

# Fast and exceptionally slow vibrational energy transfer in acetylene and phenylacetylene in solution

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The excitation of the CH-stretching mode ( $\nu_3$ ) of  $C_2H_2$  in  $CCl_4$  leads to fast population ( $< 2$  ps) and very slow depopulation (240 ps) of the symmetric CC-stretching mode ( $\nu_2$ ). The long lifetime of  $\nu_2$  is due to the absence of anharmonic interaction to neighboring states (symmetry forbidden). The corresponding CC-stretching mode of  $C_6H_5-C_2H$  has a lifetime of 15 ps. The phenyl group relaxes the symmetry restrictions and introduces new decay channels.

## I. INTRODUCTION

The study of the vibrational relaxation of selectively excited states provides interesting information about the nature of the intramolecular and intermolecular interactions of molecules in the liquid state. Recent experiments<sup>1</sup> have shown that the life time of typical CH-stretching modes can vary over two orders of magnitude depending upon intramolecular couplings (Fermi resonances).

In this note we want to report on acetylene and phenylacetylene. In acetylene we find a population lifetime of the C=C-stretching mode at  $1968\text{ cm}^{-1}$  which represents the longest population lifetime observed so far of a polyatomic molecule in the liquid state at room temperature. Acetylene is particularly well suited for the study of collision induced vibrational relaxation pathways by the following reasons:

(1) The molecule is sufficiently small so that all vibrational states up to the energy region of about  $4000\text{ cm}^{-1}$  can be assigned in the gas phase.<sup>2</sup>

(2) From the rotational structure of vibrational overtones and combination bands an anharmonic force field can be determined empirically.<sup>3</sup>

(3) The high symmetry ( $D_\infty$ ) introduces high selectivity in the interaction of different states.

(4) The appearance of low-frequency bending modes ( $\nu_4, \nu_5$ ) and high-frequency stretching modes ( $\nu_1, \nu_2, \nu_3$ ) (Fig. 1) allows to study energy transfer from fundamentals to high combination tones. In particular, the high Raman cross section of the  $\nu_2$  mode helps to detect the fast population and slow depopulation of this mode.

(5) In the energy region of the CH-stretching modes ( $3300\text{ cm}^{-1}$ ) anharmonic mixing of triple combination tones with the CH-stretching modes is needed in order to get efficient energy transfer. Thus information on the importance of the intramolecular interactions can be obtained.

(6) The  $\nu_2$ -stretching mode of the C=C band has several combination tones in its neighborhood but none of them can couple due to symmetry selection rules. From the observed lifetime one may infer whether symmetry aspects are important for the transfer process even though the molecule is dissolved in a liquid.

(7) There are lifetime data available for a few states of acetylene in the gas phase.<sup>4</sup> The comparison of those lifetimes with the values in the liquid should be of interest.

## II. EXPERIMENTAL

Our experimental system has been discussed previously. Acetylene and phenylacetylene in  $CCl_4$  solution is excited by an infrared pulse of 5 ps duration which is tuned to the infrared active CH-stretching mode near  $3300\text{ cm}^{-1}$ . The population of the C=C mode near  $2000\text{ cm}^{-1}$  is inferred from the scattered anti-Stokes Raman signal generated by a delayed probe pulse at  $\nu = 18990\text{ cm}^{-1}$  (5 ps duration). Mixing the infrared exciting pulse and the green probing pulse in a nonlinear crystal provides the system's cross-correlation func-

