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Multiple-Photon Infrared Laser Photophysics and Photochemistry. I

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This paper begins our review paper on the multiple-photon excitation of molecules by intense infrared laser light. The whole review will be given in installments. In this first part we bring forward certain general concepts on spectroscopy, molecular physics and chemical kinetics essential for understanding the later material.

Contents

SECTION 1. INTRODUCTION

The interaction of light with molecules is a particular physical process which ranges from the relatively simple process of the interaction of diatomic molecules in the gas phase up to the interaction of light with complex biomolecules in condensed media, which is not easily studied by direct physical methods. Research in this field stems not only from our desire for knowledge but also from the great fundamental importance molecular photoprocesses have in the origins of life and mankind. This importance is clear from the relatively simple photoprocesses in the ozone layer of the Earth's atmosphere and the complicated photoprocesses in complex biomolecules responsible for plant photosynthesis and for animal and human vision.

The absorption of light gives an excess of internal energy to a molecule, resulting in many different processes but all called *photochemical* ones. Often such a process is an increase of the chemical reaction rate due to irradiation with light of a wavelength absorbed by the substance. Such a phenomenon was discovered in the beginning of the 19th century (see the monograph[1]), and possibly consisted of electron-excited molecular reactions which proceed very slowly if at all for the non-excited molecules. Another important process is *the photodissociation* of simple molecules by ultraviolet irradiation which was discovered and described in detail by A. N. Terenin in the years 1920–1940.[2] Now this field of research lying at the confluence of molecular physics, chemistry and biology is called *photochemistry*. Many monographs and thousands of papers are devoted to it.[1–6]

All the photochemical processes studied so far are associated solely with the excitation of atomic or molecular electronic states (Figure 1.1a), and therefore this photochemistry should be called more exactly *photochemistry of excited electronic states* or *electronic photochemistry*. On the other hand, in most cases in chemistry one has to deal with processes involving molecules in the electronic ground state. In the electronic ground state, the molecules are distributed over vibrational, rotational and translational degrees of freedom. If the energy in these degrees of freedom exceeds some minimum value, chemical reactions become possible. Such reactions with molecules in the ground electronic state (Figure 1.1b) play the most important part in chemical technology and, as opposed to photochemical

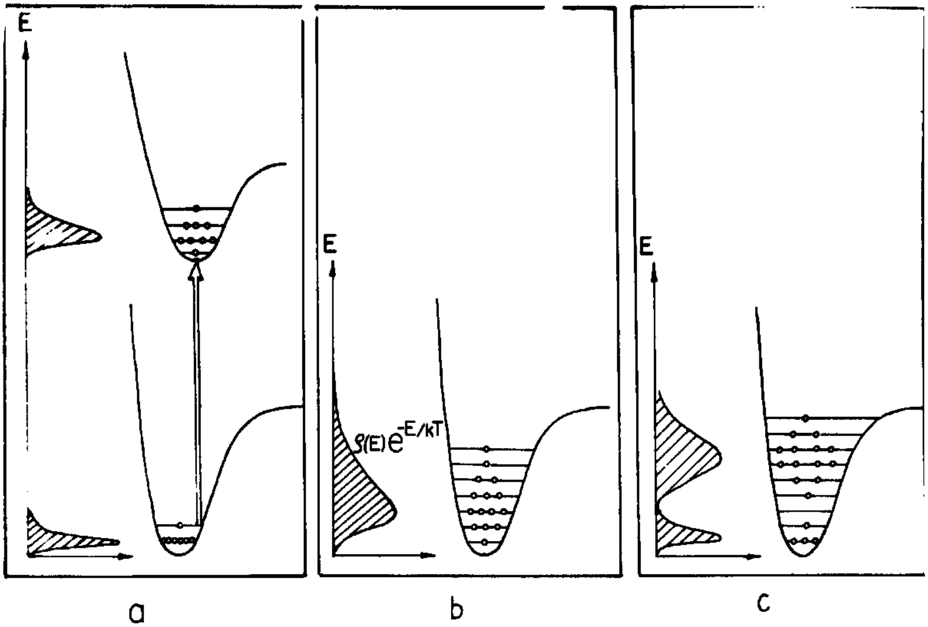

FIGURE 1.1 Types of molecular excitation resulting in faster chemical reactions: a) nonequilibrium electron excitation responsible for the photochemistry of molecules in electron-excited states—electron photochemistry; b) equilibrium thermal excitation responsible for thermal reactions; c) nonequilibrium vibrational excitation responsible for the photochemistry of molecules in the ground electron states—vibrational photochemistry.

reactions, they are termed *thermal* ones since they take place under thermal equilibrium where the contribution of radiation is negligible.*

In principle, there is one more possibility for increasing the rate of chemical reactions. Rather intense infrared (IR) radiation may induce nonequilibrium vibrational excitation of molecules at a comparatively low temperature of the substance just as can be done in exciting molecular electronic states with UV light. In this case the "translationally cold" molecule has a considerable internal energy and hence can participate in

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*It should be noted that as far back as 1919 the well-known French physicist Perrin, in order to explain an increase in the rate of some chemical reactions of complex molecules as the reactor is heated, suggested[7] that the IR radiation of the heated reactor walls excited the vibrational levels of the molecule and thus increased the reaction rate. But Longmair showed[8] that the intensity of thermal IR radiation is too small to explain the effect.

new chemical processes. Before IR lasers were developed this potential was not realized. Nevertheless, the first successful experiments were performed[9] to observe directly an increase in the rate of the *cis-trans*-isomerization of vibrationally excited HNO_2 molecules in a low-temperature matrix using an incoherent source of IR radiation. The possibility of applying this effect to photochemical isotope separation was discussed in Ref. 10. However, only the advent of high-power pulsed IR lasers and the discovery of the effect of strong excitation of polyatomic molecule vibrations by powerful resonant IR laser radiation formed the basis for the rapid development of a new field of research, the *photochemistry of highly excited molecules in ground electron state* or *multiphoton vibrational photochemistry* (Figure 1.1c).

Now dozens of laboratories in many countries are carrying out research in this field. The international efforts of physicists and chemists during the past five years have created a new field of research mixing quantum electronics, spectroscopy, and chemistry that may comprise the most important part of *laser photochemistry*. The position of multiphoton vibrational photochemistry in the broad spectrum of studies of the selective interaction of a laser light with a substance can be understood from the monograph.[11] In the present review we consider the multiphoton (MP) IR photophysics and photochemistry of polyatomic molecules. This problem has already been reviewed in some special articles[12–14] and the review monograph.[15] The monograph[15] reviews over 400 works carried out in this field during 1974–80. The present review is a revised and extended version of our review monograph,[15] which was published in Russian by the USSR Institute of Scientific Information.

It seems advisable to give first a short review of the history of multiphoton IR vibrational photophysics and photochemistry and we should note the earliest innovative and persistent, although sometimes unsuccessful, research.

1.1. History of early work

In 1964, directly after the invention of the laser, when it became possible to observe many nonlinear effects of the interaction between a strong light field and matter, Askarian[16] and Bunkin et al.[17] theoretically studied the multiquantum excitation of the vibrations of a diatomic anharmonic molecule. They considered the excitation of molecular vibrations by high-power radiation at the frequency ω-ω_{vib} and its harmonics. According to their calculations, radiation intensity should be from 10^{11} to 10^{12} W/cm^2 to dissociate a diatomic molecule (in the model of an anharmonic Morse oscillator). Even now, when such intensities are quite attainable in focusing powerful pulses of IR radiation, it is impossible to observe the multiphoton excitation of the vibrations of a diatomic molecule (Figure 1.2a).

When the first powerful IR cw laser using the CO_2 molecule at 10 μm was created, some experiments on the action of its radiation on molecular gases were performed for the first time. Bordé et al. observed[18] the visible luminescence of gaseous ammonia and its decomposition products under CO_2 laser radiation, the frequency of which coincides with a vibration-rotation absorption line of NH_3. This effect is explained[18,19] by the heating of NH_3 by laser radiation up to a high temperature. Very similar experiments were performed subsequently with the CO_2 laser and the BCl_3 molecule.[20] It was quite clear that in all these experiments the main role was played by collisions that not only de-excited the vibrations of some molecules but also provided this vibrational energy to other molecules, thus exciting them. At that time Khokhlov et al. considered[21] the possibility of collisional-radiative excitation of molecular vibrations by IR radiation. In the method considered, collisional excitation of high-lying molecular levels is possible if the rate of vibrational energy exchange (V–V exchange) $1/\tau_{V-V}$ is much higher than the relaxation rate of the vibrational excitation to heat (V–T relaxation) $1/\tau_{V-T}$. In this work conditions were found under

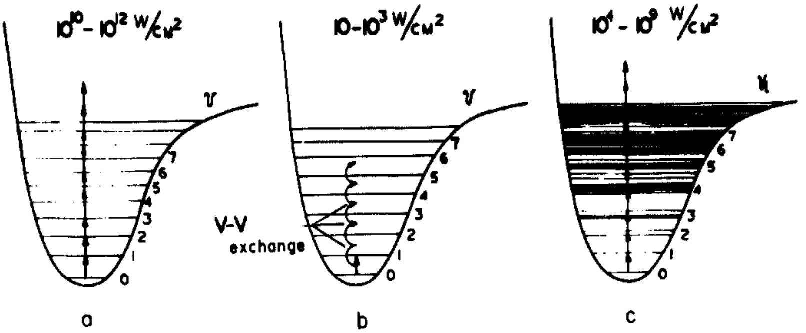


FIGURE 1.2 Basic method of molecular vibrational level excitation: a) multiphoton excitation of the vibrations of a simple molecule with required intensities of 10^{10} to 10^{12} W/cm^2; b) collisional excitation of vibrations due to vibrational exchange with molecules resonantly excited by IR radiation with the intensity from 10 to 10^3 W/cm^2; c) multiphoton excitation of the vibrations of a polyatomic molecule with required IR radiation intensity 10^4 to 10^9 W/cm^2.

which one may expect an acceleration of photochemical reactions under IR radiation that excites directly only the first vibrational level with subsequent collisional transfer of excitation to higher levels (Figure 1.2b). The intensities required in this case are not high (10 to 10^3 W/cm^2) but it is the choice of molecules complying with the condition $\tau_{V-V} \ll \tau_{V-T}$ that has a key role. Beginning with Refs. 22 and 23, many experiments on the action of continuous IR radiation on molecular mixtures to accelerate chemical reactions have been performed. However, in none of the experiments was the condition $\tau_{V-V} \ll \tau_{V-T}$ apparently fulfilled properly and opinions about the results of these experiments in the literature differ. Most researchers believe that they can be explained by purely thermal effects (see, for example, Refs. 24–26). In this review we consider instead the multiphoton selective IR photophysics and photochemistry of molecules when collisions do not play a dominant role. As for bimolecular photochemical processes induced by IR radiation, the reader may turn to the reviews.[26–29]

The creation of powerful pulsed CO_2 lasers at atmospheric pressure using a transverse discharge (TEA lasers) made it possible to start studying the action of more intense (10^6 to 10^9 W/cm^2) pulsed IR radiation on molecules. In Ref. 30 optical breakdown and visible fluorescence of some molecular gases (NH_3, SiF_4, CCl_2F_2, etc.) were observed as a CO_2 laser radiation pulse was focused onto them. It was found that the visible fluorescence occurred at intensities much lower than the optical breakdown threshold in the focus. The study of the fluorescence spectrum has shown that it belongs to electron-excited molecular dissociation products. In Ref. 31 more detailed quantitative measurements were taken for the kinetics and spectra of the fluorescence of NH_3 and C_2F_3Cl molecules irradiated by a CO_2 laser pulse. The study of the fluorescence time dependence has shown that the fluorescence appears without an observable decay at the leading edge of the laser pulse. In Ref. 32 the dissociation of N_2F_4 with a pulsed CO_2 laser was studied but the dissociation rate was measured from the occurrence of the NF_2 radicals in the ground electronic state (from UV absorption spectra rather than fluorescence). It should be noted that in Refs. 31 and 32 it was possible to observe the dissociation of polyatomic molecules at a rate much higher than that of the relaxation of the absorbed energy to heat. Yet because of the comparatively high pressure (tens of Torr) there were several V–T collisions during the time interval of observation.

The discussion of a potential mechanism of dissociation made in Refs.

31 and 32 showed at once that it would be non-trivial to explain the observed experimental data. A more detailed calculation of the kinetics of radiative excitation of molecular vibrations by IR pulses carried out in Ref. 33 shows that the participation of collisions can not provide the observed dissociation rate by any V–T relaxation, V–V exchange, or rotational relaxation process. On the other hand, the direct radiative excitation of high vibrational levels with no collisions can, in principle, provide the observed dissociation rate but encounters an evident problem: vibrational anharmonicity. The anharmonic detuning of vibrations requires very high intensities (some orders of magnitude higher than that used in these experiments) of IR radiation to induce direct multiphoton excitation.

To understand the mechanism of molecular dissociation or particularly to prove that it is possible in the interaction of an isolated molecule with an IR field, in 1972 the Institute of Spectroscopy, USSR Academy of Sciences, performed experiments on the observation of the isotopically-selective dissociation of the $^{15}NH_3$ molecule mixed with $^{14}NH_3$ using focused CO_2 laser pulses. The laser frequency was in resonance with the vibrations of the $^{15}NH_3$ molecule. The experiments yielded a negative result that is quite understandable now when we know the conditions of isotopically-selective IR molecular photodissociation. Then it was decided to carry out a detailed study into the effects of fluorescence and dissociation on another molecule, such as BCl_3. Similar experiments were performed by Canadian researchers on SiF_4.[34] At a reduced pressure (0.03 Torr) the collisionless photodissociation of these molecules was revealed from the peak of the instantaneous fluorescence, while the contribution of collisions was determined from the delayed fluorescence.

Though the techniques and results of these independent experiments[34,35] are alike there are essential differences between them. In Ref. 34 with SiF_4 the CO_2 laser frequency was out of resonance with the fundamental vibration, while in Ref. 35 with BCl_3 the dissociation was quite resonant by nature. In their work[34] the Canadian researchers explained the nonresonant character of dissociation by invoking the idea of a "vibrational quasi-continuum" beginning at rather low energies of vibrational excitation (3000 to 5000 cm^{-1}). A molecule can fall within it after multiquantum absorption of 3 to 5 IR photons (Figure 1.2c).

The resonant collisionless dissociation of BCl_3 observed in our work[35] predetermined our further program to prove the dissociation of isolated molecules in a strong IR field by observing the isotopic selectivity of dissociation in a natural mixture of the isotopic molecules $^{10}BCl_3$ and

$^{11}BCl_3$. After many unsuccessful attempts to observe this effect through direct observation of the changes in the isotopic composition of BCl_3 some experiments werë performed to study the isotope effect in the primary dissociation products from the chemiluminescence spectrum of the BO radical with a time resolution better than 10^{-7} s. This excluded any uncertainty in the interpretation of the results connected with a loss of selectivity in the final dissociation products due to secondary processes. The resulting work[36] was the first to report the isotopically-selective dissociation of BCl_3.

The experiment in Ref. 36 was of particular importance for two reasons. First, it became clear finally that there really is a phenomenon of the dissociation of an isolated molecule by a strong IR field even without the participation of collisions. Secondly, a practical method was elaborated to separate isotopes within the framework of our photodissociation approach.[37,38] The multiphoton dissociation observed in Ref. 39, where the preferential (the difference was 15%) dissociation of *trans*-2-butane by CO_2 laser radiation in mixtures with *cis*-2-butane was reported, was perhaps resonant by character. The results obtained in this work were, however, too few to make a choice between some potential mechanisms, including the one involving the participation of collisions.

After the isotopically-selective dissociation of BCl_3 in a strong IR field was discovered, it was realized that the effect was general by character and could be observed in other polyatomic molecules. Indeed, right away the Institute of Spectroscopy, USSR Academy of Sciences, successfully performed some experiments on the isotopically-selective dissociation of SF_6 and the macroscopic enrichment of sulfur isotopes.[40] These experiments were soon confirmed at the Los Alamos Scientific Laboratory, USA.[41] Heavy isotopes (such as osmium isotopes in the OsO_4 molecule) were also subjected to isotopically-selective dissociation.[42] In the same work researchers observed directly (from the variation of the UV absorption spectrum) the photoexcitation of high-lying vibrational levels of OsO_4 in an IR field of moderate intensity (about 10^6 W/cm^2). Such excitation of vibrational levels below the dissociation can apparently explain the results of the experiments[43] where isotopically-selective chemical relaxation of the BCl_3 with H_2S (or D_2S) under CO_2 laser pulses was observed.

These successful experiments on the isotopically-selective dissociation of polyatomic molecules[36,40–42] aroused considerable interest among experimentalists elaborating new methods of isotope separation and control of chemical reactions as well as among theorists interested in the nontrivial effect of collisionless resonant photodissociation of polyatomic molecules in a strong IR field. In essence, it was a new method for the formation of a highly nonequilibrium molecular distribution over vibrational levels directly by an intense IR field without translational heating (Figure 1.2c). This has become the main approach to the laser photochemistry of molecules in the ground electronic state. As far as the required radiation intensity is concerned, it lies between the above-discussed approaches and the one conventionally illustrated in Figure 1.2: the radiative multiphoton excitation of simple molecules which needs an intensity from 10^9 to 10^{12} W/cm^2 and radiative-collisional excitation which requires a rather low intensity, from 10 to 10^3 W/cm^2.

1.2. Basic processes

The multiphoton (MP) excitation and dissociation of polyatomic molecules in a strong IR field have proved rather difficult for theoretical description, and there is only a semiquantitative theory of these effects developed now. These difficulties are due to the fact that the spectrum of the vibration-rotation transitions between excited vibrational states of polyatomic molecules is almost not studied. Attempts to explain and quantitatively describe the effects of MP excitation and dissociation of molecules have motivated the first experimental data on the spectrum of transitions between excited and especially highly excited vibrational levels of polyatomic molecules and the effects themselves have become now basic methods for obtaining such spectroscopic information.

Below we shall be guided by a rather simple model of MP excitation and dissociation of polyatomic molecules within which it is possible to explain qualitatively the basic features of these effects. Figure 1.3 shows in a simple way the basic stages of MP excitation and subsequent dissociation of polyatomic molecules in a strong resonant IR field which is adopted now by the most scientists. To a certain extent this model determines the structure of the present review: first, successive excitation of multiphoton transitions in the system of lower vibrational levels (Section 5), then stimulated transitions in the vibrational quasi-continuum (Section 6) and, finally, photochemical transformations of highly excited molecules (Section 7). However, before giving a detailed description of multiphoton excitation and subsequent photochemical processes for polyatomic molecules, in Section 4 we illustrate the general physics of the processes induced by high-power IR radiation in polyatomic molecules. A reader concerned

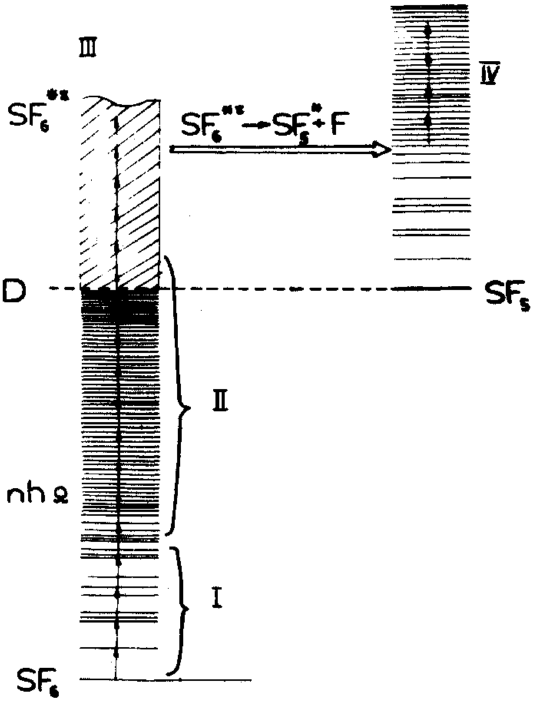


FIGURE 1.3 Model for the process of polyatomic molecule dissociation by an intense IR field: stage I—resonant excitation of low-lying vibrational transitions; stage II—strong excitation (vibrational heating) of molecules at transitions between highly excited states; stage III—monomolecular decay of overly-excited molecules; stage IV—subsequent strong excitation and dissociation of polyatomic decay products.

with the applications of multiphoton IR photoexcitation—specifically, isotope separation, photochemistry, etc.—may limit himself to this chapter and then proceed directly to Sections 8 and 9.

Now we want to turn to discussing multiphoton excitation in accordance with the model illustrated in Figure 1.3. In the lower vibrational transitions the molecule in an IR field of moderate intensity is subjected to resonant multistep excitation. This is accomplished due to compensation of the anharmonic frequency detuning of successive vibrational transitions because of changes in the molecular rotational energy, anharmonic splitting of excited degenerate vibrational states, etc. In cases when at any of the lower transitions there is no true anharmonicity compensation, two- and three-photon vibrational transitions with near-to-resonance intermediate levels will occur. At this first stage resonant and particularly isotope selective molecular excitation may occur.

As a rule, for multiphoton excitation of molecules in the lower vibrational levels only small energy fluences (intensities) of the laser pulse are needed. It is because of this that one can treat separately multiphoton resonant excitation of molecules at lower levels. This first stage of the process is under detailed consideration in Section 5. Here such important characteristics as the selectivity of multiphoton excitation and the fraction of molecules involved in this process are explained. This Section is of interest for vibrational multiphoton spectroscopy of molecules, a new approach to nonlinear laser spectroscopy. We believe that, along with theoretical representations, brief information on basic experimental methods of study of multiphoton absorption and excitation of molecules is also useful in this case.

As a polyatomic molecule is excited to upper vibrational levels the number of possible vibrational transitions from a given vibrational-rotational state increases sharply. This is conditioned by a high density of vibrational molecular levels with a great number of interacting degrees of freedom. Therefore the spectrum of vibrational transitions between highly excited states is not so resonant as it is for lower transitions. A wide-band and, hence, comparatively weaker spectrum of transitions between them is termed the "vibrational quasicontinuum". If the intensity (or the energy fluence in the absence of absorbed energy relaxation) of an IR pulse is rather high, a polyatomic molecule is able to climb up the levels of the vibrational quasicontinuum, even though the absorption cross-section of transitions between them is small.

The vibrational photoexcitation of molecules in the quasicontinuum is considered in Section 6. Besides the analysis of the spectroscopic properties of highly excited vibrational states and radiative transitions between them, we focus our primary attention on the vibrational molecular energy distribution formed by powerful IR pulses. We also discuss the problem of stochastization of vibrational energy among vibrational molecular modes and the possibility of mode-nonequilibrium distribution of vibrational energy. Also, consideration is given here to the peculiarities of multiphoton excitation of isolated molecular ions under continuous IR radiation as well as the connection of electronically excited states with highly excited vibrational states (reverse V–E conversions).

Through transitions in the vibrational quasicontinuum under a rather high-fluence IR pulse any polyatomic molecule can accumulate an energy comparable to the dissociation energy. This energy is distributed over many vibrational degrees of freedom since there are numerous combinational overtones that can participate in the absorption at the transitions in the vibrational quasicontinuum. For a molecule to dissociate during the laser pulse (with a usual duration of 10^{-7} s), its dissociation rate must be higher than 10^7 s^{-1}. In this case its vibrational energy must somewhat exceed the value of the dissociation energy known from thermochemical data. In other words, the energy of nonstationary dissociation is somewhat higher than the known energy of steady-state dissociation in an unlimited time. The decomposition of this vibrationally-super-energetic molecule lying above its dissociation limit is the third stage of the process (Figure 1.3).

If one of the fragments of the molecule is polyatomic it can participate further in multiphoton absorption of IR radiation and produce simpler fragments after dissociation. This is possible either due to excessive vibrational energy transferred by the super-energetic molecule to its polyatomic fragment so that it falls at once within the region of the vibrational quasicontinuum or due to conservation of resonance between IR radiation and the molecular bond in its polyatomic fragment. The polyatomic fragment, SF_5, for example, is able itself to absorb IR radiation for both reasons. Successive dissociation of a polyatomic molecule and its fragments is the fourth possible stage of polyatomic molecule decomposition in a strong IR field (Figure 1.3).

Section 7 describes in detail the dissociation and isomerization of polyatomic molecules under high vibrational excitation. Consideration is given here to different channels of decay of polyatomic molecules, decay products, their quantum states and various methods of study. Much emphasis is focused on the correlation of experimental results with the predictions of the statistical theory of monomolecular reactions. It should be stressed here that the possibility of fast controllable energy deposition into a polyatomic molecule by multiphoton absorption of IR radiation has given us a very handy method of research of monomolecular reactions under ideal, collisionless conditions. This may lead to a profound understanding of the theory for the monomolecular reactions of polyatomic molecules.

It should be emphasized that such a division of the process into stages (Figure 1.3), although conventional in many respects because these stages may overlap, is convenient for understanding the basic features of such a complicated process as the interaction of the field with a quantum system having a great number of degrees of freedom and subject to nonlinear destruction by an external force. This rather simple model of the process was developed gradually as a result of synthesis of some key ideas conceived by different researchers. The idea of soft compensation of anharmonicity at lower vibrational transitions, particularly due to rotational energy variation, was conceived in Ref. 44. The role of multiphoton processes at lower levels was discussed in Refs. 45 and 46. The idea of nonresonant excitation of molecules at transitions between highly excited states forming a vibrational quasicontinuum was suggested in Ref. 34 and then discussed in Refs. 47–50. The direct experiments in Ref. 50 on selective dissociation of molecules in a two-frequency field (resonant IR and nonresonant IR fields for lower transitions) supported the validity of these qualitative considerations. The role of mixing (or stochastization) of different vibrational modes under strong IR excitation of one vibrational degree of freedom was considered in Ref. 51. The degree of vibrational overexcitation of a molecule beyond the dissociation limit and the possibility of subsequent dissociation of its fragments were considered and studied in Refs. 52 and 53. It is these experiments with molecular beams that have shown that dissociation occurs through breaking the weakest molecular bond and that the formation of simpler fragments is connected with the effect of subsequent dissociation of primary fragments.

Numerous later studies into the characteristics of MP excitation and dissociation of a great number of different molecules have confirmed the validity of the described qualitative considerations. In particular, through a special choice of molecules it was possible to trace the change of contribution of each stage to the process of MP excitation and dissociation. For example, systematic studies of more complex molecules, S_2F_{10} in particular, were carried out.[54] The vibrational quasicontinuum of this molecule starts very low, in the region of the first vibrational level under excitation (Figure 1.4a). In this case the first stage of MP excitation is almost absent and such a molecule begins at once to perform transitions in the vibrational quasicontinuum. Such a situation can be realized for polyatomic molecular ions isolated from collisions and dissociated under continuous CO_2 laser radiation of comparatively low power (several W).[55]

For simple polyatomic molecules the vibrational quasicontinuum boundary lies at the level of from 3 to 5 vibrational quanta but dissociation occurs with a small excess of the vibrational energy from the IR field over the dissociation limit (1 or 2 IR photons) and the dissociation products cannot absorb effectively the IR radiation in the MP process (Figure 1.4b). For such molecules as CF_3I the dissociation process is not complicated by

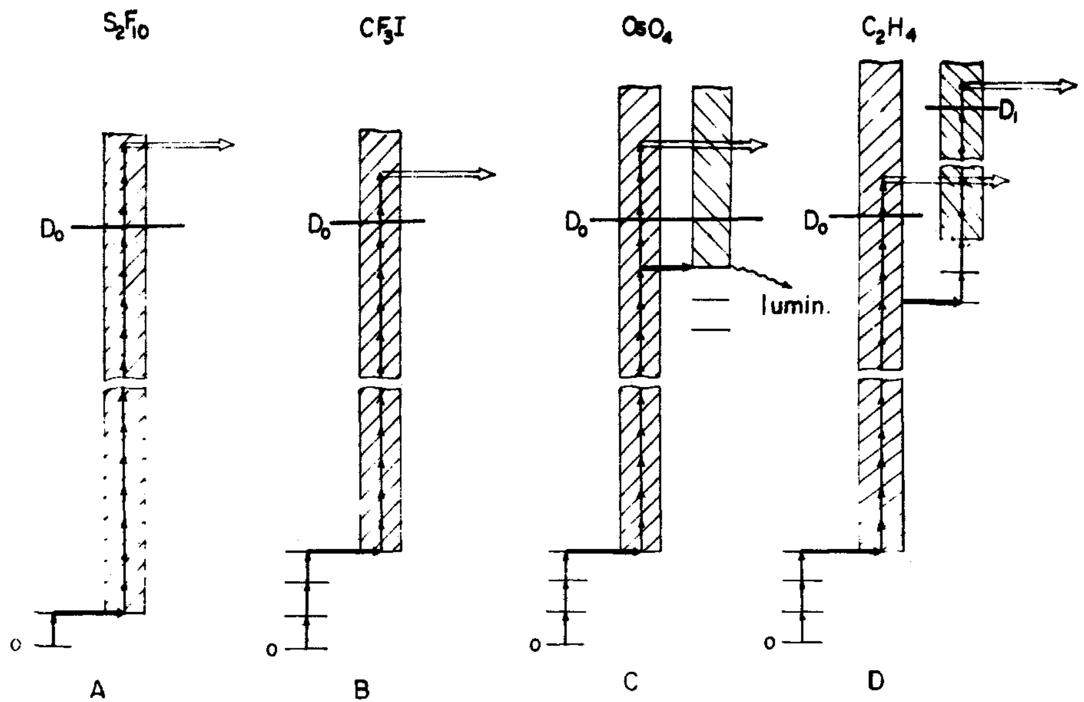


FIGURE 1.4 Various limiting cases of MP excitation and dissociation of polyatomic molecules by IR radiation: a) MP excitation of molecules with a very low vibrational quasi-continuum limit (the shaded area below the dissociation limit in the steady state case D_0); b) molecular decay at low excitation ($E - D_0 \ll D_0$) over the dissociation limit D_0 in the region of real continuum (the shaded area above D_0); c) excitation of mixed electron-vibrational molecular states which can luminesce in the visible or UV ranges; d) MP excitation of mixed electron-vibrational states and subsequent MP vibrational excitation in the electron-excited state.

strong overexcitation of the molecule above the dissociation limit D_0 and secondary dissociation of fragments. In these cases it becomes possible to compare precisely theory and experiment.[56]

Many polyatomic molecules have excited electronic states lying below the dissociation limit of the ground electron state. In these cases there is inevitable mixing of the wave functions of highly excited vibrational levels of the ground electron state and lower vibrational levels of the excited electron state. When many IR photons are absorbed, such mixed electronic-vibrational states are inevitably excited. As a result, a polyatomic molecule may become electronically excited with some probability depending on both the degree of electronic-vibrational interaction and the ratio of statistical weights of the vibrational states in the quasicontinuum and in the excited electronic state. In this state the molecule can, firstly, luminesce (Figure 1.4c); this apparently takes place as the OsO_4 molecule is excited by CO_2 laser radiation and explains[57] its fluorescence even without the necessity of dissociation and formation of electronically-excited fragments. From this standpoint we shall probably have to reconsider the interpretation of the results of the early experiments with SiF_4.[34] Secondly, an electronically excited molecule can continue with MP absorption of IR photons up to the dissociation limit of an excited electronic state (Figure 1.4d) and thus dissociate through another channel, even one with a large energy barrier. This probability can explain the collisionless formation of C_2 radicals as the C_2H_4 molecule is dissociated by CO_2 laser radiation.[58,59]

Thus, even this simplified classification shows that a polyatomic molecule in an intense IR field may undergo many different processes. Therefore, in the first consideration of the behavior of a specific polyatomic molecule in an IR field, one should first understand into which of these simplified classifications it must be placed (Figure 1.4). This necessitates, at the very least, study of the molecule's characteristics of MP excitation and dissociation over a wide range of intensity and frequency of IR field. We can then gain some insight into the molecule's basic characteristics using the theoretical and experimental data from other molecules belonging to this case. Moreover, in limiting cases it is also possible to simplify the theoretical description. As an example, for all molecules with a very low limit of vibrational quasicontinuum (Figure 1.4a), one need not consider the process of multiphoton excitation of low discrete levels since, after absorbing the first IR photon, this molecule passes to the vibrational quasicontinuum and the MP excitation is reduced to a combination of an ordinary linear IR absorption and excitation in the vibrational quasicontinuum. Similar simplification can be done in describing the MP excitation near and above the dissociation limit because, in the case of polyatomic molecules, appreciable excitation over the dissociation limit may occur before the molecule finds its decay channel during the limited time of a laser pulse while at the same time, for comparatively simple polyatomic molecules, the decay takes place at a small excess of the vibrational energy over the dissociation limit (Figure 1.4b). It must be emphasized, however, that the effects induced in a polyatomic molecule under intense IR pulses are complicated and varied, with even the qualitative understanding of these effects requiring study of the phenomenon of multiphoton absorption.

1.3. Trends of application

The effects arising when polyatomic molecules are irradiated by IR laser radiation pulses have a very wide range of applications—from spectroscopy to nuclear chemistry. It is just such promising applications as laser isotope separation that have stimulated rapid progress in multiphoton IR photophysics and photochemistry. Two important applications, laser isotope separation and chemical synthesis, are more fully discussed in the last two Sections, 8 and 9. In this Introduction we will restrict ourselves to enumerating the trends of application.

Molecular spectroscopy

As has been already noted, MP excitation of molecules by powerful IR radiation pulses has made possible the systematic study of highly excited vibrational molecular levels and the transitions between them, essentially developing the molecular spectroscopy of excited vibrational levels, both the discrete ones lying below the vibrational quasicontinuum limit and the highly-excited vibrational levels forming the quasicontinuum. The problems and possibilities of this new approach to spectroscopy and molecular physics are discussed in Sections 5 and 6.

Attention should be drawn to the possibility of studying so-called "inverse radiationless" transitions where strong vibrational excitation transforms to electronic excitation in contrast to the well-known process of radiationless relaxation of electronic energy to vibrational energy. Such processes have become the subject of experimental studies[57] (Section 6).

MP dissociation makes it possible to produce high concentrations of certain radicals (10^{14} to 10^{16} cm^{-3}). In the earliest work this effect was proposed as a method for IR photolysis of molecules. Using various polyatomic molecules, even provided that the weakest molecular bond is broken, we can vary the type of radicals over a very wide range. This opens up possibilities for systematic studies of radical spectra from the microwave region to the vacuum ultraviolet.

Chemical physics

The production of certain free radicals by pulsed radiation provides a convenient method for investigating elementary processes taking place in the gas phase, particularly the kinetics and dynamics of chemical reactions.[60] The excitation of radical fluorescence by tunable laser radiation can be used to determine the quantum state of free radicals with nanosecond time resolution. Thus, for example, the C_2 radical was detected[58,59] both in the ground ($a^3\pi_u$) and metastable ($d^3\pi_g$) electronic states in MP dissociation of C_2H_4 molecules by high-power CO_2 laser pulses. Time resolved laser induced fluorescence is now a very efficient technique in the study of gas-phase reactions (see Refs. 60 and 61).

