FORMATION OF MOLECULAR LINES IN STELLAR ATMOSPHERES

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SUMMARY

Statistical equilibrium of electronic states of diatomic molecules in stellar atmospheres is examined. Atmospheres discussed are representative of the Sun, Arcturus (K-giant) and Betelgeuse (M-supergiant).

A comparison of the relative collisional and radiative contributions to the equilibrium of the ground electronic state shows that this state is collisionally controlled and that the line source function for vibration–rotation transitions within this state is equivalent to the Planck function.

Examination of the equilibrium for excited electronic states demonstrates that the exchange between these states and the ground electronic state is most probably determined by radiative excitation. This result implies that scattering rather than pure absorption is the appropriate mechanism for the formation of lines belonging to these electronic transitions. The scattering hypothesis is given a preliminary check against solar observations.

Areas for future investigations are outlined.

I. INTRODUCTION

Diatomic molecules provide an important contribution to the absorption line spectra of the Sun and stars. With continuing improvements in the accuracy of the fundamental molecular data, and refinements in model solar and stellar atmospheres, the astronomical spectroscopist might expect to achieve a full quantitative interpretation of the molecular absorption lines.

A key component in the standard analyses of molecular lines is the assumption of local thermodynamic equilibrium (LTE). The molecular density and the relative populations of the molecular energy levels are assumed to be equal to the equilibrium values as computed for the local kinetic temperature. In addition, the LTE assumption incorporates the hypothesis that pure absorption is the appropriate prescription for line formation. The view is widely held that the rich energy level structure of a molecule guarantees the validity of the pure absorption mechanism. This paper examines this assumption.

2. THE LINE SOURCE FUNCTION

With the usual assumption of complete redistribution, the line source function for a transition between an upper level U and a lower level L is given by the relation

$$S_1 = \frac{2h\nu_{UL}^3}{c^2} \frac{1}{\left(\dfrac{n_L g_U}{n_U g_L} - 1\right)}. \tag{1}$$

The number densities, n_L and n_U, are provided by the equations of statistical equilibrium. These express the fact that the population and depopulation rates are in balance for each level in the steady state conditions which appear to exist in stellar atmospheres.

The total source functions for the line and continuum may be written

$$S_{tot} = \frac{\kappa_1 S_1 + \kappa_c S_c}{\kappa_1 + \kappa_c} \qquad (2)$$

where κ_1 and κ_c are the absorption coefficients for the line and continuum, respectively. The former with a correction for stimulated emission is given by

$$\kappa_1 = \frac{\pi e^2}{mc} n_L f_{LU} \phi_\nu \left(1 - \frac{n_U g_L}{n_L g_U} \right) \qquad (3)$$

where ϕ_ν is an absorption profile, f_{LU} is the absorption oscillator strength and other symbols have their standard meaning.

The residual line intensity is given by

$$r_{\Delta\nu} = \frac{\int_0^\infty S_{tot}(\tau_0) \exp(-t_{\Delta\nu}) \, dt_{\Delta\nu}}{\int_0^\infty S_c(\tau_0) \exp(-t_c) \, dt_c}$$

where $\Delta\nu$ is the distance from the line centre, $t_{\Delta\nu}$ is the total (line + continuum) optical depth, t_c is the optical depth in the continuum and τ_0 is the continuum optical depth at a standard wavelength λ_0.

The equivalent width is calculated by integration over the line profile

$$W_\nu = \int_{-\infty}^{+\infty} (1 - r_{\Delta\nu}) \, d(\Delta\nu).$$

When LTE is valid, $S_{tot} = S_1 = S_c = B_\nu(\tau)$ and the familiar thermodynamic equations are applicable. The simplification introduced by LTE is attractive! Dismissal of the LTE assumption necessitates the construction and solution of the equations of statistical equilibrium for the molecule. This procedure should include excitation processes within a molecule and, also, processes involving formation and destruction of the molecule.

The molecular transitions of primary concern in this paper are the electronic transitions of light molecules. The transitions have characteristic wavelengths in the ultraviolet through the near infrared regions of the spectrum. An electronic state has an associated vibrational and rotational structure. Then, a minimum labelling for a single state would be (n, v, J, S) where n denotes the electronic quantum numbers, v the vibrational quantum number, J the rotational quantum number and S the electronic spin. Standard notation is followed as upper states are denoted by single primed quantities and lower states by double primes. In principle, radiative and collisional terms involving all possible exchanges between states should appear in the equilibrium equations. In practice, considerable simplification appears possible.

3. COLLISIONAL AND RADIATIVE EXCITATION PROCESSES

3.1 *Preliminary remarks*

Investigations of the statistical equilibrium of atoms and ions include a term due to excitation by electrons. Hydrogen atoms outnumber electrons by a

considerable number (e.g. $n(H)/n(e) \sim 10^4$ at $\tau_0 = 0 \cdot 01$ in the solar atmosphere) but hydrogen atom excitation is omitted. The basic reason for this is contained in a discussion by Massey (1949).

A collision occurs with a characteristic time scale $t \sim r/v$ where r is the effective range and v is the relative velocity. The transition in the perturbed molecule (or atom) corresponds to a frequency $v \sim E/h$. Classically and, also, quantum mechanically, the expectation is that the cross-section for excitation and de-excitation will be small unless $1/t \sim v$. It is instructive to examine this limit:

$$tv \approx \frac{r}{v}\frac{\Delta E}{h} = \frac{4r}{\sqrt{T}}\Delta E \quad \text{(electrons)}$$

$$= \frac{170r}{\sqrt{T}}\Delta E \quad \text{(hydrogen atoms)}.$$

In these formulae, the effective range is given in Å units and the energy ΔE is eV.

A typical electronic transition, $(n'', v'', J'') \rightleftarrows (n', v', J')$, has $\Delta E \sim 3$ eV so that at $T \sim 5000$ K, $tv \sim 1/6$ for an electron collision and ~ 7 for a hydrogen atom collision. In a molecule, the rotational and vibrational transitions correspond to smaller excitation energies: $\Delta E_{\text{rot}} \sim 0$ to $0 \cdot 05$ eV and $\Delta E_{\text{vib}} \sim 0 \cdot 2$ to $0 \cdot 4$ eV for typical molecules. Then, the product $tv \lesssim 1$ and excitation by hydrogen (also, helium) atoms must be included. In the limit $tv \to 0$, the cross-section will decrease from a maximum near $tv \lesssim 1$ but it will remain significantly large for small tv values. On the other hand, the cross-section is essentially zero for $tv \gg 1$.

Rates for rotational and vibrational excitation by hydrogen atoms are discussed in the following sections. Corresponding rates for electrons are omitted because they are generally unimportant for stellar atmosphere problems; this was demonstrated for the CO electronic ground state by Thompson (1973).

3.2 *Rotational excitation*

A rigid rotator model provides energy levels $E = BJ(J+1)$ where B is the rotational constant and J the rotational quantum number. Molecules of astrophysical interest span the range $B = 61$ cm^{-1} (H_2) to $0 \cdot 5$ cm^{-1} (TiO). Molecules with electronic transitions in the readily accessible visible and infrared spectral regions cover a more limited range with $B \sim 15$ cm^{-1} (CH, NH, OH) as the upper limit. The spacing between adjacent levels is $\Delta E_{J+1/2} = E_{J+1} - E_J = 2B(J+1)$. Absorption or emission lines within a vibrational band attain a maximum intensity for $J_{\text{max}} \sim 0 \cdot 6\sqrt{T/B}$. For this J, the spacing is $\Delta E_{J+1/2} \sim 1 \cdot 2\sqrt{BT}$ or $\Delta E \sim 200$ cm^{-1} ($0 \cdot 025$ eV) for $B \sim 10$ cm^{-1} and $T \sim 3000$ K. In a strong band, the rotational structure may be followed well beyond J_{max} subject to an upper limit imposed by rotational pre-dissociation or the lack of completeness of the available wavelength measurements. In a typical case, the rotational structure can be followed to $J \sim 3J_{\text{max}}$. Even at this limit, the rotational level spacing is small relative to the thermal energy. The small excitation energy is a major reason why collisional excitation between rotational levels is an efficient process in stellar atmospheres.

Rotational excitation by atoms (H, He) and molecules (H_2) will be an efficient process. Stevens (1967) following earlier discussions by Beckerle (1953) and Brout (1954) provides the following estimate for the cross-section for a rotational

de-excitation

$$\sigma \sim \frac{4I}{m_r}$$

where I is the moment of inertia of the diatomic molecule and m_r is the reduced mass of the colliding system. For the system $AB + H$, $m_r \sim m_H$ and $I = m_A m_B r_e^2 / (m_A + m_B)$ so that

$$\sigma \sim \frac{4 m_A m_B}{(m_A + m_B)} r_e^2$$

where r_e is the equilibrium internuclear separation and the masses are expressed in atomic mass units. Representative cases are hydrides, $\sigma \sim 4 r_e^2$, and homonuclear molecules where $\sigma \sim 2 m_A r_e^2$. Then, a cross-section $\sigma \sim 5$ to 10 Å^2 appears reasonable. This corresponds to a probability of a rotational redistribution of essentially unity per collision.

Stevens points out that these simple arguments provide predictions which are in moderately good agreement with measurements made at room temperature. The experimental data cover the self-relaxation of N_2, O_2 and HCl and the relaxation of N_2 and O_2 by He at room temperature. The cross-section may decrease slightly at the higher temperatures of astrophysical interest.

Later discussion shows that a cross-section of this magnitude is quite sufficient to guarantee that collisions dominate the interchange between rotational levels of the ground electronic state. A precise value for the cross-section is not required. This happy circumstance is too rarely encountered in calculations of this type. A more difficult problem arises when excited electronic states are considered. The key question is whether a collisional redistribution (rotational, vibrational or electronic) can occur before the spontaneous (or stimulated) emission of a photon. In this case, more precise estimates appear necessary.

The previous estimate, $\sigma \sim 5$ to 10 Å^2, may apply to excited states. The available experimental results are few and none deal with de-excitation by H atoms. The excited $A^2\Sigma^+$ state of NO was investigated by Broida & Carrington (1963) who reported $\sigma \sim 7\cdot5 \text{ Å}^2$ for He collisions and $\sigma \sim 6\cdot6 \text{ Å}^2$ for H_2 collisions. Smaller cross-sections for the $A^2\Delta$ state of CH were reported by Brennen & Carrington (1967): $\sigma \sim 0\cdot35 \text{ Å}^2$ (He), $\sim 1\cdot3 \text{ Å}^2$ (N_2). Evenson & Broida (1966) found that the rotational de-excitation cross-section was approximately equal to the gas kinetic cross-section for $CN + N_2$ collisions.