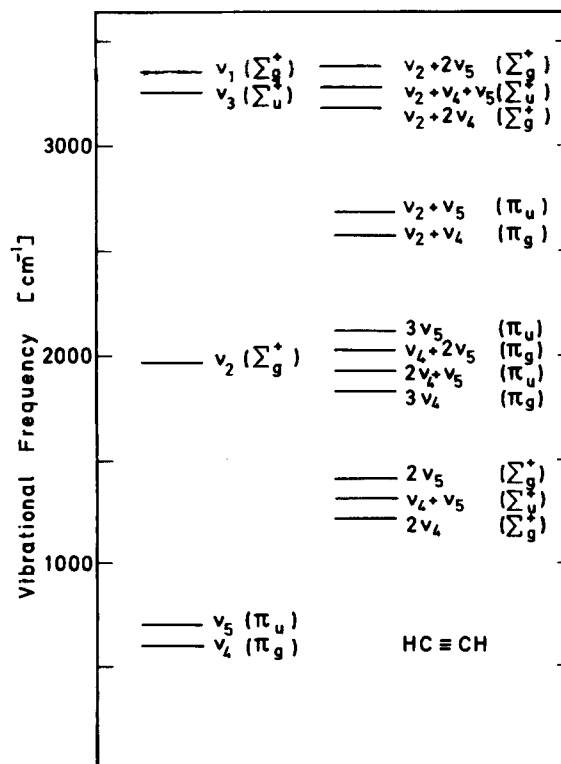


FIG. 1. Energy level diagram of the vibrational modes of acetylene.

tion (broken curves of Figs. 2 and 3). The latter determines the zero point on our time scale and indicates the time resolution of the experimental setup. The experimental data on acetylene are shown in Fig. 2. We obtain a fast population ( $< 2$  ps) of the C≡C mode at  $1968 \text{ cm}^{-1}$  and a very slow depopulation with a time constant of 240 ps. In phenylacetylene (Fig. 3) the population of the C≡C mode ( $\tilde{\nu} = 2111 \text{ cm}^{-1}$ ) again is quite fast, but the decay has a time constant of  $T_1 = 15$  ps, considerably shorter than the C≡C mode in acetylene.

### III. ENERGY RELAXATION AND DEPHASING

The vibrational energy relaxation of molecules in the liquid phase is basically a very complex process, since it involves strong anharmonic intramolecular interactions and since the intermolecular interactions are not very well known for polyatomic molecules. If the solvent is of relatively simple structure like  $\text{CCl}_4$  and vibrational relaxation via long-range resonance processes does not contribute, one may be tempted to describe the relaxation in analogy to collision induced relaxation processes in the gas phase. This point of view is supported by the observation that the vibrational relaxation rates often scale well from gas phase values if the collision numbers are properly extrapolated. A microscopic justification is not apparent, but one may argue that the most effective interactions in the liquid are of short range and for these the binary collision assumption is reasonable. We have seen earlier,<sup>1</sup> and acetylene is a good candidate to support this point of view, that the dominant factors which affect the vibrational lifetimes of CH-stretching modes of polyatomic molecules are the intramolecular interactions. Therefore, we have to incorporate these interactions into the so-called zero order states which are populated by the exciting pulse. An average potential of the medium which affects the position of the vibrational states may also be included. In this way only relatively weak fluctuations remain which induce the transitions between the molecular eigenstates of the molecule in the average potential. Since we cannot treat the dynamics of these fluctuations

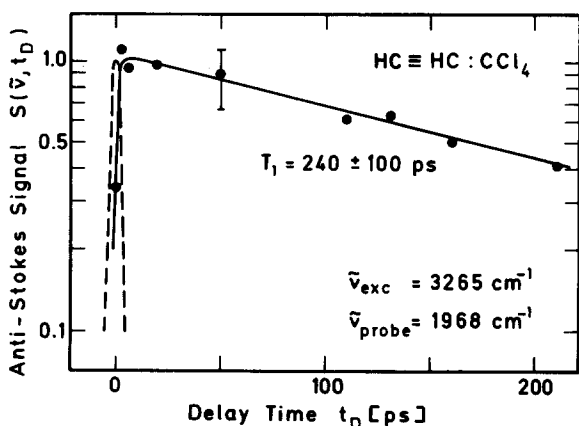


FIG. 2. Time dependence of the population of the C≡C mode of acetylene in liquid  $\text{CCl}_4$  following excitation of the  $\nu_3$  CH-stretching mode at  $3265 \text{ cm}^{-1}$ . After a rapid rise the population decays slowly with a decay time of 240 ps.