Controllable deposition of laser energy to the vibrational degrees of freedom of a polyatomic molecule has provided us with a unique possibility to study monomolecular reactions of dissociation and isomerization and to compare their rates with those predicted from the RRKM theory.[62] The problems and possibilities of this approach are discussed in Section 7. The method of MP excitation in combination with the diagnostic methods of laser spectroscopies[63] of the electronic, vibrational and rotational states of photodissociation products is especially useful here.

Nuclear chemistry

Isotope separation is one of the more important applications of nuclear chemistry and technology. The progress in the methods of MP excitation and dissociation of molecules is stimulated by their isotopic selectivity.[36] The separation of very different isotopes has by now been demonstrated: from light (H/D) isotopes in highly selective dissociation of CF_3Cl_2H molecules[64] to heavy (Os) isotopes in dissociation of OsO_4 molecules in a two-frequency IR field.[65] Laser isotope separation is one of the very important specific applications of the selective action of laser radiation on atoms and molecules (see Ref. 11). In more detail the problems of laser isotope separation by IR photodissociation of polyatomic molecules are considered in Section 8.

It should be noted, for example, that our experiments[56,66,67] on CF_3I

molecules have proved that the following are possible: 1) measurement and MP isotope-selective deposit of the dissociation energy of the weakest molecular bonds (2 eV of IR radiation energy); 2) complete (almost 100%) dissociation yield of molecules in the irradiated volume at a moderate energy flux of IR radiation pulse; 3) high isotopic selectivity of dissociation (more than 30) at rather high (5 to 10 Torr) total pressure of CF_3I gas; 4) a considerable degree of extraction (about 50%) of the wanted rare isotope (^{13}C) without appreciable decomposition (below 2%) of the rest of the molecules ($^{12}CF_3I$); 5) elimination of secondary photochemical processes that would prevent high dissociation selectivity. All this has enabled us to propose a method for the separation of light- and medium-mass isotopes on a practical scale with the use of a TEA CO_2 laser with a high (up to 200 Hz) pulse rate and its mean power of 1 kW.[68] The simplicity and technological effectiveness of this method of laser isotope separation may lead to its industrial adaptation in the near future.

It is rather simple to separate light- and medium-mass isotopes with their abundance of about 1% and more but there are more important and harder problems: particularly, the extraction of rare isotopes (for example, the D isotope with its relative content 1/5000) and isotopes of heavy elements from molecular compounds with a small isotopic shift (^{235}U from UF_6, for example). A viable method of laser separation for hydrogen isotopes requires that the separation selectivity $\alpha(D/H)$ defined as the ratio of the dissociation yields for the molecules with the wanted (D) isotope and without it (H)

$$\alpha\left(\frac{D}{H}\right) = \frac{\beta_D}{\beta_H} \tag{1.1}$$

should exceed at least 1000. The recent successful experiments[64] on MP dissociation of some deuterium-containing molecules by CO_2 laser radiation give hope for future progress in this direction.

Such highly selective laser based technology may greatly affect in the future decontamination of nuclear reactor waste containing radioactive impurities which poison the reactor and the environment—for example, tritium in heavy-water reactors.[69] Laser engineering today, of course, is in the initial stage of development, as far as such large-scale applications are concerned. The scientific fundamentals of such advanced technology, however, are being discovered today.

Chemical synthesis

MP excitation enables intense IR radiation to deposit energies of several eV to certain molecules in a mixture without depositing such a high energy to the other molecules. This situation differs from thermal excitation where all the molecules in the gas mixture have approximately the same store of vibrational energy. Therefore, new ways of chemical reactions may be expected with the participation of highly excited molecules or their dissociation products. It is the strong excitation of these chosen molecules under transient conditions of reaction and the formation of their dissociation products before excitation thermalization that can make more competitive the unusual pathways of chemical reactions from those studied under equilibrium conditions. Indeed, under steady-state conditions, as a rule, the composition of initial and final products is determined by thermodynamics. At pulsed excitation under transient nonstationary conditions time factors (i.e., the ratio between the reaction rate and the relaxation rate of some nonequilibrium state of the molecular mixture) become essential as well as the thermodynamic factors.

Highly effective IR photochemical synthesis is illustrated in Ref. 70 where selective IR MP dissociation of CF_3Br and CF_3I molecules in the presence of acceptors has been studied. Among other things this work demonstrates the possibility of highly effective (almost 100%) photochemical conversion to CF_3I molecules of CF_3Br mixed with I_2 at a pressure of more than 10 Torr. Based on this and other works[71] we may draw an optimistic conclusion on laser photochemical synthesis based upon radical reactions. Using an IR laser and appropriate molecules we can have some concentrations of very different radicals for a short time. This enables us to tailor the synthesis reaction directly to provide a maximum yield of the wanted product at a minimum use of original materials. In the case of using IR MP dissociation to prepare radicals of a desired sort, one should keep in mind that the molecules under excitation decay due to the breaking of the weakest bond. Nevertheless, this gives many possibilities for laser chemical synthesis. The problems and possibilities of the application of MP IR molecular excitation to chemical synthesis are comprehensively discussed in Section 9.

After this Introduction and before beginning with a systematic description of multiphoton IR photophysics and photochemistry and its applications, it would be useful to introduce some background in two short Sections, 2 and 3. Section 2 contains basic concepts from quantum mechanics, molecular spectroscopy, chemical physics and quantum electronics which are quite necessary for understanding the ensuing, more comprehensive, material. Section 3 deals with the elements of the theory of interaction of multilevel quantum systems with laser radiation; and, for further theoretical interpretation, simple physical effects of the interaction of light with molecules such as the Rabi frequency, multiquantum transitions, etc. are described.

SECTION 2. PHYSICAL BACKGROUND

2.1. Elements of quantum mechanics of molecules

2.1.1. Symmetry in quantum mechanics

It is often useful to begin studies of any isolated quantum system with some insights into the symmetry properties of its Hamiltonian. Ordinarily, one treats symmetry transformations as those that do not change the energy of the system. There also exists a more general definition. Let $\psi(\mathbf{r}_1, \ldots, \mathbf{r}_n)$ be an arbitrary wavefunction of a quantum system which depends on $3N$ Cartesian coordinates of N particles and let $\hat{G}$ be some linear operator which transforms function ψ into another wavefunction ψ. If operator $\hat{G}$ commutes with the system's Hamiltonian $\hat{H}$, i.e., for any wavefunction

$$\hat{H}\hat{G}\psi = \hat{G}\hat{H}\psi, \tag{2.1}$$

then $\hat{G}$ is called the *element* of the Hamiltonian symmetry group, and the collection of *all* the operators which comply with the commutation property (2.1) is called the *total symmetry group* of the Hamiltonian.

Operators which commute with the Hamiltonian correlate with conserved quantities manifested by their corresponding physical observable phenomena. For example, the invariance of the Hamiltonian under spatial-shift operators is equivalent to the principle of momentum conservation, and the invariance of the Hamiltonian under rotation operators is equivalent to the principle of angular-momentum conservation. These conservation principles are valid for any arbitrarily isolated quantum system. Of the fundamental quantum-mechanical conservation laws, one can also add the parity conservation that reflects the invariance of the Hamiltonian under the inversion transformation, i.e., under the simultaneous change of the sign of every spatial coordinate of every particle.

The name *symmetry group* is not accidental. Mathematically, the set of operators which comply with the commutation property (2.1) forms the group. This fact leads to far-reaching consequences. It appears that one can predict properties of real energy states, even without solving the Schrödinger equation, but just knowing the total symmetry group of the Hamiltonian. From these predicted characteristics one may attribute degeneracies of states and their splittings in electric and magnetic fields, as well as the ability of a system to emit, to absorb, and to scatter radiation at various transitions.

The problem of state classification can be solved using the *group representation theory*. The formulation is rather simple. *States of a quantum system are classified by irreducible representations of its Hamiltonian total symmetry group,* i.e., each level can be referred to some irreducible representation. Behind this formulation, however, there are hidden beautiful theorems and powerful analytical methods, as well as many new concepts and terms. And, particularly related to this series of papers, one should note the following points:

1. The quantum mechanical aspects of the group representation theory are excellently treated in many books.[72–76]
2. It is not hard to use the representation theory as a tool. It is ordinarily enough to know the fundamentals and how to apply formally the tables of the so-called *characters* of irreducible representations.
3. The representation theory is not all-powerful. It helps to understand molecular spectra in a detailed picture only in combination with both the approximate methods for solution of the Schrödinger equation and the actual experimental data.[77–80]
4. Do not be anxious about the notation of molecular terms which will be sometimes used below. Keep in mind that a designation is no more than that of the irreducible representation, and the necessary properties of the corresponding state can always be obtained from the tables of characters.
5. There are no *accidental* degeneracies in quantum mechanics. If, upon solution of the Schrödinger equation, the degeneracies of some levels exceed those values predicted by the representation theory, then this simply means that the symmetry group used is *not* complete. Two well-known examples are the hydrogen atom[81] and the isotropic two- or three-dimensional harmonic oscillator.[82] To some extent, this second example will be of importance here.
6. What is being referred to as the molecular Hamiltonian symmetry is ordinarily formulated for simple geometric reasons and is just an *approximation,* but this approximation is well based physically, and it agrees wonderfully with experiment. Its physical sense will be clear below.

2.1.2. The Born-Oppenheimer approximation

The classical energy of a molecule, a system consisting of N nuclei and n electrons, is schematically given by the sum of three parts: the kinetic energy of nuclei T_{nucl}, the kinetic energy of electrons T_{el}, and the potential energy U which describes Coulomb pair interactions between all particles. Accordingly, the nonrelativistic Hamiltonian of a molecule is composed of three operators:

$$
\begin{aligned}
\hat{H} &= \hat{T}_{\mathrm{nucl}} + \hat{T}_{\mathrm{el}} + U \\
\hat{T}_{\mathrm{nucl}} &= \frac{1}{2}\sum_{j=1}^{N} \frac{[\hat{\mathbf{P}}_j^{(\mathrm{nucl})}]^2}{M_j} = -\frac{\hbar^2}{2}\sum_{j=1}^{N} \frac{\Delta_j^{(\mathrm{nucl})}}{M_j} \qquad (2.2) \\
\hat{T}_{\mathrm{el}} &= \frac{1}{2m}\sum_{i=1}^{n} [\hat{\mathbf{P}}_i^{(\mathrm{el})}]^2 = -\frac{\hbar^2}{2m}\sum_{i=1}^{n} \Delta_i^{(\mathrm{el})} \\
U &= e^2 \sum_{j_1 \neq j_2} \frac{Z_{j_1} Z_{j_2}}{|\mathbf{R}_{j_1}^{(\mathrm{nucl})} - \mathbf{R}_{j_2}^{(\mathrm{nucl})}|} + e^2 \\
&\quad \sum_{i_1 \neq i_2} \frac{1}{|\mathbf{R}_{i_1}^{(\mathrm{el})} - \mathbf{R}_{i_2}^{(\mathrm{el})}|} - e^2 \sum_{i,j} \frac{Z_j}{|\mathbf{R}_j^{(\mathrm{nucl})} - \mathbf{R}_i^{(\mathrm{el})}|}
\end{aligned}
$$

Here the index j is related to a j-th nucleus, the index i is related to an i-th electron, e and m are the electron charge and mass, $\hat{\mathbf{P}}_j^{(\mathrm{nucl})}$ is the notation for momentum operators of nuclei, $\mathbf{P}_i^{(\mathrm{el})}$ means the same for electrons, $-Ze$ and M are the charges and the masses of nuclei, the vectors $\mathbf{R}_j^{(\mathrm{nucl})}$ describe the positions of nuclei in the laboratory frame, the vectors $\mathbf{R}_i^{\mathrm{el}}$ describe those of electrons, $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ is the Laplacian. Hamiltonian (2.2) is, of course, invariant under the operators of shifts, rotations, and inversion. One can also note its invariance under the permutation of any pair of electrons as well as of any pair of identical nuclei. This, however, gives little new for classification. Some additional simplifications are needed. It is rather natural firstly to make use of a great difference between the electron and nuclear masses. This fact is basic for developing the quantum theory of molecules. It evidently follows that the kinetic energy of nuclei must be considerably less than that of electrons, and, therefore, one can treat the motion of electrons, under fixed positions of nuclei, as the simplest approximation. Just this concept is usually referred to as an *adiabatic approximation* or the *Born-Oppenheimer approximation*. In Ref. 83 they have shown that by order of magnitude the ratio between the energy of nuclear motion and that of electron motion is $E_{\mathrm{nucl}}/E_{\mathrm{el}} \sim (m/M)^{1/2} = \kappa^2$, where κ is called the *Born-Oppenheimer parameter*.

Let us list the important results from this approximation, in which the electron motion is separated from that of nuclei.

1. Electronic terms can be found from the Schrödinger equation for electronic wavefunction

$$\hat{H}_{\text{el}}\, \psi_{\text{el}}\, [\mathbf{R}_i^{(\text{el})}, \mathbf{R}_j^{(\text{nucl})}] = E_{\text{el}}\, [\mathbf{R}_j^{(\text{nucl})}]\, \psi_{\text{el}}\, [\mathbf{R}_i^{(\text{el})}, \mathbf{R}_j^{(\text{nucl})}] \qquad (2.3)$$

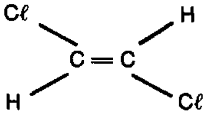
where $\hat{H}_{\text{el}} = \hat{T}_{\text{el}} + U$. Since this equation does not include nuclear-coordinates derivatives, then those coordinates can be treated parametrically. Hence, it follows that energy eigenvalues E_{el} depend on nuclei coordinates parametrically, too.

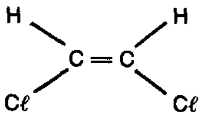
2. The very stability of a molecule gives evidence of the dependence $E_{\text{el}}[\mathbf{R}_j^{(\text{nucl})}]$ having a minimum. It is possible that this dependence has more than a single minimum. This could mean that several isomeric modifications of a molecule may exist. Transitions among modifications can be treated as quantum tunneling through a barrier. The probabilities of such transitions may often be very small. In this case, the isomers are possibly treated as different molecules.

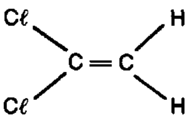
3. The nuclei positions being fixed, the solution of Eq. (2.3) gives, generally speaking, an infinite number of energy eigenvalues $E_{\text{el}}[\mathbf{R}_j^{(\text{nucl})}]$. An excited electronic term may also be stable as the ground one, or it may be absolutely unstable. As a rule, molecular transitions from the ground electronic term into excited ones lie in the visible or ultraviolet regions of the spectrum. Therefore, taking into account the goal of this series of papers, we shall restrict ourselves mainly to considering the ground electronic state.

4. When the symmetry properties of an electronic wavefunction are discussed, it is usually of the symmetry corresponding to the equilibrium nuclei configuration. Thus the symmetry of the electronic wavefunction is an *approximation,* since a deviation from the equilibrium configuration would generally lead to the symmetry group of Hamiltonian $\hat{H}_{\text{el}}$ to be changed. However, for small variations, this change is not significant and an empirical rule states that the electronic wavefunction of the ground term does not change under every symmetry transformation allowed by the equilibrium configuration, i.e., it is totally symmetric.

Typical distances between adjacent nuclei in a molecule are usually about (1–3) × 10^{-8} cm. The X-ray diffraction method is most widely used to determine experimentally the equilibrium configurations of molecules. One can also make use of spectroscopic methods. Very often the equilibrium configuration qualitatively agrees with that expected from intuitive ideas. For example, the molecules CH_4 and OsO_4 have the form of the regular tetrahedron with the atoms C and Os at the centre, and H and O at the apexes; the molecules SF_6 and UF_6 have the form of the regular octahedron; in the molecules CF_3I, CF_3Br, etc. the F-atoms constitute the equiangular base of a pyramid, whereas the atoms C and I(Br) lie on the perpendicular axis. However, in some cases our intuition cannot give a simple answer. For example, the molecule NH_3 has the pyramidical form, but the molecule BCl_3 is plane; the molecule CO_2 is linear, but the molecule H_2O is bent. Proceeding from speculations only, it is also difficult to find the isomeric modification which is energetically more profitable. Let the molecule CH_2Cl_2 be an example. One can suggest for it three possible equilibrium configurations:







The first one proves to be the most profitable.

The symmetry of the molecule equilibrium configuration is of fundamental importance in developing the theory of its vibration-rotation spectrum. The symmetry of the equilibrium configuration is described in terms of the so-called point symmetry group, elements of which are all coordinate transformations acting upon the nuclei of a molecule, and sending them into identical nuclei. Each point symmetry group has its own notation, for example, T_d for the molecules CH_4 and OsO_4, O_h for the molecules SF_6 and UF_6, C_{3v} for the molecules CF_3I and CF_3Br, and D_{3h} for the molecule BCl_3. Properties of point-group representations are comprehensively treated, for example, in Refs. 72, 74 and 76–80.

2.1.3. *The vibration-rotation Hamiltonian*

The operator of the nuclei kinetic energy $\hat{T}_{\text{nucl}}$, which was neglected when the electronic terms were obtained, is taken into consideration in this next approximation dealing with the quantization of motion of the nuclei. After the electron motion has been extracted, the Schrödinger equation for nuclear wavefunction takes the following form:

$$\hat{H}_{\text{nucl}}\,\psi = E\psi, \tag{2.4}$$

where

$$\hat{H}_{\text{nucl}} = \hat{T}_{\text{nucl}} + E_{\text{el}}\,[\mathbf{R}_j^{(\text{nucl})}] \tag{2.5}$$

The electronic term $E_{\text{el}}[\mathbf{R}_j^{(\text{nucl})}]$ in this equation conventionally plays a role of potential energy. Further progress could be achieved if a convenient approximation of the Hamiltonian (2.5) were formulated, allowing analytical solutions, with corrections being of a clear physical sense. The idea of deriving such an approximation is based upon a rather apparent relationship between amplitudes of molecular vibrations and internuclei distances under the equilibrium configuration of a molecule. Since any essential changes in internuclei distances lead to considerable changes in the Coloumb interaction, this means that the minimum of the potential energy $E_{\text{el}}[\mathbf{R}_j^{(\text{nucl})}]$ is rather deep, or, in other words, the lower energy levels of (2.4) must correspond to the motion of nuclei with *small* deviations from the equilibrium configuration. Thus, a molecule can be approximately treated as being almost rigid, and, in this approximation, the nuclei motion can be described as composed of some *rotational* motion of a molecule as a whole which does not change their mutual arrangement, and some *vibrational* motions which are small vibrations of the nuclei near their equilibrium positions in the molecule-fixed frame. (The ratio of the amplitudes of small vibrations to internuclei distances is equal within an order of magnitude to the Born-Oppenheimer parameter κ.) A molecule, of course, has three translational degrees of freedom. Since a nonlinear molecule has also three rotational degrees of freedom, then the number of vibrational ones equals $3N$-6. As is well known from classical mechanics,[84] small vibrations near equilibrium can be approximately treated as *harmonic* ones. Furthermore, from Cartesian coordinates one can constitute independent linear combinations, each of them having its own vibrational frequency. Such combinations are called *normal coordinates*.

One can transform this visual picture into the zero-order vibration-rotation Hamiltonian

$$\hat{H}^{(0)}_{\text{nucl}} = \hat{H}_{\text{tr}} + \hat{H}\ (\text{rigid rotator}) + \hat{H}\ (\text{harmonic oscillators}) \qquad (2.6)$$

Here $\hat{H}_{\text{tr}} = \hat{\mathbf{P}}^2/2M_{\text{total}}$ is the Hamiltonian of the translational motion of a molecule as a whole which is ignored below, $\hat{H}$ (rigid rotator) $= \hat{J}^2_\alpha/2I_\alpha + \hat{J}^2_\beta/2I_\beta + \hat{J}^2_\gamma/2I_\gamma$ is the Hamiltonian of a rigid molecule ($\hat{J}_{\alpha,\beta,\gamma}$ are the components of the angular momentum operator, $I_{\alpha,\beta,\gamma}$ are the principal moments of inertia), $\hat{H}$ (harmonic oscillators) $= (1/2) \sum_{i=1}^{3N-6} (\hat{p}_i^2 + \omega_i^2 q_i^2)$ is the Hamiltonian of harmonic vibrations ($\hat{p}_i = -i\hbar\, \partial/\partial q_i$ the conjugate-momentum operator which is related to an i-th normal coordinate q_i, ω_i is the frequency corresponding to the i-th normal coordinate).

Hamiltonian (2.6) is of great significance, since solutions of the Schrödinger equation for both the rigid rotator and the harmonic oscillator are rather simple. Furthermore, from Hamiltonian (2.6) one can easily estimate, by an order of magnitude, the ratio between typical values of rotational and vibrational energies by noting that one quantum of rotational energy approximately equals $\hbar^2/Ma^2$, where M is the typical nuclear mass, and a is the typical dimension of the molecule. The potential energy of vibrational motion is about $M\omega^2A^2$, where A is a typical amplitude of molecular vibrations which, in its turn, is about κa. On the other hand, a vibrational quantum is equal to $\hbar\omega$. Using $\hbar\omega \sim M\omega^2\kappa^2a^2$, we find that $\omega \sim \hbar/Ma^2\kappa^2$, and estimate the vibrational energy to be $E_{\text{vib}} \approx \hbar\omega \sim \hbar^2/Ma^2\kappa^2$. Therefore, the ratio $E_{\text{rot}}/E_{\text{vib}} \sim \kappa^2$ is again expressed through the Born-Oppenheimer parameter.

Of course, the exact vibration-rotation Hamiltonian is much more complicated than (2.6). One complication is rather obvious and comes from the fact that molecular vibrations are really *anharmonic*, i.e., the potential energy, in addition to the terms which are quadratic by deviations from equilibrium positions, does also contain terms of higher orders: cubic, quartic, etc. Anharmonicity results in two basic effects which are firstly corrections to the energies of the vibrational levels and secondly interactions of different normal vibrational degrees of freedom. Another complication originates from the possibility of the molecular vibrational motions having a non-zero angular momentum. This causes an interaction between the vibrations and the rotations. The vibration-rotation interaction can be also the result of a real nonrigidity of the molecule.

The idea of the derivation of a convenient expression for the exact vibration-rotation Hamiltonian becomes, in essence, a transformation into new generalized coordinates that would allow the separation of vibrational motion from rotational, at least in the zero-order approximation, according to the above discussions. There are, however, many mathematical fine points (see, for example, Refs. 78, 85 and 86). Three generalized coordinates are to be introduced, describing an orientation of the rotating frame, attaching the equilibrium configuration of the molecule to the laboratory frame. (Those may be Eulerian angles, for example.) The rest ($3N$-6) of the generalized coordinates would correspond to the vibrations. Besides the components $\hat{J}_\alpha$ of the total angular momentum operator, the expression for the exact vibration-rotation Hamiltonian includes also the components $\hat{l}_\alpha$ of the vibrational angular-momentum operator. The latter is introduced according to the following definition[72]:

$$\hat{\mathbf{l}} = \sum_{j}[(\mathbf{r}_j - \mathbf{r}_j^{(0)}) \times \hat{\mathbf{p}}_j], \tag{2.7}$$

where the vectors $\mathbf{r}_j^{(0)}$ and $\mathbf{r}_j$ describe correspondingly the equilibrium and instantaneous positions of a j-th nucleus in the molecule-fixed frame, and $\hat{\mathbf{p}}_j$ is the momentum operator of a j-th nucleus which is also referred to the molecule-fixed frame. The displacement vectors and the momenta of nuclei in the molecule-fixed frame can be expressed in terms of the normal coordinates and the conjugate momenta. In this representation, the operators $\hat{l}_\alpha$ are of bilinear form

$$\hat{l}_\alpha = \sum_{k,l} \zeta_{kl}^{\alpha}\, q_k\, \hat{p}_l, \tag{2.8}$$

where ζ_{kl}^{α} are *Coriolis coupling coefficients* from analogy with Coriolis forces in classical mechanics.

It is also necessary to generalize the inertial moment concept. From classical mechanics one can describe a system of masses in terms of the symmetrical inertia tensor $I_{\alpha\beta}$. It is always possible to transform a matrix $I_{\alpha\beta}$ to the diagonal form corresponding to the principal axes of inertia. In our case [see the discussion following Eq. (2.6)], it is convenient to fix the molecule-fixed frame so that the matrix $I_{\alpha\beta}$ would be diagonal for the equilibrium configuration of a molecule. But, with nuclei perturbed, the components of the matrix $I_{\alpha\beta}$ change and, in particular, its nondiagonal elements can differ from zero. Thus, it is also necessary to introduce the *effective* inertia tensor

$$I'_{\alpha\beta} = I_{\alpha\beta} - \sum_{k,l,m} \zeta_{km}^{\alpha}\, \zeta_{lm}^{\beta}\, q_k\, q_l \tag{2.9}$$

which involves that additional dependence on normal coordinates. The matrix $D_{\alpha\beta}$ will also be needed which is reciprocal to $I'_{\alpha\beta}$, and we denote its determinant as D.

Although these definitions may look cumbersome, they are essential for us to write the vibration-rotation Hamiltonian correctly. However, first it should be remembered that if the dependence of the $D_{\alpha\beta}$ matrix on normal coordinates is neglected, then it just becomes the matrix with diagonal elements which are simply equal to the reciprocal principal moments of inertia corresponding to the equilibrium configuration.

Having accepted the above definitions, we are able now to write out the vibration-rotation Hamiltonian. We shall present it in the Wilson-Howard form[78]

$$\begin{aligned}\hat{H}_{\text{nucl}} = {} & \frac{1}{2} D^{1/4} \sum_{\alpha,\beta} (\hat{J}_\alpha - \hat{l}_\alpha) D_{\alpha\beta} D^{-1/2} (\hat{J}_\beta - \hat{l}_\beta) D^{1/4} \\ & + \frac{1}{2} D^{1/4} \sum_{i=1}^{3N\text{-}6} \hat{p}_i D^{-1/2} \hat{p}_i D^{1/4} + \frac{1}{2} \sum_{i=1}^{3N\text{-}6} \omega_i^2 q_i^2 + V_{\text{anh}}(q_i) \qquad (2.10)\end{aligned}$$

The harmonic terms in the potential energy have been extracted explicitly. Thus, the expansion of $V_{\text{anh}}(q_i)$ by normal coordinates starts, in general, from third-order (or cubic) terms.

Some general features of the Wilson-Howard Hamiltonian will now be listed:

1. If in (2.10) we neglect the terms $V_{\text{anh}}(q_i)$ and $\hat{l}_\alpha$ as well as the dependence of $D_{\alpha\beta}$ on normal coordinates, we get the zero-order approximation (2.6).

2. The deviations of the nuclei from their equilibrium positions being small, one can develop the perturbation theory by expanding the Hamiltonian (2.10) into a series by normal coordinates. Besides the term $V_{\text{anh}}(q_i)$, it is also necessary to expand the elements of the matrix $D_{\alpha\beta}$. In the general case, it is rather difficult to determine the hierarchy of the different anharmonic terms and those vibration-rotation interaction terms (for details, see Refs. 87–89). The most essential corrections to zero-order Hamiltonian (2.6) are usually given by third- and fourth-order anharmonic terms. In molecules which, in principle, may have non-zero diagonal elements of vibrational angular-momentum operator the corrections originated from the terms $\hat{l}_\alpha \hat{l}_\beta$ in Eq. (2.10) are usually smaller than or of the same order of magnitude as the anharmonic corrections. The corrections caused by the terms $\hat{J}_\alpha \hat{l}_\beta$ (so-called Coriolis interaction) are usually smaller than or of the same order as the distances between adjacent rotational levels of a rigid rotator. The accounting for the dependencies $D_{\alpha\beta}(q_i)$ is important for small (but essential for spectroscopy) corrections to rotational energies as well as for some actual effects originated from vibration-rotation interaction of higher orders than Coriolis ones.

3. Hamiltonian (2.10) is invariant under transformations allowed by the point symmetry group of the equilibrium configuration of a molecule. The

vibration-rotation levels of a molecule are, therefore, classified by the irreducible representations of its point symmetry group.*

4. If an approximate calculation shows the degeneracy of a vibration-rotation state to exceed those allowed by the irreducible representations of the molecule point symmetry group, then simply, the neglected terms must be responsible for full or partial splitting.

2.1.4. Rotator and oscillator

Hamiltonian (2.6) provides a zero-order approximation separating the variables in the Schrödinger equation into purely rotational and purely vibrational ones. The operators of angular-momentum components which participate in the rotational part of the Schrödinger equation (a rigid rotator equation) are actually differential operators acting upon the angular variables that orient the molecule-fixed reference frame to the laboratory frame. The explicit form of these operators is given, for example, in Ref. 85. Since the rotational angular momentum is conserved, each level of the rotator can be marked by the value of the rotational quantum number J. Furthermore, rotation levels are degenerated in M, the component of rotational angular momentum along a space-fixed axis, and their degeneracies are equal to $2J + 1$. Qualitatively, energy spectra of rotators are different, depending on the relationships of the principal moments of inertia.

In Section 2.1.2 we cited several molecules (CH_4, OsO_4, SF_6, UF_6) with their equilibrium configurations being highly symmetric (the point symmetry group T_d for CH_4 and OsO_4, and O_h for SF_6 and UF_6). It can easily be seen that all three principal moments of inertia are equal for these molecules. The molecules having equal principal moments of inertia at their equilibrium configurations are referred to as *spherical tops*. The spectra of spherical tops has the form

$$E_J = BJ(J + 1), \tag{2.11}$$

where $B = \hbar^2/2I_\alpha = \hbar^2/2I_\beta = \hbar^2/2I_\gamma$ is the so-called rotational constant. Each state with energy E_J, except the degeneration in M, is additionally degenerated in K, the component of rotational angular momentum along an axis attached to a molecule.

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*Strictly speaking, the point group does not coincide with the total symmetry group of the Wilson-Howard Hamiltonian. As for *quasirigid* molecules, however, this fact is usually unessential for practical applications (for details, see Ref. 80).

Such molecules as CF_3I, CF_3Br (C_{3v} point group), BCl_3 (D_{3h}), CO_2 ($D_{\infty h}$), etc. are referred to as *symmetrical tops*. Two principal moments of inertia are equal for those molecules: $I_\alpha = I_\beta$. In addition to J, energy states of symmetrical tops can be marked by the quantum number K, the component of rotational angular momentum along their symmetry axis. The degeneration in K that takes place in the case of spherical tops is partially removed, however. The spectra of symmetrical tops has the form

$$E_{J,K} = BJ\,(J + 1) + (A - B)\,K^2, \qquad -J \leqslant K \leqslant J, \quad (2.12)$$

where $B = \hbar^2/2I_\alpha$, $A = \hbar^2/2I_\gamma$. Thus the spectra of symmetrical tops must be described in terms of two rotational constants B and A. The difference $(A - B)$ may be positive or negative depending on what inertia moment is smaller, respectively, to the symmetry axis or to the perpendicular one. Correspondingly, with quantum number J fixed, the energy increases or decreases versus $|K|$. Note that states of symmetrical tops with $K \neq 0$ are two-fold degenerate.

Such molecules as H_2O, $C_2H_2Cl_2$, and many others have all three principal moments of inertia different. These molecules are referred to as *asymmetrical tops* and, in this case, one cannot depend on a conservation of a component of rotational angular momentum along any molecular axis. It is generally not possible to write out explicitly the energies of levels. Nevertheless one can give a conventional classification of levels[72] but it will not be required here.

Besides the separation of rotational and vibrational variables, the zero-order Hamiltonian (2.6) allows us to separate the variables relating to different oscillators. This enables us to introduce the concept of *vibrational modes*. As is well known, the solution of the Schrödinger equation for a harmonic oscillator gives an equidistant spectrum of energy eigenvalues

$$E_v = \hbar\omega\left(v + \frac{1}{2}\right), \quad (2.13)$$

and their eigenfunctions can be expressed through Hermite polynomials H_v:

$$\psi_v(q) = \text{Const} \times \exp\left(-\frac{\omega q^2}{2\hbar}\right) H_v\left[\left(\frac{\omega}{\hbar}\right)^{1/2} q\right] \quad (2.14)$$

Thus, considering the vibrational motion of a molecule within the zero-order approximation, one can mark vibrational energy levels by a set of *vibrational quantum numbers* v_i:

$$E_{\text{vib}}(v_1, v_2, \ldots) = \hbar \sum_{i=1}^{3N-6} \omega_i \left(v_i + \frac{1}{2}\right) \tag{2.15}$$

The vibrational wavefunctions corresponding to the energy eigenvalues (2.15) are

$$\psi_{v1,v2,\ldots}(q_1, q_2, \cdots) = \prod_{i=1}^{3N-6} \psi_{v_i}(q_i), \tag{2.16}$$

where $\psi_{v_i}(q_i)$ are given by Eq. (2.14).

If all the vibrational frequencies of a molecule are different, then all its vibrational states (2.15) are nondegenerate. Applying the group representation theory to analysis of molecular vibrations, one can conclude that there are no equal frequencies only in the cases of asymmetrical tops. Since rotational sublevels of asymmetrical tops are nondegenerate too, it follows that any vibration-rotation level is nondegenerate. It should also be noted that asymmetrical tops have diagonal matrix elements of the vibrational angular-momentum operator equal to zero for all levels.

Together with nondegenerate vibrations, symmetrical tops also have one or more two-fold degenerate vibrational frequencies. For example, nine vibrational degrees of freedom of the molecule CF_3I are distributed over three totally symmetric vibrations ν_1, ν_2, ν_3 corresponding to the irreducible representation A_1 of the point symmetry group C_{3v} and three two-fold degenerate vibrations ν_4, ν_5, ν_6 which correspond to the irreducible representation E. In the harmonic approximation, a two-fold degenerate vibration is actually equivalent to the motion of a two-dimensional harmonic oscillator placed on a plane (x, y), its vibrational frequencies being identical along the two directions. A two-dimensional oscillator can be formally treated as two separated one-dimensional ones, and its energy levels and eigenfunctions can be written as

$$E(v_x, v_y) = \hbar\omega (v_x + v_y + 1) \tag{2.17}$$

$$\psi_{v_x, v_y} = \psi_{v_x}(x)\, \psi_{v_y}(y), \tag{2.18}$$

where ψ_{v_x} and ψ_{v_y} are given by Eq. (2.14). Further, it is easy to see that the levels which are attached to some fixed value of the sum $v_x + v_y$ have the same energies. Therefore, it is convenient to use a single quantum number $v = v_x + v_y$ for the notation of the energy levels of a two-fold degenerate vibrational mode. It is not hard to calculate that the vibrational level marked by v has the degeneracy equal to $g_v = v + 1$. Under fixed v, one can also make up arbitrary linear combinations of wavefunctions (2.18), each of them being also a solution of the Schrödinger equation. In the case of a two-dimensional vibrator oscillating in a plane (x, y), one can, in particular, make up such states in which the angular momentum component m_z along the perpendicular axis z is conserved. The quantum number m_z takes the values $m_z = -v, -v + 2, \ldots, v$. For excited states of doubly-degenerate modes of symmetrical tops, the vibrational angular momentum is just an analog of the quantum number m_z.