Experiments with H as a collision partner are necessary if the results are to be readily applicable to stellar atmosphere problems. At the present time, the probability for a rotational redistribution is taken as unity with the collision frequency computed from a gas kinetic cross-section. A selection rule $\Delta J = \pm 1$ may be assumed for a heteronuclear molecule, but there is experimental evidence that $\Delta J = \pm 2, \pm 3, \ldots$ transitions can occur as a result of a collision.

3.3 *Vibrational excitation*

Vibrational relaxation of gases is the subject of an extensive literature but only a minute fraction of the work refers to molecules of astrophysical interest undergoing relaxation with atomic or molecular hydrogen. Hence, uncertainties exist in an assessment of the vibrational excitation and de-excitation rates.

The rate of transfer of vibrational energy to translational energy is frequently

expressed in terms of a relaxation time $\tau_{v'}$ for the excited vibrational level. In relating $\tau_{v'}$ to a collisional de-excitation rate from v' to v'' account must be taken of the other processes occurring, i.e. $v'+1 \to v'$, $v' \to v'+1$, etc. If the harmonic oscillator approximation is adopted, the selection rule is $\Delta v = v'-v'' = \pm 1$ and the de-excitation probabilities satisfy the relation $P_{v',v'-1} = v'P_{1,0}$ where $P_{v',v''}$ is the probability of a de-excitation $v' \to v''$. Then, the rate $C_{v',v''}$ and the relaxation time $\tau_{v'}$ are related through the equation

$$C_{v',v''} = \frac{1}{\tau_{v'}(1 - \exp(-h\nu_{v'v''}/kT))}.$$

The astrophysicist in need of good estimates for the rate $C_{v',v''}$ for the astrophysically abundant molecules in a hydrogen-rich atmosphere will find almost no direct experimental results and, apparently, no reliable theoretical guide.

Millikan & White (1963) discussed the experimental results available to them and they were able to construct an empirical expression. Their result for the relaxation time was

$$\log_{10}(P\tau_1) = 5.0 \times 10^{-4} \mu^{1/2}\theta_{\mathrm{vib}}^{4/3} \left(\frac{1}{T^{1/3}} - 0.015\,\mu^{1/4}\right) - 8.00$$

where μ is the reduced mass in atomic mass units for the colliding system, θ_{vib} is the fundamental vibrational frequency of the relaxing molecule expressed as a temperature, P is the total pressure in atmospheres. A common unit for $P\tau$ is atm μs. The authors noted that the agreement was generally within 50 per cent and within a factor of 5 in all cases.

This result is tempting to the astrophysicist. The temperature range covered by many experimental measurements extended to 4000 K or higher in a few cases. This is just the range of interest for stellar atmosphere problems. However, inspection of the contributing data shows that almost none of the molecules provide observed electronic transitions in stellar spectra and in only two cases (CO, O_2) were measurements reported for relaxation by H_2. No measurements of relaxation by H atoms were known. All measurements referred to molecules in the ground electronic state. Therefore, application of the Millikan–White expression to conditions in stellar atmospheres involves a considerable extrapolation.

With the results of experiments published after 1963 some interesting comments may be made relative to this extrapolation. The relaxation of CO is discussed first. Results are available for relaxation by H (von Rosenberg, Taylor & Teare 1971), O (Center 1973) and Fe (von Rosenberg & Wray 1971) atoms. A summary of the experimental results together with the Millikan–White predictions are shown in Fig. 1. The conclusion drawn from Fig. 1 is that relaxation by H (and the other atoms) is considerably faster than predicted: the excess is a factor of 10^2 at 1400 K and increases to nearly 10^3 at 2800 K. The enhanced relaxation by atoms is found for other molecules (O_2, N_2) for which work references are listed in the CO papers just referenced. The above rates for $CO + H$ correspond to a de-excitation probability of $P_{1,0} \sim 0.01$ at $T = 1500$ K increasing to $P_{1,0} \sim 0.30$ at $T = 2800$ K, i.e. 100 to 3 collisions are required before a de-excitation occurs.

The Millikan–White sample contained no hydrides. Callear (1967) has pointed out that their empirical fit ' does not take account of the large amplitude of vibration of light molecules, and presumably will therefore not be applicable to diatomic hydrides '. Measurements of the self-relaxation of HF, HI, HCl, and HBr (see, for

example, Chow & Greene 1965; Solomon *et al.* 1971) indeed show relaxation times considerably shorter than those predicted; for example, the HI+HI relaxation time for $T = 2500$ K is about 4×10^4 faster than predicted. Self-relaxation of H_2 follows the same trend (Gaydon & Hurle 1962).
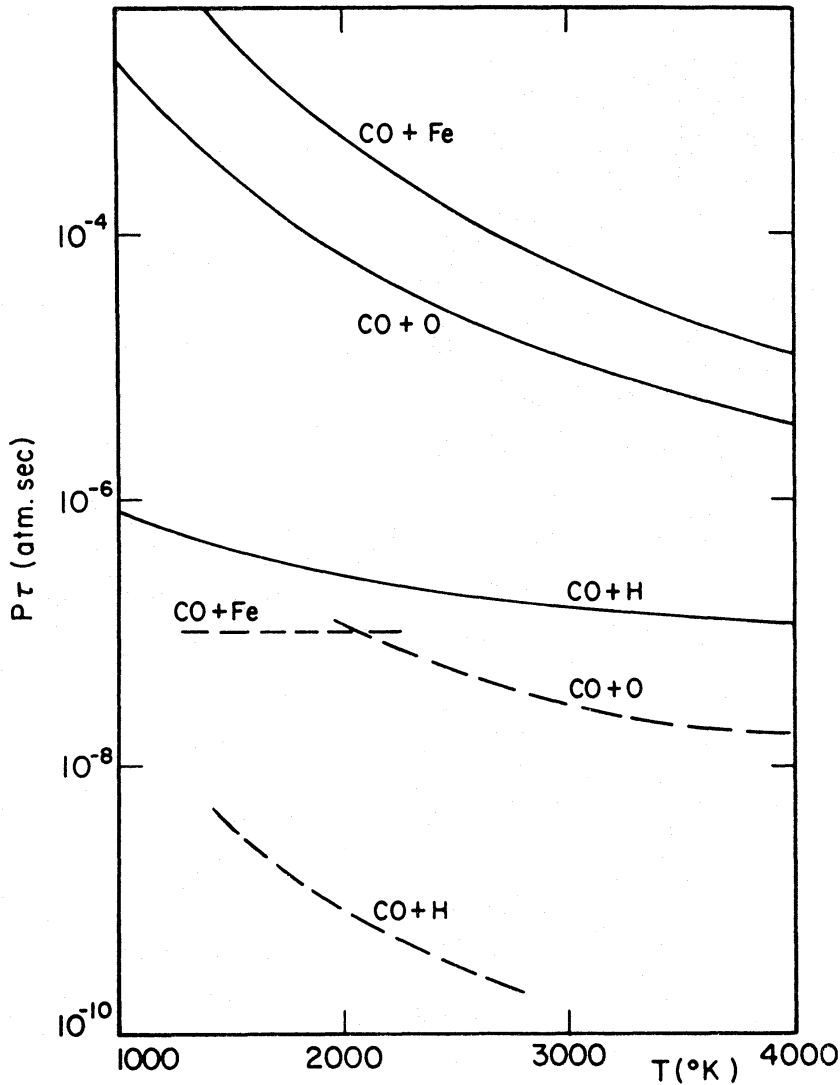
FIG. 1. *Predicted and observed vibrational relaxation times. The solid lines show the predicted relaxation times computed from the Millikan & White (1963) relation. Recent experimental measurements are summarized by the dashed lines.*

The lack of an adequate theoretical background makes an extrapolation to the astrophysically important cases (i.e. CH+H, OH+H) difficult. It is apparent that the small relaxation times for hydrides are the result of a high rate of transfer from vibrational to rotational energy, an efficient mechanism for hydrides because of the small moment of inertia of the hydrogen atom. Seeny (1973) measured the vibrational relaxation of HCl by the inert gases, He, Ne and Ar. He noted that none of the available theories for vibration rotation transfer could explain the observed strong dependence of the relaxation time on the mass of the inert collision partner. In some cases, enhanced relaxation may be due to a long range chemical interaction; for example, the self-relaxation of NO is anomalously fast compared to the

Millikan–White expression and here a specific chemical interaction has been proposed (Wray 1962).

Vibrational relaxation of excited electronic states can also exceed the expectation based on the Millikan & White empirical fit to ground state observations. This is true for cases (e.g. $N_2 + N_2$) which show relaxation times in accord with the empirical fit when the electronic ground state is involved. Calo & Axtmann (1971) investigated the vibrational relaxation of the $N_2 \ C^3\Pi_u \ (v' = 1)$ excited state. For collisions with ground state N_2 molecules, they found $\sigma_v \sim 2$ Å^2 or a probability $P_{1,0} \sim 0.05$. Comes & Fink (1972) measured the relaxation of excited $(A^1\Pi)$ CO molecules. The de-excitation cross-section for the $1 \to 0$ vibrational transition is $\sigma_v = 0.37$ Å^2 (He), 1.9 Å^2 (H_2), and 11.4 Å^2 (Ar), with the equivalent probabilities for de-excitation in the range $P_{1,0} = 0.01$ to 0.3. Broida & Carrington (1963) studied the relaxation of excited $(A^2\Sigma^+)$ NO and cross-sections $\sigma \sim 0.001$ Å^2 (He), ~ 0.005 Å^2 (N_2) and ~ 3.0 Å^2 (NO) were found.

Recent work (Lengel & Crosley 1974) on the $A^2\Sigma^+$ state of OH has shown that the vibrational and rotational de-excitation cross-sections are comparable for OH–H_2 collisions with the former averaging 8 Å^2 for low rotational levels. The vibrational cross-section is reduced by about two orders of magnitude for OH–He collisions but the rotational cross-section is little changed.

In this paper, a de-excitation rate for $v' = 1 \to v'' = 0$ from H atom collisions is evaluated for both ground and excited electronic states on the basis of the probability $P_{1,0} = 0.03$. The contribution from H_2 and He is ignored because H is apparently more effective than H_2 or He and it is the dominant constituent in the stellar atmospheres of interest. In cool dwarf atmospheres, H_2 and He could make an important contribution. The inadequacies of the presently available information especially for excited electronic states cannot be overemphasized.