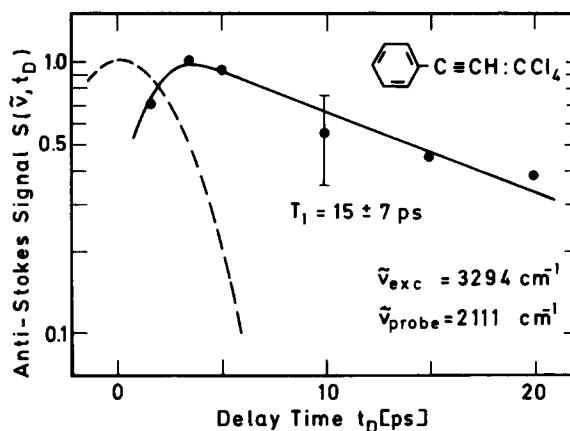


FIG. 3. Population of the C≡C mode of phenylacetylene in liquid  $\text{CCl}_4$  after excitation of a CH-stretching mode at  $3294 \text{ cm}^{-1}$ . Here the population of the C≡C mode decays with a decay time of 15 ps.

in detail, we shall refer to model calculations for the gas phase or we treat the interaction with the medium empirically by introducing a dephasing time in the rate expression for energy relaxation. The dephasing time  $T_2(r)$  we obtain from the corresponding homogeneously broadened Raman lines:  $T_2(r) = 1/2\pi\Delta\nu(r)$ . [It should be noted that  $T_2(r)$  is equivalent to  $T_2/2$  measured in coherent experiments.]

Let us assume that the intermolecular interaction can be factorized into a term  $V(\mathbf{q})$  which depends upon the normal mode coordinates  $\mathbf{q}$  of the excited molecule and one term  $U(\mathbf{R})$  which depends upon the intermolecular variables  $\mathbf{R}$ . Such a factorization can be justified if the interaction potential is an exponential function of both sets of variables  $\mathbf{q}$  and  $\mathbf{R}$ . For other potentials one may expand the interaction in terms of the normal mode coordinates. Then every expansion term factorizes and one may pick the dominant term. The expansion is rapidly convergent if the zero point amplitudes of the normal mode coordinates are small compared to the typical interaction length.

With these assumptions in mind we can describe the transition between an initial molecular eigenstate  $\psi_i$  and a final state  $\psi_f$  in terms of a correlation function expression of the molecular forces  $U(\mathbf{R})$ :

$$k_{i \rightarrow f} = \frac{1}{\hbar^2} |\langle \psi_i | V(\mathbf{q}) | \psi_f \rangle|^2 \int_{-\infty}^{+\infty} \langle U(t) U(0) \rangle e^{i\omega t} dt. \quad (1)$$

Here the energy difference between the initial and the final state is  $E_i - E_f = \hbar\omega$ . The bracket under the time integral stands for the thermodynamic average over the medium states. We assume that the time dependent correlation function of the intermolecular force field  $\langle U(t) U(0) \rangle$  decays exponentially with a relaxation time  $\tilde{\tau}$ . We obtain

$$k_{i \rightarrow f} = \frac{1}{\hbar^2} |\langle \psi_i | V(\mathbf{q}) | \psi_f \rangle|^2 \frac{2\langle U(0)^2 \rangle_{\tilde{\tau}}}{1 + \omega^2 \tilde{\tau}^2}. \quad (2)$$

If the energy difference  $E_i - E_f$  is large compared to the thermal energy  $kT$  the decay pattern is no longer

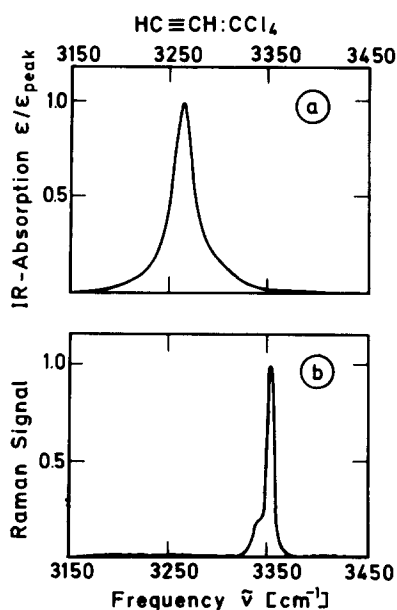


FIG. 4. Part of the infrared (a) and Raman (b) spectrum of acetylene in liquid  $\text{CCl}_4$ .

exponential and the factor  $(1 + \omega^2\tau^2)^{-1}$  should be replaced by  $\exp[-(\omega\tau)^{2/3}]$  [see Ref. 1 Eq. (9) with  $\tau = \Omega^{-1}$ ].