Thus, in the zero-order approximation, the degeneracies of the vibration-rotation levels of symmetrical tops are obtained in the general case. For example, in the case of the molecule CF_3I, the general expression which gives the degeneracies of the vibration-rotation states marked by the quantum numbers $v_1, \ldots, v_6, J, K$ has the form

$$g(v_i, J, K \neq 0) = 2 \prod_{i=4}^{6} (v_i + 1), \tag{2.19}$$

$$\text{and } g(v_i, J, K = 0) = \prod_{i=4}^{6} (v_i + 1)$$

However, applying the group representation theory to the symmetrical-top vibration-rotation spectra, one can conclude that only nondegenerate and two-fold degenerate levels are permissible. This simply means that the exact corrections to the zero-order Hamiltonian must provide additional splittings in order to agree with the group representation theory. In particular, such corrections are, of course, the anharmonic terms and terms responsible for vibration-rotation interactions.

Spherical tops, parallel with nondegenerate and two-fold degenerate vibrations, obviously possess three-fold degenerate vibrational frequencies, too. For example, in the case of the molecule SF_6 (O_h point symmetry group), one vibrational degree of freedom refers to the totally symmetrical vibrational mode ν_1 (A_{1g}-species), two refer to the two-fold degenerate mode ν_2 (E_g-species), and the remaining twelve are distributed over the three-fold degenerate vibrational modes ν_3 and ν_4 corresponding to the irreducible representation F_{1u}, ν_5 (F_{2g}-species), and ν_6 (F_{2u}-species). In the harmonic approximation, a three-fold degenerate vibration is actually equivalent to a three-dimensional isotropic harmonic oscillator. Its energy levels can be marked by the quantum number $v = v_x + v_y + v_z$, degeneracies being equal to $g_v = (v + 1)(v + 2)/2$. Under fixed v, one can make up the states marked by the additional quantum numbers l and m which are just the vibrational angular momentum and its component along some fixed axis in the rotating frame attached to a molecule. The quantum number l takes the values $l = v, v - 2, \ldots, 1$ or 0, and $m = -l, -l + 1, \ldots, l$.

One can easily obtain the general expression which gives, in the zero-order approximation, the degeneracies of vibration-rotation levels of spherical tops. For example, in the case of the molecule SF_6, the degeneracies of levels marked by the quantum numbers $v_1, \ldots, v_6$, J are

$$g(v_i, J) = \frac{1}{16}(2J + 1)(v_2 + 1) \prod_{i=3}^{6} (v_i + 1)(v_i + 2) \qquad (2.20)$$

However, the maximally degenerated true levels of spherical tops must be three-fold degenerate ones only. Just as in the case of symmetrical tops, the corrections to the zero-order Hamiltonian are responsible for splittings and in the case of spherical tops non-, two-fold and three-fold degenerate levels must be met. It is important to note that diagonal matrix elements of the vibrational-angular-momentum operator can be different from zero only for three-fold degenerate levels.

The physical effects of the corrections to the zero-order Hamiltonian (2.6) are not limited only to the splittings, which are the subject of the next Section, and are of particular interest for the degenerate vibrational modes. The main correction V_{anh} [see Eq. (2.10)] produces the coupling of different modes as well as the shifts of vibrational states, those effects being also of the greatest significance. To illustrate, let us consider the vibrational part of the Hamiltonian (2.10), restricting ourselves, for simplicity, to the case of nondegenerate modes and neglecting the dependencies of $D_{\alpha\beta}$ on normal coordinates:

$$\hat{H}_{\text{vib}} = \frac{1}{2} \sum_{i=1}^{3N-6} (\hat{p}_i^2 + \omega_i^2 q_i^2) + V_{\text{anh}}(q_i) \qquad (2.21)$$

To find the effects arising from the term V_{anh} it is natural to use perturbation theory. This leads to the following basic conclusions:

1. The expansion of the anharmonic part starts from terms which are cubic by normal coordinates. A diagonal matrix element of a cubic term vanishes for every harmonic state. Therefore, in the first-order approximation of perturbation theory, the cubic terms do not give any shifts of vibrational states.

2. State shifts produced by cubic terms in the second-order approximation should be taken into account together with shifts produced by quartic terms in the first-order approximation of the perturbation theory.

3. The main nonvanishing corrections having been calculated, the energies of vibrational states can be written explicitly as

$$E_{\text{vib}}(v_1, v_2, \ldots v_{3N\text{-}6}) = \hbar \sum_{i=1}^{3N\text{-}6} \omega_i \left(v_i + \frac{1}{2}\right) + \hbar \sum_{i=1}^{3N\text{-}6} \sum_{k=1}^{i} x_{ik} \left(v_i + \frac{1}{2}\right)\left(v_k + \frac{1}{2}\right) \tag{2.22}$$

The values x_{ik} are called the *anharmonicity constants*. Ordinarily they are negative. The intramode anharmonicity constants x_{ii} describe the shift increase versus an increase in energy of the i-th vibrational mode itself. The intermode x_{ik} $(i \neq k)$ describes the increase of level shifts within the i-th vibrational mode versus an increase in energy of the k-th vibrational mode.

4. In case of a diatomic molecule having just one vibrational degree of freedom, the *approximate* equation (2.22) comes to

$$E_v = \hbar\omega\left(v + \frac{1}{2}\right) + \hbar x\left(v + \frac{1}{2}\right)^2 \tag{2.23}$$

If one treats Eq. (2.23) as the exact spectrum originating from a certain model potential, he would take the so-called Morse oscillator, the potential energy of which is (see Figure 2.1)

$$U(q) = U_0\,(1 + e^{-2\alpha q} - 2e^{-\alpha q}), \tag{2.24}$$

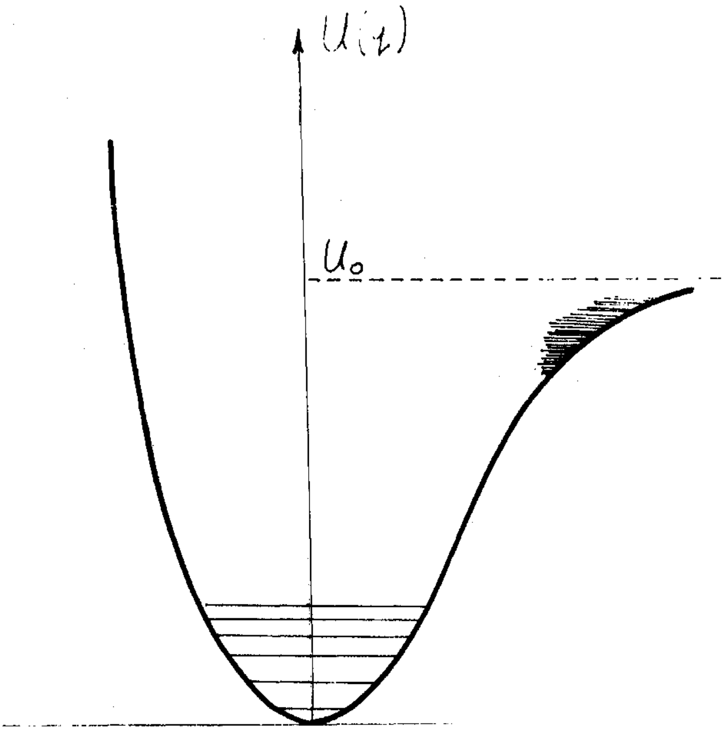

FIGURE 2.1 The model Morse potential.

where the constant values U_0 and α fix the frequency ω and the anharmonicity constant x. The Morse oscillator[90] proves to be a useful model not only for a diatomic molecule. It is also helpful in cases when a single vibrational mode of a polyatomic molecule is involved in excitation.

5. In cases, when two vibrational levels a and b are spaced so closely that the nondiagonal matrix element $\langle a\ |V_{\text{anh}}|\ b\rangle$ is comparable to the distance between them, perturbation theory becomes unvalid, and one can say that *resonance occurs*. The simplest example of resonance can be observed when for some three vibrational frequencies of a molecule the condition $\omega_1 \approx \omega_2 + \omega_3$ is met. In this case, the nondiagonal matrix element of cubic term in V_{anh} which is proportional to $q_1q_2q_3$ differs from zero, calculated for any pair of states $|v_1, v_2, v_3, v_i\rangle$, $|v_1 - 1, v_2 + 1, v_3 + 1, v_i\rangle$. If its value is sufficiently great, the marked pairs of states should be strongly *mixed*. Other examples of resonances are given in Table 2.1.

TABLE 2.1

Three-frequency and four-frequency resonances due to anharmonic interaction

Resonant condition	The lowest-order term in potential energy being responsible for interaction
$\omega_1 \approx \omega_2 + \omega_3$	$q_1q_2q_3$
$\omega_1 \approx 2\omega_2$	$q_1q_2^2$
$\omega_1 + \omega_2 \approx \omega_3 + \omega_4$	$q_1q_2q_3q_4$
$2\omega_1 \approx \omega_2 + \omega_3$	$q_1^2q_2q_3$
$2\omega_1 \approx 2\omega_2$	$q_1^2q_2^2$
$\omega_1 \approx \omega_2 + \omega_3 + \omega_4$	$q_1q_2q_3q_4$
$\omega_1 \approx 3\omega_2$	$q_1q_2^3$

They are called three-frequency and four-frequency *Fermi resonances* depending on the number of vibrational quanta participating in the exchange.

2.1.5. Splittings of vibration-rotation states

As we have mentioned above, accidental degeneracies of vibrational states from the harmonic approximation being applied to two- and three-fold degenerate vibrations are removed due to anharmonicity and the terms $\hat{l}_\alpha \hat{l}_\beta$ in the Hamiltonian (2.10) are responsible for this splitting. This can be illustrated by some specific examples. Let us consider, for example, an isolated three-fold degenerate mode of a spherical-top-type molecule which exhibits the symmetry O_h, such as SF_6 and UF_6. It can be shown that, in this case, cubic terms in V_{anh}-expansion are forbidden by symmetry. Taking quartic terms, including also those which originate from the components of the vibrational-angular-momentum operator, one can make up three independent totally symmetric combinations which may be the following ones:

$$\left(\sum_{i=1}^{3} q_i^2\right)^2, \ \hat{l}^2, \text{ and } q_1^2\, q_2^2 + q_2^2\, q_3^2 + q_3^2\, q_1^2 \qquad (2.25)$$

For description, therefore, three independent anharmonic constants must be introduced which are customarily denoted as X, G, and T, correspondingly. If the three terms (2.25) are treated separately, they are responsible for qualitatively different effects. The first term is responsible for the joint shift of every degenerate state as a whole, just as for levels of a nondegenerate mode. The second term is responsible for the splitting of components which are related to different values of vibrational angular momentum $\hbar l$. Note that these two terms are spherically symmetric. Therefore, the degeneracies $(2l + 1)$ by the component of the vibrational-angular-momentum along an axis attached to a molecule still remain. These degeneracies are partially removed by the third term which exhibits the point symmetry group of a molecule. So, in the general case, all terms (2.25) *having* been involved, vibrational levels are classified by the irreducible representations of the point symmetry group of the molecule.

Within the spherical symmetry approximation, i.e., when $T = 0$, one can write out explicitly a simple expression for vibrational energies of levels of three-fold degenerate mode. The vibrational levels are marked by two quantum numbers v and l $(l = v, v - 2, \ldots, 1 \text{ or } 0)$, and their energies are

$$E_{v,l} = \hbar\omega\left(v + \frac{3}{2}\right) + \hbar X\left(v + \frac{3}{2}\right)^2 + \hbar G l(l + 1) \qquad (2.26)$$

With $T \neq 0$ analytical formulas for vibrational energies are rather cumbersome.[91] A typical diagram of vibrational levels calculated in Ref. 92 for the ν_3-mode of the molecule SF_6 is shown in Figure 2.2.

Other degenerate vibrational states[91] are treated similarly and the conclusion is that, all quartic terms in Hamiltonian (2.10) *having* been involved, *complete* anharmonic splitting occurs (the only degeneracies still remaining are those arising from the *dimensions* of irreducible representations). Figure 2.2 shows the species which mark the components of anharmonic splitting (E-species mark two-fold degenerate levels, and F-species mark three-fold degenerate ones). It should be noted that, in the very general case, species components can be obtained without solving the problem of splitting explicitly. To do so using standard formulas (see for example Ref. 78), one has firstly to find the characters of the representation which correspond to the degenerate state under consideration. If this representation does not appear to coincide with any of irreducible ones (in other words, it is *reducible*) then one should expand it into the sum of irreducible representations and it is just this procedure that gives the species components.

Degenerate vibrational states of symmetric tops are split into non- and two-fold degenerate levels. Within an approximation which treats vibra-

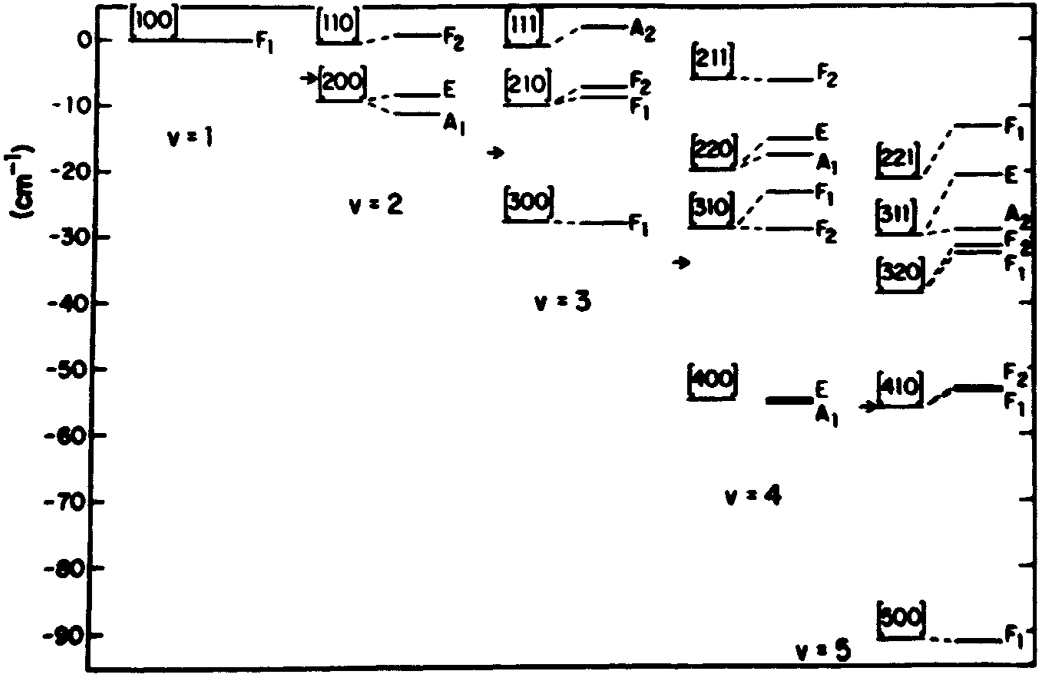

FIGURE 2.2 Diagram of anharmonic-splitting components for ν_3-mode of the molecule SF_6. Splittings of states with vibrational quantum number v from 1 to 5 are shown. Anharmonicity constants are $X = -2.8$ cm^{-1}, $G = 1.34$ cm^{-1}, and $T = 0.44$ cm^{-1}. Small arrows indicate anharmonic positions of levels without splitting, i.e., at $G = T = 0$, and $X = -2.8$ cm^{-1} (from Ref. 92).

tions and rotations separately, there are vibration-rotation states with the degeneracy $g = 4$, in addition to non- and two-fold degenerate levels. The states with $g = 4$ are two-fold degenerated vibrationally and they are also two-fold degenerated by the sign of the component of rotational angular momentum along the symmetry axis of a molecule. The term in the Hamiltonian (2.10) responsible for the partial splitting of such states takes the following form in the rigid-rotator approximation:

$$-2\,[B\hat{\mathbf{J}}\hat{\mathbf{l}} + (A - B)\,\hat{J}_\gamma\,\hat{l}_\gamma] \tag{2.27}$$

Here B and A are the rotational constants defined in Eq. (2.12), and γ denotes the symmetry axis of a molecule. As mentioned in Section 2.1.4, a pair of wavefunctions can be chosen as the basis of a two-fold degenerate vibrational state, which have defined values of the vibrational angular momentum component along the symmetry axis. In other words, referred to this basis, the operator $\hat{l}_\gamma$ is diagonal. From symmetry considerations it is also obvious that two diagonal matrix elements of the operator $\hat{l}_\gamma$ are equal in absolute magnitude, but opposite in sign. Numerical values of diagonal matrix elements l_γ can be expressed through Coriolis coupling coefficients (2.8), and, of course, they vary from level to level. Corrections to energies which are caused by term (2.27) are equal to $2A\,|l_\gamma K|$ in absolute value. The correction sign depends on that of the product $l_\gamma K$. Thus, we obtain two two-fold degenerate levels, corrections to the energy being

$$E^{(\mathrm{Cor})} = \pm 2A\,|l_\gamma K| \tag{2.28}$$

This type of splitting is called the *Coriolis splitting*.

An analogous effect also takes place in the case of three-fold degenerate vibrational levels of spherical tops. The corresponding vibration-rotation states have the degeneracies $g = 3(2J + 1)$. In this case, Coriolis interaction has the form

$$-2B\,\hat{\mathbf{J}}\hat{\mathbf{l}}, \tag{2.29}$$

and it results in splitting into three levels, corrections to the initial energy being

$$E_1^{(\mathrm{Cor})} = -2B\zeta\,(J + 1),\ E_2^{(\mathrm{Cor})} = -2B\zeta,\ E_3^{(\mathrm{Cor})} = 2B\zeta J \tag{2.30}$$

Here the constant ζ, like l_γ for symmetric tops, can be expressed through the Coriolis coupling coefficients (2.8). The value ζ is ordinarily called the *Coriolis constant*. In principle, the Coriolis constant varies from level to level. In fact, the levels are marked by energies (2.30) that correspond to the combinations of wavefunctions which are achieved through subtraction of the vibrational angular momentum $\hat{\mathbf{l}}$ from the total angular momentum $\hat{\mathbf{J}}$: $\hat{\mathbf{R}} = \hat{\mathbf{J}} - \hat{\mathbf{l}}$. The resulting vector $\hat{\mathbf{R}}$ is often called the operator of the *purely rotational angular momentum*. Levels (2.30) are just the eigenstates of the operator $\hat{\mathbf{R}}$, the corresponding quantum numbers R being equal to

$$R_1 = J - 1, \qquad R_2 = J, \qquad R_3 = J + 1 \tag{2.31}$$

The degeneracies of energy levels (2.30) which are simply equal to $(2R + 1)$ will be

$$g_1 = 2J - 1, \quad g_2 = 2J + 1, \quad g_3 = 2J + 3 \tag{2.32}$$

For the levels with $v = 1$ (the so-called *fundamental* vibrational levels) of isolated degenerate vibrational modes, the anharmonic interaction would not provide any splitting. So only the Coriolis interaction can be responsible for any effect. However, for splittings of higher levels, both interactions participate. We have actually been suggesting above that the anharmonic splitting is much stronger than the Coriolis one. This assumption has enabled us to restrict ourselves to the treatment of the Coriolis interaction applied to only slightly (not more than three-fold) degenerate vibrational states. In the general case, when it is necessary to allow for both effects jointly, the calculations are harder. Only in some particular cases can one write an explicit analytical expression for energies of split levels. One typical example can be shown with the case of spherically symmetric anharmonicity ($T = 0$) of three-fold degenerate modes of spherical tops. Here one can advance, involving both interactions simultaneously. The energy levels are marked by the quantum numbers v, l, J, and R, and their energies are

$$E_{v,l,J,R} = E_{v,l} + BJ(J + 1) + B\zeta\,[R(R + 1) - J(J + 1) - l(l + 1)], \tag{2.33}$$

where $E_{v,l}$ is given by Eq. (2.26), l takes the values $l = v, v - 2, \ldots, 1$ or 0, and R takes the values $|J - l| \leq R \leq |J + l|$. Vibration-rotation states (2.33) are $(2R + 1)$-fold degenerated by the component of the purely rotational angular momentum. It may easily be seen that, if $l = 1$, the last term in Eq. (2.33) comes to the Coriolis corrections (2.30). [In Eq. (2.33) ζ means the Coriolis constant of the fundamental vibrational levels, i.e., the state with $v = 1$.]

Consider now one more type of splitting, the so-called *octahedral (tetrahedral) splitting* which refers to molecules possessing the symmetry O_h (T_d). This type of splitting results in effects which are considerably less than those considered above. The octahedral splitting originates, in particular, from the real dependencies of the constants $D_{\alpha\beta}$ of the reciprocal effective inertia tensor on the normal coordinates. It is not difficult to understand the reasons for this splitting. When nuclei deviate from their equilibrium positions, a molecule, generally speaking, becomes asymmetric. Therefore, one can expect that degeneracies in the R-component must disappear. Octahedral splitting effects have been treated in detail[91,93] for the ground vibrational state as well as for the fundamental ones of three-fold degeneracies. It has been shown that, in the ground state, splitting effects are about 2–3 orders less than in the fundamental state. The value of splitting increases considerably versus J but even under high J it is really 1–2 orders smaller than the distance between adjacent rotational sublevels. Components of octahedral (tetrahedral) splitting can be classified using the irreducible representations of the point symmetry group O_h (T_d). Levels that originate from the same R, and referring to the same species are customarily marked by the index n running from higher energy levels to lower ones.

Concluding this Section, we wish to note the following points:

1. R is a good quantum number, if only the main Coriolis term of the vibration-rotation interaction is involved. In other words, taking into account higher orders of the vibration-rotation interaction, one ought to treat R as an approximation.
2. Studies of splittings of vibration-rotation levels are at the frontier of modern molecular spectroscopy. To a considerable extent, they are stimulated by the investigations which will be described below in this series of papers.
3. So far we have said nothing on an effect caused by the *indirect* influence of nuclear spins on vibration-rotation levels (see, for example, Ref. 72). If the nuclei of a molecule possess non-zero spins, one can write

a series of total nuclear spin I-values. Since nuclear spins perturb nuclear motion to a negligible amount, their *direct* influence (the so-called *hyperfine splitting*) on energies of levels is very weak, and really one can treat states which differ by I as *different* modifications of a molecule. However, it can be proved that each modification is allowed by symmetry to occupy only some vibration-rotation species. For example, in the case of spherical tops, an octahedral (tetrahedral) splitting component of a given symmetry species corresponds to a quite definite value of I. It should also be noted that, hyperfine splitting neglected, each vibration-rotation level is additionally degenerate in I-component. This degeneracy $g_I = 2I + 1$ is ordinarily called *nuclear statistical weight.*

4. We believe that inversion splitting of levels, seldom essential for spectroscopy except of a few particular cases, is known to the reader. A classical example, the ammonia molecule, is perfectly presented by Feynmann et al.[94] We will not be coming across this effect in our discussions.

2.2. Spectroscopy of molecular vibration-rotation transitions

2.2.1. Selection rules

Transitions between molecular levels occurring under the action of an external electromagnetic field can be treated dually, both treatments being quite useful. One may start from the problem of *quantization* of a free electromagnetic field,[95,96] the solution of which can be obtained using the expansion of the field into plane waves, a procedure well known from classical electrodynamics. The quantization of electromagnetic field leads to a continuous spectrum of states, each of them being marked by the set of the occupation numbers of *field oscillators*. Using this interpretation, one treats the system *molecule plus field* as a closed one, and a stationary perturbation which describes the molecule-field interaction produces transitions between different states without changes in energy. For example (see Figure 2.3), such transitions may correspond to *emission,* when the molecule goes down from the upper level b to the lower level a, and one photon with the frequency $\omega_{ba} = (E_b - E_a)/\hbar$ is created, or to *absorption,* when the molecule goes up from a to b, and one photon with frequency ω_{ba} is annihilated. It may also be *Stokes Raman scattering,* when the transition $a \rightarrow b$ is accomplished by the annihilation of the ω-photon parallel with the creation of the photon with the smaller frequency $\omega - \omega_{ba}$, as well as *anti-Stokes Raman scattering,* when, unlike the Stokes case, a

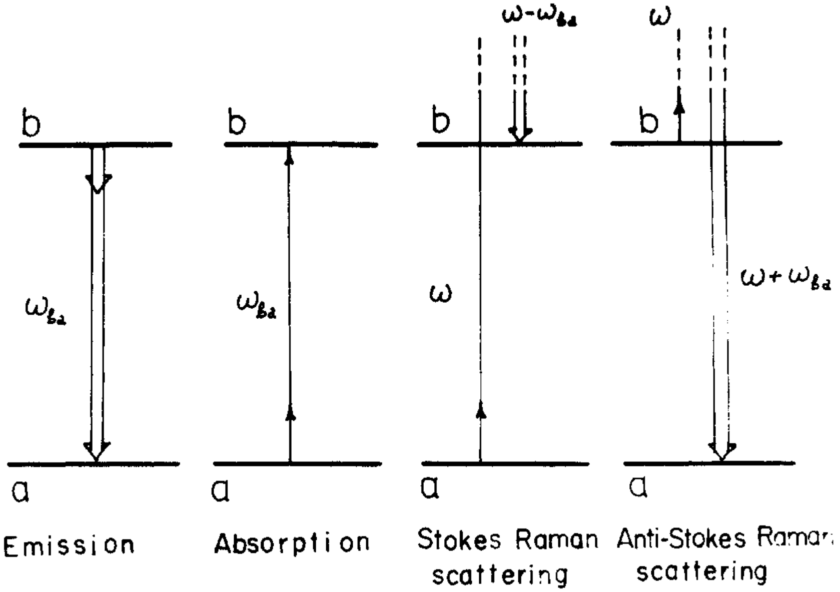

FIGURE 2.3 Processes of emission, absorption, and Raman scattering. Annihilation of photons are shown by single lines, and creation of photons are shown by double lines. Arrows show real transitions occurring between levels.

higher-frequency photon ($\omega + \omega_{ba}$) is created, and the molecule goes down.

Another, so-called *semiclassical,* picture uses the classical formulation where the field is treated as an external source with the amplitude *depending on time* explicitly. In this series of papers we shall restrict ourselves to this treatment. As applied to the processes of absorption and stimulated emission, it is really equivalent to the quantum description, because the field amplitude is usually high enough for the creation or annihilation of a single photon to be neglected. So, let the field be classical and write out the term in the Hamiltonian which describes the molecule-field interaction:

$$\hat{H}_{\text{int}} = -\frac{e}{2mc}\sum_i \hat{\mathbf{P}}_i^{(\text{el})}\,\mathbf{A}(\mathbf{R}_i^{(\text{el})}, t) + \frac{Ze}{2c}\sum_j \frac{\hat{\mathbf{P}}_j^{(\text{nucl})}}{M_j}\,\mathbf{A}(R_j^{(\text{nucl})}, t) \qquad (2.34)$$

Here $\mathbf{A}(\mathbf{R}_i^{(\text{el})})$ is the vector potential at the position of an i-th electron, and $\mathbf{A}(\mathbf{R}_j^{(\text{nucl})})$ is the same for a j-th nucleus. Further we can note that wavelengths in the infrared region, where vibration-rotation transitions lie, are ordinarily four or five orders larger than characteristic molecular dimensions. Thus, it is a good approximation to equate the fields acting on all electrons and nuclei. Neglecting in Eq. (2.34) the dependence of **A** on coordinates within a molecule, one comes to the widely used *dipole approximation*. We do not give here the rather simple transformations which lead to the following final form of the interaction part of the Hamiltonian:

$$\hat{H}_{\text{int}} = -\hat{\boldsymbol{\mu}}\mathbf{E} \tag{2.35}$$

This form fully justifies the name of the used approximation, since the molecule-field interaction is simply reduced to that of the dipole moment $\boldsymbol{\mu}$ of a molecule with the electric component **E** of the field. Within the dipole approximation, a molecule is allowed to emit light at the transition $b \rightarrow a$, or to absorb light at the transition $a \rightarrow b$, only if the transition nondiagonal matrix element of its dipole-moment operator is different from zero, i.e.,

$$\langle b\,|\hat{\boldsymbol{\mu}}|\,a\rangle \neq 0 \tag{2.36}$$

In the case of linearly polarized light (z is the polarization axis), Eq. (2.36) takes the form

$$\langle b\,|\hat{\mu}_z|\,a\rangle \neq 0, \tag{2.37}$$

while for circularly polarized light (x, y are axes of the polarization plane) it comes to

$$\langle b\,|\mu_x \pm i\mu_y|\,a\rangle \neq 0 \tag{2.38}$$

These requirements are called *selection rules* for emission and absorption. The quantum description of electromagnetic field does not change their formulation.

So far we have said almost nothing about the spectrum of field required to produce real transitions. If the field intensity is small, then the field should be *resonant*. In other words, its spectrum must contain the transition frequency ω_{ba}. In the general case, if I_ω is *spectral intensity* of field, the transition probability in a definite time is proportional to $|\mu_{ba}|^2 I_{\omega_{ba}}$. Under rather strong intensities, however, transitions can be produced even by a field with a frequency detuned from the resonance. Of course, in this series of papers we shall very often be interested in various aspects of interaction of molecules with radiation fields, and the *resonance criterion* will soon be absolutely clear for the reader. Here we wish solely to note that the object of the linear molecular spectroscopy which is the subject of this Section is just the examination of resonances. Therefore, weak light sources must ordinarily be used and, of course, the narrower their spectrum the more exact spectroscopic information can be obtained.

Now let us formulate some general points concerning selection rules:

1. In contrast to absorption, Raman scattering does not display sharp resonant properties with respect to the incident radiation frequency. In this case, resonance manifests itself in the difference between frequencies of incident and scattered radiation. Selection rules for Raman scattering involve not the dipole moment but another value which is called the *polarizability tensor*[98] (see Section 2.2.5).

2. Transitions between molecular levels obey rigorous selection rules by the rotational quantum number J. In particular, for absorption and emission, these selection rules are

$$\Delta J = 0, \ \pm 1 \tag{2.39}$$

(besides, the transitions $J = 0 \longrightarrow J = 0$ are rigorously forbidden), and for Raman scattering

$$\Delta J = 0, \ \pm 1, \ \pm 2 \tag{2.40}$$

3. For the most part, the other important selection rules are *approximate*, since they appear as consequences of the specific approximations used for wavefunctions of vibration-rotation levels which have been discussed in above Sections. Naturally, to obtain approximate selection rules the separation of the motion of nuclei into vibrational and rotational parts is a starting point.

4. Further we shall not discuss selection rules by the angular momentum component M along a fixed axis in the laboratory frame. Those rules are universal for any quantum system. In particular, for absorption of linearly polarized light $\Delta M = 0$, where M is the component of the angular momentum along the polarization axis, and for absorption of circularly po-

larized light $\Delta M = \pm 1$, where M is referred to the axis along the direction of wave propagation.

2.2.2. *Infrared molecular spectra within the approximation of a rigid rotator and anharmonic oscillator*

To find selection rules in vibration-rotation IR spectra it is convenient to operate with the dipole-moment components $\hat{\mu}_{\alpha,\beta,\gamma}$ along the axes of the molecule-fixed frame. The dipole-moment components $\hat{\mu}_{x,y,z}$ along the axes of the laboratory frame are related to $\hat{\mu}_{\alpha,\beta,\gamma}$ by equations

$$
\begin{aligned}
\hat{\mu}_x &= \phi_x^\alpha\, \hat{\mu}_\alpha + \phi_x^\beta\, \hat{\mu}_\beta + \phi_x^\gamma\, \hat{\mu}_\gamma \\
\hat{\mu}_y &= \phi_y^\alpha\, \hat{\mu}_\alpha + \phi_y^\beta\, \hat{\mu}_\beta + \phi_y^\gamma\, \hat{\mu}_\gamma \\
\hat{\mu}_z &= \phi_z^\alpha\, \hat{\mu}_\alpha + \phi_z^\beta\, \hat{\mu}_\beta + \phi_z^\gamma\, \mu_\gamma
\end{aligned}
\tag{2.41}
$$

where $\phi_{x,y,z}^{\alpha,\beta,\gamma}$ are the direction cosines. The direction cosines depend on angles which describe the orientation of the molecule-fixed frame relative to the laboratory one, and the components $\hat{\mu}_{\alpha,\beta,\gamma}$ depend on vibrational coordinates. Therefore, if we use the approximation for wavefunctions which shows the separation of vibrational and rotational variables, then a procedure to calculate nondiagonal matrix elements of the dipole-moment operator is just separated into calculation of the matrix elements of the components $\hat{\mu}_{\alpha,\beta,\gamma}$ for purely vibrational transitions, and calculation of those of the direction cosines for purely rotational transitions.

Let us begin with considering the vibrational dipole moment. Using the concept of small vibrations, we write out the vibrational dipole moment as the expansion by the normal coordinates, i.e.,

$$
\boldsymbol{\mu} = \boldsymbol{\mu}_0 + \sum_{i=1}^{3N-6} \left(\frac{\partial \boldsymbol{\mu}}{\partial q_i}\right)_0 q_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 \boldsymbol{\mu}}{\partial q_i\, \partial q_j}\right)_0 q_i\, q_j + \ldots \tag{2.42}
$$

The first term in Eq. (2.42) describes the permanent dipole moment associated with the equilibrium configuration. From general considerations it is rather obvious whether a molecule will possess a nonvanishing permanent dipole moment. The molecules H_2O, NH_3, CF_3I, CF_3Br, etc. are among those. On the contrary, dipole moments of such molecules as CO_2, BCl_3, CH_4, OsO_4, SF_6, UF_6, etc. are equal to zero under their equilibrium configurations. Of course, the permanent part of the dipole moment cannot give nonzero matrix elements between different vibrational states, so it is responsible only for purely rotational spectrum.

The next linear terms in Eq. (2.42) may differ from zero for some particular normal coordinates, and for other normal coordinates vanish. Accordingly, the former vibrations are called *active* in the IR spectrum, and the latter ones are called *inactive*. The problem to be determined, which of the vibrations of a molecule are active, can be solved with the use of the group representation theory, but very often one can conclude by intuition only. For example, in case of the molecule CF_3I, under the totally symmetric vibrations ν_1, ν_2, ν_3 (A_1-species), the component μ_γ along the symmetry axis is changed. Otherwise, under two-fold degenerate vibrations ν_4, ν_5, ν_6 (E-species) the change is to occur in the perpendicular components μ_α and μ_β. Thus, all vibrations of CF_3I are IR-active. The case of the molecule SF_6 is more complicated. It is evident that under the totally symmetric vibration ν_1 (A_{1g}-species), when all the atoms F oscillate synchronously along the bonds S–F, the dipole moment remains to be zero, so the ν_1-mode is IR-inactive. Using the group representation theory, one can show that there are the other IR-inactive vibrational modes $\nu_2(E_g)$, $\nu_5(F_{2g})$, and $\nu_6(F_{2u})$. Only the vibrations ν_3 and ν_4 which belong to F_{1u}-species are IR-active, involving the simultaneous change in all three dipole-moment components.