3.4 Electronic excitation

Experimental work on the excitation of electronic states by electron collision is meagre. In order to assess the importance of this collisional excitation, the method (Seaton 1962) of treating the collisional excitation as a radiative process was adopted. This approximation gives a cross-section

$$\sigma(i \to j) = \frac{4\pi^2}{k_i^2\sqrt{3}} \frac{f(j,i)}{(E_j - E_i)} g(k_j, k_i)$$

where E_j and E_i are in atomic units and $k_i^2 = k_j^2 + 2(E_j - E_i)$. The Kramers–Gaunt factor $g(k_j, k_i)$ is defined by Seaton. The optical oscillator strength is $f(j,i)$. Seaton noted that empirical Gaunt factors were very similar for three atomic transitions (H, $1s \to 2p$; He, $1^1S \to 3^1P$; Na, $3s \to 3p$) for which good experimental cross-sections were available. He pointed out that although the Gaunt factors were similar, the maximum cross-sections ranged over three orders of magnitude.

This approach should be applicable to electronic transitions in molecules. Unfortunately, experimental work is so limited that a thorough test of the approach is impossible. Mumma, Stone & Zipf (1971) measured excitation cross-sections for the CO Fourth-Positive ($A^1\Pi \to X^1\Sigma^+$) system. They noted that the relative cross-sections $\sigma_{v',v''}$ were proportional to the Franck–Condon factors (hence, $f_{v',v''}$) which is consistent with the approximation. All their measurements refer to excitation from $v'' = 0$. Absolute cross-sections show good agreement with the

above equation; for example, the cross-section for excitation from $v'' = 0$ to $v' = 0$ has a maximum value near 30 eV of $\sigma = 6 \times 10^{-18}$ cm^2. The Seaton method with the measured oscillator strength, $f_{0,0} = 0.016$ gives $\sigma = 5.3 \times 10^{-18}$ cm^2. This agreement is maintained at higher electron energies.

In an estimation of rate constants at the temperatures prevailing in stellar atmospheres the dominant contribution is provided by electrons with energies just above the threshold value. Unfortunately, the experimenters did not make measurements in this energy range. However, the theoretical cross-section does match the measurements from the lowest energy ($\sim 3 \times$ threshold) to high energies.

Estimates of the excitation rate will be based upon the above equation and estimates for the electronic oscillator strength.

3.5 *Quenching collisions*

The loss of the electronic energy in a collision is known as quenching. Several processes contribute collectively to quenching.

An obvious contributor is the direct inverse process of electron excitation discussed in the previous section. The rate may be estimated from the excitation rate and the principle of detailed balancing. Furthermore, the reasons for omitting hydrogen atom excitation of the electronic excited states are valid when the de-excitation process is considered as a direct application of detailed balance will show.

A collision induced change in the spin multiplet (i.e. $^2\Pi_{1/2} \rightleftarrows {}^2\Pi_{3/2}$, $^3\Delta_1 \rightleftarrows {}^3\Delta_2$) can also contribute to what are known as quenching collisions. Strictly speaking, since the electronic energy is basically unchanged by this process, the collision does not result in quenching. However, certain experiments may be unable to distinguish this from a full quenching. Very little experimental work has been reported on spin multiplet relaxation in molecules. References to four experiments are given by Slanger & Black (1973a) who studied the process $d^3\Delta \rightleftarrows d^3\Delta$ in CO induced by Ar and He atoms. The limited experimental data available suggest that spin-multiplet relaxation is an efficient process with a cross-section in the range $\sigma_{\text{spin}} \sim \sigma_{\text{rot}}$ to $\sigma_{\text{spin}} \sim \sigma_{\text{rot}}/10$ where σ_{rot} is the cross-section for rotational relaxation. Experiments with H as a collision partner are required.

Another form of quenching arises because excited electronic states may have close-lying neighbours. A collision may induce a transition to a neighbouring state and lead to an apparent quenching. The importance of this process for spectroscopic studies is that these cross-relaxations may couple two states excited by radiation at two different wavelengths—an unwelcome growth in complexity!

Two recent examples illustrate the problem. Luk & Bersohn (1973) studied the quenching of the excited CN $B^2\Sigma$ state by rare gases. These gases cannot participate in a direct exchange of the electronic energy because the excitation energy of the $B^2\Sigma$ state is small relative to the separation between ground and first excited state of the rare gases. Earlier arguments of this section suggest a direct conversion of electronic to translational energy is most improbable. The observed quenching was attributed to processes of the type

$$\text{CN}(B, v, K') + X \rightleftarrows \text{CN}(A, v+9 \quad \text{or} \quad v+10, K) + X$$
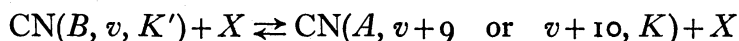
where A denotes the $A^2\Pi$ excited state. Spectroscopic studies have shown the existence of strong interaction between specific rotational states with B and A states. The cross-relaxation will occur between these states.

Relaxation processes for excited states of CO were studied by Slanger & Black (1973b). Room temperature rate constants were measured for the relaxation $d^3\Delta(v = 7) \to e^3\Sigma^-(v = 4)$. A probability $P_{d,e} \sim 0.01$ was found when the collision partner was Ar, N_2, H_2 or CO. He was markedly less efficient with $P_{d,e} \sim 0.0005$.

Other quenching modes can be anticipated. A collision resulting in the dissociation of H_2 is a possibility for the more highly excited electronic states. Quenching of excited $a^3\Pi$ CO by the process

$$CO(a^3\Pi) + H_2 \to CO(X^1\Sigma^+) + 2H$$
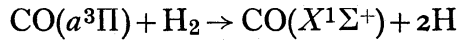
was observed by Slanger & Black (1971) and is discussed in a stellar atmosphere context by Thompson (1973). If the survey is limited to the electronic transitions observed above the ultraviolet atmospheric cut-off, this dissociation process can be excluded on the basis of energetics.

3.6 *Radiative rates*

The radiative contribution to the equations of statistical equilibrium includes pure rotational transitions, vibration–rotation transitions and electronic transitions. Other contributions (i.e. photodissociation) may have to be included for some molecules.

The pure rotation transitions are very weak. For a transition in a $^1\Sigma$ ground state, the coefficient for spontaneous emission is

$$A_{J'J''} = \frac{64\pi^4}{3h} \mu^2 \sigma^3 \frac{J''+1}{2J'+1}$$

where μ is the permanent dipole moment and σ (cm^{-1}) is the frequency for the transition with $\sigma \sim 2BJ'$.

The maximum intensity in a band is reached near $J_{max} \sim 0.6\sqrt{T/B}$ where

$$A_{J'J''} \sim 5 \times 10^{-7} \mu_D^2 (BT)^{3/2}$$

where μ_D is the dipole moment expressed in Debyes ($1D = 10^{-18}$ esu). A typical molecule may have $\mu_D \sim 1$, $B \lesssim 15$ cm^{-1}, $T \lesssim 4000$ or

$$A_{J'J''} \lesssim 10 \text{ s}^{-1}.$$

Transition probabilities for several ground state vibration–rotation transitions have been measured in the laboratory. No measurements have been reported for excited electronic states. The general expression for the vibrational transition probability is

$$A_{v'v''} = \frac{64\pi^4\sigma^3}{3h} \langle v'|M(r)|v''\rangle^2.$$

Here, an estimate is based upon the assumption that the molecular vibrator is a harmonic oscillator for which the selection rule is $\Delta v = v' - v'' = \pm 1$. Also, the electric dipole moment $M(r)$ is assumed to show a linear variation with internuclear separation:

$$M(r) = M_0 + M_1(r - r_e).$$

Evaluation of the matrix element gives

$$A_{v'v''} \sim 8 \times 10^{-6} \frac{\sigma^2 M_1^2 v'}{m_r} \text{ s}^{-1}$$

where the reduced mass m_r is expressed in atomic mass units. A substitution for representative values of σ, M_1 and m_r gives $A_{1,0} \sim 10$ to 100 s^{-1}; for example, the SiO molecule has $\sigma \sim 10^3$ cm^{-1}, $M_1 \sim 2 \cdot 5$ Å and $m_r \sim 9 \cdot 6$ or $A_{v',v''} \sim 5$ s^{-1}. Hedelund & Lambert (1972) reported calculations using a Morse potential and they gave $A_{1,0} = 5 \cdot 1$ s^{-1}.

Radiative excitation within an electronic transition is estimated from the expression

$$R(n'' \to n') = \frac{\pi e^2}{mc} \sum_{v'} f_{v'v''} \frac{4\pi J_\nu\ v'v''}{h\nu_{v'v''}}$$

where $f_{v'v''}$ is the absorption band oscillator strength. A sum over the rotational structure is implied here. If the atmosphere is optically thin in the lines of this electronic transition, the mean intensity J_ν is equal to the mean continuum intensity J_ν^c. If the atmosphere is optically thick to line radiation, J_ν takes the form

$$\sum \int J_{\Delta\nu} \phi_{\Delta\nu} \, d\Delta\nu$$

where $\phi_{\Delta\nu}$ is the absorption line profile, $J_{\Delta\nu}$ is the mean intensity at a frequency $\Delta\nu$ from the line centre and the sum is made over the rotational structure. In general, $J_{\Delta\nu} < J_\nu^c$ so that the rate

$$R(n'' \to n') = \frac{4\pi^2 e^2}{mc} \sum_{v'} f_{v'v''} \frac{J_\nu^c\ v'v''}{h\nu_{v'v''}}$$

provides an upper limit to the radiative excitation rate.

One measure of potential departures from LTE is provided by the ratio of radiative excitations out of the ground electronic state to the collisional rate of redistribution within the rotational and vibrational structure of the ground electronic state. A calculation of this ratio should include all electronic transitions from the ground state. Often, the known electronic transitions have small oscillator strengths; for example, the three CH transitions identified in the solar spectrum ($A^2\Delta–X^2\Pi$, $B^2\Sigma^-–X^2\Pi$, $C^2\Sigma^+–X^2\Pi$) have a total of $f \sim 0 \cdot 02$. A calculation based on these transitions provides an incomplete assessment of the radiative rate because the electronic f-values should satisfy the oscillator strength sum rule:

$$\sum_{n'} f(n'' \to n') = 1.$$

Apparently, the transitions in CH with large f-values are part of the Rydberg series which is located shortward of about 1370 Å (Herzberg & Johns 1969). CH is probably typical in that the strong electronic transitions are in the ultraviolet and presently unobserved. Fortunately, the mean intensity in the ultraviolet is small in the atmospheres of cool stars and even with an oscillator strength of unity, the Rydberg transitions most probably provide a negligible contribution to a radiative excitation rate. An additional factor is that photoionization of neutral metal atoms will provide a large continuous opacity in the ultraviolet so the $J_\nu \sim B_\nu(T)$ can be anticipated for the ultraviolet and the radiative excitation rate will approach closely the LTE value. Molecules other than the light hydrides may have strong transitions in the near ultraviolet, which should be included in the calculations; possible molecules in this class would be MgH, SiH, TiO.

