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A Note on Saturation in Microwave Spectroscopy

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The investigation of Van Vleck and Weisskopf, on the shape of collision-broadened absorption lines, is extended to high power levels of the exciting radiation. Transitions among the molecular states are then induced at a rate that is not negligible compared with the collision rate, thus invalidating the assumption of thermal equilibrium. The theory is based on a quantum transcription of the previous semiclassical treatment, the essential tool being the density matrix. When the resonant frequencies of the molecule are widely spaced, an absorption line is ultimately broadened as the power level increases. Correspondingly, the peak absorption coefficient decreases, the power absorbed per unit volume approaching saturation with increasing incident power. It is shown that the broadening of an absorption line is not to be attributed to any intrinsic modification of the line shape, but rather to a frequency dependent alteration of the energy level populations. A molecule for which all resonant frequencies coincide, a one-dimensional harmonic oscillator, is treated in Appendix II. No saturation effect occurs here, since the absorption is independent of the molecular distribution among the oscillator energy levels.

THE shape of collision-broadened absorption lines has been investigated by Van Vleck and Weisskopf[1] for weak monochromatic radiation. Their results are of importance for the interpretation of the extensive data recently acquired on microwave absorption spectra. However, the investigation of Van Vleck and Weisskopf does not include a discussion of two aspects of these experimental studies—saturation and frequency modulation. At high power levels of the exciting radiation, transitions among the molecular states are induced at a rate that is not negligible compared with the collision rate, thus invalidating the assumption of thermal equilibrium. This note contains a theoretical analysis of the resultant modification of the absorption coefficient. A discussion of frequency modulation is given in a companion note by R. Karplus.

To facilitate the extension of the theory, we shall first derive the results of Van Vleck and Weisskopf, replacing their semiclassical treatment by a suitable quantum transcription. The linear absorption coefficient for radiation of angular frequency ω, in a gas of molecular density N, is

$$\alpha = 4\pi(\omega/c)NIm\chi, \tag{1}$$

where χ is the molecular susceptibility. The latter is determined by the dipole moment

$$\mathbf{p}(t) = Re(\chi\mathbf{F}e^{-i\omega t}), \tag{2}$$

induced by the field

$$\mathbf{F}(t) = \mathbf{F}\cos\omega t = Re(\mathbf{F}e^{-i\omega t}), \tag{3}$$

which may be either electric or magnetic. The assumptions of Van Vleck and Weisskopf are most compactly expressed in quantum language with the aid of the density matrix.[2] Thus, to calculate the dipole moment at time t, we suppose that a strong collision has occurred at a previous time $t_0 = t - \vartheta$. This assumption of complete thermal equilibrium, immediately following the collision, is described by

$$\rho_0(t_0) = Ce^{-H(t_0)/kT}, \quad 1/C = Spe^{-H(t_0)/kT}, \tag{4}$$

where $H(t)$ is the Hamiltonian of the molecule, including the energy in the external field,

$$H(t) = H_0 - \mathbf{p}\cdot\mathbf{F}(t) = H_0 + V\cos\omega t. \tag{5}$$

In the latter formula, H_0 is the Hamiltonian of the isolated molecule and $\mathbf{p}$ is the dipole moment operator. The subsequent development of the density matrix in time is determined by

$$i\hbar(\partial/\partial t)\rho = H\rho - \rho H. \tag{6}$$

The final task of the theory lies in the calculation

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[1] J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Physics **17**, 227 (1945).

[2] Cf. R. C. Tolman, *Principles of Statistical Mechanics* (Oxford University Press, New York, 1930), Chapter IX.

of the average dipole moment at time t,

$$\mathbf{p}(t)=Sp\mathbf{p}\bar{\rho}(t), \tag{7}$$

where the bar indicates that one must eventually average over t_0, the time of the last collision, in accordance with the assumption of random collisions spaced by an average time interval τ.