From only the fact that $(\partial\mu/\partial q_i)_0 \neq 0$ one can't yet say between what specific pairs of vibrational states transitions are allowed. It is necessary that the matrix element of the involved normal coordinate q_i would differ from zero. As is well known, within the harmonic approximation this requirement leads to the following selection rule by the vibrational quantum number:

$$\Delta v_i = \pm 1, \tag{2.43}$$

the explicit dependence on the upper-level index being

$$\langle v_i \,|q_i|\, v_i - 1\rangle = \left(\frac{\hbar v_i}{2\omega_i}\right)^{1/2} \tag{2.44}$$

Within the harmonic approximation, the frequencies of all the transitions (2.43) are equal to ω_i. Anharmonicity of molecular vibrations brings about two effects. Firstly, it is responsible for different frequencies of different transitions. Secondly, the selection rule (2.43) proves to be, strictly speaking, destroyed and it is this second effect which is responsible for the relatively weak *overtones* and *combination bands* in IR spectra that will be discussed in the next Section. Let us turn now to the first effect. It is easy to obtain its consequences from Eq. (2.22) for the energies of anharmonic vibrational states. The transition frequency from the ground state to the fundamental one with $v_i = 1$:

$$\nu_0^{(i)} = \omega_i + 2x_{ii} + \frac{1}{2} \sum_{k \neq i} x_{ik} \tag{2.45}$$

$\nu_0^{(i)}$ is called the *fundamental frequency* of the band. Let the lower state to be excited, within the vibrational mode under consideration, be v_i. Then the frequency of the transition $v_i \rightarrow v_i + 1$ is

$$\nu_{v_i}^{(i)} = \nu_0^{(i)} + 2x_{ii}\, v_i \tag{2.46}$$

It can easily be seen that the frequencies (2.46) make up an arithmetic progression, and, since the anharmonicity constant x_{ii} is usually negative, the progression must decrease. Frequency shifts of transitions appear due to excitation of other modes, too. Let, for example, the i-th mode be not excited and another j-th mode be excited. Then the frequency of the transition $|v_i = 0, v_j\rangle \rightarrow |v_i = 1, v_j\rangle$ will be

$$\nu_{0,v_j}^{(i)} = \nu_0^{(i)} + x_{ij}\, v_j \tag{2.47}$$

At room temperature the lower vibrational levels of molecules have, as a rule, rather appreciable populations. Therefore, transitions from these levels can show up in IR absorption spectra as the so-called *hot bands* shifted to the long-wave spectral region with respect to the fundamental band.

We now discuss the rotational structure of vibrational bands. Under room temperature this structure is always observed in IR absorption spectra, since rotational motion is sufficiently excited. The presence of a few branches is the very feature common to vibration-rotation transitions of molecules. In the general case, there should at least be three branches in the spectrum of a vibrational band in accordance with the general selection rule (2.39). These are the *P-branch* which corresponds to a change in the rotational quantum number $\Delta J = -1$ with the vibrational excitation, the *Q-branch,* where J does not change, and the *R-branch* with $\Delta J = +1$. Within the rigid-rotator approximation, there can be no change in the rotational energy of a molecule, when a transition occurs in the *Q*-branch. One might expect transitions for different unchanged *J* to degenerate into a single line in the absorption spectrum. However, this is not actually observed. As can be seen from Figure 2.4, where the shape of the ν_3-mode absorption band of the molecule SF_6 is shown, the *Q*-branch is broadened to some extent. The point is that, because of its real nonrigidity, a molecule distends slightly in the vibrationally excited state equivalent to a slight increase of inertia moments. So, vibration-rotation transitions, *J* unchanged, are associated with a slight decrease of the rotational energy. If, in the case of spherical tops for example, we denote the rotational constant in the ground state as

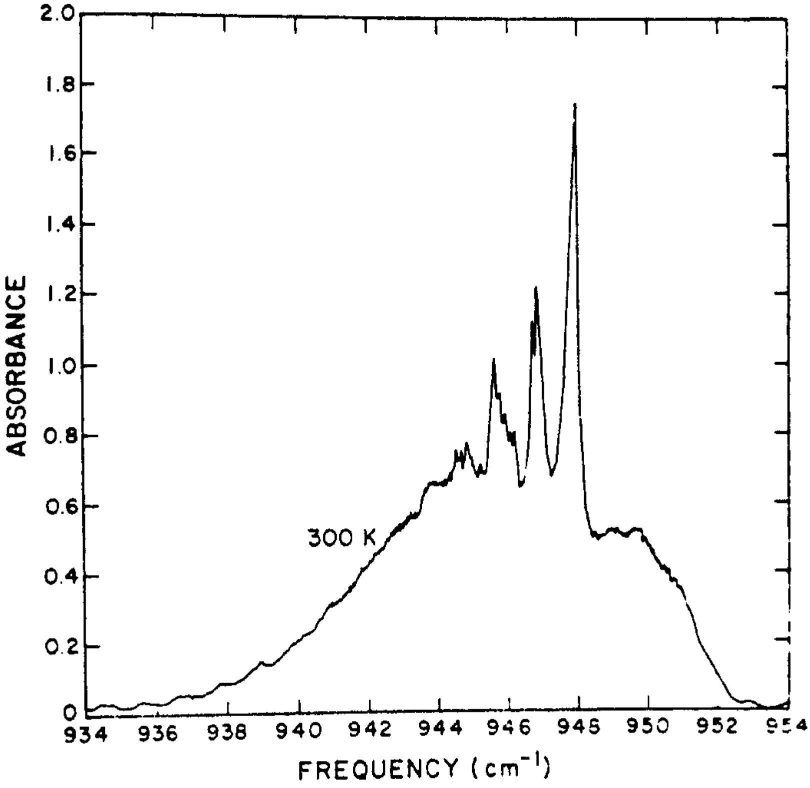

FIGURE 2.4 The spectra of the ν_3-band of SF_6. In addition to *P*-, *Q*-, and *R*-branches of the fundamental band, *Q*-branches of above-mentioned hot bands are also seen.

B_0, and in the fundamental vibrational state as B_1, then we find the following frequencies of transitions in the Q-branch:

$$\nu\,(v_i = 0, J \rightarrow v_i = 1, J) = \nu_0^{(i)} - (B_0 - B_1)\,J(J+1) \qquad (2.48)$$

In the P- and R-branches the nonrigidity of a molecule shows up only as rather small corrections to the frequencies of different separated lines. For the P-, and R-branches we shall use the rigid-rotator approximation, suggesting $B_0 \approx B_1 = B$.

The additional rotational selection rules and, accordingly, the rotational structure of vibrational bands are dictated by the symmetry features of the molecule itself as well as the vibration of interest. The rotational structure in the spectra of asymmetrical tops is so complex that we refer the interested reader to Herzberg[77] who has treated all these cases extensively. As for us, we shall restrict ourselves to listing the basic results which hold for fundamental absorption bands of spherical and symmetrical tops.

1. In the case of spherical tops, within the rigid-rotator approximation, the transition frequencies in the P- and R-branches are

$$\begin{aligned} \nu\,(v_i = 0, J \rightarrow v_i = 1, J-1) &= \nu_0^{(i)} - 2BJ && (P\text{-branch}) \\ \nu\,(v_i = 0, J \rightarrow v_i = 1, J+1) &= \nu_0^{(i)} + 2B\,(J+1) && (R\text{-branch}) \end{aligned} \qquad (2.49)$$

Thus, the transition frequencies make up an arithmetic progression, the distance between adjacent lines being equal to $2B$. The inclusion of the Coriolis interaction forces one to substitute B for the effective rotational constant $B_{\text{eff}} = B(1 - \zeta)$ in Eqs. (2.49). In Section 2.2.4 we shall turn to a more detailed discussion of the Coriolis splitting.

2. In addition to the selection rule (2.39), transitions in the bands of symmetrical tops which originate from nondegenerate vibrational modes (the so-called *parallel* bands) follow the selection rule by the angular-momentum component along the symmetry axis of the molecule

$$\Delta K = 0 \qquad (2.50)$$

So, the lines in the P- and R-branches with the same J but different K would coincide in frequency. However, just like the Q-branch, these lines split due to the nonrigidity of the molecule, and we have

$$\begin{aligned}
\nu\,(v_i = 0, J, K \rightarrow v_i = 1, J - 1, K) &\approx \nu_0^{(i)} - 2BJ - [(A_0 - A_1) \\
&\quad - (B_0 - B_1)]K^2 \ (P\text{-branch}) \\
\nu\,(v_i = 0, J, K \rightarrow v_i = 1, J, K) &= \nu_0^{(i)} - (B_0 - B_1)\,J(J + 1) \\
&\quad - [(A_0 - A_1) \\
&\quad - (B_0 - B_1)]K^2 \ (Q\text{-branch}) \\
\nu\,(v_i = 0, J, K \rightarrow v_i = 1, J + 1, K) &\approx \nu_0^{(i)} + 2B\,(J + 1) \\
&\quad - [(A_0 - A_1) \\
&\quad - (B_0 - B_1)]K^2 \ (R\text{-branch})
\end{aligned} \tag{2.51}$$

3. Transitions in the bands of symmetrical tops that originate from twofold degenerate vibrational modes (the so-called *perpendicular* bands) follow the selection rule

$$\Delta K = \pm 1 \tag{2.52}$$

by the quantum number K. Therefore, six branches are observed, the frequencies of which are given in Table 2.2.

4. So far we have been discussing only the selection rules. However, they are not informative about the intensities of different vibrational bands or of different rotational lines in the bands. The line intensity is predominantly proportional to the squared *vibrational dipole moment;* the definition of this in the case of a degenerate mode is the summation over the degeneracy index *m:*

$$\mu_i^2 = \frac{\hbar}{2\omega_i} \sum_{m\,=\,1}^{1,2,3} \left| \left(\frac{\partial \mu}{\partial q_{im}} \right)_0 \right|^2 \tag{2.53}$$

The value μ_i^2 gives the integrated intensity of the vibrational band. The intensities of different allowed vibrational bands may differ greatly. For example, as noted above, all six vibrational bands of the molecule CF_3I are not forbidden by symmetry considerations and the bands ν_1 and ν_4 are much stronger than the other ones. The integrated intensity of a band is distributed among many rotational lines, the intensity of each individual transition being proportional to the product $f_{JK}\mu_{i,JK}^2$, where f_{JK} is the relative

TABLE 2.2

Frequencies of transitions in different branches of perpendicular bands of symmetric tops

Branch	Changing in rotational quantum numbers	Transition frequencies*
^{P}P-branch	$\Delta J = -1, \quad \Delta K = -1$	$\nu_0^{(i)} - 2BJ - (A - B)(2K - 1)$
^{R}P-branch	$\Delta J = -1, \quad \Delta K = +1$	$\nu_0^{(i)} - 2BJ + (A - B)(2K + 1)$
^{P}Q-branch	$\Delta J = 0, \quad \Delta K = -1$	$\nu_0^{(i)} - (B_0 - B_1)J(J + 1) - (A - B)(2K - 1)$
^{R}Q-branch	$\Delta J = 0, \quad \Delta K = +1$	$\nu_0^{(i)} - (B_0 - B_1)J(J + 1) + (A - B)(2K + 1)$
^{P}R-branch	$\Delta J = +1, \quad \Delta K = -1$	$\nu_0^{(i)} + 2B(J + 1) - (A - B)(2K - 1)$
^{R}R-branch	$\Delta J = +1, \quad \Delta K = +1$	$\nu_0^{(i)} + 2B(J + 1) + (A - B)(2K + 1)$

*The difference between rotational constants for the ground and fundamental vibrational states is taken into account only in cases of ^{P}Q - and ^{R}Q - branches.

population of the rotational sublevel marked by the quantum numbers J and K, and $\mu_{i,JK}$ involves the rotational dipole moment for the transition from this sublevel. The values $\mu_{i,JK}$ depend not only on the lower sublevel but also on the branch from where the transition occurs, and they are related to the vibrational dipole moment by the so-called *Hönl-London factors* A_{JK}:

$$\mu_{i,JK}^2 = A_{JK}\,\mu_i^2 \tag{2.54}$$

One can find the Hönl-London factors from the general expressions for the matrix elements of the vector components.[72] They are tabulated for transitions in the various branches of the bands of symmetrical tops in Table 2.3.

5. The Hönl-London factors obey two important sum rules. The first one refers to the P-, Q-, or R-branch taken individually, and averages over all values of K allowed by the given J. It is apparent that

$$\begin{aligned}
\langle A_J\rangle &= \frac{1}{2J+1}\sum_{K=-J}^{J} A_{JK} = \frac{2J-1}{2J+1} && (P\text{-branch})\\
\langle A_J\rangle &= 1 && (Q\text{-branch})\\
\langle A_J\rangle &= \frac{2J+3}{2J+1} && (R\text{-branch})
\end{aligned} \tag{2.55}$$

TABLE 2.3

Factors A_{JK} for symmetric tops

Band	Branch	A_{JK}
Parallel band	P-branch	$(J^2 - K^2)/J(2J + 1)$
	Q-branch	$K^2/J(J + 1)$
	R-branch	$[(J + 1)^2 - K^2]/(J + 1)(2J + 1)$
Perpendicular band	^PP-branch	$(J + K - 1)(J + K)/4J(2J + 1)$
	^RP-branch	$(J - K)(J - K - 1)/4J\ 2J + 1)$
	^PQ-branch	$(J - K + 1)(J + K)/4J(J + 1)$
	^RQ-branch	$(J - K)(J + K + 1)/4J(J + 1)$
	^PR-branch	$(J - K + 2)(J - K + 1)/4(J + 1)(2J + 1)$
	^RR-branch	$(J + K + 1)(J + K + 2)/4(J + 1)(2J + 1)$

These equations also show the distribution of intensities in the vibration-rotation spectra of spherical tops. In the case of a rigid spherical rotator all lines marked by a fixed J coincide within the fixed branch and the intensity of a degenerate line is given by the factor $\langle A_J \rangle$. It can easily be seen that the factor $\langle A_J \rangle$ is just equal to the ratio of the degeneracy of the upper level participating in the transition to the degeneracy of the lower one.

6. The second sum rule refers to any J,K-level. If we sum the Hönl-London factors for transitions from this level over all possible branches, we shall find for both the parallel and perpendicular bands that

$$\sum_{\text{all branches}} A_{JK} = 1, \text{ or } \sum_{\text{all branches}} \mu_{i,JK}^2 = \mu_i^2 \tag{2.56}$$

This rule implies that the integrated intensity of the vibrational band *does not depend* on the *rotational distribution* of the molecules. It should be noted that this feature, to a good approximation, is applied to any arbitrary *vibrational distribution,* too. Of course, the *shape* of the absorption band *depends* on distribution. We shall return to a more detailed discussion of this point.

2.2.3. *Overtones and combination bands*

As mentioned above, the vibrational selection rule (2.43) is approximate and just a specific property of the harmonic-oscillator wavefunctions. Nevertheless, it forms an essential part of vibration-rotation spectroscopy. Anharmonic corrections are ordinarily so small that the transition bands with total changes greater than unity of the vibrational quantum numbers are considerably weaker than the allowed fundamental ones.

Let us consider the transitions between levels of an isolated vibrational mode. The transitions from the ground state into excited ones with v more than unity are called *overtones*. The transition $v = 0 \rightarrow v = 2$, for example, is called the first overtone, $v = 0 \rightarrow v = 3$ is called the second overtone, etc. Using the perturbation theory, one can develop a procedure to find dipole moments of overtone transitions. In general, for anharmonic corrections, the *true* wavefunctions $\psi_{\text{true}}^{(v)}$ can be presented as superpositions of the harmonic wavefunctions ψ_v (2.14):

$$\psi_{\text{true}}^{(v)} = \sum_{k=0}^{\infty} c_k^{(v)} \psi_k(q) \tag{2.57}$$

Then, for the transition $v = 0 \longrightarrow v = n$, the nondiagonal matrix element of the dipole-moment operator is given, according to Eq. (2.44), by

$$\langle \psi_{\text{true}}^{(v)} | \hat{\mu} | \psi_{\text{true}}^{(0)} \rangle = \mu_{\text{vib}} \left(\sum_{k=1}^{\infty} k^{1/2} c_{k-1}^{(0)} c_{k}^{(v)} + \sum_{k=1}^{\infty} k^{1/2} c_{k-1}^{(v)} c_{k}^{(0)} \right) \qquad (2.58)$$

If we limit ourselves to the first order perturbation theory, we have

$$c_{v}^{(v)} \approx 1, \quad c_{k}^{(v)} \approx \frac{\langle v | V_{\text{anh}} | k \rangle}{\hbar \omega_{kv}} \text{ for } k \neq v \qquad (2.59)$$

Writing out the term V_{anh} as a power-series expansion by the normal coordinates, one can easily conclude that the first overtone, for example, can be allowed due to cubic anharmonicity. The second overtone in the first order of the perturbation theory is allowed due to quartic anharmonicity, but, in the general case, it is also necessary to take into account the second-order corrections of the perturbation theory which arise from the cubic term, and so on. Also, it can be shown that the cubic term vanishes because of the symmetry of a molecule. For example, in the case of the IR-active modes of molecules possessing a center of symmetry, anharmonic interaction cannot activate the first overtone at all.

It often appears that the intensities of some overtones are much higher than that calculated from Eq. (2.58). In such a case, the true wavefunction $\psi_{\text{true}}^{(v)}$ of the upper vibrational state takes a contribution from the wavefunction $\psi_1(q_i)$ of the fundamental state of another IR-active vibrational mode, with this contribution being responsible for the added dipole-moment value. Let us consider, as an example, the overtone $0 \longrightarrow v_5 = 2 (2\nu_5)$ of the molecule CF_3I (see Figure 2.5a). The harmonic position of the level is only 5 cm^{-1} higher than that of the nearby fundamental level with $v_1 = 1$. This separation proves to exceed only slightly the nondiagonal matrix element $\langle v_1 | V_{\text{anh}} | 2\nu_5 \rangle$ of anharmonic interaction and the band $2\nu_5$ is strong enough for the *R*-branch of the band ν_1 to be rather distinctly distorted.

The mechanism of developing the *combination bands* in IR spectra is, in essence, identical. We give, as an example, the band $\nu_2 + \nu_6$ of the molecule SF_6 (see Figure 2.5b). The level of the molecule SF_6 where both vibrations being excited with $v_2 = 1$ and $v_6 = 1$ lies about 40 cm^{-1} higher than the fundamental ($v_3 = 1$) level of the mode ν_3. The cubic term in V_{anh}-expansion which couples these three modes causes the ν_3-wavefunc-

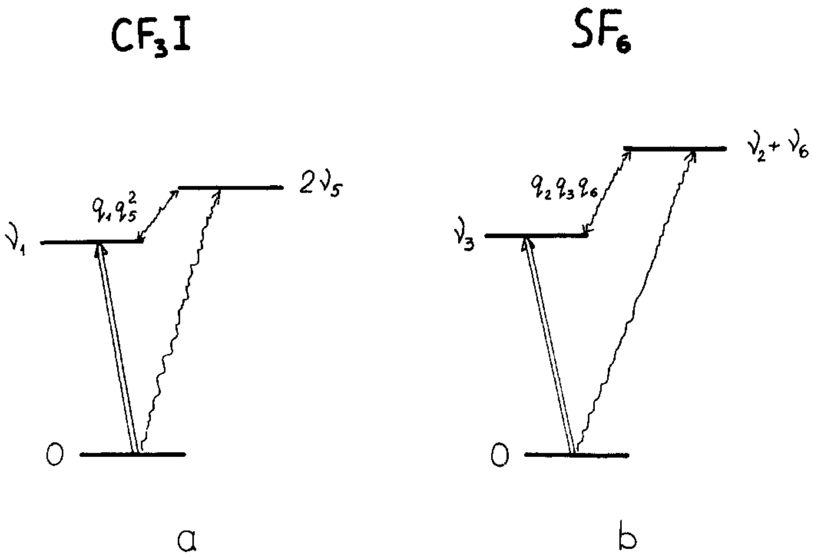

FIGURE 2.5 Mechanisms for the activation of overtones and combination bands due to intermode anharmonicity. Double lines show transitions which are allowed within the harmonic approximation.

tion to give a small contribution to the true wavefunction of the state $\nu_2 + \nu_6$. As a result, the band $\nu_2 + \nu_6$ is present in the IR spectrum. Its intensity is, however, about two orders smaller than that of the band ν_3.

In the preceding section we have pointed out that, using the group representation theory, one can conclude what molecular vibrations are IR-active. These same considerations may also be applied to overtones and combination bands. For example, the molecule SF_6 exhibits only species F_{1u} to be IR-active, if an initial state is the ground one. The problem is to judge whether the species F_{1u} enters into the full representation of a combination vibrational state. The full representation of the state $\nu_2 + \nu_6$ which is reducible is expanded into the following sum: $F_{1u} + F_{2u}$. Thus, this state is to be IR-active. In contrast, the reducible representation of the state $\nu_4 + \nu_6$ is expanded into the sum $A_{2g} + E_g + F_{1g} + F_{2g}$ where the species F_{1u} does not appear, and, even though this is separated from ν_3 only by 14 cm^{-1}, the anharmonic interaction is unable to allow it to be observed in the IR spectrum. It is also easy to show that the first overtone of the mode ν_3 is IR-inactive. This is a particular case of the above-mentioned rule for molecules possessing a center of symmetry.

The following notes complement the discussion of overtones and combination bands:

1. In literature one may often see designations of transitions—for example, $\nu_i + \nu_j - \nu_k$—which are conventionally called *difference bands*. One should keep in mind that this is just a notation which is interpreted as the transition $|v_i = 0, v_j = 0, v_k = 1\rangle \rightarrow |v_i = 1, v_j = 1, v_k = 0\rangle$. Thus, difference bands are always *hot bands*.

2. Since difference-band transitions involve two excited levels, to judge whether the transition is allowed it is not sufficient to know only the selection rules for transitions from the ground state. Some additional selection rules are needed, and, for example, for the molecules belonging to the point group O_h (SF_6, UF_6) those between arbitrary vibrational states are

$$F_1 \leftrightarrow A_1, E, F_1, F_2;\ F_2 \leftrightarrow A_2, E, F_2;\ \text{and also } u \leftrightarrow g \qquad (2.60)$$

From such selection rules which are specific for different point symmetry groups and from species-expansions of the participating states, one can conclude whether or not the anharmonic interaction will activate the transition of interest.

3. Not only the anharmonic interaction, but also the terms which are higher-order with respect to the linear ones in the dipole-moment expansion (2.42) by the normal coordinates can be responsible for overtones and combination bands. This kind of anharmonicity, which Herzberg[77] has named *electric*, does not affect the general symmetry selection rules, but, strictly speaking, it should be invoked along with V_{anh} when numerical estimates of band intensities are made.

2.2.4. *Structure in vibration-rotation spectra of degenerate modes*

In Section 2.1.5 we discussed splittings of vibration-rotation levels of degenerate modes due to the effects of anharmonicity and vibration-rotation interaction. In the structure of fundamental bands only vibration-rotation interaction will show up, however, since anharmonicity does not affect the degeneracy of a vibrational state with $v = 1$. The dominating term among those in the Hamiltonian that couple rotations and vibrations is the Coriolis interaction. It splits the vibration-rotation levels with $v = 1$ and the total angular momentum J into three levels marked by the quantum numbers $R = J - 1, J, J + 1$ [see (2.31)], the energies given by Eqs.

(2.30). Looking at only the general selection rule (2.39) by the total angular momentum, one would believe nine transitions from the level $|v = 0, J_J\rangle$ to be possible. If the other terms that also couple rotations and vibrations but differ from the Coriolis one are neglected, then the following additional selection rule can be derived:

$$\Delta R = 0 \tag{2.61}$$

This selection rule allows for only three transitions

$$\begin{aligned} |v = 0, J_J\rangle &\rightarrow |v = 1, (J - 1)_J\rangle \ (P\text{-branch}) \\ |v = 0, J_J\rangle &\rightarrow |v = 1, J_J\rangle \qquad\quad (Q\text{-branch}) \\ |v = 0, J_J\rangle &\rightarrow |v = 1, (J + 1)_J\rangle \ (R\text{-branch}) \end{aligned} \tag{2.62}$$

Their frequencies appear to be in coincidence with Eqs. (2.48, 2.49), if one includes the small additional constant term $-2B\zeta$ into the fundamental frequency value and substitutes B for $B_{\text{eff}} = B(1 - \zeta)$ in Eqs. (2.49) [see also the discussion following Eqs. (2.49)].

The selection rule (2.61) is not rigorous. Hecht[99] noted this point when he interpreted the structure of the ν_3-mode spectrum of the molecule CH_4 measured in Ref. 100. There had been observed weak transitions in this spectrum, and it had been possible to explain some of them as those with $\Delta R \neq 0$. The mechanism which activates transitions with $\Delta R \neq 0$ is caused by vibration-rotation interaction of higher orders, as it has been recently shown in Ref. 101.

Since lines with $\Delta R \neq 0$ are weak, it follows that the vibration-rotation interaction does not lead, for rough observations, to complication of the structure of the fundamental IR absorption bands. A finer structure than the rotational one appears only in high-resolution spectra. Its presence is caused by octahedral (tetrahedral) splitting (see Section 2.1.5). An example is given in Figure 2.6[102] where the narrow portion in the P-branch of the ν_3-band of the molecule SF_6 is shown. To understand the designations of lines in this figure, we should be reminded (see Section 2.1.5) that the higher-order vibration-rotation interaction removes the degeneracy in the R-component. Each splitting component is described, in our case, in terms of the irreducible representations of the point group O_h. Transitions between components of the lower and upper vibration-rotation states obey symmetry selection rules. These selection rules may seem somewhat unusual to a

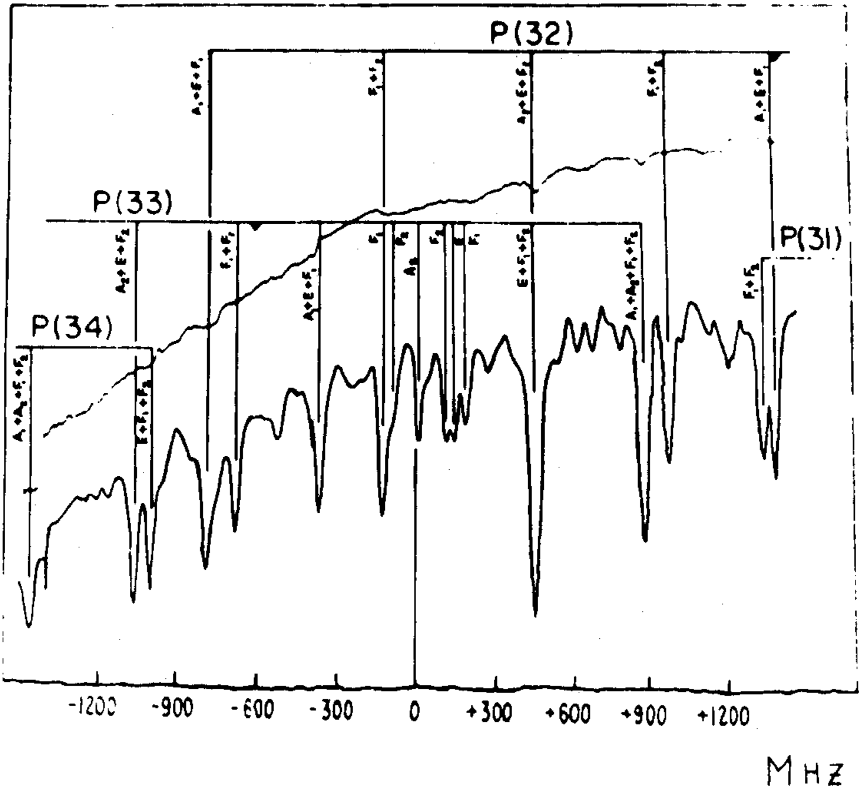

FIGURE 2.6 A small region of a high-resolution absorption spectrum of the ν_3-band of SF_6 (from Ref. 102).

reader who is accustomed to the selection rules from *vibrational* symmetry derived in terms of the dipole-moment-operator matrix elements with respect to the molecule-fixed frame. We should, however, bear in mind that the rotations and vibrations are not yet separated and we must use the dipole-moment operator as it is written out explicitly by Eq. (2.41), i.e., with respect to the laboratory frame. In these terms, the symmetry selection rule takes the form

$$\Delta C = 0 \tag{2.63}$$

where C denotes conventionally the species of involved *vibration-rotation* levels. Thus, under transition, the splitting component retains its symmetry.

Therefore, each line can be classified by symmetry species of both the lower and upper levels, and they are just these designations that are shown in Figure 2.6. It can also be seen from the figure that every J exhibits several lines referring to each individual species. To distinguish between them one can introduce the additional mark n running in parallel within both the upper and lower manifolds, for example, from their tops. Then the additional selection rule (see Ref. 93)

$$\Delta n = 0 \tag{2.64}$$

proves to hold. This selection rule is *nonrigorous*. However, it should be noted that transitions with $\Delta n \neq 0$ are probably very weak, and so far they have not been identified in spectra; there are also no theoretical speculations as yet in the literature about any rule-violation mechanism.

Let us turn now to a discussion of the role of anharmonic splitting. This implies splittings of transitions between excited states of a degenerate mode. General symmetry selection rules for transitions between components of anharmonic splitting can be obtained with the use of the representation theory. In the case of the point group O_h, for example, the transitions are possible in accordance with (2.60). We have shown in Figure 2.2 a diagram of the anharmonic-splitting components calculated for the ν_3-mode of the molecule SF_6. Allowed transitions with $\Delta v = 1$ are shown in Figure 2.7.

Anharmonic splitting is also responsible for large-scale structure in overtones of degenerate modes. For example, the second-overtone $2\nu_3$-band of the molecule SF_6 should split into two components F_{1u}, each exhibiting its own rotational structure. Such structure has been observed,[103] and its origin has been referred to by the authors as anharmonic splitting.

We have treated principal effects of splittings of different types on IR spectra. Furthermore, we would like to discuss briefly some more specific points:

1. Within the model of spherically symmetric anharmonicity [i.e., when the energy levels are given by Eq. (2.33)], the vibrational angular momentum is conserved, and the following selection rule holds

$$|\Delta l| = 1, \tag{2.65}$$

in addition to the selection rules (2.39) and (2.61). Dipole moments of transitions have been calculated for this case in Ref. 104.

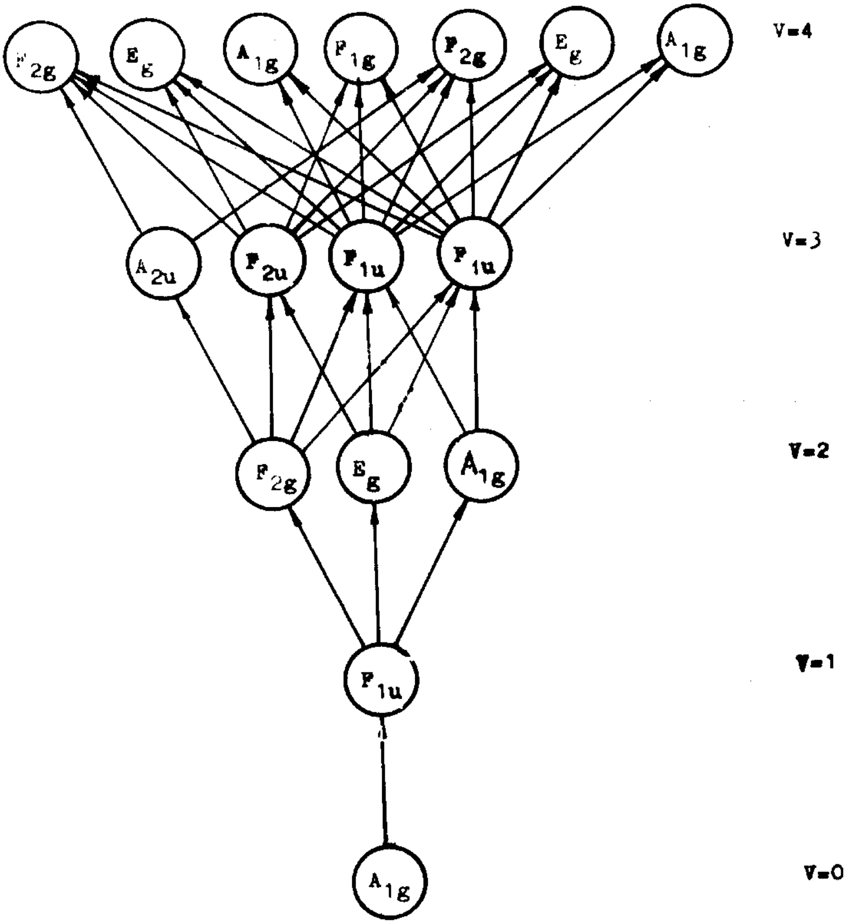

FIGURE 2.7 Selection rules for dipole transitions between anharmonic-splitting components (to the diagram of levels presented in Figure 2.2).

2. The octahedral structure shows an interesting feature. It may be seen from Figure 2.6 that some lines are grouped in clusters. This observation agrees rather well with theoretical predictions.[105]

3. Fixing J as well as a rotational branch, one may find transition dipole moments of all octahedral components to be equal. Actually, however, high-resolution spectra show interchange of intensities of lines of different

species. This is due to the fact that total nuclear spins can differ and, therefore, *nuclear statistical weights* are different, too (see also the discussion in Section 2.1.5).

4. Insight into the structure of vibration-rotation spectra of degenerate modes has become an urgent problem in view of the experiments on multiple photon excitation of molecules which are the main subject of this series of papers. Many theoretical studies of the process of MP excitation focus on this structure, among other points.

2.2.5. *Spectra of Raman scattering*

So far we have principally discussed IR absorption spectra of molecules, but Raman scattering is also a powerful tool of molecular spectroscopy. The process of Raman scattering (RS) is the effect when light with an arbitrary frequency ω (usually in the visible range) falls on the sample, and scattered light is observed at frequencies $\omega \pm \omega_i$ shifted by the value of the normal-vibration frequency. Scattering of photons is followed by some real transition between vibration-rotation levels, and one must distinguish (return to Figure 2.3) between Stokes scattering at the frequency $\omega - \omega_i$ and anti-Stokes scattering at $\omega + \omega_i$, depending on whether the molecular energy increases or decreases. To observe anti-Stokes scattering one must be sure, of course, that there are vibrationally excited molecules in the gas. Furthermore, it should be clear that ω_i denotes the collection of frequencies of all allowed transitions from populated levels.

A successful treatment of RS includes the procedure of quantization of electromagnetic field. Since there are two photons which participate in an elementary act of RS, the process is described in terms of the second order perturbation theory.[96] As mentioned in Section 2.2.1, nondiagonal matrix elements of the operator of the symmetrical polarizability tensors £ are responsible for Raman transitions. The components of this tensor define the dipole vector **P** induced by the electric part **E** of an external electromagnetic field, according to

$$\begin{aligned} P_x &= \pounds_{xx}E_x + \pounds_{xy}E_y + \pounds_{xz}E_z \\ P_y &= \pounds_{yx}E_x + \pounds_{yy}E_y + \pounds y_z E_z \\ P_z &= \pounds_{zx}E_x + \pounds_{zy}E_y + \pounds_{zz}E_z \end{aligned} \tag{2.66}$$

To allow for a Raman transition £-components (at least one) should give non-vanishing matrix elements.

As in finding the elementary dipole-moment selection rules for IR transitions, it is convenient to operate with the polarizability tensor components along the axes of the molecule-fixed frame. In the same manner, as in the dipole-moment case, separation of rotation and vibration being assumed, the vibrational polarization-tensor part may be expanded into a series by the normal coordinates, i.e.,

$$£_{jk} = (£_{jk})_0 + \sum_{i=1}^{3N-6} \left(\frac{\partial £_{jk}}{\partial q_i}\right)_0 q_i + \ldots \tag{2.67}$$

Since the first permanent term cannot give nonzero matrix elements between different vibrational states, it is responsible for *purely rotational* RS as well as for *Rayleigh scattering* which is purely elastic and not followed by any transition at all. For vibrational transitions, RS is described by the linear terms in expansion (2.67), and, as in the case of IR transitions, use of the harmonic approximation implies that only transitions of unity vibrational quantum number change [see Eq. (2.43)] can occur.