If the possibility of strong ultraviolet transitions is neglected, a typical molecule appears to have

$$f_{\text{el}} = \sum_{v'} f_{v'v''} \sim 0 \cdot 02$$

for all transitions in the wavelength interval (visible to near infrared) covering the flux maximum for the stars of interest. This value is adopted for calculations of the radiative excitation rate.

3.7 *Molecule formation and destruction*

A complete formulation of the NLTE problem must include an analysis of the rates for molecular formation and destruction. A preliminary survey is attempted here of the likely collisional and radiative contributions to these rates.

Second-order exchange reactions of the type

$$AB + M \rightleftarrows AM + B$$
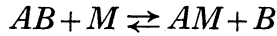
are likely to dominate. Third-order reactions $(A + B + M \rightleftarrows AB + M)$ are effective at high densities but in the atmospheres of giants and supergiants these processes are ineffective.

Rate constants for the second-order reactions are often written in the simple form:

$$K_{AB,M} = aT^n \exp(-E/RT)$$

where E is approximately equal to the activation energy for the reaction

$$AB + M \rightarrow AM + B.$$
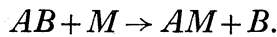
The measurements of rate constants invariably refer to a thermal average of the rate over the vibrational and rotational energy levels where

$$K_{AB,M} = \frac{\sum_v \sum_J K_{AB,M}(v, J) N_{AB}(v, J)}{\sum_v \sum_J N_{AB}(v, J)}.$$

If these processes are to be correctly inserted into the statistical equilibrium equations, the rates $K_{AB,M}(v, J)$ must be known. Of course, when the rate constant is independent of v and J, the identity $K_{AB,M}(v, J) = K_{AB,M}$ is self-evident. In the more likely event that certain vibrational levels are favoured, use of the averaged $K_{AB,M}$ is an approximation. However, at the moderate temperatures of interest, few vibrational levels can be involved and the averaged $K_{AB,M}$ should not introduce serious error. The destruction rate for a level (v, J) is

$$R_{AB,M} = K_{AB,M}(v, J) N_M \simeq K_{AB,M} N_M \text{ s}^{-1}$$

where the units for $K_{AB,M}$ are assumed to be cm^3 molecule^{-1} s^{-1}.

This rate is conveniently compared with the rate for collisional de-excitation of vibrational $v = 1$ level. Adopting the previous assumptions for this rate (R_{vib}, see Figs 2 and 4), the ratio is

$$r_{AM,M} = \frac{R_{AB,M}}{R_{\text{vib}}} \simeq 2 \times 10^{12} aT^{n-0.5} \exp(-E/RT) \frac{N_M}{N_H}.$$

Simple theories exist which can provide estimates for the second-order reaction rates. Tsuji (1964) and Thompson (1973) discuss applications of one theory in an astronomical context. The present discussion considers possible reactions involving the OH radical which is assumed to be representative of the astronomical hydrides. OH was also selected because quite extensive measurements have been made.

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The data adopted were taken from a recent compilation of rate constants (Baulch *et al.* 1972).

Two reactions are considered: $H + OH \rightarrow O + H_2$ and $O + OH \rightarrow O_2 + H$, which are slightly exothermic in the indicated direction. The rate given by Baulch *et al.* for the former is

$$K_{OH,H} = 1\cdot4 \times 10^{-14}\, T \exp\left(\frac{-3500}{T}\right)$$

for the range $400 < T < 2000$ and an uncertainty of ± 30 per cent is suggested.

Data for the $O + OH \rightarrow O_2 + H$ reaction is sparse and Baulch *et al.* decline to present a recommended rate from direct measurements. The reverse reaction $O_2 + H \rightarrow OH + O$ has been extensively measured. With an application of detailed balancing, the recommended $K_{O_2,H}$ rate can be converted to the $K_{O,OH}$ rate. This gives

$$K_{OH,O} = 2\cdot9 \times 10^{-11} \exp\left(-640/T\right)$$

for the range $700 < T < 2500$ K and subject to an uncertainty of ± 30 per cent.

In a calculation of $r_{O,OH}$, the number of free oxygen atoms is simply taken as $N_O = (A_O - A_C) N_H \sim 2.10^{-4} N_H$ where complete association of C into CO is assumed. These rates give the following values of r:

$T =$	1000	1500	2000	2500
$r_{O,OH}$	$1\cdot9.10^{-4}$	$2\cdot8.10^{-4}$	$1\cdot9.10^{-4}$	$1\cdot9.10^{-4}$
$r_{H,OH}$	$0\cdot03$	$0\cdot10$	$0\cdot22$	$0\cdot35$

The $H + OH \rightarrow H_2 + O$ reaction is apparently competitive with vibrational de-excitation. At the present time, more precise estimates for vibrational de-excitation cross-sections are needed.

In cool stars, H_2 may be abundant. Then, the $H_2 + OH \rightleftarrows H_2O + H$ reaction can occur. The recommended rate (Baulch *et al.* 1972) gives a ratio increasing from $r = 0\cdot17\, N_{H_2}/N_H$ at $T = 1000$ K to $r = 0\cdot51\, N_{H_2}/N_H$ at $T = 2500$ K. In supergiants like α Ori, the H_2 abundance is low and this reaction is not important. In cooler stars and especially those of higher surface gravity, this will be an important process. Also, direct measurements show that vibrational de-excitation by H_2 molecules can be considerably less efficient than for H atoms. Measurements refer to stable molecules (CO, O_2) and the position with respect to the hydrides (OH, CH) is uncertain. Then, a possibility exists that chemical reactions may control in part the vibrational excitation of molecules in the cool stars.

Third-order reactions appear not to be of importance in the low density atmospheres for which NLTE effects might appear. Two possible processes involving OH are $OH + H + M \rightarrow H_2O + M$ and $H + O + M \rightarrow OH + M$ where M is a third-body which on abundance considerations is likely to be either H, He or H_2. Examination of the rates for these and other third-order reactions listed by Baulch *et al.* shows a rate constant typically 10^{-31} to 10^{-32} cm^6 mol^{-1} s^{-1} for $T \sim 2000$ K. This corresponds to a ratio with respect to direct vibrational de-excitation of $r \sim 10^{-20}\, N_M$ to $10^{-21}\, N_M$ for the former process. Even with $M = H$, this gives a very small ratio for the gas pressures anticipated in giant and supergiant atmospheres. Similar conclusions were reached by Tsuji (1964) and Thompson (1973). In dwarfs, third-order reactions may be dominant; for example, in the Sun, $H + H + H \rightarrow H_2 + H$

is the dominant process in establishing the equilibrium of H_2 and indirectly the H^- ions via $H^- + H \rightleftarrows H_2 + e$.

Ion-molecule reactions (i.e., $AB + C^+ \rightleftarrows AB^+ + C$, $AB + C^+ \rightleftarrows A^+ + B + C$, etc.) can be expected to have large rate constants; a value of 10^{-9} mol^{-1} cm^3 is not unusual. In the upper solar photosphere, the major ions are Fe^+, Si^+ and Mg^+ with a combined abundance $n_+ \approx 10^{-4} n_H$. In cooler stars these elements will be predominantly neutral and other elements —Al, Na, Ca, K—will provide the ions with an abundance $n_+ \sim 10^{-5} n_H$. The total rate for ion-molecule reactions is $R \sim 10^{-9} n_+ \sim 10^{-13} n_H$ to $10^{-14} n_H$ s^{-1}. By comparison with the rate for the $H + OH \rightarrow H_2 + O$ reaction, ion–molecule reactions are seen to be a minor contributor to the molecular equilibrium.

The radiation field enters into the molecular equilibrium via photodissociation and photoionization processes. Although information on the relevant cross-sections is seriously incomplete, general considerations can be advanced to support a claim that these radiative processes produce only minor perturbations to the statistical equilibrium equations. For this discussion, molecules are divided into two groups according to their dissociation energy.

Molecules with a large dissociation energy comprise the first group and include the abundant astrophysical molecules—CO, CN, TiO and SiO. The most important photodissociation or photoionization processes involving the ground state of the molecule are located in the ultraviolet ($\lambda \lesssim 1500$ Å). The rate for molecular destruction will be low because the ultraviolet radiation field is weak in cool stars. The continuum opacity in the ultraviolet is large and the region of molecular line formation for transitions in the visible and infrared corresponds to a large optical depth at ultraviolet wavelengths. This will guarantee that the radiation field is closely Planckian and the low rates for photodissociation and photoionization will be close to their LTE values. These factors suggest that these processes are not important factors in the statistical equilibrium of the ground state. Numerical estimates for CO (Thompson 1973) in M giants confirm this conclusion.

A second group of molecules with a small dissociation energy may be dissociated more effectively by the radiation field. Molecules in this second group include OH, CH, MgH and CaH. Information on photodissociating transitions is sparse. CH is outlined as an example.

The CH spectrum was discussed by Herzberg & Johns (1969) and a summary of the photodissociation possibilities involving the ground electronic state was presented by Solomon & Klemperer (1972). Predissociation via ultraviolet transitions occurs but this contribution can be ignored for the reasons outlined above. Predissociation by longer wavelength transitions ($\lambda \lesssim 4000$ Å) can occur and involves the electronic transitions $B^2\Sigma^- - X^2\Pi$ and $C^2\Sigma^+ - X^2\Pi$. Inspection of the transition probabilities suggests that the rate for dissociation will not exceed that for radiative excitation to excited electronic states. Hence, the effect of photodissociation on the statistical equilibrium for the molecule can be safely described as slight. Since MgH, CaH and other hydrides have lower dissociation energies than CH, photodissociation is potentially of greater importance because the important transitions may lie closer to the peak wavelength for the photospheric radiation.

Although accurate cross-sections are unavailable for many of the collisional and radiative processes involved in dissociation and ionization of diatomic molecules, the discussion suggests that these processes provide only a perturbation to the statistical equilibrium of a molecule.

4. STELLAR ATMOSPHERES AND THE LINE SOURCE FUNCTION

4.1 *Model stellar atmospheres*

Exploratory calculations relating to the line source function are reported for model atmospheres of the Sun, Arcturus and Betelgeuse. Departures from LTE are not expected to be severe for the Sun but the high quality of the observations and the accuracy of the solar model atmosphere encourage a search for quite small non-LTE effects. As the ratio of collisional to radiative processes decreases, departures from LTE should become more prominent. Hence, attention in this survey is focused on the atmospheres of the cool giant and supergiant stars.