Let us further introduce the dephasing time  $T_2(r)$  of a reference state  $|r\rangle$ . This state should fulfill two conditions. Its dephasing time should be experimentally available and the dephasing should be induced by interaction of the medium with the same atoms as the population relaxation. If this is so the same function  $\langle U^2 \rangle$  will appear in both rate expressions and we can substitute into Eq. (2) the dephasing time and obtain

$$k_{i \rightarrow f} = \frac{|\langle \psi_f | V(\mathbf{q}) \psi_i \rangle|^2 T_2^{-1}(r) (1 + \omega^2\tau^2)^{-1}}{|\langle \psi_r | V(\mathbf{q}) \psi_r \rangle - \langle \psi_0 | V(\mathbf{q}) \psi_0 \rangle|^2}. \quad (3)$$

The matrix element in the denominator is just the matrix element of the dephasing rate. In a previous paper<sup>1</sup> we used for the state  $|r\rangle$  the final state. This gives us a particularly simple expression if the final state is an overtone or higher order combination tone that mixes weakly with the initial Raman or IR active fundamental. One can see that the admixture of  $\psi_f$  to  $\psi_i$  gives the largest contribution to the matrix element. The coefficient that determines this admixture can be related to the ratio  $R$  from the IR or Raman intensities of the final to the initial state. Then the diagonal matrix elements of the final state of Eq. (3) drops out leaving the simple relation

$$k_{i \rightarrow f} = R T_2^{-1}(f) (1 + \omega^2\tau^2)^{-1}. \quad (4)$$

This formula can not be applied directly in our case, since the final states are not observed in the present situation. The IR spectrum [Fig. 4(a)] shows only one broad line ( $\Gamma \approx 30 \text{ cm}^{-1}$ ) for the transition to  $\nu_3$  (quite likely rotationally broadened). In the Raman spectrum [Fig. 4(b)] the transition to  $\nu_1$  is not as broad ( $\Gamma_1 = 6 \text{ cm}^{-1}$ ) and a shoulder at the low energy side is observed. One might argue that this shoulder is a combination tone like  $\nu_2 + 2\nu_5$  of  $\Sigma_g^+$  symmetry which interacts with the  $\nu_1$

state. In principal, this could be our decay channel. This interpretation is very strained because the combination tone  $\nu_2 + 2\nu_5$  should be higher in energy than  $\nu_1$ . We shall see later that it should also be much broader. Finally, its interaction with  $\nu_1$  is predicted to be so strong that its location and intensity would be in conflict with such an assignment.

A more consistent interpretation is the following: From the gas phase spectra<sup>5</sup> it is known that the combination tone  $\nu_1 + \nu_5$  is lower in energy than the sum of the fundamentals by  $12 \text{ cm}^{-1}$ . For  $\nu_1 + \nu_4$  the difference is even larger. Consequently, we may see here hot bands. They should have a thermal population of 4.4%, but due to the degeneracy we get a factor of 2 and both modes  $\nu_4$  and  $\nu_5$  contribute to the observed shoulder.

In order to get a theoretical estimate on the relaxation rates we go back to Eq. (3) and use as reference state the CH-stretching mode  $\nu_1$ . The observed bandwidth of  $6 \text{ cm}^{-1}$  is assumed to be homogeneous and is interpreted to be due to pure dephasing<sup>6</sup> and the energy transfer process  $\nu_1 - \nu_3$ . We obtain a consistent picture in our calculations for a pure dephasing of  $\bar{\Gamma}_1 = 3 \text{ cm}^{-1}$ .

In the next section we shall determine the anharmonic mixing between  $\psi_i$  and  $\psi_f$  and evaluate the rates in Sec. V.