The theory of RS is treated, in detail, in many books (see, for example, Refs. 77–79 and 106). We shall restrict ourselves to some general remarks:

1. To be RS-active a vibrational mode should meet the requirement that at least one of the polarizability-tensor components changes due to vibration. The problem of determining the vibrational species which are RS-active can be solved using the group representation theory.

2. In cases of molecules which possess a center of symmetry, the *alternative forbidding rule* is valid, according to which IR-active modes are RS-inactive, and vice versa. For example, in the case of the molecule SF_6, there are three RS-active modes [$\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(F_{zg})$] which are IR-inactive. This rule, however, does not mean that the every vibrational mode is active either in the IR spectrum or in RS. For example, both IR and Raman transitions are forbidden for the fundamental band of the mode $\nu_6(F_{zu})$ of the molecule SF_6.

3. One empirical rule may often be used, being applied to those molecules which do not possess a center of symmetry. According to this rule, strong IR fundamental bands show up weakly in RS spectrum, and vice versa. In the case of the molecule CF_3I, for example, bands $\nu_2(A_1)$ and $\nu_5(E)$ are the strongest ones in RS. These bands are not forbidden for IR transitions, but they appear rather weakly. In any case, they are much

weaker than the strong bands $\nu_1(A_1)$ and $\nu_4(E)$ which are, in turn, weak in RS.

4. In addition to P-, Q-, and R-branches, the selection rule (2.40) based on total angular momentum J also allows the O-branch ($\Delta J = -2$) and S-branch ($\Delta J = +2$) to be observed in RS spectrum. The observed band structure, in some specific cases, is not so rich. What is more, there is allowed only the Q-branch in bands originating from totally symmetrical vibrations of spherical tops (as ν_1-mode of SF_6). The structure of RS bands of symmetric tops, however, may be complicated because of changes in the quantum number K. Selection rules by K are treated by Herzberg[77] for all examples we will encounter.

5. We will not dwell on any detailed discussion of RS structure. In this series of papers we shall deal with RS spectroscopy of rather rough resolution and the information will be obtained mainly from the integrated intensities of vibrational bands. In this connection we should stress the important feature that, unlike IR absorption spectra, the integrated intensity of a Raman band *depends* on the vibrational energy stored by the mode which is monitored. The fact that anti-Stokes RS arises only from vibrationally excited molecules may give a convincing argument. We shall give a more detailed discussion of this point later.

2.2.6. Isotopic shifts

It is well known that substances which occur in nature are mixtures of different isotopic species. The isotopes of any element differ only by the number of neutrons in their nuclei, and, thus, they are chemically very identical. But in spectroscopy, different isotopes of a molecule are *different* molecules. The differences between their transition frequencies are called *isotopic shifts*. Isotopic shifts are not only present in vibrational spectra of molecules but they may also be observed in atomic and molecular electronic spectra, with the vibrational spectra showing the strongest isotopic effect.

To explain this effect in vibrational spectra, one usually pictures the classical harmonic oscillator as a spring-suspended mass m. The vibrational frequency of such an oscillator is proportional to $(k/m)^{1/2}$ where k is the force characteristic of the spring. Therefore, k fixed, a smaller mass m_1 oscillates faster than a greater mass m_2, the ratio between frequencies being $\omega_1/\omega_2 = (m_2/m_1)^{1/2}$.

The potential energy of interaction of nuclei in a molecule does not practically depend on the isotopes, since nuclear motion is governed by Coulombic forces. Thus, heavier isotopic molecules would have smaller vibrational frequencies. Specific vibrations can show nondiffering frequencies, however, if the isotopically substituted nuclei do not participate in the motion. For example, with the totally symmetric vibration $\nu_1(A_{1g})$ of SF_6, all the F nuclei oscillate synchronously along the S—F bonds while the S nucleus is fixed. So for two molecules $^{32}SF_6$ and $^{34}SF_6$ differing only in the isotopes of sulphur, the ν_1-modes of each have equal frequencies.

One general feature of isotopic shifts is rather trivial. In spectra of molecules with isotopically different light nuclei the isotopic shifts may exceed the full band-width produced by the rotational distribution. For example, the centers of the ν_3-bands of $^{32}SF_6$ and $^{34}SF_6$ are shifted by 14 cm^{-1} whereas the width of each of them is about 10 cm^{-1}, at room temperature. The largest isotopic shifts are observed in spectra of deuterium-substituted molecules relative to their hydrogen modifications. Otherwise, spectra of molecules which isotopically differ in heavy nuclei show strong overlappings. For example, the centers of the ν_3-bands of $^{238}UF_6$ and $^{235}UF_6$ are shifted only by 0.7 cm^{-1}.

One is able to calculate isotope shifts if the dependence of potential energy on internuclear distances is explicitly known. Furthermore, isotope shifts for different vibrational modes are related by the *Teller-Redlich product rule* (for details see Ref. 77) which simplifies their calculation in some particular cases. But more often one has to study the reverse problem, i.e., investigating the potential surface through spectroscopic data on isotopic shifts. In Section 8, where isotopically selective vibrational excitation of molecules is discussed, we shall also use experimental data.

2.3. Spectroscopy of highly excited vibrational states

As has been demonstrated in the previous sections, the treatment of vibration-rotation molecular spectra, not too difficult within the harmonic-oscillator and rigid-rotator approximations, becomes rather more complicated when anharmonicity and vibration-rotation interactions are involved. Of course, the role of these effects may be affected by vibrational energy of a molecule that, in its turn, can result in further complications of spectra. Nevertheless, due to the enormous number of transitions between highly excited states, one may expect descriptions using *statistical* approaches to reproduce main features of spectra. Indeed, the experiments on action of powerful pulses of laser IR radiation on polyatomic molecules which are the subject of this series of papers give many arguments in favor of a statistical description and focus one's attention on the concept of a *quasicontinuum* of vibration-rotation transition. In this section we shall treat the principal physical effects which can be responsible for the qualitative evolution of spectra from separated transitions in the region of lower levels to quasicontinuum in the region of highly excited states. It should be noted that quantitative insight into this problem is, for the present, still in its initial stage, and the first concrete results[107] have been obtained just from the now existing experimental possibility of high excitation of molecules by laser IR radiation.

2.3.1. Density of vibrational states of polyatomic molecules

Knowing the frequencies of molecular vibrations and limiting oneself to the harmonic approximation, one can in principle easily draw the step function $N(E)$ which gives the number of the vibrational states with energies $E_{\text{vib}} < E$. Sorting out various collections of the vibrational quantum numbers, then approximating the function $N(E)$ by the smoothed curve $R(E)$ and differentiating, one finds the function $\rho(E) = dR/dE$ the *density* of vibrational states or, in other words, the number of states per unit of energy. Keeping in mind of course that anharmonicity, generally speaking, splits degenerate states, one should take into account the degeneracies when $N(E)$ is calculated.

Since consecutive counting of vibrational states is rather cumbersome, any analytical estimates are useful. For example, it is obvious that the greater the number of vibrational degrees of freedom the more rapidly the density of states increases. It is useful to clear up this point explicitly. Qualitatively, the function $\rho(E)$ can be more easily estimated, if one suggests all $s = 3N - 6$ vibrational frequencies to be equal to a certain average value ω_{av}. For such a s-fold degenerate harmonic oscillator, the degeneracy g_n of the state with the energy $n\hbar\omega_{\text{av}}$ is given by the following simple combinatory formula:

$$g_n = \frac{(s + n - 1)!}{(s - 1)!\, n!} \tag{2.68}$$

If $n \gg s$, i.e., excited levels are very high, we can rewrite Eq. (2.68) approximately as

$$g_n \approx \frac{(n + s/2)^{s-1}}{(s-1)!}, \text{ or } \rho(E) \approx \frac{(E + \hbar s\omega_{\text{av}}/2)^{s-1}}{(s-1)!\,(\hbar\omega_{\text{av}})^s} \tag{2.69}$$

If in the second of these equations we assume that ω_{av} plays the role of the arithmetic-mean frequency in the numerator and the geometric-mean one in the denominator, then we come to the following *semiclassical* approximation[108] which is widely used for estimates of the densities of molecular states:

$$\rho_{\text{semiclass}}(E) = \frac{(E + E_0)^{s-1}}{(s-1)!\,\prod_{i=1}^{s}(\hbar\omega_i)}, \tag{2.70}$$

where E is read from the energy of the ground state $E_0 = (1/2)\sum_i(\hbar\omega_i)$. Thus the number of vibrational degrees of freedom governs the power law, according to which the state density grows.

The semiclassical approximation provides satisfactory estimates if the requirement $E \gtrsim s^{1/2}E_0/2$[109] holds. In the case of the molecule SF_6, for example, the lower limit of this requirement corresponds to vibrational energies of about 9000 cm^{-1} and, in the case of the molecule CF_3I, to energies of about 4500 cm^{-1}. To find densities of vibrational states within the lower region one may use other good approximations (see, for example, Refs. 109–113). Most often the Whitten-Rabinovitch approximation[111] is used which gives the following $\rho(E)$ dependence:

$$\rho(E) = \frac{[E + E_0 - \beta f(\eta)E_0]^{s-1}}{(s-1)!\,\prod_{i=1}^{s}(\hbar\omega_i)}[1 - \beta f'(\eta)], \tag{2.71}$$

where the parameter β is given by $\beta = (s-1)\langle\omega^2\rangle/s\langle\omega\rangle^2$, and f is the universal function which depends on the variable $\eta = E/E_0$, determined empirically and tabulated[111] (see also Ref. 113). The function $f(\eta)$ monotonically decreases from the value $f \approx 0.3$ for small η to zero for $\eta \approx 8$. Dependences $\rho(E)$ for some molecules which have been calculated with the use of the Whitten-Rabinovitch approximation are shown in Figure 2.8.

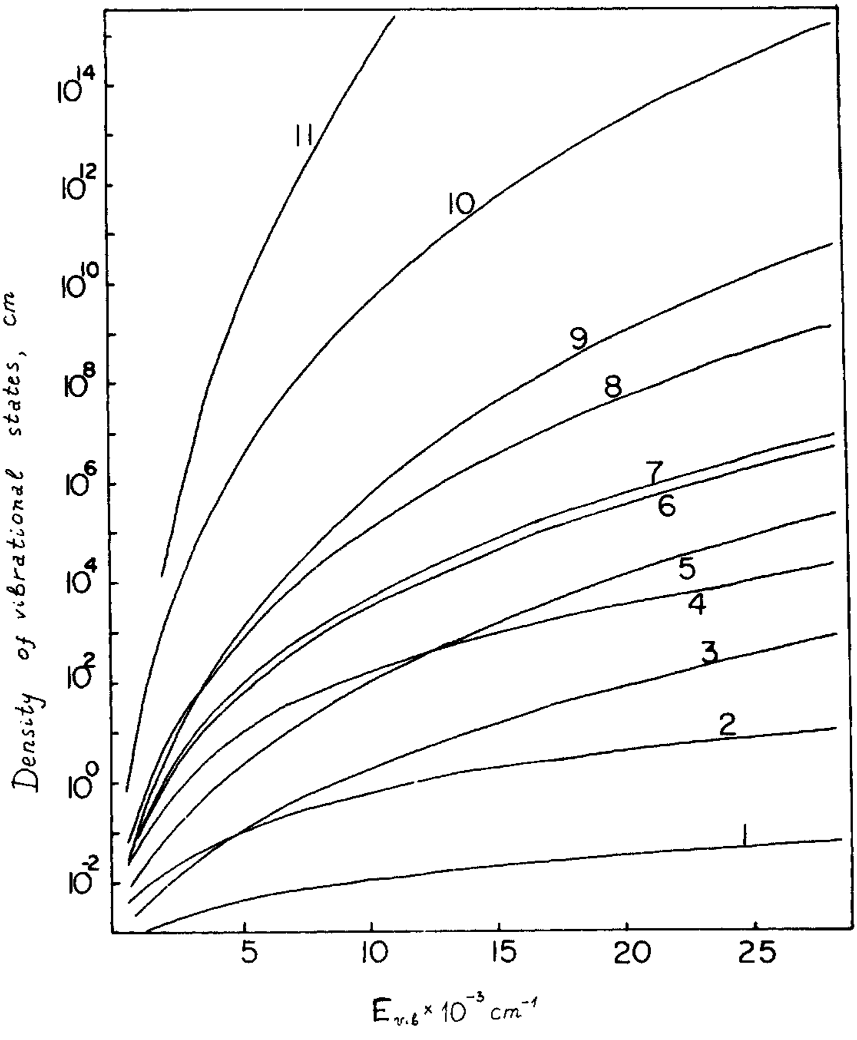

FIGURE 2.8 Dependencies of the density of vibrational states on the vibrational energy for various polyatomic molecules. 1—D_2O; 2—OCS; 3—CH_3F; 4—BCl_3; 5—C_2H_4; 6—CF_3I; 7—OsO_4; 8—C_2F_3Cl; 9—SF_6; 10—UF_6; 11—S_2F_{10}.

Additional brief remarks fall into comments on the anharmonicity role:

1. Anharmonicity, lowering vibrational levels, gives, of course, an increase in their density. This effect is more pronounced for molecules with a smaller number of atoms and drops more and more as the number of vibrational degrees of freedom increases, since less and less portions of excitation energy fall, on the average, within individual modes.
2. In the course of calculations which call for estimates of the densities of vibrational states, anharmonicity is usually ignored. The anharmonic corrections are reduced[110] to a factor which increases versus the vibrational energy. The general behavior of the dependence $\rho(E)$, however, retains its mean features. For examples of specific calculations, see Ref. 114.

2.3.2. What does stochasticity of nuclear motion in a molecule mean?

In the region of lower levels, the vibrational wavefunctions of a polyatomic molecule are rather well described by the harmonic approximation. The situation may arise sometimes when specific levels are spaced so closely that anharmonic interactions result in their strong mixing. The Fermi resonance between levels ν_1 and $2\nu_2$ in the molecule CO_2 is the classical example of this kind, and a less known example is the Fermi resonance $\nu_1 \approx 2\nu_5$ in the molecule CF_3I (see Section 2.2.3). As the vibrational energy of a polyatomic molecule grows, the closeness of levels is not accidental but rather a must. A large increase in the density of states gives rise to many neighbors of every level, and insight into the features of vibrational motion requires one to answer the key question, whether the anharmonic interaction is able to produce strong mixing of these closely spaced states. This question is nontrivial. Nevertheless, in cases of molecules with an appreciable number of atoms (say, >4), probably only the numerical aspects are ones to be discussed. Qualitatively, when both the density of states and the anharmonicity increase with vibrational energy a situation arises in which the separation of motion into individual modes will become meaningless.

This conclusion is supported by a great number of numerical experiments of nonlinear vibrational systems with many degrees of freedom (see, for example, Ref. 115 and references within it). The general feature of these calculations is that, if initially one vibrational mode has been rather highly excited, the switching on of anharmonic interaction leads to fast transfer of the energy into all other modes. The motion becomes complex and unpredictable in the sense that *any amount* of difference in initial conditions will be followed by *strong* divergence of the phase trajectories of the system. It also appears that during a sufficiently long time of observation the *distribution* of the system on the phase-space hypersurface which crosses the initially given value of energy is *uniform*, on the average. Such behavior of systems is called *stochastic* and believed to be described with the use of statistical approaches.

It is important to point out what the stochasticity of the vibrational motion of nuclei in a molecule means in terms of stationary quantum mechanics. For simplicity, in this section we shall assume separation of molecular rotation and vibration. A molecule, being an isolated stable quantum system, has discrete *stationary* levels. *True* vibrational wavefunctions can be always represented as expansions into a series (generally speaking, infinite) by harmonic wavefunctions;

$$\psi^{(k)}_{\mathrm{true}}\,(q_i) = \sum_j c_{jk}\psi^{(j)}_{\mathrm{harm}}(q_i) \tag{2.72}$$

This expansion has nothing specific yet of stochasticity. Such expansion takes place in any case, as the anharmonic part of the Hamiltonian is nonvanishing. But, in the region of lower levels, where the perturbation theory holds, *one* of the coefficients c_{jk} in the expansion (2.72) is close to unity, and the rest of them are comparatively small. Even if for specific states in this region the perturbation theory is broken because of strong Fermi resonance, then only *two* terms are essential in the right hand of Eq. (2.72). The characteristic feature of the expansion (2.72) in the stochasticity region is that *many* harmonic wavefunctions corresponding to close harmonic levels give approximately uniform contributions to the sum. This results in the next feature of true wavefunctions (2.72) in the stochasticity region, the fact that, within each true eigenstate, the distribution of energy over different vibrational modes must be *approximately* equilibrium. The possibility of statistical description implies that deviations from the equilibrium within true stationary states are also just statistical fluctuations.

Now let us suggest that before time $t = 0$ we have produced strong vibrational excitation within a mode ν_k of a molecule which is described by the harmonic wavefunction $\psi^{(v\nu_k)}_{\mathrm{harm}}$. Expanding $\psi^{(v\nu_k)}_{\mathrm{harm}}$ into a series by true wavefunctions, we find

$$\psi^{(v\nu_k)}_{\mathrm{harm}}\,(q_i) = \sum_j \tilde{c}_{j,v\nu_k}\,\psi^{(j)}_{\mathrm{true}}(q_i), \tag{2.73}$$

where coefficients $\tilde{c}_{j,v\nu_k}$ can be obtained through the inversion of the matrix c_{jk} of Eq. (2.72). The wavefunction that we have produced at $t = 0$ is *not* stationary and evolves in time, according to

$$\Psi(q_i,t) = \sum_j \tilde{c}_{j,v\nu_k} \psi^{(j)}_{\text{true}}(q_i) \exp\left(-\frac{i}{\hbar} E_j t\right) \tag{2.74}$$

The beats of the different terms in Eq. (2.74) lead to decay of any ν_k-mode excitation produced initially. If ΔE denotes the energy interval the states are spaced which mainly contribute to the expansion (2.73), then the decay time is simply

$$\tau_D \sim \hbar/\Delta E \tag{2.75}$$

To appreciate the time-scale of energy exchange between vibrational modes of a molecule in the stochastic region let us take for an estimate $\Delta E = 5$ cm^{-1} that corresponds, for example, to the nondiagonal matrix element of the three-frequency anharmonic interaction between states ν_3 and $\nu_2 + \nu_6$ of the molecule SF_6. We shall find $\tau_D = 10^{-12}$ s.

In the next section we shall present a more detailed discussion on specific mechanisms of stochastization of molecular vibrational motion. We restrict ourselves here to a few general notes:

1. Although in this series of papers we use the quantum-mechanical terminology convenient to describe the applications of stochasticity to spectroscopy, it should be mentioned that the basic theoretical results have been established with the classical approach (for details, see Ref. 115).
2. We shall not draw *particular* attention to situations of *partial* stochasticity but it should be clear to the reader that, as the vibrational energy increases, the transformation from the well-working separate-mode description to a statistical one does not occur suddenly. Insight into these intermediate regions will probably be attained through experiments in the near future.
3. In the literature, the decay of the excitation of an individual vibrational mode is often referred to as *intramolecular* (or *unimolecular*) *relaxation.* We shall also use this name occasionally but we stress once again that this

decay process is just the evolution in time, according to Eq. (2.74), of the superposition of true vibrational states, which had been coherent initially.

2.3.3. Mechanisms of stochastization of vibrational motion

In his last year, Fermi raised the problem of stochastization of motion in nonlinear vibrational chains. Together with Pasta and Ulam he carried out some numerical experiments[116] which showed a rather unexpected behavior. They put an excitation of the lowest mode of the chain as the initial condition and found in the presence of some small anharmonicity that, even though the energy was passing into other modes in the course of time, only a few lower ones were actually participating in energy redistribution. At the same time Kolmogorov[117] proved the theorem of *perpetual* stability of motion in nonlinear vibrational systems, with one essential *proviso,* however: *if there are no intermode resonances*. It has been shown in later works (for example, Ref. 118) that it is just the intermode resonances that are mainly responsible for stochastization but Fermi's model had not complied with resonant requirements, i.e., defects of resonances have exceeded the anharmonic interaction chosen. Based on numerous computer experiments, Chirikov (see, for example, Ref. 119) has formulated the empirical criterion of stochastization: *anharmonic interaction should overlap at least several resonances with the smallest defects*. There is, of course, an uncertainty in the word *several*. The simplest way to understand what it means is to turn to a specific example. Let us take the molecule CF_3I. Four of its modes ν_1, ν_3, ν_5, and ν_6 interact through the following three-frequency Fermi resonances which are allowed by symmetry:

$$\begin{aligned} &(1)\ 2\nu_5 - \nu_1 \approx 5\ \mathrm{cm}^{-1}; \\ &(2)\ \nu_5 - 2\nu_6 \approx 10\ \mathrm{cm}^{-1}; \\ &(3)\ \nu_3 + \nu_6 - \nu_5 \approx 11\mathrm{cm}^{-1} \end{aligned} \qquad (2.76)$$

Let us consider the anharmonic coupling of vibrational states in the vicinity of $v\nu_1$, assuming, for simplicity, harmonic positions of levels. This coupling is produced by anharmonic terms like those given in Table 2.1. It can be seen from Figure 2.9 that the level $v\nu_1$ interacts by a chain of connections with many other closely-spaced levels. (Only the beginning of the chain is shown in the figure). It is rather clear that, if the nondiagonal matrix elements of anharmonic interaction are smaller, on the average,

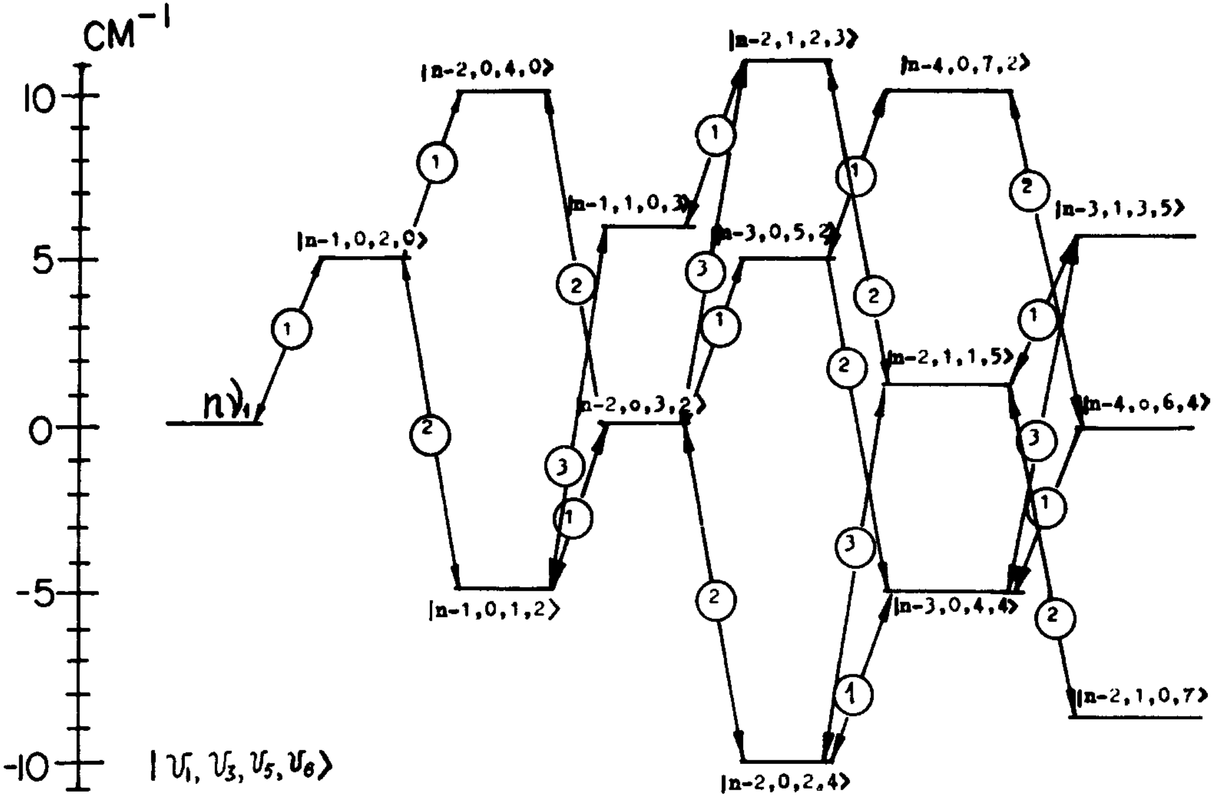

FIGURE 2.9 Mechanism of mixing, through the chain, of harmonic vibrational states of CF_3I due to the Fermi resonances (2.76). Numbers inside circles correspond to those in (2.76).

than the characteristic distance ΔE between levels in the chain (in our case, $\Delta E \approx 10 \text{ cm}^{-1}$), then perturbation theory forces the contribution of the $v\nu_1$-wavefunction to other states to decrease, roughly speaking, in a geometric progression, as the number of required steps increases. Otherwise, if the non-diagonal matrix elements exceed the value ΔE, the formal procedure of perturbation theory would lead to a divergency. This means that mixing by the chain will be effective, and this is in agreement with Chirikov's criterion.

Thus, insight into the mechanisms of stochastization in a given molecule starts from the picture of its intermode resonances. It is necessary to keep in mind that, in the general case, interaction of levels diminishes as the order of resonances grows. Indeed, for any two harmonic levels, even with considerably different sets of vibrational quantum numbers, one can write out explicitly the anharmonic term which will produce a nonvanishing nondiagonal matrix element. It may turn out, however, that interaction through intermediate resonances of lesser orders will be much more efficient. For example, in the case of the molecule SF_6, using the harmonic approximation, one finds levels $v\nu_3$ and $(v - 3)\nu_3 + 2\nu_2 + \nu_5 + 3\nu_6(d)$ (see Figure 2.10) detuned by 1 cm^{-1}. These levels are coupled by a chain of three three-frequency Fermi resonances. Simple estimates (see Ref. 107) based on known cubic-anharmonic constants show that levels $v\nu_3$ and d are probably mixed even for $v = 4$. At the same time, these levels are possibly directly coupled only by the ninth-order anharmonic term which may be negligible, of course. Multistep resonances with small intermediate defects similar to the one just considered should be considered in the analysis of intermode resonances.

Some quantitative points of this effect may be understood using the approach of extracting a highly excited level of an individual mode and treating the rest of the levels as the *bath*. Strictly speaking, such an approach is proper only if the interaction within the bath is much stronger than the level-bath interaction. As an example let us assume, for simplicity, that the extracted level $v\nu_1$ undergoes a single resonance with the level $(v - 1)\nu_1 + \nu_2 + \nu_3$ (c). (We denote the nondiagonal matrix element of anharmonic interaction by $V_{v\nu_1,c}$.) The interaction within the bath will lead to a broadening of the resonance (see Figure 2.11). In other words, with allowance made for the interaction within the bath, the level $v\nu_1$ is coupled with many closely spaced states. (We denote the interaction matrix elements by $V_{v\nu_1,b}$ and the typical distance between adjacent levels by ρ^{-1}.) Recall that stochasticity implies an irreversible decay of an initially excited

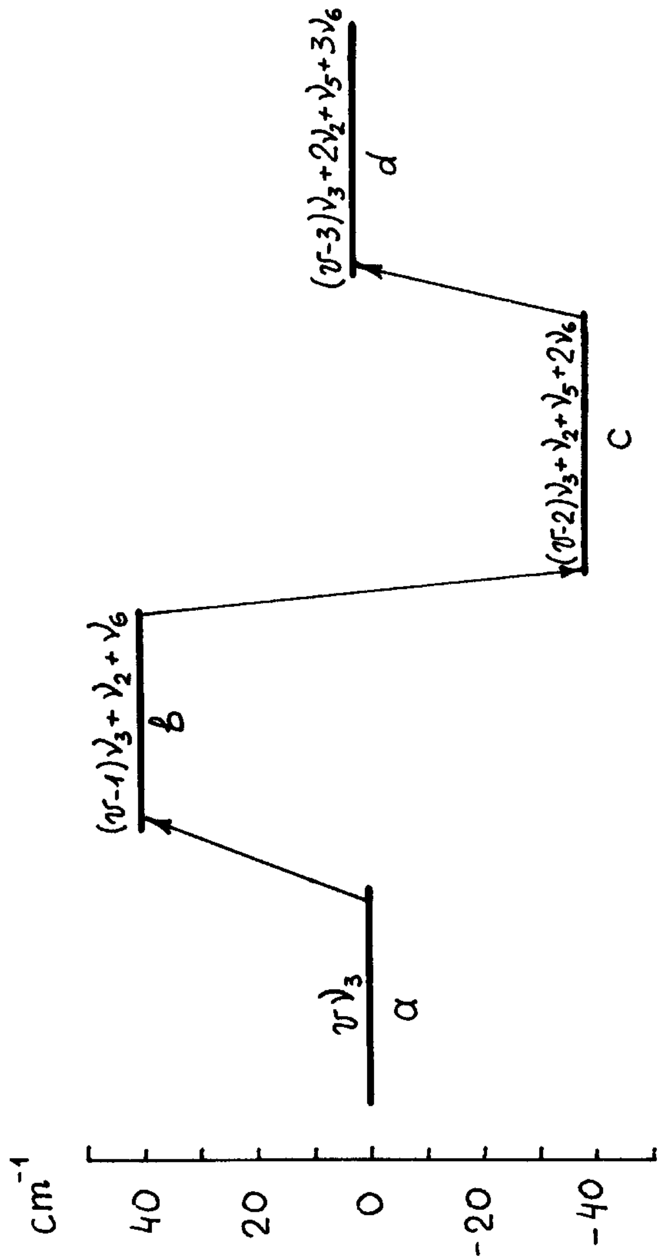

FIGURE 2.10 Diagram of levels illustrating the effect of three-step resonance in the case of SF_6.

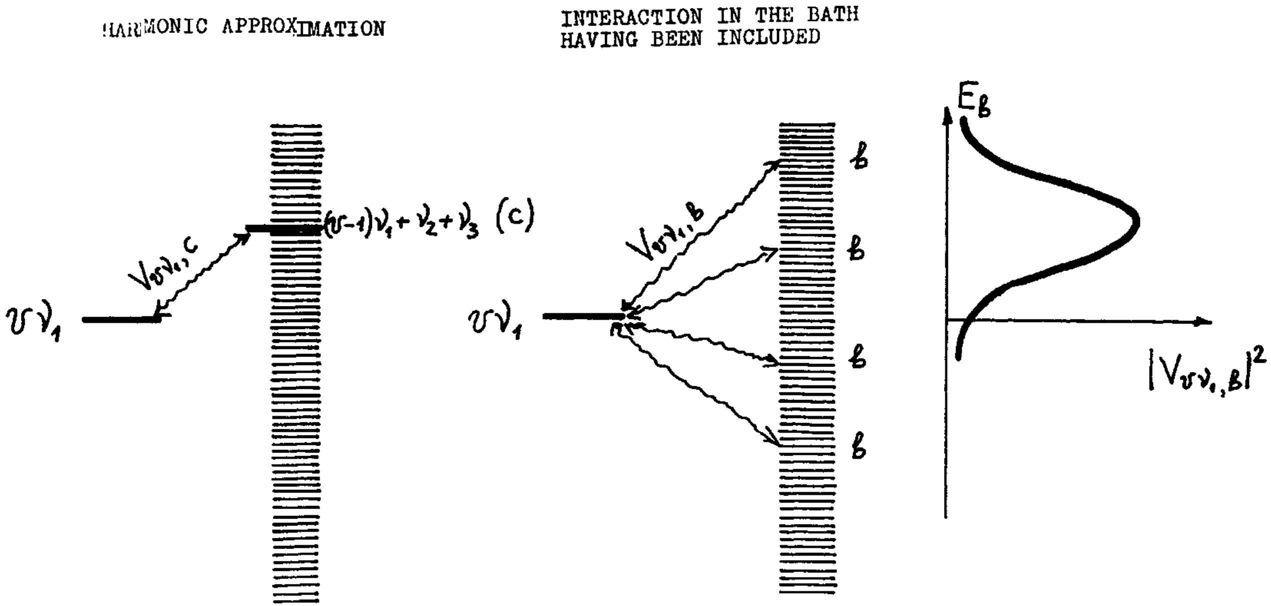

FIGURE 2.11 Interaction of the separated vibrational level with the bath.

state of an individual mode and (see, for example, Ref. 72) that, as a level interacts with a continuous spectrum, the irreversible decay follows the exponential law with a rate of

$$W = \frac{2\pi}{\hbar}|V_{if}|^2, \tag{2.77}$$

where V_{if} is the interaction matrix element between the initial discrete state $|i\rangle$ and the final continuous-spectrum state $|f\rangle$ with the same energy. Actually, because of the finite W, the initial state decays into a band of continuous spectra with width $\Delta E \approx 2\pi\hbar W$. In our case, the spectra of bath eigenstates is discrete. It is not hard to modify Eq. (2.77) (see, for example, Ref. 120) to

$$W = \frac{2\pi}{\hbar} \,| V_{v\nu_1,b}|^2 \,\rho, \tag{2.78}$$

but it remains to be seen whether Eq. (2.78) will be applicable to describe any actual decay. It is apparent when the discontinuity of spectrum may be ignored. The decay band must be wider than the distance between adjacent levels, i.e., the condition

$$2\pi\hbar W \gg \rho^{-1}, \text{ or } |V_{v\nu,b}| > \rho^{-1} \tag{2.79}$$

should be met. In the opposite case, when the condition (2.79) is invalid, it is not likely that any irreversible decay of the initial state will occur.

The condition (2.79), in fact, can be treated as a criterion of stochasticity. In literature Eq. (2.78) is often referred to as *Fermi's golden rule*. This equation contains the density ρ of vibrational states. It should be noted that a W-dependence on ρ is curious as higher ρ gives a greater number of bath states in the primary interaction matrix element. The redistribution of coupling matrix elements due to interactions within the bath should comply with a rather general quantum-mechanical sum rule which is derived in many textbooks on quantum mechanics:

$$|V_{v\nu_1,c}|^2 = \sum_b |V_{v\nu_1,b}|^2 \tag{2.80}$$

We have treated some qualitative aspects of the stochastization effect. Theory is under development, and we can list some unresolved points:

1. Are there any reasonable physical restrictions on the order of intermode resonances which may be essential for the stochastization effect?
2. There are no works in the literature which would present the role of vibration-rotation interaction in the stochastization of vibrational motion.
3. Anharmonic interaction is able to mix states with the same vibrational symmetry. It is surely of interest to determine what mechanisms are responsible for the mixing of different vibrational species.

One of the main problems is locating the stochastic region limits for different molecules. The first results are from the effect of a strong IR field excitation of molecules, so it will be advantageous to discuss actual experiments below, after the physics of this process and the experimental techniques have been given.