The solar model was taken from Gingerich *et al.* (1971). A model with effective temperature $T_e = 4100$ K and surface gravity $\log g = 2 \cdot 0$ was chosen as representative of the K giant Arcturus. Finally, a model with $T_e = 3500$ K and $\log g = 0 \cdot 0$ was adopted to represent the cool M supergiant Betelgeuse. This latter model was kindly provided by Professor Hollis R. Johnson (see Faÿ & Johnson 1973; Johnson 1974).

4.2 *Statistical equilibrium for the electronic ground state*

In spite of considerable uncertainty in the rate constants, simplification of the statistical equilibrium equations appears possible. This section examines a possible approximation to the line source function and absorption coefficient.

Rates for processes affecting the equilibrium of the ground electronic state are displayed in Fig. 2. The collisional rates for rotational and vibrational redistribution are compared with radiative rates for excitation within the ground state and to excited electronic states. These rates were reviewed in the earlier sections. The collision frequency was calculated assuming a molecular diameter of $3 \cdot 5$ Å and a diameter of 1 Å for the colliding atom. The molecular mass was put at 15 atomic mass units. These are representative figures.

The radiative rates shown correspond to spontaneous emission for a pure rotation transition and vibration–rotation transition together with radiative excitation to an excited electronic state. The pure rotation rate, $A_{rot} < 10$ s^{-1}, is the approximate upper limit derived earlier for the spontaneous emission probability. The approximate limit, $A_{vib-rot} = A_{1,0} < 100$ s^{-1}, is illustrated for the vibration–rotation transitions.

Rates for vibrational de-excitation are shown for the $v' = 1 \rightarrow v'' = 0$ transition. For low vibrational levels both radiative and collisional de-excitation probabilities should scale approximately as the harmonic oscillator approximation:

$$P_{v',v'-1} = v'P_{1,0}.$$

Then, the ratio of the collisional to radiative rates for the $1 \rightarrow 0$ transition should be a reasonable measure of their relative importance for neighbouring low lying levels. As the dissociation limit is approached, this ratio could change. Excitation to excited electronic states calculated by the prescription given earlier is shown for three representative wavelengths for the exciting radiation or, equivalently, for three different excitation energies for the excited electronic state. Electron excitation to these excited states is small (see Fig. 3).

The rates shown in Fig. 2 demonstrate that the statistical equilibrium of molecular ground electronic states is collisionally controlled throughout these stellar photospheres. Qualifications to be attached to this statement are outlined

below. When collisions dominate, the relative level populations are described by the Boltzmann equation for the local kinetic temperature. Vibration–rotation transitions of astrophysical interest occur within ground electronic states. Since collisions dominate, the line source function for these transitions is equal to the
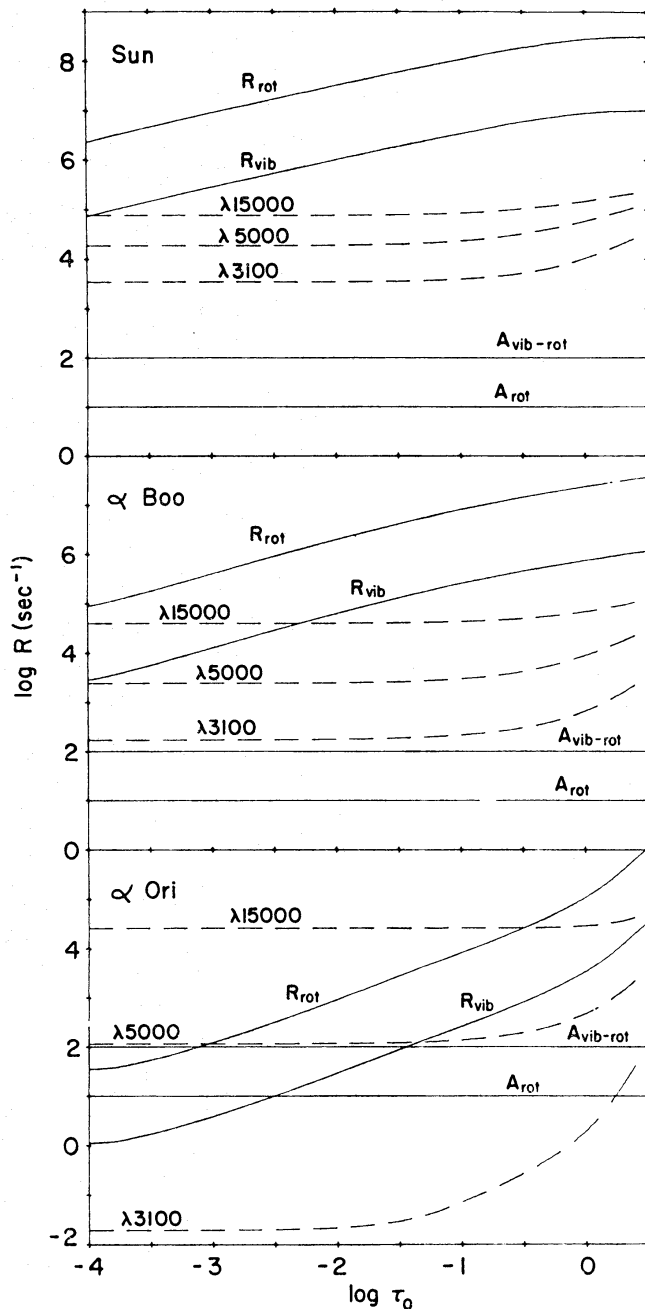
FIG. 2. *Excitation rates for a typical electronic ground state for the three model atmospheres: top—Sun, middle—α Boo and bottom—α Ori. Rates for a rotational and vibrational redistribution within the ground electronic state are shown by the curves labelled R_{rot} and R_{vib} respectively. The rates for radiative excitation to an excited electronic state for three wavelengths (15 000, 5000 and 3100 Å) are shown by the broken lines. Upper limits to the transition probability for spontaneous emission (Einstein A) in a vibration–rotation transition and a pure rotation transition are shown as $A_{vib-rot}$ and A_{rot} respectively. The rate for electronic excitation to the excited electronic state is not plotted, but is shown in Fig. 3. The optical depth, τ_0, is at 5000 Å in Figs 2, 3, 4 and 5.*

Planck function evaluated for the local kinetic temperature; pure absorption prevails. In late-type giants and supergiants, the cores of the fundamental vibration–rotation transitions of CO are formed in the uppermost layers of the photosphere. In this case, complete collisional control may not be assumed and a more specific examination appears necessary.

The claim for collisional control is well supported by the rates calculated for the model solar atmosphere. The photospheric molecular lines are formed in the layer $-1 > \log \tau_0 > -3$ in which the collisional processes dominate.
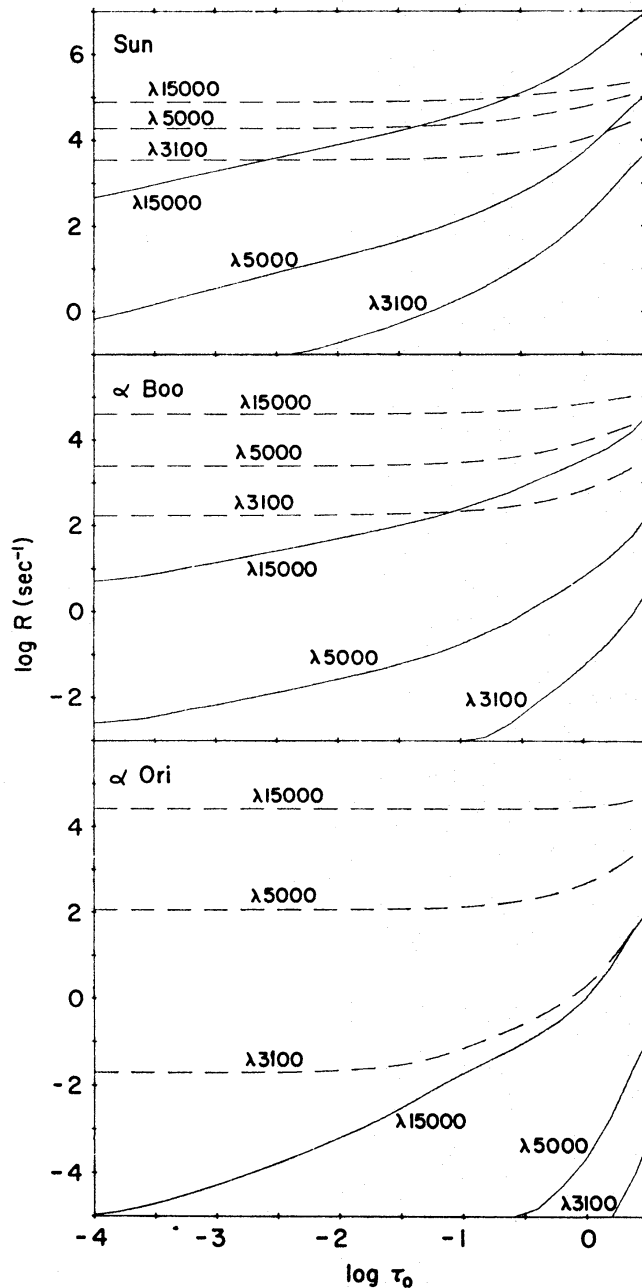
FIG. 3. *Excitation rates to a typical excited electronic state for the three model atmospheres. Radiative excitation in the optically thin limit is shown by the broken lines for the three wavelengths—3100, 5000 and 15 000 Å. Rates for excitation through electron collisions for excitation energies corresponding to these wavelengths are shown by the solid lines.*

A similar situation prevails for Arcturus. However, the vibrational collisional de-excitation rate is less than the radiative excitation for $\tau \lesssim 10^{-3}$ and $\lambda \gtrsim 8000$ Å. The CN molecule is an important example with a characteristic wavelength for an electronic transition in the near infrared. Fortunately, the CN molecules are located in the deeper layers where the CO molecules begin to dissociate. In these layers, collisional processes surely dominate. The TiO molecule, which is detectable in spectral types later than about K5, has important near infrared electronic transitions. The calculations suggest that radiative excitation in the TiO transitions may contribute to the equilibrium of the ground state.

The lower gas pressures in the atmosphere of α Ori provide for interesting competition between radiative and collisional processes. Since collisions are not dominant by overwhelming margins, molecules must be examined individually. Present discussion is restricted to a sketch of three molecules.