This program is greatly simplified by first performing the average over the time of the last collision, using the fact that the probability that the last collision occurs in the time interval $t-\vartheta$, $t-\vartheta-d\vartheta$ is $e^{-\vartheta/\tau}d\vartheta/\tau$. The density matrix may be considered to depend parametrically upon the initial time t_0, say $\rho(t,t_0)$, and is subject to the equation of motion (6) together with the initial condition (Cf. Eq. (4))

$$\rho(t_0,t_0)=\rho_0(t_0). \tag{8}$$

Now

$$\bar{\rho}(t)=\int_0^\infty \rho(t,\,t-\vartheta)e^{-\vartheta/\tau}d\vartheta/\tau, \tag{9}$$

and

$$(\partial/\partial t)\bar{\rho}(t)=\int_0^\infty [(\partial/\partial t)\rho(t,t_0)]_{t_0=t-\vartheta}e^{-\vartheta/\tau}d\vartheta/\tau$$
$$-\int_0^\infty [(\partial/\partial\vartheta)\rho(t,\,t-\vartheta)]e^{-\vartheta/\tau}d\vartheta/\tau, \tag{10}$$

whence

$$(\partial/\partial t)\bar{\rho}(t)=-(i/\hbar)[H(t)\bar{\rho}(t)-\bar{\rho}(t)H(t)]$$
$$-(1/\tau)[\bar{\rho}(t)-\rho_0(t)]. \tag{11}$$

We have thus succeeded in constructing an equation of motion for the averaged density matrix $\bar{\rho}(t)$, which is the quantity directly concerned in the evaluation of the average dipole moment. However, it is somewhat more convenient to introduce

$$D(t)=\bar{\rho}(t)-\rho_0(t) \tag{12}$$

which obeys the equation of motion

$$(\partial/\partial t)D(t)=-(i/\hbar)[H(t)D(t)-D(t)H(t)]$$
$$-(1/\tau)D(t)-(\partial/\partial t)\rho_0(t) \tag{13}$$

and measures the deviation of the density matrix $\bar{\rho}(t)$ from instantaneous thermal equilibrium.

We shall first solve this equation of motion under the conditions of Van Vleck and Weisskopf, namely, a weak monochromatic radiation field. On employing a matrix scheme in which the unperturbed Hamiltonian, H_0, is diagonal, the equation of motion (13) becomes

$$(\partial/\partial t+i\omega_{mn}+1/\tau)D_{mn}(t)=-(\partial/\partial t)[\rho_0(t)]_{mn}$$
$$-(i/\hbar)\textstyle\sum_k(V_{mk}D_{kn}(t)-D_{mk}(t)V_{kn})\cos\omega t, \tag{14}$$

where

$$\omega_{mn}=(E_m-E_n)/\hbar \tag{15}$$

designates the angular frequency associated with the transition from state m to state n of the unperturbed molecule. The assumption of a weak radiation field implies that the density matrix differs little from that of the isolated molecule at temperature T:

$$\rho^{(0)}=C^{(0)}e^{-H_0/kT},\quad 1/C^{(0)}=Spe^{-H_0/kT}. \tag{16}$$

The latter operator is represented by the diagonal matrix

$$\rho_{mn}{}^{(0)}=\rho_m{}^{(0)}\delta_{mn},\ \rho_m{}^{(0)}=e^{-E_m/kT}/\textstyle\sum_n e^{-E_n/kT}. \tag{17}$$

Thus, we may neglect the terms in Eq. (14) in which D is multiplied by the magnitude of the field. In addition, the matrix $\rho_0(t)$ may be simplified since the energy of the molecule in the external radiation field will always be small compared to kT. It is shown in Appendix I that, to a sufficient approximation,

$$[\rho_0(t)]_{mn}=\rho_m{}^{(0)}\delta_{mn}$$
$$+(\rho_m{}^{(0)}-\rho_n{}^{(0)})(V_{mn}/\hbar\omega_{mn})\cos\omega t. \tag{18}$$