2.3.4. Quasicontinuum of vibration-rotation transitions

The qualitatively drastic change in structure of the vibrational eigenwavefunctions in the stochasticity region results in radical changes in the overall spectroscopic picture compared to that in the region of lower levels. Since, according to Eq. (2.73), each harmonic wavefunction contributes to a great number of true states, then a *manifold* of transitions is allowed. For energies below the dissociation limit, the spectrum of transitions is, strictly speaking, discrete. It could become continuous, if the distances between adjacent levels were smaller than their natural radiative widths which are typically about 10^{-7}–10^{-9} cm^{-1}. It can be seen from Figure 2.8 that the value ρ^{-1} is, as a rule, several orders greater, even for highly excited levels. Nevertheless, we shall use the name *vibrational quasicontinuum* whenever transitions in the stochastic region are discussed. This is justified due to a real line-width of the laser radiation (see Section 2.8).

The fact that there are many allowed transitions does not mean their spectra are structureless. Figure 2.12 shows the emission spectra of the gas SF_6 heated to the temperature 1780 K[121] that corresponds to an average vibrational energy of about 14 600 cm^{-1}. It may be seen that the emission is concentrated about the IR-active ν_3-band. The spectra are shifted to the long-wave side by anharmonicity, and they are broadened as compared to the absorption spectra of cold SF_6. There are probably two causes of

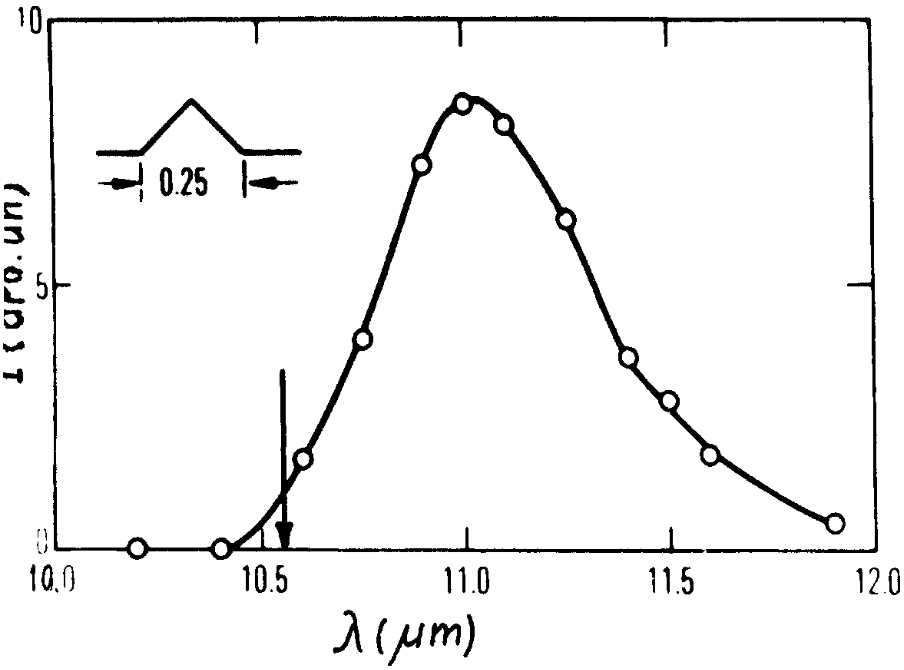

FIGURE 2.12 Emission spectrum of ν_3-band of the gas SF_6 heated to the temperature 1780 K. The arrow indicates the position of Q-branch of the fundamental band (from Ref. 121).

broadening. First, in such a simple experiment, one is forced to deal with the real Boltzmann distribution of molecules over vibrational levels, and states with different energies undergo different anharmonic shifts. This broadening can be appropriately called *inhomogeneous*, according to the usual terminology. The second cause arises from the *homogeneous* width of spectrum of transitions from each individual level. One would, in principle, avoid inhomogeneous broadening, if molecules had been *selectively* excited into a single high level, and then the condition would come only from homogeneous broadening. Such spectra are of fundamental importance for insight into structure of true states in the stochastic region. Unfortunately, proper measurements have not as yet been carried out. Based on existing experiments which deal with real vibrational distributions, one is able to estimate just the upper limits for homogeneous widths and may conclude that modes retain their individuality in spectra, not only for IR absorption and emission (see also Ref. 122), but for Raman scattering, too.[123]

The spectra near the ν_{IR}-band of quasicontinuous IR transitions above any vibration-rotation level $|i\rangle$ lying in the stochastic region can be roughly described in terms of three parameters: the *position of the maximum* $\nu_{\max}^{(i)}$, the *half-width* $\delta_{\text{hom}}^{(i)}$, and the value of the *integrated intensity* which is proportional to the sum of squared transition dipole moments $\sum_l |\langle l|\hat{\mu}|i\rangle|^2 = (\mu_{\text{int}}^{(i)})^2$, where $E_l \approx \text{E}_i + \hbar\nu_{\text{IR}}$. These parameters vary, in principle, from level to level. But it is an important feature of the stochastic region that an averaged statistical description may be used. There are two physical reasons. The first is the very structure of these true vibrational states in the stochastic region which are superpositions of many harmonic states with close energies, and which are in approximate vibrational equilibrium over all modes. The second argument, essential in view of the experiments and theoretical studies presented below, is that in any actual experiment, when a pulsed laser acts during an interval of time and, in addition, has a finite line-width as well as a rather strong intensity, a *group* of many closely spaced levels is in fact excited. Therefore there is just cause to use averaged parameters for some vibrational energy E_{vib}.

One of these dependences $\langle \mu_{\text{int}}^2(E_{\text{vib}})\rangle$ can be estimated in a rather simple manner. Within the harmonic approximation, sum the squared dipole moments of upward allowed transitions between vibrational states with E_{vib} into those with $E_{\text{vib}} + \hbar\nu_{\text{IR}}$ and then use the above-mentioned [see Eq. (2.80)] general quantum-mechanical rule, that the interaction of close states does not change the value of this sum. We obtain the following equation:

$$\rho(E_{\text{vib}})\,\langle \mu_{\text{int}}^2(E_{\text{vib}})\rangle = \mu_{\text{IR}}^2 \sum_{k=0}^{[E_{\text{vib}}/\hbar\nu_{\text{IR}}]} (k+1)\,\rho^1(E_{\text{vib}} - k\,\hbar\nu_{\text{IR}}) \qquad (2.81)$$

Here μ_{IR} is the vibrational dipole moment of the ν_{IR}-mode [see Eq. (2.53)], ρ^1 denotes the density of vibrational states produced by the rest of the modes other than ν_{IR}, and the factor $(k + 1)$ presents the dependence of squared transition dipole moment on the vibrational quantum number of the ν_{IR}-mode. Curves $\langle \mu_{\text{int}}^2(E_{\text{vib}})\rangle$ calculated for two cases are shown in Figure 2.13.

It is also easy to understand the law of the dependence $\langle \nu_{\max}(E_{\text{vib}})\rangle$. It has been demonstrated in Section 2.2.2 [see Eqs. (2.46 and 2.47)] that main anharmonic corrections give linear dependences of frequencies, of

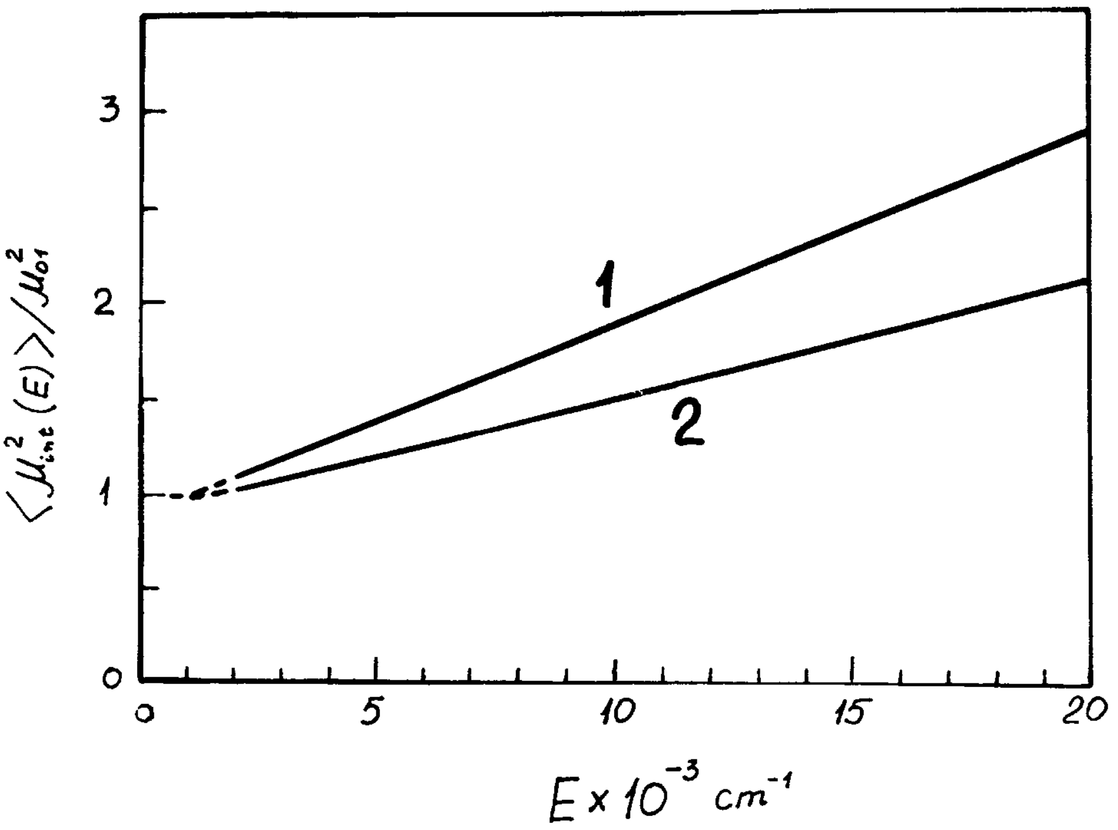

FIGURE 2.13 Dependencies $\langle \mu_{int}^2 (E) \rangle$ for two cases: 1—ν_1-band of CF_3I; 2—ν_3-band of SF_6.

successive vibrational transitions, on the vibrational quantum numbers of different modes. If, in accordance with the above arguments, we are going to operate with the averaged value, it is natural to use

$$\langle \nu_{\max}(E_{\text{vib}}) \rangle = \nu_0^{(\text{IR})} - \langle x \rangle E_{\text{vib}}, \tag{2.82}$$

$$\langle x \rangle = -\frac{1}{s}\left(2x_{ii} + \sum_{k \neq i} \frac{\omega_i}{\omega_k} x_{ik}\right),$$

where the index i refers to the ν_{IR}-mode under consideration. Thus, one again comes to a linear dependence on E_{vib}, in terms of the averaged anharmonicity constant.

The third parameter $\langle \delta_{\text{hom}}(E_{\text{vib}}) \rangle$ is more complicated. First, so far we have said nothing about the *shape* of these absorption contours. Second, transitions are possible within various rotational branches in the vibrational quasicontinuum as well as in the region of lower levels. We shall turn to a more detailed discussion of this point, when comparing the spectroscopic models of the quasicontinuum with experiments on the excitation of molecules by a strong IR field. Here we restrict ourselves to listing the basic assumptions, without going into details, but not simplifying the general picture:

1. The consensus is that the absorption contour originating from an individual vibration-rotation line shows the Lorentzian shape. Physical arguments here are usually associated with the exponential law of intramolecular relaxation of vibrational energy (see, for example, Ref. 124). Direct measurements[125,126] of spectra of overtones lying in the stochastic region support the Lorentzian dependence.
2. The overall contour of an absorption from a stochastic-region-level is produced by superposition of Lorentzians originating from transitions within different rotational branches. In the simplest case of three-fold degenerate vibrational modes of spherical tops as well as parallel bands of symmetric tops, three Lorentzians are participating.
3. The value $\langle \delta_{\text{hom}}(E_{\text{vib}}) \rangle$ which presents the broadening of each rotational component grows versus the vibrational energy due to increasing anharmonic interactions that force more and more distant states to mix. A power law which governs $\langle \delta_{\text{hom}} \rangle$-dependence on E_{vib} is probably caused by Fermi resonances responsible for the stochastization effect in a specific molecule.

Summarizing, we can write out explicitly the assumed spectral dependence of the squared dipole moment μ_{Ω}^2. Restricting ourselves to the three-branch case (P-, Q-, and R-branches) and neglecting the dependence of the rotational constant B on the vibrational energy, we come to

$$\begin{aligned}\mu_{\Omega}^2 = {} & \frac{\langle \mu_{\mathrm{int}}^2(E_{\mathrm{vib}})\rangle \, \langle \delta_{\mathrm{hom}}(E_{\mathrm{vib}})\rangle}{3\pi} \\ & \left\{ \frac{1}{[\Omega - \langle \nu_{\max}(E_{\mathrm{vib}})\rangle + 2BJ]^2 + \langle \delta_{\mathrm{hom}}(E_{\mathrm{vib}})\rangle^2} \right. \\ & + \frac{1}{[\Omega - \langle \nu_{\max}(E_{\mathrm{vib}})\rangle]^2 + \langle \delta_{\mathrm{hom}}(E_{\mathrm{vib}})\rangle^2} \\ & + \frac{1}{[\Omega - \langle \nu_{\max}(E_{\mathrm{vib}})\rangle - 2B(J + 1)]^2 + \langle \delta_{\mathrm{hom}}(E_{\mathrm{vib}})\rangle^2} \end{aligned} \tag{2.83}$$

Recall that all averaged symbols refer to upward transitions from states at E_{vib} within a single band, a separation of vibrations and rotation is assumed, and the rotational quantum numbers are fixed, i.e., are not subjected to averaging. Finally, it is evident that, if one integrates μ_{Ω}^2 over Ω, the result will be $\langle \mu_{\mathrm{int}}^2(E_{\mathrm{vib}})\rangle$.

2.4. Statistical theory of unimolecular decay

The stability of a molecule, as it has been discussed in Section 2.1.2, arises from a minimum in the electron-energy surface $E_{el}[\mathbf{R}_j^{(\mathrm{nucl})}]$, depending on the nuclei positions. $E_{el}[\mathbf{R}_j^{(\mathrm{nucl})}]$ acts, in nuclear motion, as a potential energy. One can calculate the electron energy, when, in particular, two fragments A and B of a molecule AB are separated so that their interaction may be neglected. Both fragments may appear to be stable with minimum energies E_A and E_B corresponding to their equilibrium configurations. Then the difference $D_{A,B} = E_A + E_B - E_{AB}$ is called the *energy of dissociation* into the fragments A and B. Taking various possible decay channels into these fragments, one can establish the *lowest* of $D_{A,B}$ which is conventionally called the *dissociation limit* D. If the vibrational energy of a molecule exceeds the dissociation limit, then spontaneous decay can occur. Of course, we may ask what is the rate of such a unimolecular decay, what is its dependence on excess vibrational energy over the dissociation limit, and what decay features may be common from molecule to molecule. A natural starting point is the assumption that the dissociation limit lies in the region of stochasticity of vibrational motion. This assumption forms the basis for the statistical theory of unimolecular reactions which provides rather good agreement with experiments. We shall present the principal formula of this theory and discuss some of its consequences. First let us turn to some specific examples.

In some cases the dissociation limit calls for only a single atom to be detached. For example, in the case of the molecule SF_6, the dissociation into the radical SF_5 and a fluorine atom is the lowest channel, requiring the energy $D \approx 32\,000\ \text{cm}^{-1}$ (for comparison, the dissociation of SF_6 into SF_4 and F_2 requires $36\,750\ \text{cm}^{-1}$). In the case of the molecule CF_3I, the lowest channel corresponds to a decay into the radical CF_3 and the iodine atom ($D \approx 18\,500\ \text{cm}^{-1}$). Other molecules may have dissociation limits that call for the chemical bond between two radicals to be broken. A typical example is the breaking of the bond between two nitrogen atoms in the molecule N_2F_4 leading to the formation of two radicals NF_2. In these examples, a molecule will dissociate if the required energy is concentrated at the weakest bond d_0. The dissociative decay should then occur very fast, in approximately one period of vibration. It is clear from the ideas developed in the foregoing section, however, that at high excitations of a molecule, the most probable states are those at energy equilibrium over different vibrational degrees of freedom. Therefore a fluctuation or redistribution is necessary which will give energy to the decay channel, and one is forced to wait, on an average, much longer than one period of vibration.

The approach which treats a molecule as a closed equilibrium system and its dissociation as a result of a statistical fluctuation was first formulated by Landau.[127] Calculations were later worked out in detail, and the terminology itself changed. The concept of *activated complex* was introduced into the theory. An activated complex corresponds, in fact, to the configuration of nuclei in a molecule when the energy sufficient for dissociation is localized at the weakest bond d_0. The activated-complex states are those which exhibit $E_{d_0} > D$. The energy excess, $E_{\text{vib}} - E_{d_0}$ in this case, is distributed over the internal vibrational degrees of freedom of the complex. The activated-complex states reserve a relatively small volume V_0 of the phase space within the hypersurface $E = E_{\text{vib}}$. Ignoring the dissociation, one can easily understand that, according to stochasticity of nuclear motion, a molecule should be activated during the time which is proportional to this volume V_0, and, therefore, the dissociation rate will increase versus V_0. The dissociation rate may be calculated explicitly with an additional basic assumption along with the stochasticity concept. *The activated-complex lifetime is long as compared to the typical time for energy exchange between different vibrational modes due to anharmonic interaction.* Thus, in addition to the qualitative assumption on the general character of nuclear motion near the dissociation limit, the statistical theory of unimolecular reactions results in a rather simple expression applied to the dissociation process (see Refs. 109, 113 and 128 for derivation details):

$$k\,(E_{\mathrm{vib}}) = R(E_{\mathrm{vib}} - D)/2\pi\hbar\rho(E_{\mathrm{vib}}) \tag{2.84}$$

In this equation $k(E_{\mathrm{vib}})$ means the statistically averaged rate of dissociation of molecules with the energy E_{vib}. This rate is proportional to the total number $R(E_{\mathrm{vib}} - D)$ of activated-complex vibrational states lying between D and E_{vib}, or, in other words, to the number of energetically allowed decay channels. Furthermore, the dissociation rate is inversely proportional to the density of molecular vibrational levels at E_{vib}.

Formula (2.84) is rather general and one needs, to use it, the energy spectra of the vibrationally excited molecule and activated complex. The theory which starts from the quantum-mechanical approach to find these spectral characteristics is called the *RRKM theory* after its authors.[129] One version of the RRKM theory ordinarily used to make estimates does not overstep the limits of the harmonic approximation. Equations giving densities of molecular states have been discussed in Section 2.3.1. The equation describing the number R of activated-complex states can be obtained through a simple integration of the corresponding state-density one. We shall restrict ourselves to the semiclassical approximation which gives the following equation for the rate of unimolecular decay:

$$k(E_{\mathrm{vib}}) = \tilde{\omega}\left[\frac{E_{\mathrm{vib}} - D + E_0^{(\mathrm{compl})}}{E_{\mathrm{vib}} + E_0^{(\mathrm{mol})}}\right]^{s-1} = \tilde{\omega}f(E_{\mathrm{vib}}), \tag{2.85}$$

where s is the number of vibrational degrees of freedom of the molecule; $E_0^{(\mathrm{mol})}$, $E_0^{(\mathrm{compl})}$ are the ground-state energies of the molecule and activated complex; and the frequency factor $\tilde{\omega}$ is formed explicitly by s vibrational frequencies of the molecule and $(s - 1)$ frequencies of the complex through the following equation:

$$\tilde{\omega} = \frac{L}{2\pi}\left[\prod_{i=1}^{s} \omega_i^{(\mathrm{mol})}\right] \Bigg/ \left[\prod_{i=1}^{s-1} \omega_i^{(\mathrm{compl})}\right] \tag{2.86}$$

Here L is the number of possible ways for a particular dissociation (for example, the decay $SF_6 \rightarrow SF_5 + F$ implies $L = 6$).

The frequency factor $\tilde{\omega}$ is evidently within an order of magnitude to typical frequencies of molecular vibrations, i.e., $\tilde{\omega} \sim 10^{13}$–$10^{14}$ s^{-1}. The physical sense of the second factor $f(E_{\mathrm{vib}})$ in Eq. (2.85) is clear. This factor describes a rapidly increasing dependence of the decay rate on the molecular energy, over the dissociation limit, due to the increasing of the number of energetically allowed decay channels. But numerical values f are small; they are smaller, as a rule, for molecules with the greater number N of atoms. This is understandable in terms of the fluctuation mechanisms of decay. Rough curves $f(E_{\mathrm{vib}})$ are shown in Figure 2.14 for different N. Those dependences may be treated as universal if the ground-state energies which differ from molecule to molecule are ignored. They are, however, suitable for the simplest estimates. As examples, more accurate calculations of decay rates for cases of SF_6[130] and C_6F_5H[131] are shown in Figure 2.15 and illustrate the qualitative conclusions drawn above.

We have considered some simplest instances when dissociation of molecules is naturally treated in terms of a break of the weakest bond. But there may be situations when dissociation is associated with a rearrangement of chemical bonds. A typical example is the decay which leads to detachment of the diatomic molecule whose atoms have not been chemically coupled initially. For example, the dissociation limit of CF_2Cl_2 calls for decay into the radical CF_2 and molecule Cl_2. In this and similar cases, the nuclear configuration making up the activated complex is probably separated from that in the molecule with a potential barrier. If the vibrational energy of the molecule exceeds the dissociation limit but is lower than the barrier-energy, then the decay rate is limited by a rather slow tunneling through the barrier. Therefore, the principal formula of the theory of unimolecular decay may be used only in the above-barrier region.

The final notes refer to the practical applications of Eqs. (2.85 and 2.86):

1. The basic assumption of the theory using a statistical description near the dissociation limit is probably applicable to molecules with the number of atoms $\geqslant 4$ (see, for example, Ref. 132 where the dissociation rates of

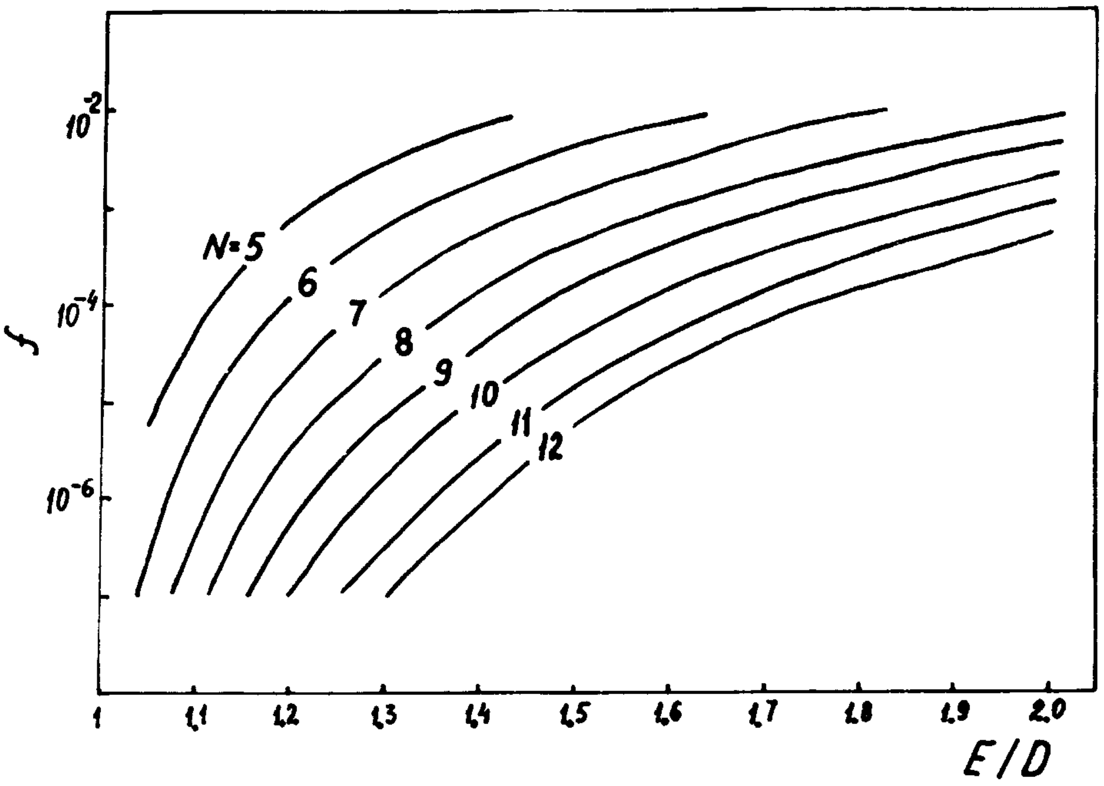

FIGURE 2.14 Estimated dependencies of function f entering into Eq. (2.85) for the rate of unimolecular decay on the ratio E/D of vibrational energy to dissociation one. Dependencies are presented for molecules with different numbers N of atoms.

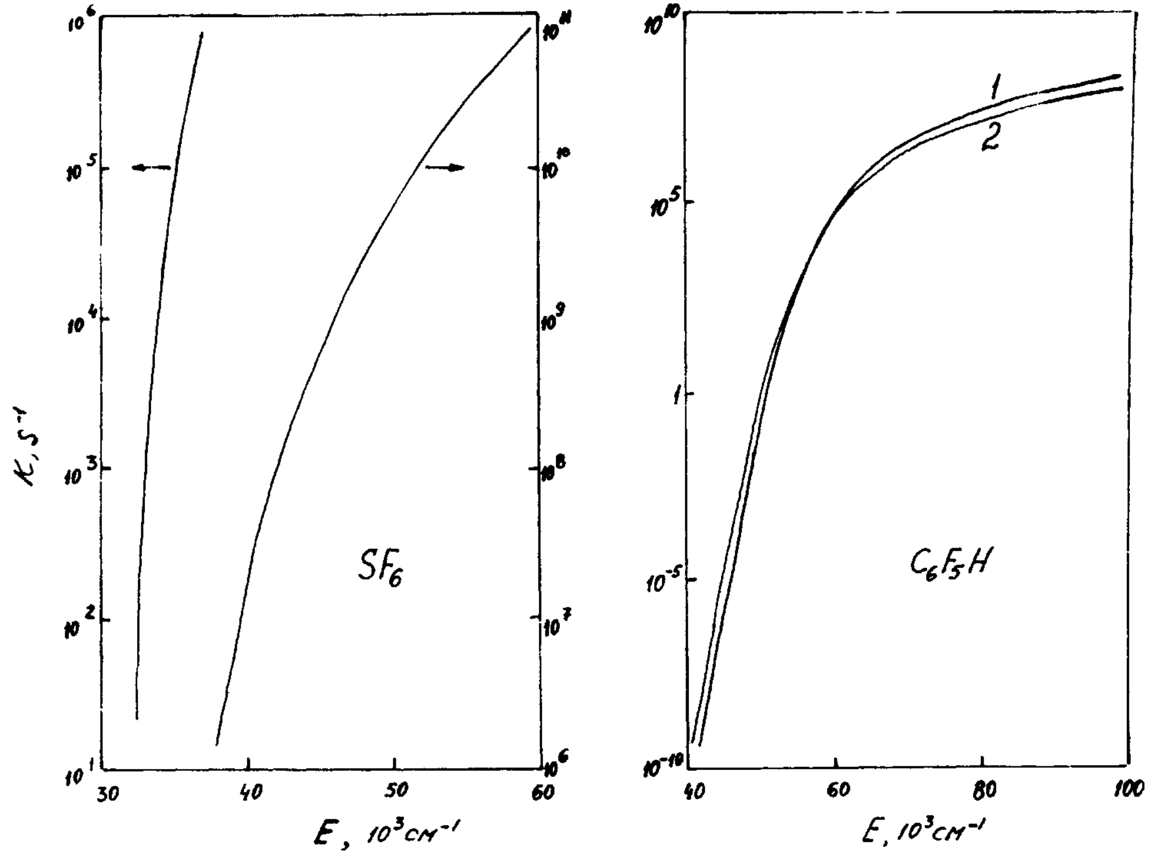

FIGURE 2.15 Dependencies of the rates k of unimolecular decay on the vibrational energy for the molecules SF_6 (from Ref. 130) and C_6F_5H (from Ref. 131). Curves 1 and 2 correspond to different sets of vibrational frequencies of activated complex (see Ref. 131).

different molecules were calculated numerically in terms of classical motion in a multidimensional model potential).

2. In addition to the barrier situation, the RRKM theory cannot be used when the dissociation calls for a nonadiabatic transition to another electronic term. It should be noted (see, for example, Ref. 109) that nonadiabatic effects arising from electronically-excited terms near the dissociation limit may, in general, affect the value of the decay rate. Therefore, one must examine carefully calculations using the RRKM theory and probably treat them rather as rough estimates.

3. Even though one believes formulas (2.85 and 2.86) to be true, it is often difficult to estimate vibrational frequencies of the activated complex. We can only point out special computer programs[133] aimed at finding the most favored configurations of activated complexes.

2.5. Classification of relaxation processes in molecular gases

In the experiments that are the subject of this series of papers, a pulse of powerful laser IR radiation produces a distribution in a molecular gas that, in general, may differ greatly from statistical equilibrium. The distribution observed at the end of laser pulse must, of course, depend on the initial distribution which is defined by the initial temperature T_0. It may be important for observations whether the molecule may be treated as isolated from its surroundings during the laser pulse, or if the molecule undergoes collisions with other molecules in the gas. After the pulse is over, collisions act on the distribution to bring it into an equilibrium corresponding to the energy stored in the gas during the pulse. It should also be noted that usually a limited gas volume is irradiated and diffusion processes will begin after the pulse.

It is difficult in this short section to embrace the whole variety of relaxation processes, even in only a descriptive way. The detailed treatment is presented in many books and reviews, for example Refs. 109, 128, 134–138. Experimental studies of collisional relaxation processes may use, for example, the techniques of supersound, shock wave, and crossing beams. Now lasers are often used, too. Successful instances of the use of lasers in different double-resonance versions can be found in Refs. 139 and 140. Lasers are also suitable for investigation into coherent transient effects which often gives useful information on relaxation processes.[141] To apply formula (2.88) to a greater or smaller accuracy one should use all those equations (see Section 2.1) which to a greater or smaller accuracy changes between translational, rotational, and vibrational degrees of freedom as well as relaxations of distributions within each of them. We shall treat a specific relaxation process which is a *phase* or *transverse* relaxation, too. But first we shall discuss features of equilibrium distributions and concepts which are common for all collisional processes.

2.5.1. *Statistical equilibrium distribution*

In statistical equilibrium, without external fields, and at the temperature T, the distribution in a gas over velocities v_x, v_y, v_z, and different quantum states $|i\rangle$ is defined by a distribution function $F(v_x, v_y, v_z, i)$ normalized to unit volume and is the product of the Maxwell-distribution function

$$F_{\text{Maxw}}(v_x, v_y, v_z) = \left(\frac{M}{2\pi kT}\right)^{3/2} \exp\left[-\frac{M(v_x^2 + v_y^2 + v_z^2)}{2\,kT}\right], \quad (2.87)$$

where M is the gas-molecule-mass and k is the Boltzmann constant, and the Boltzmann-distribution function

$$F_{\text{Boltzm}} = \frac{g_i}{Z_{\text{Boltzm}}} \exp(-E_i/kT) \quad (2.88)$$

The Maxwell-distribution function gives the expected density of molecules with the velocity components lying within the elementary volume $dv_x\, dv_y\, dv_z$ of the velocity space. The Boltzmann-distribution function gives the probability of finding a molecule in the quantum state $|i\rangle$ with the energy E_i, and is usually normalized to unity. In Eq. (2.88), g_i means the degeneracy of the level, and the statistical sum is just the normalization factor:

$$Z_{\text{Boltzm}} = \sum_j g_j \exp(-E_j/kT) \quad (2.89)$$

To apply formula (2.88) to a greater or smaller accuracy one should use all those equations (see Section 2.1) which to a greater or smaller accuracy give the spectra of vibration-rotation molecular states. For our purposes it will be quite sufficient to use the approximation separating rotation and vibrations, i.e., $E_{\text{vib-rot}} = E_{\text{vib}} + E_{\text{rot}}$. With this approximation, one can operate with a *vibrational distribution* and a *rotational distribution*, independently. Assuming this, one, in essence, uses just the rigid-rotator approximation, i.e., neglects in the Wilson-Howard Hamiltonian (2.10) the terms $\hat{l}_\alpha$ and dependencies of $D_{\alpha\beta}$ on the normal coordinates. The approximation of harmonic oscillators allows us to reduce the Boltzmann-distribution function to a more simplified form, since one can now operate with distributions within separated modes, too. The Boltzmann distribution $F_{\mathrm{Boltzm}} = F_{\mathrm{rot}}F_{\mathrm{vib}}$ from the approximations of a rigid rotator and harmonic oscillators is widely used for the simplest estimates. The vibrational part is especially simple, since the evaluation of the statistical sum is trivial:

$$F_{\mathrm{vib}}(v_i) = \left\{ \prod_{i=1}^{s} \left[1 - \exp\left(-\frac{\hbar\omega_i}{kT} \right) \right] \right\} \exp\left(- \frac{\hbar \sum_{i=1}^{s} v_i\omega_i}{kT} \right) \qquad (2.90)$$

Using Eq. (2.90) one can easily calculate the average vibrational energy within the i-th mode:

$$\langle E_i \rangle = \hbar\omega_i \left[1 - \exp\left(-\frac{\hbar\omega_i}{kT} \right) \right] \sum_{v_i=1}^{\infty} v_i \exp\left(-\frac{v_i\hbar\omega_i}{kT} \right) = \frac{\hbar\omega_i}{\exp\left(\frac{\hbar\omega_i}{kT} \right) - 1} \qquad (2.91)$$

Hence, for high temperatures $kT \gg \hbar\omega_i$ we get the *classical limit* $\langle E_i \rangle \approx kT$. Half of this value falls on the kinetic energy of vibrations, and the second half falls on the potential one. For temperatures $kT \lesssim \hbar\omega_i$, the vibrational energy is much less than its classical value.

The statistical sum cannot be calculated analytically for the rotational part of the Boltzmann distribution but, considering the classical limit when the value kT is considerably greater than the characteristic distance between adjacent rotational levels, one can integrate instead of taking the sum. We shall not show general formulas (see Ref. 142 for details) but just restrict ourselves, for illustration, to the case of spherical tops. In this case, for $kT \gg B$, we have

$$Z_{\mathrm{rot}} = \sum_{J=0}^{\infty} (2J + 1)^2 \exp[-BJ(J + 1)/kT] \approx 4 \int_0^{\infty} J^2 \exp(-BJ^2/kT)dJ = \pi^{1/2}\left(\frac{kT}{B}\right)^{3/2} \qquad (2.92)$$

Thus, the rotational Boltzmann distribution comes to

$$F_{\text{rot}}(J) \approx \pi^{-1/2}\left(\frac{B}{kT}\right)^{3/2} (2J + 1)^2 \exp\left[-\frac{BJ(J + 1)}{kT} \right] \tag{2.93}$$

Its maximum falls on

$$J_{\max} \approx \left(\frac{kT}{B}\right)^{1/2} \tag{2.94}$$

that in the case of the molecule SF_6 ($B = 0.09$ cm^{-1}), for example, corresponds to $J_{\max} \approx 50$. The average rotational energy evaluated with the use of the distribution (2.93) is approximately equal to its classical value $(3/2)kT$. It should be noted, however, that formulas like (2.93) do not take into account statistical weights of rotational levels which are different in connection with nuclear spins (see the discussion in the end of Section 2.1.5). This point can be treated in each separate case but we shall not do it here and treat Eq. (2.93), without any further discussion, as averaged over a few close rotational levels.