The OH radical provides strong absorption lines attributable to the fundamental (Beer *et al.* 1972) and first-overtone (Lambert 1974) vibration–rotation bands. Recent laboratory measurements give a spontaneous emission probability $A_{1,0} = 43$ s^{-1} (Roux, d'Incan & Cerny 1973). Radiative excitation to excited electronic states appears negligible; the leading transition $A^2\Sigma - X^2\Pi_i$ with an origin near 3000 Å and an f-value of about 10^{-3} gives a negligible contribution according to Fig. 2. An interesting competition could occur between collisional and radiative vibration–rotation transitions. Since the adopted collisional rate is probably an underestimate for a hydride, collisional processes probably dominate. Rotational equilibrium seems assured.

The CN red system is a significant contributor to the supergiant spectrum. The bands cover a wide wavelength interval across the peak in the flux curve, say $7000 \lesssim \lambda \lesssim 17\,000$ Å. However, two factors reduce the significance of the effect of radiative excitation in the red system on the ground electronic state. The oscillator strength is about an order of magnitude less than the value adopted for Fig. 2. Secondly, the CN molecules are located deep in the atmosphere ($\log \tau_0 > -1$) where collisional effects are increasing.

The TiO molecule provides an enormous number of lines. Unlike CN, TiO exists throughout the atmosphere. Some transitions are quite strong; for example, Price, Sulzmann & Penner (1971) give the oscillator strength of the γ-system at 7147 Å as $f = 0.089 \pm 0.036$. In this case radiative excitation to excited electronic states may exceed the vibrational and, even, the rotational collisional redistribution rates. A detailed analysis will require that the simplifying optically-thin approximation be replaced by a full treatment of the radiative transfer within the TiO lines.

4.3 *Statistical equilibrium in excited electronic states*

Discussion of the statistical equilibrium of excited electronic states is conveniently begun with a consideration of the relative importance of radiative and collisional excitation from the ground electronic state. The rate constants were discussed earlier and the rates versus optical depth for the three atmospheres are compared in Fig. 3. An assumption is that the excited state is reached exclusively from the ground state. This is not strictly correct; for example, the upper state of the CN red system, $A^2\Pi$, can be excited through a cascade from the $B^2\Sigma^+$ state where the $B^2\Sigma^+ - X^2\Sigma^+$ transition is the CN violet system. In addition, a single vibrational level in an excited state may be excited from several vibrational levels

in the ground state; excitation to the CN $A^2\Pi$ state is an example of this behaviour. In this initial survey, these and other fine points are overlooked.

A principal result to be extracted from Fig. 4 is that electronic states in the majority of molecules should be excited primarily by the radiation field with electron collisional excitation as a minor contributor. Clearly, this is the case for
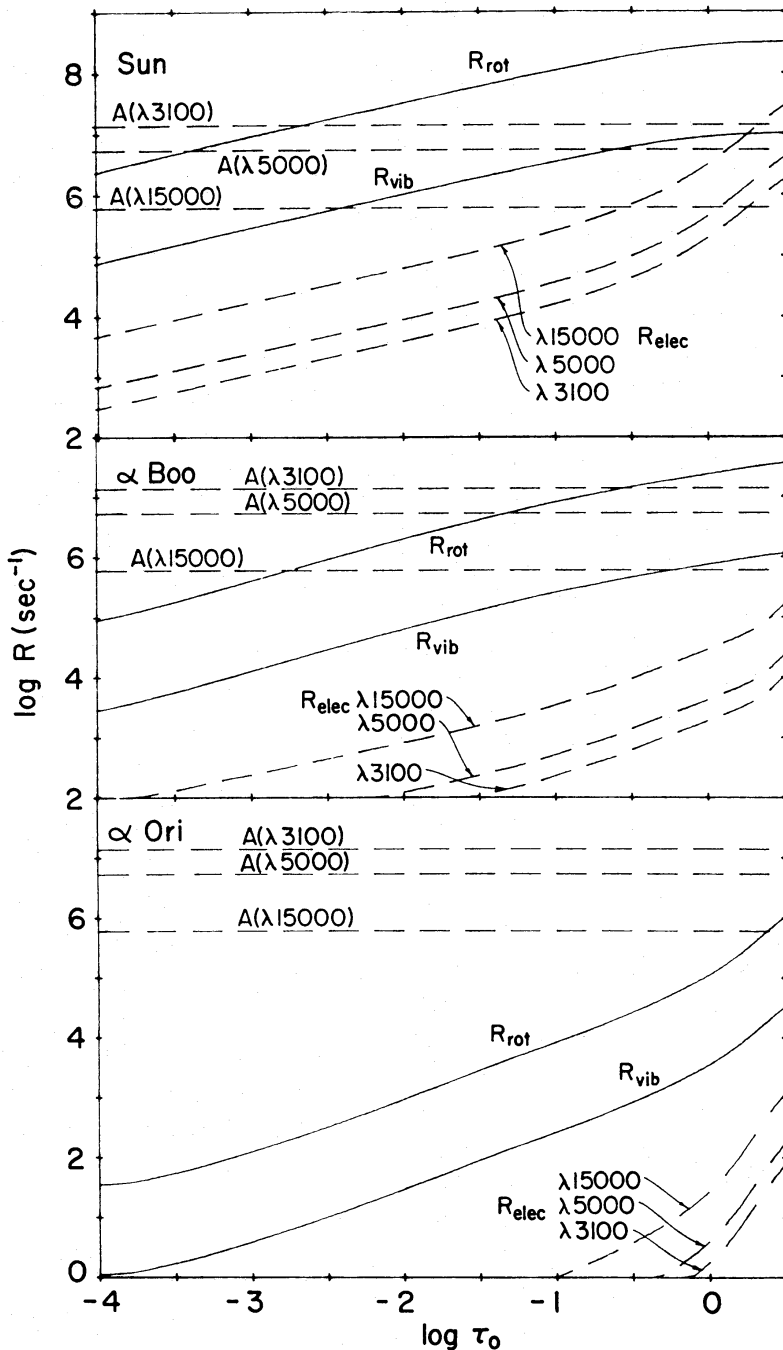

FIG. 4. *De-excitation rates for a typical electronic excited state for the three model atmospheres. Collisional redistribution within the excited state with a change of rotational or vibrational energy is represented by the rates R_{rot} and R_{vib} respectively. The rate for decay by spontaneous emission of a photon is shown by the broken lines for the adopted wavelengths (3100, 5000, 15 000 Å). The rate for de-excitation by electron collision is given by the curves labelled R_{elec} for the three excitation energies corresponding to the wavelengths 3100, 5000 and 15 000 Å.*

α Boo and α Ori. In the deep layers of the solar atmosphere, electron collisions are competitive for low energy (long wavelength) transitions. The radiative excitation is calculated on the assumption that the atmosphere is optically thin to molecular line radiation but the radiative rates will not decrease substantially when optical depth effects are considered. The rate for collisional excitation must be in error by several orders of magnitude before it is competitive with radiative excitation. Therefore, the simple method for estimating these rates is probably adequate.

Contributors to the de-excitation of the excited electronic state are compared in Fig. 4. A return to the ground state through spontaneous emission of a photon is much more probable than a de-excitation via an electron collision; this result could be anticipated from Fig. 3 and the principle of detailed balance. Collisions may also lead to a redistribution within the vibronic structure of the excited electronic state; rates R_{rot} and R_{vib} refer to a rotational and a vibrational transfer, respectively. In addition, spin multiplet relaxation is possible in non-singlet states and the rate is probably between the R_{rot} and R_{vib} values. A collision may also induce a transfer to a close-lying level of another excited electronic state; the rate will vary from molecule to molecule and, also, show sharp specificity within an excited electronic state.

The importance of collisions within excited electronic states varies considerably among the three sample atmospheres. In the extreme case represented by α Ori, the collisional redistribution is apparently negligible and the equilibrium of excited electronic states is radiatively controlled. Then the source function is that appropriate for line formation by scattering. Most molecular energy-level structures can probably be reduced to a two-level model with an accuracy consistent with the other approximations introduced in this survey. When this is appropriate, the line source function (equation (1)) reduces to

$$S_1 = \int J_\nu \phi_\nu \, d\nu.$$

When the optically thin assumption is valid S_1 simplifies to

$$S_1 = J_\nu{}^c$$

where $J_\nu{}^c$ is the mean intensity in the continuum. The corresponding line absorption coefficient κ_1 (equation (3)) reduces to

$$\kappa_1 = \frac{\pi e^2}{mc} n_{\text{L}} f_{\text{LU}} \phi_\nu \left(1 - \exp\left(-\frac{h\nu}{kT_{\text{r}}} \right) \right)$$

where T_{r} is the radiation temperature describing the mean continuum intensity $J_\nu{}^c$. The relative number densities, n_{L}, are given by the Boltzmann equation as discussed earlier. In molecules, several vibrational transitions may contribute about equally to the excitation of a particular vibrational level in the upper state, then the source function is an appropriate weighted mean of the continuum intensity at the several wavelengths.

Construction of an adequate model for a molecule is an interesting problem of interlocking levels. One interesting case is highlighted here. The CN violet ($B^2\Sigma^+ - X^2\Sigma^+$) and the CH G band ($A^2\Delta - X^2\Pi$) have dominant $\Delta v = v' - v'' = 0$ sequences. In these cases, the weaker $\Delta v = -1$ sequence is observed or is potentially detectable in stellar spectra. Absorption in the $\Delta v = 0$ sequence lines

will control the excitation to the excited electronic state and, hence, strongly influence the source function for the $\Delta v = -1$ and other sequences. Since the atmosphere must be optically thick in the $\Delta v = 0$ sequence in order to provide detectable $\Delta v = 1$ lines, the optically thin approximation will have to be dropped in treating this case.

In the solar atmosphere, collisional redistributions within the excited state vibronic structure will occur prior to a return to the ground electronic state via spontaneous emission. A rotational redistribution can be considered as highly probable and a vibrational redistribution as quite probable before re-emission. Some redistribution is likely to occur for molecules in the atmosphere of α Boo. Since nearby rotational and vibrational levels are excited from the ground state by radiation of similar wavelength and intensity, the redistributions within the vibronic structure are unlikely to change the source function dramatically from the pure scattering form previously discussed for α Ori; the calculation of $S_1 = J_\nu{}^c$ should adopt a mean frequency to account for the interlocking. This should be especially valid for the optically thin case.

5. PREDICTION AND OBSERVATION

5.1 *Scattering and absorption: basic differences*

When local thermodynamic equilibrium prevails, the line (and total) source function is identical to the local Planck function: $S_1 \equiv B_\nu(T)$. This is probably the appropriate form for vibration–rotation transitions in stellar atmospheres. Arguments have been presented in favour of line formation by scattering for the electronic transitions in which case the line source function is $S_1 = J_\nu{}^c$ for weak lines.