#### IV. ANHARMONIC MIXING IN ACETYLENE

Acetylene is an interesting example for local mode vibrations.<sup>7</sup> The harmonic or anharmonic force field is usually given in terms of the valence coordinates, which correspond to local modes. The anharmonic coupling constants in this representation are dominated by the diagonal anharmonicities of the three stretching bonds. In terms of normal modes, however, one finds very strong nondiagonal interaction constants between the CH-stretching modes and overtones or combination tones of the CH-bending modes. The physical origin of this effect has to do with the presence of very low frequency bending modes. Their zero point amplitudes are quite large and thus bending motion causes also changes in the distances between the atoms. Mathematically this fact is described by the nonlinear terms of the transformation between normal mode coordinates and valence bond coordinates. It turns out that this nonlinear contributions are particularly large for linear molecules.

Having these facts in mind we can determine the anharmonic coupling constants between the normal mode coordinates and the mixing coefficients between the individual states in the following way. We start from an empirical anharmonic force field  $v$  which is given in terms of valence coordinates.<sup>3</sup> Denoting the valence coordinates by  $r_i$  we obtain

$$v = \frac{1}{2} \sum_{i,j} K_{ij} r_i r_j + \frac{1}{6} \sum_{i,j,k} K_{ijk} r_i r_j r_k + \frac{1}{24} \sum_{i,j,k,l} K_{ijkl} r_i r_j r_k r_l. \quad (6)$$

In Table I we list the important cubic and quartic

TABLE I. Anharmonic force constants (from Ref. 3).

$K_{111} = K_{222} = -34.8 \text{ mdyn } \text{Å}^{-3}$
$K_{333} = -97.8 \text{ mdyn } \text{Å}^{-3}$
$K_{1111} = K_{2222} = 161.5 \text{ mdyn } \text{Å}^{-4}$
$K_{3333} = 436 \text{ mdyn } \text{Å}^{-4}$

terms. The indices 1 and 2 refer to the CH-stretching coordinate,  $r_3$  is the C=C distance. The potential is defined in terms of normal mode coordinates as

$$\nu = \frac{1}{2} \sum_p k_{pp} q_p^2 + \sum_{n \leq m \leq p} k_{nmp} q_n q_m q_p + \sum_{n \leq m \leq p \leq q} k_{n,m,p,q} q_n q_m q_p q_q. \quad (7)$$

If we expand the valence coordinates also in terms of the normal mode coordinates we obtain up to third order:

$$r_i = \sum_p \frac{\partial r_i}{\partial q_p} q_p + \frac{1}{2} \sum_{p,r} \frac{\partial^2 r_i}{\partial q_p \partial q_r} q_p q_r + \frac{1}{6} \sum_{p,q,r} \frac{\partial^3 r_i}{\partial q_p \partial q_q \partial q_r} q_p q_q q_r. \quad (8)$$

We can now evaluate the partial derivatives, substitute these expressions into Eq. (6) and compare the result with Eq. (7). In this way we get the anharmonic coupling constants. In Table II we show those which are of interest here. It should be noted that  $k_{345}$  is unusually large. Its energy is larger than the energy of the normal modes  $\nu_4$  and  $\nu_5$ . It does, however, play no important role in mixing the vibrational states, since the energies of the  $\nu_3$  state and the combination of  $\nu_4$  and  $\nu_5$  are separated by  $1938 \text{ cm}^{-1}$ . For the fundamental of  $\nu_2$  we have to mix  $\nu_2$  with the  $\Sigma_g^+$  components of the overtones of  $\nu_4$  and  $\nu_5$ . This can be done by simple perturbation theory. For the mixing of  $\nu_1$  and the  $\Sigma_g^+$  component of  $\nu_2 + 2\nu_5$  or that of  $\nu_3$  with the  $\Sigma_u^+$  component of  $\nu_2 + \nu_4 + \nu_5$  we have to apply perturbation theory of almost degenerate states. In these calculations we used the energies from the gas phase.<sup>3</sup> In Table III the anharmonically mixed states are expressed in terms of the harmonic zero order states.

## V. ENERGY RELAXATION RATES FOR $\nu_1, \nu_2$ , and $\nu_3$

We assume that the interaction  $V(q)$  has the exponential form

$$V(q) = V_0 \exp\left\{-\frac{1}{\sqrt{2}} \sum_i \beta_i q_i\right\}. \quad (9)$$

The parameters  $\beta_j$  depend upon an angular function and normal mode parameters like the frequency and the reduced mass. In a simple collinear collision of a diatomic with an atom, they would consist essentially of the

TABLE II. Anharmonic potential constants for normal mode coordinates.