Let us return to vibrational distribution and estimate how much the vibrationally-excited states of molecules are populated, for example, at room temperature. The population of the ground state can be evaluated with the use of equation

$$F_{\text{vib}}(v_i = 0) = \prod_{i=1}^{s} \left[1 - \exp\left(-\frac{\hbar\omega_i}{kT} \right) \right] \tag{2.95}$$

Hence, one can see that the population of the ground state is less, in general, the greater the number of atoms and low-frequency vibrations with the energy of one quantum being of the order of or smaller than kT. For example, in the gas D_2O, at the temperature $T = 300$ K, there are about 99% of all the molecules in the ground state, while in SF_6 there are only about 30%. The vibrations of UF_6 are, on the average, appreciably lower in frequency than those of SF_6. As a consequence, in the gas UF_6, at the same temperature, there are even <1% of all the molecules in the ground state.

When high vibrational states are strongly excited, one can use the density of vibrational states to arrive at the shape of the distribution. It is convenient to treat formally the distribution as continuous, i.e., the distribution function will give the probability of finding a molecule within the interval dE_{vib} of vibrational energy. In terms of the density of states, the Boltzmann vibrational distribution is described by

$$F_{\text{vib}}(E_{\text{vib}}) = \frac{\rho(E_{\text{vib}})}{Z_{\text{vib}}} \exp\left(-\frac{E_{\text{vib}}}{kT}\right), \qquad Z_{\text{vib}} = \int_0^{\infty} \rho(E_{\text{vib}}) \exp\left(-\frac{E_{\text{vib}}}{kT}\right) dE_{\text{vib}} \tag{2.96}$$

The main characteristics of this distribution may be estimated by first neglecting E_0 in the semiclassical expression (2.70) for $\rho(E_{\text{vib}})$. Then we shall find

$$F_{\text{vib}}(E_{\text{vib}}) \sim \frac{1}{(s-1)!} \left(\frac{E_{\text{vib}}}{kT}\right)^{s-1} \exp\left(-\frac{E_{\text{vib}}}{kT}\right) \tag{2.97}$$

The maximum of this distribution falls on the value $E_{\max} = (s - 1)kT$, and the mean energy $\langle E_{\text{vib}} \rangle = skT$ and we have the classical result, according to which each vibrational degree of freedom takes kT. Of course, if one does not ignore in Eq. (2.70) the energy E_0 of the ground state and, as well, uses the more accurate Whitten-Rabinovitch approximation (2.71), then quantum effects will appear, and the mean vibrational energy will probably be appreciably less than skT. It should be also noticed that the Boltzmann distribution for a polyatomic molecule has a substantial qualitative distinction from the diatomic case. For a diatomic molecule having a single vibration, the distribution function decreases monotonicly versus the vibrational energy, while, for a polyatomic molecule, it exhibits a pronounced maximum almost coinciding with the mean energy. This is a feature of the growth of $\rho(E_{\text{vib}})$. Of course, under equilibrium conditions, populations of individual vibrational levels should be less than the population of the ground state.

It should also be noted that the relative width of the distribution (2.96) decreases with an increase in the number of vibrational degrees of freedom. It is convenient to characterize the relative half-width of any distribution $f(x)$ through the ratio d of the standard deviation $(\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$ to the mean value, i.e.,

$$d = \left[\frac{\langle x^2\rangle}{\langle x\rangle^2} - 1\right]^{1/2} \tag{2.98}$$

In our case, we can easily find that

$$d_{\text{vib}} \approx s^{-1/2} \tag{2.99}$$

2.5.2. *General features of collisional processes*

The problem of a collision of two particles A and B in general usually takes approximately the following form. Before the collision, i.e., at rather a large distance, let the particles be in the quantum states $|a\rangle$ and $|b\rangle$ with velocities v_A and v_B, so that the motion following their classical trajectories brings them so close at some instant of time (see Figure 2.16) that one can no longer neglect their interaction. This interaction can lead to a change in trajectories as well as quantum states of both the particles. During and after the collision, only the total energy, momentum, and angular momentum of whole system are conserved in principle, and one can describe the change in velocities and quantum states in terms of the probabilities $W(a, b, v_A, v_B; a', b', v'_A, v'_B)$. The probability W also depends on the *collision radius* $\hat{r}$ (see Figure 2.16). It is just these probabilities that are the subject of collision theory. The classical treatment of the trajectory

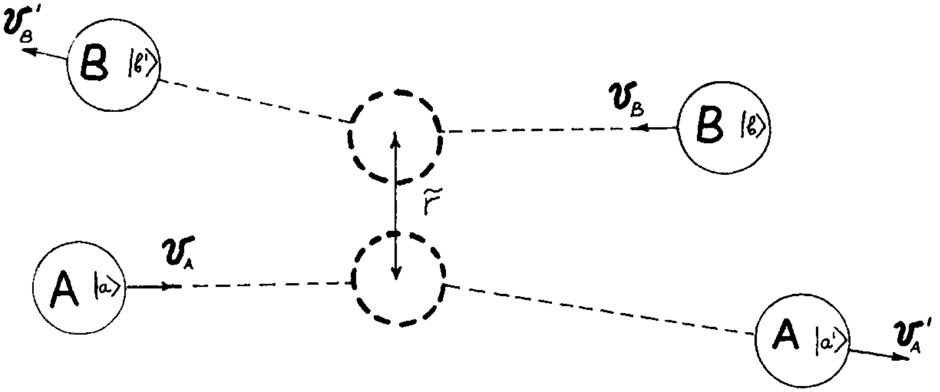

FIGURE 2.16 The treatment of collision of two molecules A and B in terms of their classical trajectories.

may often be reasonably used, but the rigorous quantum-mechanical treatment of translational motion can also be applied.

Let us now formulate the basic concepts of the simplest estimates:

1. To evaluate the probabilities of quantum transitions occurring due to a collision one needs, first of all, the *intermolecular potential V* from electrostatic forces. Adhering to the classical description of translational motion, one treats V as a matrix $V_{a,b;a',b'}$, elements of which depend on the distance R between the centers of mass of the colliding molecules. The diagonal elements $V_{a,b;a,b}$ of this matrix describe, in the first order perturbation theory, the interaction of molecules in the states $|a\rangle$ and $|b\rangle$, while the nondiagonal elements are responsible for the transitions between levels occurring during collisions. Of course, different matrix elements of any intermolecular potential may depend on R in different ways. Nevertheless, a common qualitative feature is that all intermolecular forces are short-range; their radii are, within an order of magnitude, the geometrical dimensions of molecules.

2. The electrostatic forces responsible for intermolecular interaction may be determined from the molecular wavefunctions, from which the spatial distribution of charges can be, in principle, obtained. This problem is very complex; therefore, to introduce an intermolecular potential one ordinarily uses models. The simplest one is the *rigid-sphere approximation,* according to which the interaction potential jumps to infinity at $R_0 = r_A + r_B$, where r_A and r_B are treated as geometrical *radii* of colliding molecules, and equals zero at $R > R_0$. Various other model potentials based on different physical considerations are widely used (see, for example, Refs. 134 and 143), the choice of model being influenced by the relaxation process specifically studied. For example, to describe the diagonal matrix elements of an intermolecular potential one often uses the Lennard-Jones potential

$$V(R) = 4V_{\mathrm{L-J}}\left[\left(\frac{r_A + r_B}{R}\right)^{12} - \left(\frac{r_A + r_B}{R}\right)^{6}\right] \qquad (2.100)$$

which contains the Van-der-Waals attraction component and the repulsive component depending more rapidly on R (see Figure 2.17). In Eq. (2.100), the values r_A and r_B can also be understood as molecular radii. It must be stressed that any model potential, both its diagonal and nondiagonal parts, must contain a parameter treated as the molecular radius.

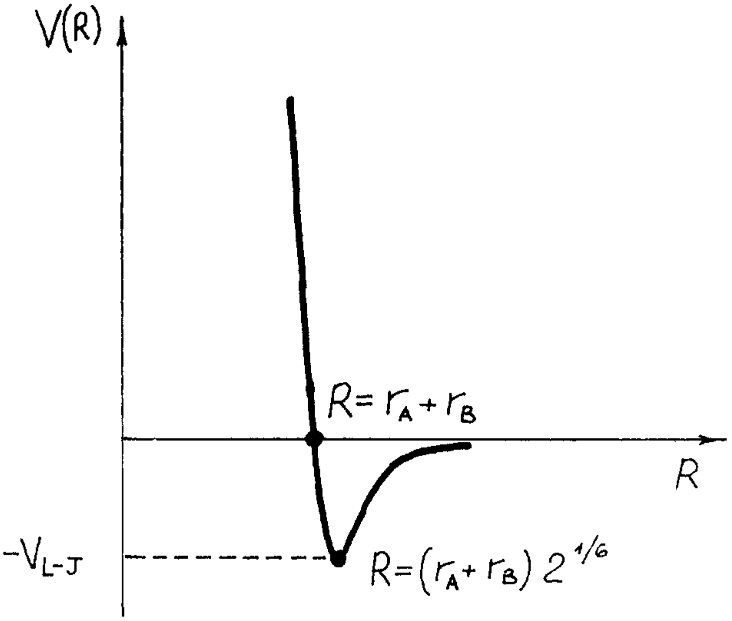

FIGURE 2.17 The Lennard-Jones model potential.

3. If the radius of collision of molecules A and B is smaller than the value $(r_A + r_B)$, the molecules are said to undergo a *hard collision*. In the analysis of such a collision, the purely classical picture of the elastic collision of billiard balls is useful. These collisions, without changes in the internal states of the particles, are called elastic. As a result of elastic collision, the velocities of particles change according to the laws of conservation of energy and momentum. Averaging over all possible directions and values of molecular velocities in the gas, the jump in kinetic energy of a molecule when it rigidly collides with an identical one, is of the order of kT, i.e., the mean kinetic energy. This notion of the molecule, as a rigid sphere, enables us to introduce such important concepts as the *gas-kinetic cross-section* and the *free-flight time*. These concepts are, of course, known to everybody from elementary textbooks. Let us take, for example, the expressions for a one-component gas with density N and temperature T:

$$\sigma_0 = 4\pi r^2, \ \tau_{\text{free}} = \frac{1}{4N\sigma_0}\left(\frac{\pi M}{kT}\right)^{1/2} \tag{2.101}$$

Rather substantial changes in molecular velocities due to hard collisions result in an important consequence. If the molecular velocity distribution differs from the equilibrium one at some instant of time, then equilibrium is re-established during the free-flight time.* The pressure of 1 Torr corresponds to a density of molecules $N \approx 3.5 \times 10^{16}$ cm^{-3}, at a temperature of 300 K; then for example, molecules with radius $r \approx 3 \times 10^{-8}$ cm and mass equal to 100 atomic units, this time will be $\tau_{\text{tr}} \sim \tau_{\text{free}} \approx 0.7 \times 10^{-7}$ s. In this series of papers we shall assume a Maxwell velocity distribution. Thus, even if the distribution in the gas is nonequilibrium, on the whole, we shall use, without any correction, the concept of *translational temperature* T_{tr}.

4. Collisions followed by transitions between internal states of the molecules are called *inelastic*. As a result of inelastic collision, the kinetic energy of the system changes, i.e., $\Delta E_{\text{tr}} = (E_a - E_{a'}) + (E_b - E_{b'}) = E_{a,b} - E_{a',b'}$. If the translational motion of molecules is treated classically, one naturally comes to the idea of presenting the result of inelastic collision in terms of the transition produced in the system of two molecules *(quasimolecule)* by the nonstationary interaction *V(t)* which increases as the molecules draw together, and then decreases as they move away. Let us consider, for simplicity, a two-level quasimolecule and use, for orientation, the formula for the transition probability given by the nonstationary perturbation theory (see, for example, Ref. 72):

$$W(a,b;a',b') = \frac{1}{(E_{a,b} - E_{a',b'})^2}\left|\int_{-\infty}^{\infty} \frac{\partial V_{a,b;a',b'}}{\partial t} \exp\left[\frac{i}{\hbar}(E_{a,b} - E_{a',b'})t\right] dt\right|^2 \tag{2.102}$$

It may be seen from this formula that the value of the transition probability depends primarily on the relation between the rate of switching on of *V(t)* and the frequency of the transition under consideration. The typical rise time of *V(t)*, say, for a rigid collision of identical molecules is approxi-

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*This statement requires a more accurate definition, if the gas is a mixture of molecules with essentially different masses (see Refs. 128 and 138 for details).

mately equal to the ratio of the molecular radius to the average velocity of relative motion of molecules, in gas, i.e.,

$$\tau_{\text{coll}} \approx r(M/kT)^{1/2}, \tag{2.103}$$

and the parameter

$$\chi_{\text{adiab}} = \frac{|E_{a,b} - E_{a',b'}|}{\hbar} \tau_{\text{coll}} \tag{2.104}$$

may be used for estimates. Discussing molecular spectra, we spoke (see Section 2.1.2) about the standard treatment of the electron terms within the adiabatic approximation, since characteristic frequencies of motion of electrons are much higher than those of nuclei. By analogy, one can also appeal to *adiabaticity of collision,* if $\chi_{\text{adiab}} \gg 1$. During an adiabatic switching on of $V(t)$ the levels of the quasimolecule have time to adapt themselves to changes in interaction and the transition probability is small and generally it is proportional to the value $\exp(-\chi_{\text{adiab}})$. In the opposite case of *nonadiabatic collision*, the transition probability is much greater:

$$W(a,b;a',b') \sim \left| \frac{V^{(\max)}_{a,b;a',b'}\, \tau_{\text{coll}}}{\hbar} \right|^2 \tag{2.105}$$

It is natural that, if W evaluated with the use of Eq. (2.105) turns out to be higher than unity, this simply means that the system is expected to have about the same probability $\sim 1/2$ in both the initial and final states, as a result of collision. It should also be noted that, if N transitions complying with the conditions $\chi_{\text{adiab}} \lesssim 1$ and $|V^{(\max)}_{a,b;a',b'}\tau_{\text{coll}}/\hbar| \gtrsim 1$ are exhibited, the actual realization of each of them is about N^{-1}.

5. If the levels in a quasimolecule (we are interested in the transition between them) are very close, the requirements diminish which calls for rapid switching on (a steep potential) as well as an appreciable value of interaction. Therefore, not only hard collisions but also those with radius exceeding $(r_A + r_B)$ can, in principle, effectively produce transitions with very small changes in the total internal energy of the system. Thus, cross-sections of such processes can *exceed* the gas-kinetic one.[139,144] Here are two particularly interesting degenerate cases where the energy in a quasimolecule does not change at all: transitions between sublevels with different

angular-momentum components along an axis of the laboratory frame, and resonant energy exchange $|a,a'\rangle \rightarrow |a',a\rangle$ between two identical molecules.

2.5.3. *Phenomenological description of relaxation processes*

Averaging of probabilities of inelastic processes over the Maxwell velocity distribution and radii of collisions leads to a phenomenological description of relaxation processes which will be sufficient for our purposes in this series of papers. We will dwell on the formal calculations being worked out to provide the averaging but notice that the result of the averaging can be expressed through various physical quantities. Usually the so-called *reaction constant* $k_{A,B}(a,b;a',b')$ in $\mathrm{cm}^3\mathrm{s}^{-1}$ is used. This value has the following physical meaning. The reaction constant multiplied by the densities N_a and N_b of the molecules in the states $|a\rangle$ and $|b\rangle$ gives the *number of events* $|a,b\rangle \rightarrow |a',b'\rangle$ per cubic centimeter of volume per second. The reaction constant describing a *direct process* which is accompanied by a decrease in energy is greater, of course, than that describing a *reverse process* which is accompanied by an increase in energy, since the Maxwell velocity distribution does not allow any pair of colliding molecules to undergo the reverse process. The inequivalence of direct and reverse processes is reflected in the *detailed-balance principle*, according to which

$$k_{A,B}(a,b;a',b') = \frac{g_{a'}g_{b'}}{g_a g_b} k_{A,B}(a',b';a,b) \exp\left[-\frac{(E_{a'} - E_a) + (E_{b'} - E_b)}{kT} \right], \tag{2.106}$$

where E_i, g_i are the energies and degeneracies of participating levels. Thus, two reaction constants differ greatly if $|E_{a,b} - E_{a',b'}| > kT$ and are almost equal, with a regard for the degeneracies, if $|E_{a,b} - E_{a',b'}| \ll kT$. The detailed-balance principle follows directly from the fact that under statistical equilibrium the number of direct events must be equal to that of reverse ones, in addition to the explicit form of the Boltzmann distribution.

If the distribution of molecules over energy levels differs initially from the equilibrium one, then the kinetics of the transient process to equilibrium can be described in terms of time-dependent populations $N_a(t)$ of individual levels. Let us consider, for simplicity, a one-component gas. In this case, the kinetics of populations is governed by the equations

$$\frac{dN_a}{dt} = -N_a \sum_{b,b'} N_b \sum_{a' \neq a} k(a,b;a',b') + \sum_{b',b} N_{b'} \sum_{a' \neq a} k(a',b';a,b)N_{a'} \tag{2.107}$$

One would hardly try to use this equation in its general form, since such a great number of constants is needed. The main problem of a theoretical description of relaxations in any system, then, is the categorizing into some hierarchy of relaxation processes by their characteristic transition times to *partial* balances. For example, for molecules, as mentioned in the foregoing section, one can assume the equilibration of the translational degrees of freedom to be the fastest process. The hierarchy can be extended (supported by numerous experiments), and one can add three more processes: rotational relaxation and attendant equilibration of rotational and translational degrees of freedom; vibrational relaxation which leads to equilibrium within vibrations; and energy exchange between vibrations on the one hand and translational and rotational motion on the other hand. All these processes have the same common feature that equilibration usually follows the exponential law that has been tested through a variety of kinetic models.

Before discussing individual relaxation processes, let us formulate the basic approximations which are often used in practice:

1. *Linearized approximation.* Averaging of the reaction constants over all initial and final states of the colliding partner leads to the following simplified form of the kinetic equation (2.107):

$$\frac{dN_a}{dt} = -NN_a \sum_{a' \neq a} \tilde{k}(a;a') + N \sum_{a' \neq a} \tilde{k}(a';a)N_{a'} \tag{2.108}$$

Here N is the density of molecules in a gas, and the products $\tilde{k}\,(a;a')N$ mean numbers of transitions $|a\rangle \rightarrow |a'\rangle$ per second. This approximation is trivial, of course, if the reaction constants depend only slightly on the initial and final states of the collision partner B. Then $\tilde{k}(a;a') \approx k(a,b;a',b')$ for all $|b\rangle$ and $|b'\rangle$. In addition, there may be two other situations when this approximation is physically justified. First, a case when the relaxing molecules A are mixed with excessive buffer gas B, say atomic, the excitation of which may be neglected. Another case is a one-component gas with its distribution differing slightly from the equilibrium one. Then one can roughly accept $N_b = N_b^{(eq)}$, and $\tilde{k}(a;a') = N^{-1} \sum_b k(a,b;a',b')N_b^{(eq)}$.

2. *Linear approximation*. This approximation assumes that the time derivatives in Eqs. (2.108) depend only on populations N_a and do not depend on the distribution function over other states. In essence, for the case when the distribution differs slightly from the equilibrium one, it is the natural next step following the linearized approximation. Within the linear approximation, the kinetic equations can be treated separately for each individual level and are of the form

$$\frac{dN_a}{dt} = \frac{N_a^{(eq)} - N_a}{\tau_a}, \tag{2.109}$$

where the constant τ_a really means the time of relaxation of population N_a to its equilibrium value $N_a^{(eq)}$. If at time $t = 0$ $N_a = N_a^{(0)}$, then, following to (2.109), $N_a(t) = N_a^{(0)}\exp(-t/\tau_a) + N_a^{(eq)}[1 - \exp(-t/\tau_a)]$. Thus, it is just a linear approximation of the relaxation processes and the exponential law of equilibration may be seen explicitly. Note that formally Eq. (2.107) can always be rewritten in the form (2.109), but with τ_a latently depending on time. The use of the linear approximation assumes, in fact, that the dependence of τ_a on the shape of distribution and, hence, on time may be neglected.

3. *Quasiequilibrium approximation*. This approximation assumes that partial balances within different degrees of freedom will have been attained before the energy exchange between them occurs. Within this approximation, the energy exchange between different degrees of freedom is likely governed by kinetic equations like

$$\frac{dE_1}{dt} = \frac{E_1^{(eq)} - E_1}{\tau_{12}}, \qquad \frac{dE_2}{dt} = \frac{E_2^{(eq)} - E_2}{\tau_{12}}, \tag{2.110}$$

where, for simplicity, two degrees of freedom are involved, and $E_1^{(eq)}$ and $E_2^{(eq)}$ are the equilibrium energies, their sum being equal to $E_1 + E_2$ at any instant of time. As in Eq. (2.109), the value τ_{12} is the relaxation time, which, in general, probably depends on energies E_1 and E_2. If this dependence may be neglected, then one again comes to the exponential law of equilibration.

4. *One-quantum approximation*. This approximation which works rather well in some particular cases assumes that, when the molecule A collides with a partner, the transitions, with overwhelming probabilities, are into the adjacent upper and lower quantum states. We shall not write out general equations here but later we shall come across one specific case while treating vibration-vibration relaxations. Just note the one-quantum approximation is closely related to the widely used *diffusion approximation*, when to simplify the mathematics one substitutes the discrete distribution function by the continuous one.

2.5.4. Rotational relaxation

As mentioned in Section 2.5.1, distances between adjacent populated rotational levels are usually much smaller than kT. On the other hand, at the instant of a rigid collision, the energy of relative translational motion of molecules which is also, on the average, of the order of kT converts into that of intermolecular interaction. Therefore, one may expect rotational levels to become strongly perturbed during a collision, wavefunctions of the quasimolecule to be strongly mixed within kT, and colliding molecules to forget their initial precollision states. As a result, the molecule may be found, after the collision, in an arbitrary rotational level within one kT from the initial one. A similar conclusion on the mean value of jumps in rotational energy due to hard collisions can be drawn from a purely classical picture when molecules are simulated by rough spheres, dumb-bells, etc. (see, for example, Refs. 134, 135, 138 and 145). Such a picture of rotational relaxation is usually referred to as the *mechanism of strong collisions*.[146]

Starting from the general features discussed in Section 2.5.2, one may conclude that the mechanism of strong collisions is realistic, if the processes leading to rotational relaxation can be treated as nonadiabatic. For transitions between, at least, rather close rotational levels, this is generally so. Let us compare, for example, the inverse frequency $\omega_{\max}^{-1}$ of the transition between adjacent rotational levels of spherical tops near the maximum of rotational distribution [see Eq. (2.94)] with the typical τ_{coll} (2.103). Omitting numerical coefficients, we find $\omega_{\max} \sim \hbar^{-1} (BkT)^{1/2}$. Now, if the mass of the molecule is not concentrated in its center, then $B \sim \hbar^2 / Mr^2$, hence $\omega_{\max}\tau_{\text{coll}} \sim 1$. Thus, the collisions followed by actual transitions between, at least, adjacent rotational states probably comply with the criterion of nonadiabaticity $\chi_{\text{adiab}} \lesssim 1$, and, in the general case, any rotational transition with

$$\Delta E_{\text{rot}} \approx \hbar/\tau_{\text{coll}} \tag{2.111}$$

can be treated as nonadiabatic. Thus, we have obtained the lower estimate for jumps in the rotational energy due to rigid collisions. However, the value ΔE_{rot} (2.111) is considerably less than kT suggested by the mechanism of strong collisions. Indeed, taking for estimate the molecule velocity $v \approx 3 \times 10^4$ cm/s and molecule radius $r \approx 3 \times 10^{-8}$ cm, one has $\tau_{\text{coll}} \approx 10^{-12}$ s, and from (2.111) $\Delta E_{\text{rot}} \approx 5$ cm^{-1}, while $kT \approx 200$ cm^{-1} at room temperature. Remember, however, that there is rather a big factor unaccounted for, since, at the instant of the closest approach of two molecules, their interaction is great. If we accept the matrix element of intermolecular interaction entering Eq. (2.105) for the transition probability to be kT, then we estimate $W \gg 1$. This means that a transition with the jump $\Delta E_{\text{rot}} \sim \hbar/\tau_{\text{coll}}$ requires a much shorter time than τ_{coll}, and there is time for $N \sim kT/\Delta E_{\text{rot}}$ transitions with the jumps ΔE_{rot} to occur during a collision, hence the average change in rotational energy per collision proves again to be about kT.

Thus, the correspondence of the mechanism of strong collisions to the nonstationary quantum picture of collision becomes clear. It is necessary that the rotational transitions comply with the nonadiabaticity criterion, and the matrix elements of intermolecular interaction would be of the order kT. Realistically, for rotational transitions, the matrix elements of intermolecular interaction are probably somewhat smaller than kT, and in the literature you can find a more careful value, i.e., rotational relaxation needs *several* gas-kinetic collisions. But, if we are interested in relaxation within the lower rotational levels where the transition frequencies are small, then, as mentioned in Section 2.5.2, the transition cross-sections can slightly *exceed* gas-kinetic. In summary it may be said that the estimate of the time of rotational relaxation $\tau_{\text{rot}} \sim 3 \times (10^{-7}–10^{-8})$ s related to a gas pressure about 1 Torr will not be in big error.

Two final notes may be rather obvious, but the last note refers to a situation when the rough picture is probably insufficient:

1. Since rotational relaxation is inevitably accompanied by energy exchange with the translational degree of freedom, there is no sense in separating these two processes. Therefore, we shall always assume that the translational and rotational degrees of freedom will be in equilibrium.
2. The distance between adjacent levels in rotational energy increases so that, in general, the requirements for collision nonadiabaticity are harder.

The effect of slower equilibration within the upper rotational levels, as compared to the lower levels, has been observed, for example, in experiments on the molecule N_2.[147]

3. In some cases, for example dipole molecules, the collisions, with their cross-sections higher than the gas-kinetic one, exhibit certain selection rules. When such collisions play the main role for real rotational relaxation, the situation is usually referred to as the *mechanism of weak collisions*. A complete analysis of this mechanism together with actual selection rules is given by Oka[139] who treats the gas NH_3 as a typical example.

2.5.5. Vibrational-vibrational relaxation

By analogy with IR spectroscopy, where one makes the use of the expansion of the dipole moment of the molecule by the normal vibrational coordinates (see Section 2.2.2), the procedure of expansion of intermolecular interaction is carried out in the theory of collisions accompanied by vibrational transitions. This procedure is quite natural, since the intermolecular potential has the molecule dimension as its characteristic spatial scale, and the amplitude of molecular vibrations is typically much smaller. In general, the intermolecular potential V depends on the distance R between the centers of mass of the molecules and on the normal coordinates $q_i^{(A)}$ and $q_i^{(B)}$, and the following expansion is assumed to be justified:

$$
\begin{aligned}
V(R,q_i^{(A)},q_i^{(B)}) \approx V_0(R) &+ \sum_i \left(\frac{\partial V}{\partial q_i^{(A)}}\right)_0 q_i^{(A)} \\
&+ \sum_l \left(\frac{\partial V}{\partial q_i^{(B)}}\right)_0 q_i^{(B)} + \frac{1}{2}\sum_{i,j} \left(\frac{\partial^2 V}{\partial q_i^{(A)}\partial q_j^{(A)}}\right)_0 q_i^{(A)} q_j^{(A)} \\
&+ \frac{1}{2}\sum_{i,j} \left(\frac{\partial^2 V}{\partial q_i^{(B)}\partial q_j^{(B)}}\right)_0 q_i^{(B)} q_j^{(B)} + \frac{1}{2}\sum_{i,j} \left(\frac{\partial^2 V}{\partial q_i^{(A)}\partial q_j^{(B)}}\right)_0 q_i^{(A)} q_j^{(B)} \\
&+ \ldots
\end{aligned}
\tag{2.112}
$$

Within the harmonic approximation, each term in Eq. (2.112) is responsible for several quite definite vibrational transitions. First, let us consider the last term written out. Since, within the harmonic approximation, only matrix elements of a normal coordinate between adjacent vibrational states are nonvanishing, then this term, in particular, describes a one-quantum vibrational exchange between colliding molecules. From this class of processes, one type is especially distinguished, when identical molecules collide and vibrational-energy exchange occurs within one mode. Within the harmonic approximation, such a process is *resonant*, since it does not call for any change in vibrational energy, and, therefore, it satisfies the nonadiabaticity criterion $\chi_{\text{adiab}} \ll 1$. Formally, within the harmonic approximation, the parameter χ_{adiab} is even equal to zero. But there is a real anharmonicity of vibrations and the intramode exchange is more appropriately called *quasiresonant*. In accordance with Eqs. (2.105) and (2.112), the probabilities of intramode exchanges due to collisions are proportional to $(\partial^2 V/\partial q_l^{(A)}\partial q_l^{(B)})_0$ squared. We cannot go into any detailed estimates here but note that physically the tunneling through a potential barrier between the surfaces of internal potentials of two colliding molecules is needed. Nevertheless, due to nonadiabaticity, the probabilities for the process under consideration are rather appreciable. Characteristic relaxation times $\tau_{V\text{-}V}$ for transition to equilibrium within individual modes are about 10^{-6} s per the pressure 1 Torr.

The vibrational-vibrational exchange may be referred to as quasiresonant not only when identical molecules collide, but also in cases of pairs of molecules with close values of vibrational frequencies. There is, for example, the well known process of quasiresonant transfer of vibrational energy from the molecule N_2 excited in the electric discharge to the molecule CO_2 that plays the important role in the operation of the CO_2-laser. Another important practical point is the vibrational-vibrational exchange between molecules with different isotopic compositions. The energy defect ΔE at vibrational-vibrational exchange can be compensated by changes in rotational energy. Hence one may understand that the criterion of quasiresonance lies in the condition $\Delta E < kT_{\text{tr}}$. Characteristic relaxation times for quasiresonant one-quantum exchanges between different molecules, as well as for the intramode exchange, are about 10^{-6} s per the pressure 1 Torr.

The higher-order terms in the expansion (2.112) may also be responsible for processes of vibrational-vibrational *intermode* exchange. In particular, the specific third-order terms exhibit processes, when, for example, one vibrational quantum ω_1 exchanges into two quanta ω_2 and ω_3, the sum of which is close to ω_1, etc. (See, for example, the detailed experimental study on the molecule CH_3F[148] which demonstrates the variety of actual intermode exchanges.) For lower vibrational levels, the processes of intermode and intramode relaxation are quite distinguishable by their characteristic times. Since, in the general case, intermode relaxation is caused by terms of orders higher than for intramode relaxation, it is the slower process. Characteristic times for intermode exchange correspond to the range $p\tau_{V\text{-}V'} \sim 10^{-5}$–$10^{-6}$ Torr × s.

It is very important to note that, for the region of stochasticity of vibrational motion, where the equilibrium distribution of vibrational energy over modes is caused by the very structure of the true energy eigenstates (see Section 2.3.2), the process of intermode relaxation is not particularly important. Keeping this in mind, we shall often use the name vibrational-vibrational *(V-V)* relaxation without any additional specifications and denote, as τ_{V-V}, the characteristic time of equilibration of the system to the equilibrium Boltzman distribution (2.96).

The final notes refer to two subtle points.

1. When the relaxation of a gas of one-dimensional anharmonic oscillators through the one-quantum-exchange mechanism is worked out, the inclusion of anharmonic shifts leads to an interesting effect. If the vibrational energy, in particular, exceeds its equilibrium value defined by the energy stored in the translational degree of freedom, then *V-V* exchanges form a distribution which differs from the Boltzmann one. This distribution called the *Treanor distribution*[149] is, in essence, *quasiequilibrium* and relaxes to the Boltzmann one as the exchange of energy between the vibrational and translational degrees of freedom proceeds. The Treanor distribution may sometimes be useful for analysis of intermode relaxation, too (see, for example, Ref. 148). On the whole, however, the problem of the shape of a quasiequilibrium vibrational distribution remains unclear for polyatomic molecules. So, in this series of papers, we shall assume the Boltzmann dependence to be the most realistic and describe the distribution after *V-V* relaxation in terms of the *vibrational temperature* T_{vib}.
2. In the literature, there are many approaches to the analysis and estimation of characteristic times of *V-V* relaxation for lower levels. Nevertheless, for highly-excited vibrational levels lying in the stochasticity region, the theoretical studies are only beginning (see, for example, Ref. 150). The possibility of strong vibrational excitation of molecules by IR field has given, in essence, the first prerequisites for experimental studies in this region. In the following Sections we shall discuss some specific experiments.

2.5.6. *Vibrational-translational relaxation*

Since reaction constants for direct and reverse processes are not equal [see Eq. (2.106)], vibrational exchanges, on the average, are inevitably followed by a transformation of a portion of vibrational energy into translational motion. But, if after the process of *V-V* relaxation the vibrational temperature exceeds the translational one ($T_{\text{vib}} > T_{\text{tr}}$), then the transition to the total equilibrium is possible only through a process of *vibrational-translational* relaxation. The second and third terms in the expansion (2.112) are responsible for this process. If the molecular vibrational frequencies are greater than $kT_{tr}/\hbar$, this process does not comply with the quasiresonant criterion. Therefore, vibrational-translational relaxation is usually the slowest of the processes under consideration and requires a great number of gas-kinetic collisions. We will not discuss the numerous theoretical calculations for the probabilities of the deactivation of vibrational excitation which were started from the work by Landau and Teller,[151] and which usually issue from the assumption that this process is adiabatic. Only note, for orientation, that the characteristic times τ_{V-T} for vibrational-translational relaxation correspond to the range $p\tau_{V-T} \sim 10^{-3}$–10^{-5} Torr × s and take into account several general remarks:

1. Some cases are treated in literature (in more detail, see, for example, Ref. 128), when, as a result of collision, the vibrational excitation transforms mainly into the rotational degrees of freedom rather than into translational motion. Those cases are referred to as *V-R relaxation,* and, in general, the name *V-T,R relaxation* is also used. But, since the translational and rotational degrees of freedom come into their mutual equilibrium rather quickly, then the use of the name *V-T relaxation* is quite justified, and we shall adhere to it below.
2. To describe the kinetics of vibrational-translational relaxation the quasiequilibrium approximation (see Section 2.5.3) is quite suitable with Eq. (2.110). It should be noted, however, that experimental data have been obtained (see, for example, Ref. 152) which show faster *V-T* relaxations, as the vibrational energy increases.
3. If the statistical equilibrium is initially disturbed inside an irradiated volume of molecular gas (for example, inside the laser beam), the physical description is often justified which suggests, at first, an equilibration in irradiated volume and, later on, the temperature equalizing over the whole volume. Here the ratio of the time of the slowest relaxation process, i.e., *V-T* relaxation, to the characteristic time of diffusion serves as a criterion whether this description can be used. Below, where a comparison will be needed, the appropriate estimates will be discussed.

2.5.7. Phase relaxation

So far, treating relaxation processes, we have been interested in the kinetics of *populations* of molecular levels. But, the description of gas in terms of populations is not the most general in the view of quantum mechanics.