Essential qualitative differences in the predicted strengths of weak molecular lines for the two source functions can be readily seen by inspection of plots of the Planck function and the mean continuum intensity. A comparison for three wavelengths and the solar atmosphere model is shown in Fig. 5: B_λ and J_λ are plotted instead of the B_ν and J_ν referred to in the text. At wavelengths shortward of the peak in the emergent intensity of flux distribution, J_ν exceeds B_ν in the outer atmosphere, the ratio J_ν/B_ν at the boundary increases as the wavelength decreases. Longward of the intensity peak, J_ν is less than B_ν over a substantial part of the atmosphere with $J_\nu/B_\nu > 1$ again in the boundary region. Close to the wavelength of the intensity peak J_ν and B_ν are similar over a large portion of the atmosphere.

Equivalent width predictions with a line source function $S_1 = J_\nu{}^c$ will be smaller than their pure absorption counterparts at wavelengths for which $J_\nu{}^c > B_\nu$ in the region of line formation. Apparently, most electronic transitions are observed shortward of the intensity peak so that the pure scattering hypothesis provides for a decrease in equivalent width. Certain molecular transitions for example (the CN red system), are located to the red of the peak and in these cases, the predicted equivalent width can be increased when the scattering hypothesis replaces the pure absorption case. Of course, the intensity is determined from an integration of the total source function (equation (2)) which is a combination of the line and continuum source functions. The assumption that $S_c = B_\nu(T)$ for the continuum is valid for the Sun and Arcturus (Lambert & Pagel 1968) but significant departures may occur for the bound–free continuum of the H^- ion in the supergiant α Ori.

In the next section, the scattering hypothesis is given a preliminary test against the solar spectrum. At the present time, the analyses of stellar molecular spectra
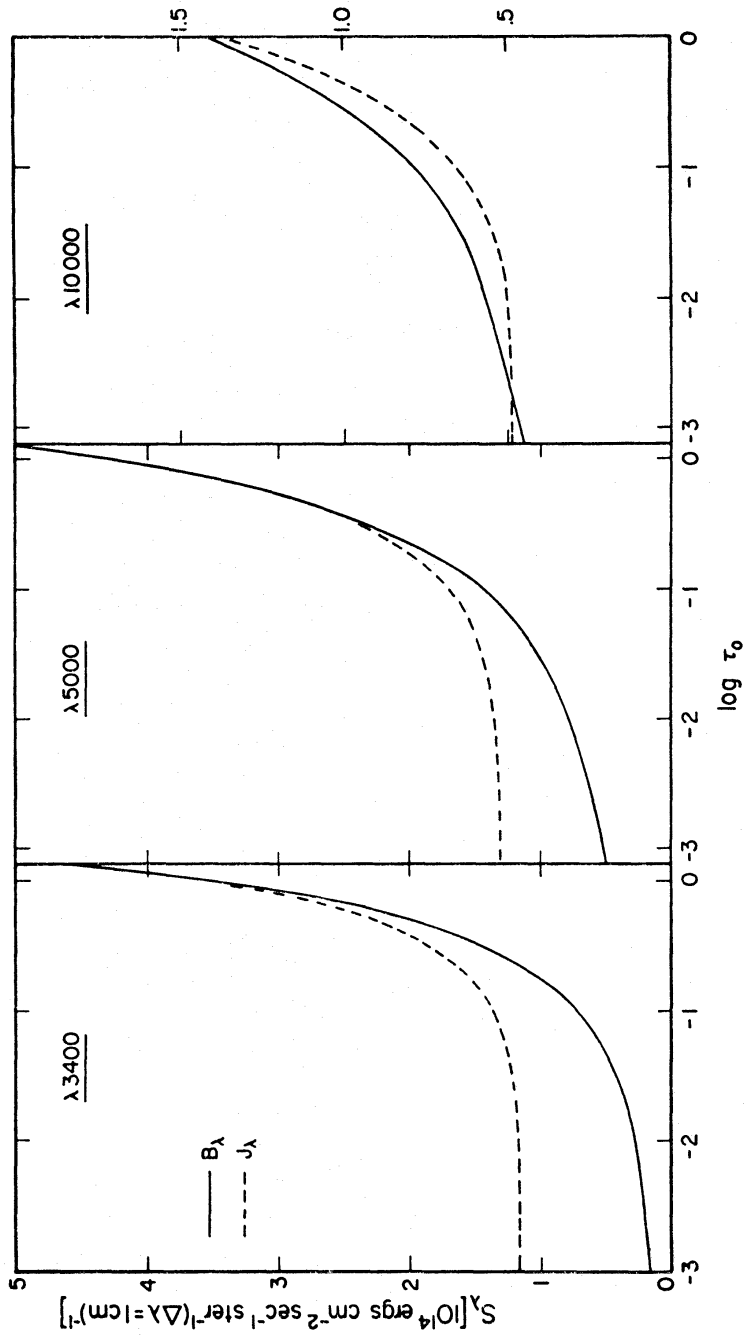
FIG. 5. *Depth dependence of the Planck function and the mean continuum intensity for the solar atmosphere at the wavelengths 3400, 5000 and 10 000 Å.*

are subject to major uncertainties (model atmosphere, abundance, etc.) that must take precedence over claims for NLTE effects.

5.2 *The solar spectrum*

5.2.1 *The solar photosphere.* Solar molecular lines are formed in the interval $0 \cdot 03 \lesssim \tau_\lambda \lesssim 0 \cdot 3$. Sample calculations have been made with $S_1 = B_\nu(T)$ and $S_1 = J_\nu{}^c$. Since the continuum source function contributes significantly to the total source function (equation (2)) in the region of line formation, the differences between B_λ and J_λ shown in Fig. 5 are diluted substantially when equivalent widths are calculated.

Differences in the predicted equivalent widths for the centre of the disk are quite small. Introduction of the scattering hypothesis provides for a reduction of 20 per cent at 3400 Å, 10 per cent at 5100 Å and an increase of 10 per cent at 10 000 Å for typical weak lines. These small changes should be reduced when radiative transfer within the lines is taken into account. Such changes are essentially undetectable. A condition for their detection is a few per cent accuracy in a combination of other factors entering into the equivalent width calculation: abundances of the constituent atoms, the oscillator strength, the molecular dissociation energy and the model atmosphere. This condition cannot be met.

Centre-limb variation of the equivalent widths offers a more realistic test to which abundance errors, etc., do not contribute significantly. The scattering and pure absorption predictions differ because the gradients of J_ν and B_ν are different across the atmosphere.

A test was made on the MgH and C_2 photospheric lines. The MgH $A^2\Pi_i$–$X^2\Sigma^+$ o–o band and the C_2 Swan o–o band lines approximate well the assumption that the atmosphere be optically thin in the molecular lines. Centre-limb observations were acquired with the Oxford spectrometer (Blackwell, Mallia & Petford 1969). The MgH observations were discussed in part by Lambert, Mallia & Petford (1971). New material is reviewed by Lambert & Mallia (1975, in preparation).

The MgH o–o band is almost solely responsible for the excitation of the $v = 0$ level in the $A^2\Pi_i$ excited state and, hence, the wavelength of this band was used for the calculation of the source function $S_1 = J_\nu{}^c$. Cascading from higher electronic states is neglected but this possibility should be examined when information on the MgH electronic transitions is more complete.

The lower state of the C_2 Swan system is not the electronic ground state of the molecule. The excitation potential for the Swan lower state is just 600 cm^{-1} or $0 \cdot 08$ eV. The transition to the ground state is forbidden so that strong, direct radiative coupling cannot occur. The collision cross-section for this transition is, perhaps, similar to that for forbidden transitions in the ground state configurations of atoms. Here, it is assumed that collisions dominate the coupling between the two states and that the simple ideas developed in this paper may be applied directly to the Swan system. In addition to the o–o band, the o–1 and o–2 bands contribute to the excitation of the $v = 0$ level in the upper state of the Swan system. A very small error is committed by ignoring their contribution and the wavelength of the o–o band is adopted for the calculation of the source function $S_1 = J_\nu{}^c$.

Observations and the predicted centre-limb variations for MgH and C_2 are compared in Fig. 6. Since the lines are weak, measurement errors (principally, location of continuum level and blending by other lines) are appreciable even
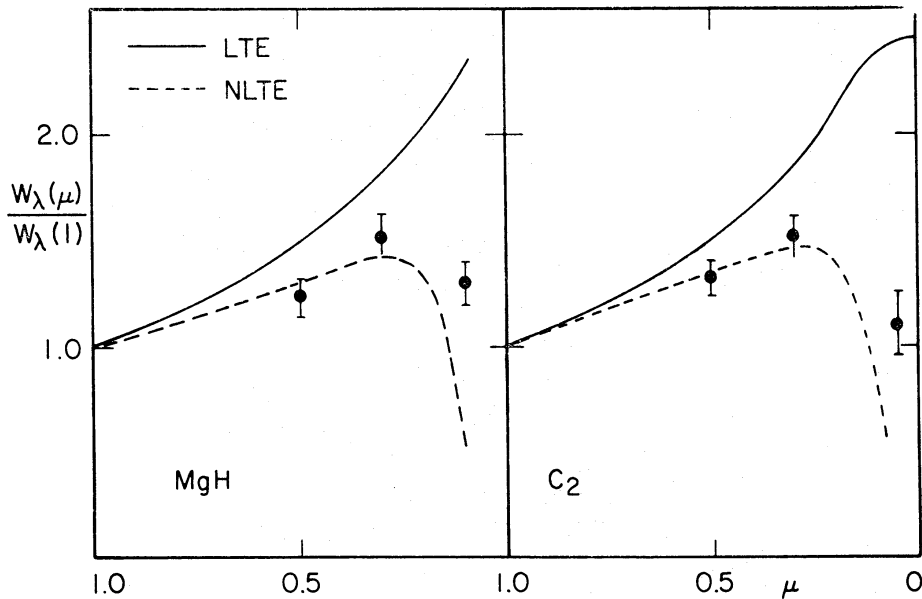
FIG. 6. *Observed and predicted centre-limb variation for weak MgH and C₂ lines. Predictions based upon the pure absorption hypothesis are shown by the solid line. Those based upon the scattering hypothesis are shown by the dashed line. The abscissa is positioned on the disk in the standard notation:* $\mu = \cos\theta$.

though the statistical photon noise of the spectra is very small. The error bars on the data points refer to the scatter of the measurements within the sample of about 10 lines. Observations were attempted close to the limb. The Oxford spectrometer was designed to permit such observations with a minimum of uncertainty due to image motion and seeing.