$k_{244} = 88.16 \text{ cm}^{-1}$	$k_{2345} = -77.71 \text{ cm}^{-1}$
$k_{255} = 59.64 \text{ cm}^{-1}$	$k_{1244} = -17.61 \text{ cm}^{-1}$
$k_{345} = 969.50 \text{ cm}^{-1}$	$k_{1255} = -38.48 \text{ cm}^{-1}$

TABLE III. Anharmonically mixed eigenstates.

$ \nu_1\rangle_{\text{anh}} = 0.915  \nu_1\rangle + 0.227  (\nu_2 + 2\nu_5)(\Sigma_g^+)\rangle$
$+ 0.076  (\nu_2 + 2\nu_4)(\Sigma_g^+)\rangle + \dots$
$ \nu_2\rangle_{\text{anh}} = 0.968  \nu_2\rangle + 0.079  2\nu_4(\Sigma_g^+)\rangle$
$+ 0.079  2\nu_5(\Sigma_g^+)\rangle + \dots$
$ \nu_3\rangle_{\text{anh}} = 0.818  \nu_3\rangle + 0.422  (\nu_2 + \nu_4 + \nu_5)(\Sigma_u^+)\rangle + \dots$

ratio of the zero point amplitude of  $q$  to the interaction length. In our case we consider the  $\text{H} \cdots \text{CCl}_4$  interaction with the interaction length  $L = 0.2 \text{ Å}$ . Following the procedure<sup>7</sup> of transforming local amplitudes of the interacting atoms in terms of normal modes we obtain the values for the modes  $\nu_1, \nu_2, \nu_3, \nu_4$ , and  $\nu_5$  shown in Table IV. The angle  $\delta$  is measured from the axis of the molecule. The rate expression must be averaged over  $\delta$  within the interaction region.

We should note at this point that the diagonal matrix elements get their main contribution from the second expansion terms of the interaction  $V(q)$ . Since the pure dephasing rates depend upon the square of these matrix elements ( $\sim \beta_i^2$ ) we can determine the relative pure dephasing rates of the fundamentals from the relation

$$\bar{\Gamma}_i = \bar{\Gamma}_1 \bar{\beta}_i^2 / \bar{\beta}_1^2. \quad (10)$$

The bar over  $\bar{\beta}_i^2$  refers to the average over the angles in the interaction region. Table IV shows the predicted linewidths after setting  $\bar{\Gamma}_1 = 3 \text{ cm}^{-1}$ . The observed width of the  $\nu_2$  mode ( $\Gamma_2 = 1.2 \pm 0.5 \text{ cm}^{-1}$ ) is consistent with the predicted one. It is also clear from this estimation of the total homogeneous width  $\Gamma_i = \bar{\Gamma}_i + \sum_k k_{i-k}$  that the states involving  $2\nu_4$  and  $2\nu_5$  should be very broad and cannot be observed.

The final rate expressions follow from Eq. (3) by substituting the mixed eigenstates from Table III, evaluating the matrix elements, and integrating over the interaction region from  $0^\circ$  to  $55^\circ$ . Higher angles do not couple to the stretching of the hydrogen atoms appreciably. In addition, we evaluated the transfer rates between  $\nu_3$  and  $\nu_1$  as well as the one between  $\nu_2$  and the combination tone  $2\nu_4 + \nu_5$ , which does not couple to  $\nu_2$ . The results are

TABLE IV. Intermolecular coupling parameters.