Molecules of the gas may be found not only in pure states but also in superposition. Realistically, even if at any instant of time the molecule were in a fixed quantum state, after the first collision its state would be uncertain, and one would speak only about the probabilities of occupation of the different molecular levels. Therefore, the description in terms of populations suggests averaging over all the molecules. On the other hand, the wavefunction of a molecule which is, in the general case, a superposition

$$\Psi = \sum_j a_j \psi_j \exp\left(-\frac{i}{\hbar} E_j t\right) \tag{2.113}$$

cannot be re-established through only the probabilities $|a_j|^2$ of occupation of different molecular energy states. One also needs the phase relationships between the probability amplitudes a_j in Eq. (2.113). The phase relationships may be defined, if one adds, for example, the combinations

$$\rho_{jk} = a_j^* a_k \tag{2.114}$$

The collection of values averaged over all molecules is called the *density matrix*, and the description with the use of the density matrix is the most general in quantum statistics. The diagonal elements of the density matrix obviously describe the populations of states. The nondiagonal elements are equal to zero at statistical equilibrium, and no collision processes whatever can make them nonzero. However, the case is somewhat different, when the molecules interact with coherent radiation. In the next chapter we shall give much consideration to this point. Here we will only point out that, as a result of this interaction, the nondiagonal elements of the density matrix are probably nonzero and raise the question of what is the physics of their relaxation to the zero statistical-equilibrium values.

First, it is rather clear that any collision which, with a probability of about unity, leads to a change in the state of the molecule also leads to loss of *phase memory*. But, in principle, another mechanism may be supposed which does not assume the occurrence of any transition. The simplest way to understand its nature is to consider the two-level system during a far adiabatic collision along a classical trajectory which just slightly perturbs the position of the levels. In the general case, the shifts of levels during the interaction are not equal, and, as a result of collision, the final value of nondiagonal matrix element relates to its initial value as

$$(\rho_{jk})_{\text{final}} = (\rho_{jk})_{\text{initial}} \exp\left[\frac{i}{\hbar}(V_j - V_k)t\right], \tag{2.115}$$

where, within first order perturbation theory,

$$V_j = \int_{-\infty}^{\infty} \langle j|\hat{V}(t)|j\rangle dt, \quad V_k = \int_{-\infty}^{\infty} \langle k|\hat{V}(t)|k\rangle dt \tag{2.116}$$

Since slightly different collision trajectories result in different values V_j and V_k, it becomes clear that the criterion of destroyed phase memory lies in the condition $(V_j - V_k)\bar{r}/v_{\text{rel}} \gtrsim 2\pi\hbar$, where V_j and V_k also depend on the collision radius $\bar{r}$, and v_{rel} is the mean velocity of relative motion. The formal allowance for the second mechanism probably forces one to treat phase relaxation irrespective of a relaxation of populations. Nevertheless, as far as the vibrational-rotational levels of polyatomic molecules are concerned, there are no convincing arguments that the second mechanism plays any essential role. Detailed discussion of this point based on experimental results which follow from studies of the coherent transient effects is given in Ref. 141.

The final note of this section is about the terminology. By analogy with the nuclear magnetic resonance, the previously considered relaxation process is often referred to as *transversal relaxation*. The designation is also T_2 for the time of transversal relaxation. For phenomenological description, one naturally accepts a usual relaxation equation, as

$$\frac{d\rho_{jk}}{dt} = -\frac{\rho_{jk}}{T_2} \tag{2.117}$$

2.6. Broadening of spectral lines in the IR range

In Section 2.2 we discussed vibrational-rotational spectra of molecules assuming the levels to be discrete. Strictly speaking, even if one treats the isolated molecule, its spectral lines are broadened due to the finite lifetime in excited states. This broadening called *natural* or *radiative* gives the widths, which are very small in the IR range being typically about $(\Delta\omega)_{\text{nat}} \sim 10^{-7}$–$10^{-9}$ cm^{-1}, for dipole-allowed transitions. Radiative broadening in IR spectra of molecular gases is negligible compared to broadenings arising from other physical causes. The first one arises from the *Doppler effect* which arises from a molecule moving with velocity v_z along the axis of propagation of radiation shifts its apparent field frequency, within the first approximation by the small ratio v/c, by the value $\Delta\omega$ with respect to the field frequency ω_0 in the laboratory frame:

$$\Delta\omega = \omega_0 \frac{v_z}{c} \tag{2.118}$$

Since the molecules in gas are distributed by velocities in accordance with the Maxwell distribution (2.87), then resonant frequencies for the gas, on the whole, are distributed by the Gauss law, and this distribution, normalized to unity, has the following form:

$$G_\omega^{(\mathrm{Doppl})} = \frac{c}{\omega_0}\left(\frac{M}{2\pi kT}\right)^{1/2} \exp\left[-\frac{M(\omega - \omega_0)^2 c^2}{2kT\,\omega_0^2}\right] \tag{2.119}$$

with its half-width at the half-maximum

$$(\Delta\omega)_{\mathrm{Doppl}} = \frac{\omega_0}{c}\left(\frac{2kT}{M}\,ln2\right)^{1/2} \tag{2.120}$$

This value, for the transition with frequency 10^3 cm^{-1}, in gas molecules of 100 atomic units, at a temperature 300 K, is $(\Delta\omega)_{\mathrm{Doppl}} \approx 7 \times 10^{-4}$ cm^{-1}.

Since Doppler broadening is from the difference in resonant frequencies of different molecules in a gas, it is *inhomogeneous*. Otherwise, the broadening caused by radiative decay is *homogeneous*. But, for molecular gases, another type of homogeneous broadening, i.e., collisional broadening, is much more essential. In the previous section we have treated various relaxation processes occurring in molecular gases. By analogy with spontaneous decay, collisions also result in a finite lifetime of a molecule in any quantum state and, hence, in a broadening of spectral lines. But even if we assume that collisions are not followed by changes in states, the mechanism of collisional broadening will exist, all the same, caused by phase relaxation. The effect of phase relaxation on the broadening of spectral lines can be understood within the simple two-level picture considered in Section 2.5.7. This picture considers that, during collision, the lower and upper level of the molecular transition undergo different shifts, i.e., the transition frequency seems to drift. Since at any instant of time there are always pairs of colliding molecules in the gas, the spectral line must be broadened. Of course this is a very rough picture, from which any information on the form of a homogeneously broadened line can hardly be obtained. We restrict ourselves here only to the theory of collisional broadening (see, for example, Ref. 153) with the shape of the contour of homogeneous broadening given by the Lorentzian

$$G_\omega^{(\mathrm{hom})} = \frac{1}{\pi} \frac{(\Delta\omega)_{\mathrm{hom}}}{(\omega - \omega_0)^2 + [(\Delta\omega)_{\mathrm{hom}}]^2}, \tag{2.121}$$

where $(\Delta\omega)_{\mathrm{hom}}$ is the half-width of line at the half-maximum which, of course, depends on gas pressure. If one takes, for example, our lower estimate for the rotational-relaxation time $\tau_{\mathrm{rot}} \approx 3 \times 10^{-8}$ s at the pressure 1 Torr (see Section 2.5.4), then $(\Delta\omega)_{\mathrm{hom}} \approx 2 \times 10^{-4}$ cm^{-1}, i.e., several times smaller than the typical Doppler half-width.

In Section 2.2.2 we characterized the intensity of an individual vibration-rotation line $|i\rangle \rightarrow |k\rangle$ in terms of the squared matrix element $|\mu_{ik}|^2$ of the dipole-moment operator. Taking broadening into consideration, one may say that the value proportional to $|\mu_{ik}|^2$ will be the line intensity integrated over its spectrum. It is convenient to describe the intensity distribution inside the line contour in terms of the frequency-dependent *absorption cross-section* $\sigma_{ik}(\omega)$ which is introduced as

$$\sigma_{ik}(\omega) = \frac{4\pi^2\omega_0^2}{\hbar c} |\mu_{ik}|^2 \, G_\omega, \tag{2.122}$$

where the function, normalized to unity, G_ω gives the line-shape. If the homogeneous and inhomogeneous widths differ greatly, the dependence (2.119) or (2.121) with the greater width should be chosen for G_ω. In general, the line-shape is given by the *convolution* of contours of homogeneous and inhomogeneous broadening. The absorption cross-section (2.122) is expressed in cm^2. The physical sense of this value is that it describes an attenuation (or amplification) in the intensity I_ω of the monochromatic light wave with the frequency ω, as it propagates through the molecular gas along the axis z, according to the law

$$I_\omega = I_\omega^{(0)} \exp[-\sigma_{ik}(\omega)(N_i - N_k)z], \tag{2.123}$$

where N_i and N_k are the densities of molecules in the lower and upper levels of the transition under consideration. The value $\sigma_{ik}(\omega)(N_i - N_k)$ is also called the ***absorption coefficient***. If the populations are inverted, i.e., $N_i < N_k$, then the absorption coefficient is negative, the wave is amplified, and the value $\sigma_{ik}(\omega)(N_k - N_i)$ is called in this case the ***gain coefficient***.

Our final notes are not directly related to this series of papers but they are included for completeness:

1. A rather typical situation for molecular gases is when two or more transitions lie within the Doppler widths of individual lines. For example, in the high-resolution-spectra of SF_6 shown in Figure 2.6, splittings of lines in clusters are screened by Doppler broadening. In such cases, the routine spectroscopy is not able to provide resolution of the individual lines. Here the various methods of modern laser spectroscopy can improve the situation with special techniques *free from Doppler broadening*, based on nonlinear effects.[154–156]
2. The methods of spectroscopy which are free from Doppler broadening are also important in another aspect. At the beginning of Section 2.5, among the investigation methods of relaxation processes in molecular gases, we mentioned the spectroscopic methods based, in particular, on double-resonance techniques. From the discussion given in this section, it is clear that useful information on collisional relaxation processes can also be obtained from an analysis of the shapes of homogeneously broadened lines. For example, in Ref. 157 a nonlinear dependence of the homogeneous width on the gas pressure was measured, and the authors explained this experimental observation using only the new concept of a physically very interesting process, *velocity-changing collisions*, which has not even been mentioned above. This process is an (see also Ref. 141) elastic scattering of molecules to small angles which is not followed by any transitions nor any phase destruction.

2.7. Methods of spectroscopy of vibrational-rotational distribution in molecular gases

Spectroscopic methods are perhaps the most universal for insights into the distribution of gas molecules over vibrational-rotational levels. Indeed, knowing the positions of levels and the transition cross-sections and measuring the gas spectra, one can, in principle, obtain very full information on the distribution function and its evolution in time with those restrictions, of course, imposed by the spectral and time resolution of the experimental apparatus as well as the broadening of spectral lines. Nevertheless, no *detailed* information on the populations of individual levels during various nonequilibrium processes have been significantly obtained with spectroscopic methods, despite these methods' evident power. (This is surely a prospect for the very near future.) There are at least two causes: the intricacy of experimental equipment needed, and the deficiency in precise spectroscopic information on the transitions between vibrationally excited molecular states. Fortunately, however, if we simplify the problem and are interested in *rough* information on the molecular vibrational distribution such as, for example, mean vibrational energy, distribution of energy over modes, qualitative shape of the energy distribution function, etc., the detailing appears even to be unnecessary, and one can manage with rather simple means. We will now discuss some suitable possibilities. We should especially point out their principal importance for the region of stochasticity of vibrational motion, where the quasicontinuity of the transition spectra (see Section 2.3.4) makes the way individual levels are spectroscopically probed hardly realistic. At the same time, being interested in the rotational distributions within the lower vibrational states, one can hardly think of any alternative to probing the individual transitions.

We need to ascertain how the shape of the vibrational-distribution function affects the integrated intensities and the shape of vibrational bands. We will be concerned not only with IR absorption spectra but also with spontaneous emission IR spectra and Raman scattering spectra. In Section 2.2.2, when considering the intensities of individual vibrational-rotational lines in IR spectra, we noted the sum rule (2.56) for the Hönl-London factors, according to which the integrated intensities of vibrational absorption bands are not dependent on the rotational distribution. Within the harmonic approximation, this conclusion is applied to an arbitrary vibrational distribution. Realistically let F_v be arbitrary distributions of populations of oscillator levels marked by vibrational quantum numbers v. With Eq. (2.44) for dipole moments of transitions as well as Eq. (2.122), we obtain for the integrated absorption coefficient normalized to unit density the following equation:

$$\alpha = \sum_{v=0}^{\infty} (F_v - F_{v+1}) \int \sigma_{v,v+1}(\omega)d\omega = \alpha_0 \sum_{v=0}^{\infty} (v+1)(F_v - F_{v+1}) = \alpha_0 \sum_{v=0}^{\infty} F_v = \alpha_0 = \text{const} \qquad (2.124)$$

Combining Eqs. (2.124) and (2.56), we can conclude that the integrated absorption coefficient in an IR-active vibrational band is only slightly sensitive to the shape of vibrational-rotational distribution. Anharmonicity that especially affects the structure of states in the region of stochasticity of vibrational motion acts mainly as a redistribution of transition cross-sections, rather changing the shapes of bands (see the discussion in Section 2.3.4). However, the conclusion drawn surely makes sense only if the vibrational band in the stochastic region is not so broadened that it overlaps adjacent bands.

The physical cause of the integrated absorption coefficient being only slightly sensitive to the shape of the vibrational distribution may be seen from Eq. (2.124) directly. Although the transition cross-section grows versus the vibrational energy, the increase in the cross-sections of the absorbing transitions is exactly compensated by the same increase in those of the emitting ones that always give negative contributions to the absorption. Let us assume now that one can manage to separate upward and downward transitions. Then, for the downward transitions, for example, the total intensity S expressed in appropriate units will be, within the harmonic approximation,

$$S = \sum_{v=1}^{\infty} |q_{v,v-1}|^2 F_v \sim \sum_{v=1}^{\infty} vF_v = \langle v \rangle \qquad (2.125)$$

This means that, if S is treated as the intensity of the band integrated over the spectrum, this value will be proportional to the average energy stored in that vibrational mode. We know two processes which enable us to observe only downward transitions. These are spontaneous IR emission and anti-Stokes Raman scattering. Thus, *the integrated intensity of a spontaneous-emission band originated from an IR-active mode as well as the integrated intensity of an anti-Stokes Raman band originated from a RS-active mode must be approximately proportional to the energy stored in the mode*, i.e.,

$$S_{\text{spont}}^{(\text{IR})} \sim \langle E_{\text{vib}}^{(\text{IR})} \rangle, \qquad S_{\text{AS}}^{(\text{RS})} \sim \langle \mathrm{E}_{\text{vib}}^{(\text{RS})} \rangle \qquad (2.126)$$

In the case of Stokes Raman scattering, the integrated intensity of the band which, of course, is some spectral distance from the anti-Stokes Raman one also grows versus the energy:

$$S_S^{(\mathrm{RS})} = \sum_{v=0}^{\infty} |q_{v,v+1}|^2 F_v \sim \sum_{v=0}^{\infty} (v+1) F_v = 1 + \langle v \rangle \sim \hbar\omega_{\mathrm{RS}} + \langle E_{\mathrm{vib}}^{(\mathrm{RS})} \rangle \quad (2.127)$$

Thus, we know, in principle, a way for the vibrational energy in an individual mode to be measured. The vibrational modes of molecules are active with respect to at least one of the two considered processes. Therefore, one may, in principle, obtain complete information on the distribution of vibrational energy between modes. Qualitative information on the vibrational distribution over energies which cannot be judged by band intensities can be obtained from shapes of bands. IR-absorption spectroscopy as well as Stokes Raman spectroscopy are more suitable for probing shapes, since these methods enable us to detect not only vibrationally-excited molecules, but also those in the ground vibrational state. The potentials existing here are evident and arise from the anharmonic shift increasing versus the vibrational energy. It is clear, of course, that these potentials are limited to a certain extent because of real band-widths caused by the rotational distribution. Therefore, from band shapes, one can judge the rough qualitative features of only highly nonequilibrium distributions. We shall come across, while discussing specific experiments, such cases where far-reaching physical conclusions can be drawn from the band shapes.

So far we have said nothing about the spectroscopy of electronic transitions lying in the visible and UV spectral ranges. Below, in the following Sections, we shall appeal to electronic spectroscopy to obtain some additional information on vibrational distributions produced through IR-radiation action on molecular gases. Therefore, it would not be out of place to summarize here the principal possibilities of probing vibrational distributions with the use of the spectroscopy of electronic transitions:

1. The fact that the spectra of electronic transitions from the ground state must exhibit a long-wave limit is clear from the presence of a minimum in potential energy of an electronically-excited term. Some cases may be pointed out—when the transition of interest goes to a stable electronic term, or if the excited term is unstable (see Figure 2.18 where possible situations are schematically shown for the case of a diatomic molecule). Usually only the first case (but not always[160]) exhibits a sharp long-wave limit (see Figure 2.18a). In the second case (see Figure 2.18c) and often in the first case (see Figure 2.18b) when the equilibrium molecular configurations of the two terms differ substantially, the absorption is rather

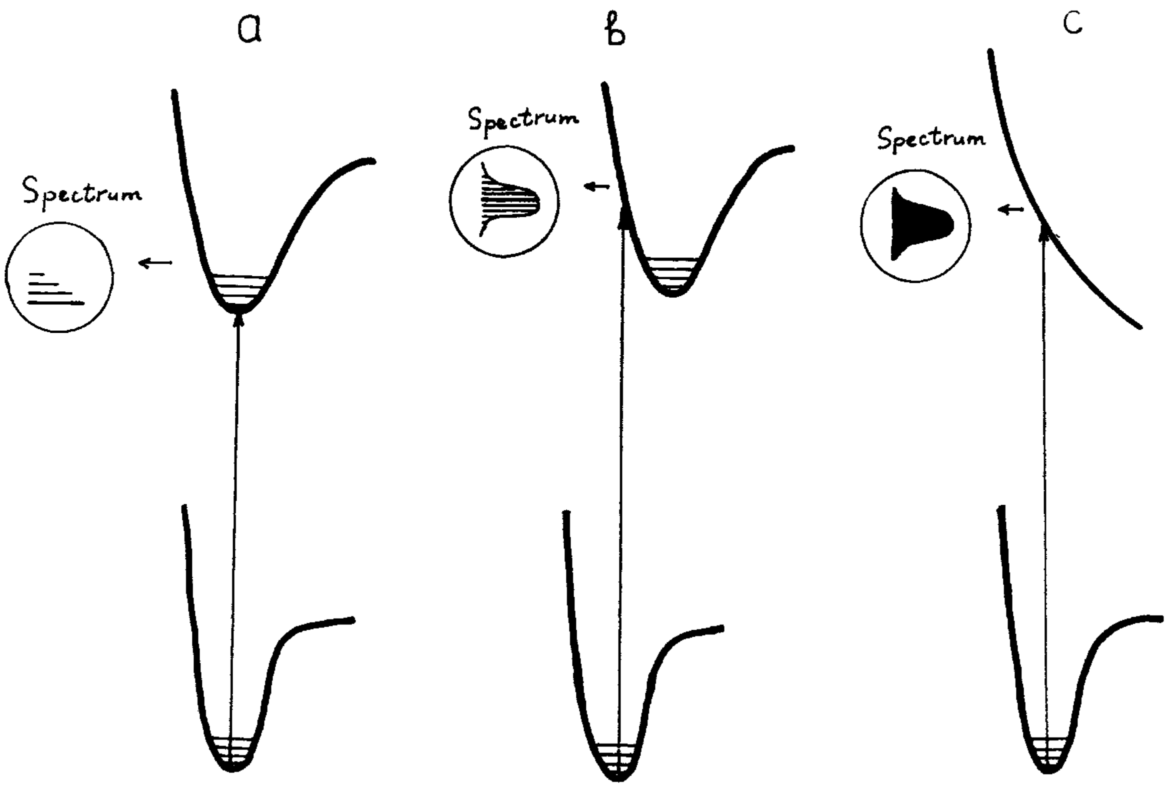

FIGURE 2.18 Different cases of electronic transitions in a diatomic molecule. (a) Transition into a stable electronic term with a slight change in the equilibrium configuration of the molecule. (b) Transition into a stable electronic term with a strong change in the equilibrium configuration. (c) Transition into an unstable electronic term. Arrows show the most probable transitions, according to the Franck-Kondon principle.[158,159]

greatly shifted because of the physically changed relative positions of the minima and the decrease in absorption cross-section at the long-wave side may be approximately described by the Gaussian tail (see Ref. 161). If a molecule is vibrationally excited it energetically approaches the electronically-excited term. As a consequence, one may expect changes in the spectra at the long-wave side of the band. Such changes can be more easily interpreted if the situation is that shown in Figure 2.18a. In this case, if, for example, the molecule has been excited into the level $v = 1$, then the new band $v = 1 \rightarrow v' = 0$ simply appears in the electronic spectrum, etc. A typical example[162] is the change in the UV-absorption spectra of NH_3 having been vibrationally excited. For the situations shown in Figure 2.18b,c, from an increase in the absorption cross-section at the long-wave side, one can also gain insight into how highly molecules are vibrationally excited. However, any quantitative analysis calls for explicitly knowing the surfaces of potential energies of two electronic terms but this can be reasonably known (see, for example, Ref. 163) only for the diatomic molecule or for those particular cases, when one may assume that the electronic excitation affects just one bond in a polyatomic molecule. Therefore, in most cases, the increase in absorption at the long-wave side only gives qualitative information on the vibrational excitation in the ground electronic state.

2. The possibilities of probing the intermode vibrational distribution in the ground electronic state with the use of electronic spectroscopy are far from being evident. In principle, one may expect that different vibrational modes, in view of their vibrational excitation, probably manifest themselves in different ways in electronic spectra. The general theories are rather complicated (see, for example, Ref. 164 for review). But again, in the particular case when one may assume with a good accuracy that the electronic excitation affects only one bond, it is easy to understand that the situation becomes somewhat simpler. A good example of this kind is probably the molecule CF_3I.[165] In this case, the lowest electronic transition occurs into an unstable term that corresponds to decay of the molecule into the radical CF_3 and the iodine atom, and the extraction of the iodine atom deforms the CF_3-configuration slightly. Therefore, one may expect that the electronic spectrum is sensitive mainly to vibrational excitation of the C-I stretching mode ν_3 and probably to excitation of the two-fold degenerate bending vibration ν_6 of the same bond. It should be noted that spectroscopy of electronic transitions gives possibilities, in principle, of probing intermode vibrational distributions. Perhaps in the future insight

into the structure of electronically excited states will come from the opposite procedure, i.e., producing a nonequilibrium intermode distribution, checking it with the use of the above-described methods of IR and RS probing, plus spectroscopy of electronic transitions.

3. An interesting case, particularly with an eye towards probing distributions of molecules in highly excited vibrational states, is (see Figure 2.19) when the bottom E_1 of the excited electronic term is placed below the dissociation limit. In this case, owing to *nonadiabatic* interaction between two electronic terms, provided that interaction matrix elements V_{01} for each pair of levels are greater than typical distance ρ_0^{-1} between adjacent vibrational levels in the ground term, the electronically-distinguished states

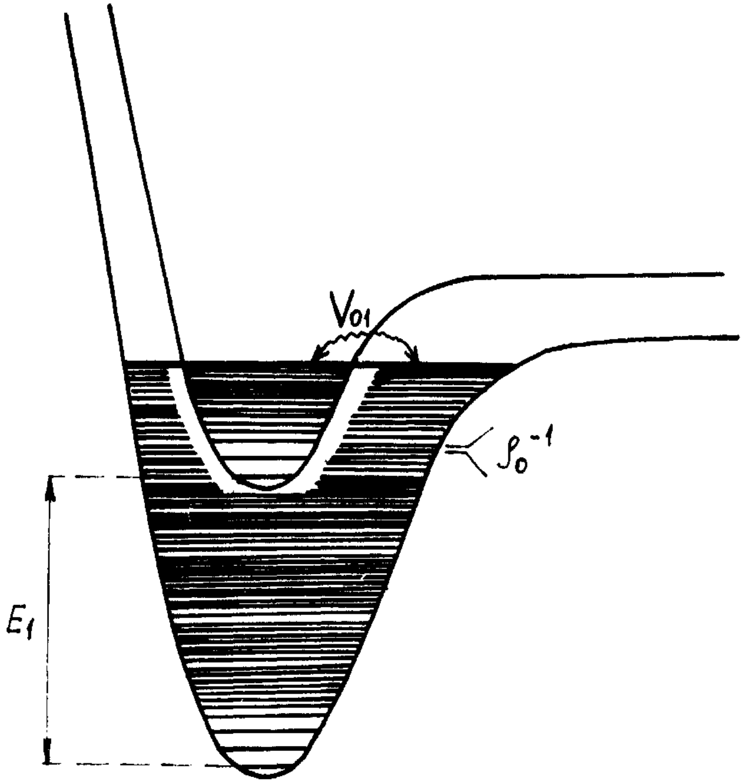

FIGURE 2.19 The situation when effective mixing of the states of two electronic terms is possible.

are strongly mixed. This effect is quite similar to the mixing of vibrational wavefunctions within one electronic term (see the discussion in Section 2.3.2), and only relatively weak interaction is required for mixing due to the great density of vibrational states in the ground electronic term near a realistic bottom of the excited one. Now, since any level of the ground term contains some character of the electronic excitation from some overlap of their wavefunctions, it can decay spontaneously into lower vibrational states, a photon being emitted. The smaller the overlap of the states the longer, of course, the radiative lifetime. If, within the adiabatic approximation, τ_1 denotes the time of decay of electronically-excited states, then time τ_0 (E_{vib}) of decay of highly-excited vibrational states with the energy E_{vib} of the ground term is given by simple equation

$$\tau_0\,(E_{\text{vib}}) = \tau_1\,\frac{\rho_0\,(E_{\text{vib}})}{\rho_1\,(E_{\text{vib}} - E_1)} \tag{2.128}$$

Since the density of vibrational states in the excited term is essentially less than that in the ground one, the decay time is probably several orders longer than typical times 10^{-6}–10^{-8} s for allowed electronic transitions. One can hardly be as sure now of how often the situation shown in Figure 2.19 is really met. Some experiments will be described in the following Sections. The molecule OsO_4 is one typical example.[166]

2.8. Characteristics of laser radiation

Multiple-photon photophysics and photochemistry have come into being only with the progress in high-power IR lasers and rest exclusively upon the unique characteristics of laser radiation. In this section we shall restrict ourselves to listing these characteristics, mainly taking for illustration the TEA CO_2-laser as an instrument used in most of the experiments discussed in the following Sections. In this laser the electric-discharge pumping *inverts* the population of the state $v_3 = 1$ of the antisymmetric stretching mode ν_3 with respect to the state $v_1 = 1$ of the symmetric stretching mode ν_1 as well as the state $v_2 = 2$ of the two-fold degenerate bending mode ν_2. Within the harmonic approximation the dipole emission at the inverted transitions which are usually denoted as $00^01 \rightarrow 10^00$ and $00^01 \rightarrow 02^00$ is forbidden. The anharmonicity of vibrations (see Section 2.2.3), in this specific case, makes the transitions exhibit a gain coefficient in the center of homogeneously broadened individual vibrational-rotational lines of $\gtrsim 10^{-2}$

cm^{-1}, at atmospheric pressures. For a working medium 1 m long, such a coefficient provides a considerable one-pass amplification.

Our purpose here is not to discuss in more detail the principles of the operation of various lasers. We may recommend several manuals[167–169] for a detailed study of the elements of quantum electronics and laser physics. In the discussions of this series of papers, the laser is no more than an instrument characterized by the energy of pulse, the duration τ_p of pulse, the spectrum of radiation, and the frequency-tuning range (i.e., an ability to generate different frequencies), be it a TEA laser, optically pumped laser, chemical laser, or a parametric oscillator, etc. The *energetic* characteristic of the laser used will be the most important for us. It is just this characteristic that is the key, when estimating the potential of any new technical development for the needs of the multiple-photon photophysics and photochemistry. It would be hard to evaluate *a priori* the required range of energies of laser pulses. Laser IR action on molecular vibrations is a complex process embracing resonant multistep transitions in the region of lower vibrational-rotational levels, multiphoton transitions with detunings at intermediate states, and comparatively weak transitions in the vibrational quasicontinuum (see Section 2.3.4). No further than in the next theoretical Section, we shall partially estimate the energetics of laser pulses required for different elementary processes. However, final estimates should rest mainly upon knowledge obtained from the experiments. We can point out *post factum* that, roughly, for molecules differing in number of atoms, symmetry, width of vibrational absorption bands, etc., laser fluences enabling us to act effectively on molecular vibrations range from $\Phi \sim 10^{-2}$ $\mathrm{J/cm^2}$ to $\Phi \sim 10^{2}$ $\mathrm{J/cm^2}$. A commercial TEA CO_2-laser has output fluences of the order 1 $\mathrm{J/cm^2}$, and higher fluences in a cell with the gas to be studied may be easily achieved through focusing of the laser beam. Therefore, CO_2-laser has proved to be very suitable for the first as well as most subsequent experiments.

Below we list other important features of the radiation of pulsed lasers which has assured progress in the multiple-photon photophysics and photochemistry.

1. *Short duration of pulse.* In quantum electronics, there have been developed a number of methods with different controllable durations available from the continuous-wave one to the pulsed ones. In Section 2.5, we treated various relaxation processes in molecular gases and cited the characteristic relaxation times. Limitations on laser-pulse duration are imposed

by what relaxation processes are undesirable to us in a specific experiment. If we want to avoid molecular collisions *at all* during a laser pulse, i.e., we are interested in the effect of radiation on the isolated molecule, then, at 1 Torr, the pulse duration must be, at the very least, several times shorter than 10^{-7} s. If we have excited *selectively* the molecules of one specific kind in a gas mixture and wish to avoid a transfer of vibrational energy to different molecules, then, at the same pressure, the pulse duration must be shorter than 10^{-6} s. Finally, if it is *only* essential that strong deactivation of vibrational energy should not occur during a laser pulse, then, at the same pressure, pulses are quite suitable with durations shorter than 10^{-5} s. If we desire to increase the gas pressure (to realize, for example, multiple-photon IR photochemical processes at atmospheric pressures), then the required laser-pulse duration lies probably in the subnanosecond region. Therefore, the development of such high-energy lasers is, no doubt, of special importance. Furthermore, in Section 2.3.1, we have roughly estimated the time of intramolecular relaxation of vibrational energy in the region of stochasticity of nuclear motion. In most cases, this time probably lies in the picosecond or subpicosecond range. Therefore, one may hope for strong selective excitation of individual bonds or functional groups in molecules only by using picosecond lasers.

The CO_2-laser possesses the obvious merit for multiple-photon photophysics and photochemistry that pulses of practically any duration are available from it, as short as tens of picoseconds. A standard TEA CO_2-laser operating at atmospheric pressure generates radiation pulses which consist, as a rule, of two parts. The leading part is ordinarily from 70 to 200 ns long, and the tail is from 0.5 to a few microseconds. The durations of both the leading and tail part as well as the distribution of energy between them depend on many factors. For example, if one increases the concentration of nitrogen in the active-medium mixture which ordinarily consists of CO_2, N_2, and He, then the energy in the tail will become larger. Pulses of 10 to 50 ns long can be easily obtained, if one cuts off the standard laser pulse, producing a discharge in the gas by appropriate focusing of the laser beam. Furthermore, the CO_2-laser radiation pulse usually exhibits a finer time-structure caused by partial synchronization of longitudinal modes, and shorter pulses (about 1 ns) can be obtained by separating and then amplifying a single peak. At present, some methods have also been developed for obtaining pulses with durations of 10^{-9}–10^{-10} s and shorter. For example, one of the coherent transient effects called *free induction decay* can be used.[170]

2. *Tunability of radiation frequency.* Methods of quantum electronics and nonlinear optics make laser radiation available at any frequency in the IR, visible, UV, and recently even in the vacuum UV regions. From discussions on actual experiments, *purposeful* and *controllable* multiple-photon excitation of molecular vibrations requires pulsed tunable IR lasers. The problem of the generation of powerful pulses which are continuously tunable within the whole IR range has not yet been solved. But, frequencies of some powerful molecular lasers (CO_2-, CO-, HF-, and DF-lasers) can be discretely tuned to different rotational lines of those vibrational bands pumped to inverted populations. The simplest way of tuning is with the use of a grating which acts as a selective element of the cavity. When the pressure of the laser medium is increased to several atmospheres, the homogeneous collisional broadening becomes so large that adjacent vibrational-rotational lines overlap each other, and this way, one may obtain a continuous tunability[171] (for review, see also Ref. 172). To widen the spectral regions of the powerful molecular lasers one may also use various isotopic modifications of the working molecules. Another effective development is to use the above-mentioned lasers for resonant optical pumping of other molecules. In this way, powerful laser pulses can be generated in the regions which are long-wave with respect to the pumping frequencies. The present state of optically-pumped IR molecular lasers can be found in Ref. 173. No doubt, future progress in laser technique and applied nonlinear optics will make it possible to generate IR radiation pulses with the energies required for multiple-photon photophysics and photochemistry at any wavelength in the IR range.

3. *Spatial coherence.* Its high spatial coherence enables the laser beam to propagate in the form of nearly a *plane wave,* the divergency not much exceeding the so-called minimum one caused only by *diffraction.* This feature enables us to form directed radiation beams and irradiate extensive samples; that is of especial importance for practical realizations of multiple-photon IR photochemical processes. Using an optical system of mirrors and lenses, one can focus a spatially coherent light wave onto an area with a diameter as small as one wavelength. Focusing a beam of the laser, even one not highly energetic, like a parametric oscillator, can yield fluences sufficient for observing multiple-photon processes.

4. *Monochromaticity and temporal coherence.* The width of the radiation spectrum of a pulsed laser is, in essence, limited by the inverse duration of pulse. But in most cases, pulsed lasers operate on many longitudinal modes which occupy some part of the amplification band of the working

medium. For example, TEA CO_2-lasers usually generate several tens of longitudinal modes taking up a spectral interval from 10^{-2} cm^{-1} to 10^{-1} cm^{-1}. A number of methods have been developed to obtain the single-mode generation with the width-limit. However, for experiments on multiple-photon excitation of polyatomic molecules, there is, as a rule, no need for such narrow radiation lines, since vibrational-rotational spectra are usually complex in structure and exhibit great densities of absorption lines. A few experiments carried out on the effects of the narrowing of the laser-radiation spectrum will be discussed in the following sections. At the same time, it should be emphasized that almost all theoretical treatments assume laser radiation to be monochromatic, for example, the electric component of laser field is

$$\mathbf{E} = \mathbf{E}(t) \cos (\Omega t - kz), \tag{2.129}$$

where Ω is the field frequency, k is the wave-vector, z is the coordinate of propagation of wave, and $\mathbf{E}$ is the field amplitude, in the general case, slowly varying. In particular, the problems that are the subject of the next section are treated just this way. A simplified description of the laser field enables us to advance analytically to some extent, but, where it is important we will be sure to discuss the possible effects of a more complex spectral structure of the laser pulse. The wave (2.129) has the maximum time coherence, and this feature is actually typical for a single-mode laser, since the phase of its field does not undergo any essential fluctuations during the pulse. As will be shown in the next section, the temporal coherence of a laser pulse may, in principle, play some role when treating the excitation of only lower vibrational levels of molecules but for not the vibrational quasicontinuum.

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