Pure absorption (LTE) and scattering (NLTE) predictions are shown. The observations are in good agreement with the latter and in disagreement with the former. Of course, the LTE (and NLTE) predictions are model dependent. Withbroe (1968) compared LTE predictions for several model atmospheres with observations for MgH, C₂ and other molecules. He was unable to fit the observations with a standard model. However, a reasonable fit was obtained with a model atmosphere constructed of three columns or streams as an attempt to mimic the solar granulation. This result means that Fig. 6 constitutes weak confirmation of the scattering hypothesis.

The CN red system can probably serve as a discriminant between the NLTE hypothesis and solar granulation models. The o–o band is near 10 900 Å and (see Fig. 5) the inequality $J_\nu^c < B_\nu$ prevails across a large part of the line forming region. As a result, the NLTE predictions show the equivalent width to increase more steeply towards the limb than the corresponding LTE predictions. The difference in the two predictions is small; the ratio $W_\lambda(\mu)/W_\lambda(1)$ at $\mu = 0\cdot2$ differs by just 10 per cent for the two hypotheses. The observations obtained with the Oxford spectrometer show the centre-limb variation to be in agreement with either prediction; the accuracy is insufficient to distinguish between the LTE and NLTE predictions. Calculations for the CN red system and the three stream model were not reported by Withbroe. Since the single stream LTE predictions are similar for the 5000 Å lines (MgH and C₂) and the 10 900 Å CN lines, it is most probable that the three stream (LTE) calculations are also quite similar. Then, the latter

would predict a variation similar to NLTE prediction in Fig. 6. The observed variation shows a much steeper increase in accord with the NLTE or scattering hypothesis.

If the molecular lines are formed by scattering, the atomic Fraunhofer lines should influence the radiative excitation rate to the excited electronic state. The effect of the reduced excitation should be apparent on another unblended molecular line from the same upper state. No such effect could be detected using the new measurements of the MgH lines. The explanation for this negative result is provided by Fig. 4 which shows that a redistribution among the rotational levels is highly probable before spontaneous emission so that the effect of a strong Fraunhofer lines is spread over several rotational levels. Correlations might be found in super-giant spectra where the probability of a rotational redistribution is much reduced.

If scattering is important, the calculations of weak lines show that the lines should go into emission inside the limb; emission occurs because the line source function exceeds the Planck function throughout the upper photosphere. The effect is quite pronounced for transitions in the blue region; for example, the CN violet system. Many of the systems violate the present restriction of an optically thin atmosphere. Weak CN violet system lines can probably be found even in this crowded region of the spectrum. Of course, rotational and vibrational redistribution via collisions may connect their upper states to those of saturated lines. It would be of interest to examine the centre-limb behaviour of a sample of the weakest CN, CH, OH or NH lines.

5.2.2 *Sunspots.* Sunspot umbrae and penumbrae are obvious locations in which the assumption of LTE should be suspect. Clearly, the umbral radiation field is highly anisotropic; the umbral dots or flashes are an intrinsic source of anisotropy and, also, the photospheric and penumbral radiation may penetrate the uppermost layers of the umbra. Detailed analyses of umbral molecular spectra will be required to delineate the extent of the breakdown from LTE. An interesting indicator is reviewed here.

The dominant role played by collisions in the equilibrium of the electronic ground state of molecules was stressed earlier. It follows from this that the rotational temperature which is deduced from the equivalent widths of rotational lines within a band will approximate closely the kinetic temperature at the mean level of formation: in other words, the possibility that the lines are formed by scattering will not be readily detectable from a comparison of relative line intensities. Sotirovski (1971) derived rotational temperatures from TiO, MgH and CN lines and the results are very close to predictions based upon the LTE assumption.

Departures from LTE should become apparent when equivalent widths are compared with predictions on an absolute basis. This requires an adequate model umbral atmosphere, accurate element abundances and a reliable oscillator strength for the transition. Interesting results are provided by a preliminary analysis.

Weak lines attributable to MgH and SiH are identified in the photospheric spectrum. The oscillator strength of the SiH transition and the dissociation energy of SiH are adequately determined and SiH equivalent widths can be predicted with reasonable certainty. There is good correspondence with observations. A similar comparison is impossible for the MgH lines because neither the oscillator strength nor the dissociation energy is known with sufficient precision. However, the

photosphere may be regarded as a spectroscopic source of known conditions which can be used to derive the unknown quantities for MgH. Then, LTE predictions can be made for the umbral SiH and MgH lines. Observations of these lines were made with the Gornergrat spectrometer and corrections were applied for scattered photospheric and penumbral light. In both cases, particular searches were made for weak umbral lines so that the curve of growth was well defined. Details of these calculations will be presented elsewhere (Lambert & Mallia 1975, in preparation). These show that the MgH and the SiH umbral lines can be matched with the LTE predictions but the product of abundance and oscillator strength must be decreased by about a factor of 10 from the value giving an acceptable fit to the photospheric lines. This is also evident from a comparison of independent abundance analyses for MgH in the photosphere (Lambert, Mallia & Petford 1971) and a sunspot umbra (Sotirovski 1971). Calculations have also been made for umbra and photospheric lines of C_2, CN and CH for which umbral observations and predictions are in close accord (Lambert & Mallia 1973).

A working hypothesis can be formulated involving line formation by scattering. Quantitative calculations have not yet been attempted. The CO molecule controls the equilibrium of C to such an extent that the observed CN and CH lines (C_2 is not present in umbral spectra) are formed in the deepest umbral layers in which the radiation field is nearly isotropic and the photospheric/penumbral influence is negligible. MgH and SiH lines are formed higher in the umbra. The suggestion is that these molecular lines are formed by scattering with the mean intensity of the radiation field as a dominant parameter. Lateral flowing photospheric/penumbral radiation could contribute to the mean intensity in the upper layers. Umbral dots will also play a role. This hotter radiation will increase the line source function (at least, for weak lines) and a weakening of the line relative to LTE predictions will result. Of course, the inflowing radiation may also reduce the molecular density directly via radiative dissociation and ionization processes and indirectly via ionization of the neutral metal atoms.

In addition to calculations to test the feasibility of this idea, observations of other molecules should be analysed. Potentially important molecules are CaH and TiO but, unfortunately, the vital oscillator strength information is almost entirely lacking and neither molecule is present in the photospheric spectrum.

5.2.3 *The chromosphere.* Molecular emission lines contribute to the spectrum of the low chromosphere. Relative line intensities are customarily interpreted to yield a rotational temperature (see, for example, Blackwell (1955), Parker (1955) and Thomas (1958)). Absolute line intensities should provide information on the gas density in addition to the temperature; the early study by Pecker & Athay (1955) requires extensive revision to take account of changes in the molecular dissociation energies and oscillator strengths.

The effects attributable to scattering may be summarized. The absolute intensity of a band will be determined by the mean intensity of the exciting photosphere continuum radiation with its superposed Fraunhofer spectrum. The importance of the Fraunhofer lines varies from transition to transition. The CN violet system o–o band will be strongly affected because the CN lines themselves are strong in the spectrum. On the other hand, the C_2 Swan band can probably be analysed without a discussion of the photospheric lines. If the exciting radiation is described by a radiation temperature ($J_\nu^c \equiv B_\nu(T_r)$), the emission line intensities from the

low chromosphere will be enhanced on the scattering hypothesis relative to the pure absorption case because the inequality $T_r > T$ holds, where T is the local kinetic temperature. The inequality will be reversed in higher layers because the kinetic temperature increases outwards.

The rotational temperature should be close to the kinetic temperature because rotational redistribution in the excited electronic state is reasonably likely before spontaneous emission and a return to the ground state. If molecular lines can be followed to a sufficient height that these collisions occur infrequently, the rotational temperature will approach the radiation temperature.

Unfortunately, such severe uncertainties exist in an LTE analysis that a check on the scattering hypothesis will be very difficult: the physical conditions in the chromosphere are uncertain; existing observational data on the molecular lines is inadequate; precise height location of the spectra is necessary but difficult to achieve.

6. CONCLUSIONS

The molecular lines in stellar spectra are important—often, unique—carriers of information pertaining to the chemical composition and the physical conditions in the stellar atmosphere. The conversion procedure from spectrum to numerical results on the composition and structure of the atmosphere must adopt a family of assumptions. This paper has examined assumptions relating to the molecular line source function and absorption coefficient.

The examination of the statistical equilibrium for electronic states of diatomic molecules has led to two major results. Stripped of the necessary qualifications, these results can be expressed in the statements: (i) the equilibrium for levels within the ground electronic state is collisionally controlled, and (ii) the equilibrium of excited electronic states is dominated by radiative processes linking these states with the ground electronic state. These results are usefully reformulated in terms of the line source function.

Vibration–rotation transitions occurring within the ground electronic state have been identified in infrared stellar spectra. Collisions dominate the equilibrium of the vibration–rotation levels so that the appropriate line source function is the Planck function. In classical terms, these lines are formed by pure absorption.

The molecular transitions dominating the visible and near infrared spectra of cool stars are transitions between electronic states. The controlling radiative influence on the excited electronic states results in a line source function which is not the Planck function but which involves the mean intensity of the radiation across the line(s). In classical terms, the lines are formed by scattering. This runs counter to numerous statements within the literature that pure absorption is the appropriate line formation mechanism.

Finally, this paper has highlighted several areas requiring detailed study. Calculations of this nature can only be as reliable as the cross-sections adopted for the microscopic processes. It is imperative that more extensive and accurate collision cross-sections for rotation, vibration–rotation and electronic excitation be made available for the collision partners (e, H, H_2, He) of astrophysical interest. At the present time, the most critical need apparently exists for reliable cross-sections for excitation to excited electronic states from the ground state. Vibrational de-excitation rates for light molecules subject to hydrogen atom for collisions is another important gap to be closed by experiment.

When scattering is important, the problems of radiative transfer and statistical equilibrium become coupled. Methods must be developed which will permit this coupling to be treated for model molecules consisting of a realistic set of energy levels with their full variety of collisional and radiative interlocking in atmospheres which are not optically thin to all molecular radiation. These methods are of application to the problem of molecular line blanketing and its effect on the structure of cool stellar atmospheres; line blanketing calculations in which the electronic transitions are described by LTE will almost certainly overestimate the blanketing effect of the molecular lines. Since certain abundance information for cool stars is provided almost uniquely from molecules, a full treatment of the scattering problem is important for abundance studies and the nucleosynthetic and stellar evolutionary interpretation of the abundances.

The ideas discussed in this paper have also led to proposals for new observational checks on molecular line formation; for example, a programme of extreme limb observations of solar photospheric molecular lines in the ultraviolet. Sunspot studies are potentially valuable but the complex structure (umbral dots, etc.) of spots should not be underestimated.

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