$\beta_i$	$\bar{\Gamma}_i (\text{cm}^{-1})$ Pure dephasing	$\Gamma_i (\text{cm}^{-1})$ Total homogeneous linewidth
$\beta_1 = 0.222 \cos \delta$	$\bar{\Gamma}_1 = 3$	$\Gamma_1 = 6$
$\beta_2 = 0.141 \cos \delta$	$\bar{\Gamma}_2 = 0.49$	$\Gamma_2 = 0.49$
$\beta_3 = 0.240 \cos \delta$	$\bar{\Gamma}_3 = 4.1$	$\Gamma_3 = 5.5$
$\beta_4 = 0.456 \sin \delta \cos \varphi$	$\bar{\Gamma}_4 = 17.7$	$\Gamma_4 = 25.6$
$\beta_5 = 0.512 \sin \delta \cos \varphi$	$\bar{\Gamma}_5 = 28.1$	$\Gamma_5 = 29.5$
	$\bar{\Gamma}_{2\nu_4} = 31.2$	$\Gamma_{2\nu_4} = 99.6$
	$\bar{\Gamma}_{2\nu_5} = 49.6$	$\Gamma_{2\nu_5} = 134.4$

TABLE V. Relaxation rates  $k_{i \rightarrow f}$ .

Transitions $i \rightarrow f$	Rates $k$ ( $s^{-1}$ )	Lifetimes $\tau$ ( $10^{-12}$ s)
$\nu_3 \rightarrow \nu_2 + \nu_4 + \nu_5$	$2.65 \times 10^{11}$	3.78
$\nu_3 \rightarrow \nu_1$	$5.56 \times 10^{11}$	1.8
$\nu_1 \rightarrow \nu_2 + 2\nu_4$	$1.51 \times 10^9$	663
$\nu_1 \rightarrow \nu_2 + 2\nu_5$	$2.08 \times 10^{11}$	4.80
$\nu_2 + 2\nu_5 \rightarrow \nu_2 + \nu_4 + \nu_5$	$7.15 \times 10^{12}$	0.47
$\nu_2 + \nu_4 + \nu_5 \rightarrow \nu_2 + 2\nu_4$	$2.22 \times 10^{12}$	0.45
$\nu_2 + \nu_4 + \nu_5 \rightarrow \nu_2 + \nu_5$	$1.84 \times 10^{12}$	0.54
$\nu_2 + \nu_5 \rightarrow \nu_2$	$1.71 \times 10^{12}$	0.76
$\nu_2 \rightarrow 2\nu_4$	$1.52 \times 10^9$	657
$\nu_2 \rightarrow 2\nu_5$	$4.10 \times 10^9$	244
$\nu_2 \rightarrow 2\nu_4 + \nu_5$	$1.07 \times 10^9$	938

summarized in Table V. In addition, we have included estimates on transfer rates between different combination tones which we need in order to discuss the complete relaxation pathway of acetylene.

During excitation of  $\nu_3$  the energy will already distribute among the states  $\nu_1$ ,  $\nu_3$ ,  $\nu_2 + 2\nu_4$  ( $\Sigma_g^+$ ),  $\nu_2 + 2\nu_5$  ( $\Sigma_g^+$ ), and  $\nu_2 + \nu_4 + \nu_5$  ( $\Sigma_u^+$ ) (Fig. 1). The population of  $\nu_2 + 2\nu_4$  takes place via  $\nu_2 + \nu_4 + \nu_5$ . This process is also very rapid since it involves changes of two quanta only. In the experiment the population of  $\nu_2$  will be observed when the fundamental  $\nu_2$  or a combination tone containing  $\nu_2$  is populated. There are many energy states in the energy regime of  $3000 \text{ cm}^{-1}$  which consist of five quanta of  $\nu_4$  or  $\nu_5$  or their combinations. Energy transfer from the  $\nu_2$  containing states into five quanta states would cause a decay of the  $\nu_2$  signal. However, these processes are slower than the transfer of one quantum of energy of  $\nu_4$  or  $\nu_5$  into rotational and translational energy. It takes only a few picoseconds. The latter process causes energy relaxation from the  $3000 \text{ cm}^{-1}$  regime to the fundamental of  $\nu_2$  which is located at  $1968 \text{ cm}^{-1}$ . We like to mention here that the energy transfer involving the deactivation of one quantum of  $\nu_4$  or  $\nu_5$  is only little enhanced by the fact that  $\text{CCl}_4$  has a vibrational state in near resonance with  $\nu_5$ . Most efficient is the transfer of the vibrational energy into rotational and translational energy of  $\text{C}_2\text{H}_2$ . This is so because the zero point amplitude of the modes of  $\text{CCl}_4$  is so small compared to the intermolecular interaction length that the coupling to these vibrational modes is small as well.