With these simplifications, Eq. (14) becomes

$$(\partial/\partial t+i\omega_{mn}+1/\tau)D_{mn}(t)$$
$$=\omega(\rho_m{}^{(0)}-\rho_n{}^{(0)})(V_{mn}/\hbar\omega_{mn})\sin\omega t. \tag{19}$$

The steady-state solution of the latter equation is

$$D_{mn}(t)=\frac{\omega}{\omega-\omega_{mn}+i/\tau}(\rho_n{}^{(0)}-\rho_m{}^{(0)})$$
$$\times(V_{mn}/2\hbar\omega_{mn})e^{-i\omega t}$$
$$+\frac{\omega}{\omega-\omega_{mn}-i/\tau}(\rho_n{}^{(0)}-\rho_m{}^{(0)})$$
$$\times(V_{mn}/2\hbar\omega_{mn})e^{i\omega t}, \tag{20}$$

whence

$$\bar{\rho}_{mn}(t)=\rho_m{}^{(0)}\delta_{mn}+\left(\frac{\omega}{\omega-\omega_{mn}+i/\tau}-1\right)\times(\rho_n{}^{(0)}-\rho_m{}^{(0)})(V_{mn}/2\hbar\omega_{mn})e^{-i\omega t}+\left(\frac{\omega}{\omega-\omega_{mn}-i/\tau}-1\right)\times(\rho_n{}^{(0)}-\rho_m{}^{(0)})(V_{mn}/2\hbar\omega_{mn})e^{i\omega t},\quad(21)$$

and, finally,

$$\begin{aligned}\mathbf{p}(t)&=\sum_{m,n}\mathbf{p}_{nm}\bar{\rho}_{mn}(t)\\&=\sum_{m,n}\mathbf{p}_{nm}\mathbf{p}_{mn}\cdot\mathbf{F}e^{-i\omega t}\times\left(1-\frac{\omega}{\omega-\omega_{mn}+i/\tau}\right)\frac{\rho_n{}^{(0)}-\rho_m{}^{(0)}}{2\hbar\omega_{mn}}\\&\quad+\sum_{m,n}\mathbf{p}_{mn}\mathbf{p}_{nm}\cdot\mathbf{F}e^{i\omega t}\times\left(1-\frac{\omega}{\omega-\omega_{mn}-i/\tau}\right)\frac{\rho_n{}^{(0)}-\rho_m{}^{(0)}}{2\hbar\omega_{mn}}\end{aligned}\quad(22)$$

in which the indices m and n have been interchanged in the second term. In virtue of the spherical symmetry of an isolated molecule, it is possible to replace $\mathbf{p}_{nm}\mathbf{p}_{mn}\cdot\mathbf{F}$ with $(1/3)\mathbf{p}_{nm}\cdot\mathbf{p}_{mn}\mathbf{F}$, or $(1/3)|\mathbf{p}_{mn}|^2\mathbf{F}$. We therefore obtain a formula for $\mathbf{p}(t)$ of the form (2), with

$$\begin{aligned}\chi&=\sum_{m,n}\tfrac{1}{3}|\mathbf{p}_{mn}|^2\left(1-\frac{\omega}{\omega-\omega_{mn}+i/\tau}\right)\frac{\rho_n{}^{(0)}-\rho_m{}^{(0)}}{\hbar\omega_{mn}}\\&=\sum_{m,n}\tfrac{1}{6}|\mathbf{p}_{mn}|^2\left(2-\frac{\omega}{\omega-\omega_{mn}+i/\tau}-\frac{\omega}{\omega+\omega_{mn}+i/\tau}\right)\frac{\rho_n{}^{(0)}-\rho_m{}^{(0)}}{\hbar\omega_{mn}}.\end{aligned}\quad(23)$$