In discussing the transfer out of  $\nu_2$  we have to consider triple combinations like  $2\nu_4 + \nu_5$ ,  $3\nu_4$ ,  $3\nu_5$ , or  $2\nu_5 + \nu_4$  and the  $\Sigma_g^+$  components of  $2\nu_4$  and  $2\nu_5$  which are separated in energy from  $\nu_2$  by  $525$  and  $743 \text{ cm}^{-1}$ , respectively. The triple combinations are close in energy but have  $\Pi_g$  or  $\Pi_u$  symmetry and, therefore, cannot mix with  $\nu_2$  ( $\Sigma_g^+$ ). Our calculations predict that the transfer into the state  $2\nu_5$  is the most effective pathway.

## VI. RELAXATION PATHWAYS IN PHENYLACETYLENE

In the experiment the CH-stretching mode on the acetylene side was excited. Again a fast population of the

$\text{C}\equiv\text{C}$  mode was observed. The signal from the  $\text{C}\equiv\text{C}$  mode ( $2111 \text{ cm}^{-1}$ ) decays now by more than an order of magnitude faster than the corresponding  $\nu_2$  mode in acetylene. We conclude from this observation: The energy transfer between the CH mode of acetylene to the CH modes of the benzene ring cannot compete on the time scale of  $5 \text{ ps}$  with the transfer to the triple combination tones involving the  $\text{C}\equiv\text{C}$  stretching mode. We could argue that the population of this mode proceeds similarly as in acetylene via the combination of the  $\text{C}\equiv\text{C}$  mode with an overtone of the CH-bending mode. This transfer is followed by transfer of the energy from the CH-bending mode to the medium or other low lying modes of the molecule.

For the relaxation of the  $\text{C}\equiv\text{C}$  mode we have to consider several pathways. Thinking in terms of the analogy with acetylene we suggest the energy goes into the CH-bending mode. The enhancement of this process compared to acetylene could be due to the fact that the third overtone of this bending mode can now interact with the  $\text{C}\equiv\text{C}$ -stretching mode, since the symmetry has been relaxed. We would need only a very small mixing of  $3\%$  and could explain the enhancement of the rate by more than an order of magnitude compared to  $\text{C}_2\text{H}_2$ . An alternative interpretation is based on the following observation. From the Raman spectrum of phenylacetylene<sup>8</sup> we can construct a combination of the C-C skeletal mode of benzene at  $1595 \text{ cm}^{-1}$  and another mode at  $485 \text{ cm}^{-1}$  which could well be the C-C stretching mode connecting the acetylene and the benzene ring. This combination tone at  $2080 \text{ cm}^{-1}$  could be the new energy accepting state.

This mechanism has the advantage that only three quanta of energy have to be changed and a cubic coupling could cause the interaction. It seems that we have good energy matching conditions and the coupling proceeds via band stretches which are directly linked. We like to mention also that the C-C skeletal mode of  $1595 \text{ cm}^{-1}$  is Raman active in phenylacetylene, while this is not so in benzene. In a preliminary experiment on phenylacetylene the CH-stretching mode of the benzene ring has been excited and the population of this skeletal mode could be observed. This observation supports the relaxation pathway we predicted for benzene in a previous publication.<sup>9</sup>

## VII. SUMMARY

Several processes occur in acetylene:

- (1) Very rapid energy exchange between CH-stretching modes in  $\text{C}_2\text{H}_2$  ( $\nu_3 \rightarrow \nu_1$ ).
- (2) Transfer into triple combination tones  $\nu_1 \rightarrow \nu_2 + \nu_4 + \nu_5$  strongly enhanced by anharmonic coupling.
- (3) Efficient intermolecular energy transfer from bending modes into translation and rotational states of acetylene.
- (4) A bottleneck effect for the  $\nu_2$  mode which is due to symmetry restrictions. It leads to a very long decay time, in agreement with the high collision number  $P$

(with Ar  $P=13\,100$ ) required for the  $\nu_2$  deactivation in the gas phase.<sup>4</sup>

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