In particular,

$$Im\chi=\sum_{m,n}\frac{1}{6\hbar}|\mathbf{p}_{mn}|^2\frac{\omega}{\omega_{mn}}\left[\frac{1/\tau}{(\omega-\omega_{mn})^2+1/\tau^2}+\frac{1/\tau}{(\omega+\omega_{mn})^2+1/\tau^2}\right](\rho_n{}^{(0)}-\rho_m{}^{(0)}),\quad(24)$$

and

$$\alpha=\frac{2\pi}{3}\frac{\omega^2}{c}\frac{N}{kT}\sum_{m,n}|\mathbf{p}_{mn}|^2\left[\frac{1/\tau}{(\omega-\omega_{mn})^2+1/\tau^2}+\frac{1/\tau}{(\omega+\omega_{mn})^2+1/\tau^2}\right]\frac{1-e^{-\hbar\omega_{mn}/kT}}{\hbar\omega_{mn}/kT}\rho_n{}^{(0)},\quad(25)$$

which is essentially the final result of Van Vleck and Weisskopf.

An important specialization of this formula refers to the situation in which the resonant frequencies of the molecule are widely spaced, in comparison with the resonance width $\Delta\omega=1/\tau$. If the applied frequency lies in the vicinity of a particular resonance frequency, $\omega_0=(E_a-E_b)/\hbar$, only terms involving $\omega-\omega_0$ will appreciably contribute to the summation in Eq. (25). However, the energy levels E_a and E_b will be degenerate, in general, and we must further specify the states contributing to (25) by a degeneracy index, say κ and λ, respectively. Thus

$$\alpha=\frac{4\pi}{3}\frac{\omega^2}{c}\frac{N}{kT}\Big[\sum_{\kappa,\lambda}|\mathbf{p}_{a\kappa,b\lambda}|^2\Big]\frac{1/\tau}{(\omega-\omega_0)^2+1/\tau^2}\times\frac{1-e^{-\hbar\omega_0/kT}}{\hbar\omega_0/kT}\frac{e^{-E_b/kT}}{\sum_m e^{-E_m/kT}}.\quad(26)$$

SATURATION

We shall now extend our treatment to include the effects of a strong monochromatic radiation field. The discussion will, however, be limited to the situation embodied in Eq. (26), that is, where $\omega-\omega_0$ is comparable with $1/\tau$, but all other such differences, $\omega-\omega_{mn}$, are large compared to $1/\tau$. In addition, we shall impose an inocuous restriction on the field strength that amounts to requiring that the external radiation field be small compared to the internal molecular field; we ignore any time variation of $\mathbf{p}(t)$ that involves harmonics of the fundamental frequency ω. This restriction is expressed by the assumption

$$D_{mn}(t)=R_{mn}+P_{mn}{}^{(+)}e^{-i\omega t}+P_{mn}{}^{(-)}e^{i\omega t},\quad(27)$$

which is to be inserted in the equation of motion

(14). The resultant set of equations are:

$$P_{mn}^{(+)}=\frac{1}{2\hbar(\omega_{mn}-\omega-i/\tau)}\left[\frac{\omega}{\omega_{mn}}V_{mn}(\rho_m^{(0)}-\rho_n^{(0)})-\sum_k(V_{mk}R_{kn}-R_{mk}V_{kn})\right],$$

$$P_{mn}^{(-)}=-\frac{1}{2\hbar(\omega_{mn}+\omega-i/\tau)}\left[\frac{\omega}{\omega_{mn}}V_{mn}(\rho_m^{(0)}-\rho_n^{(0)})+\sum_k(V_{mk}R_{kn}-R_{mk}V_{kn})\right],\quad(28)$$

$$R_{mn}=-\frac{1}{2\hbar(\omega_{mn}-i/\tau)}\sum_k[V_{mk}(P_{kn}^{(+)}+P_{kn}^{(-)})-(P_{mk}^{(+)}+P_{mk}^{(-)})V_{kn}].$$

With the impressed frequency in approximate resonance with the transition frequency $\omega_0=(E_a-E_b)/\hbar$, only the matrix elements $P_{ab}^{(+)}$, $P_{ba}^{(-)}$, R_{aa}, and R_{bb} are of significance, if we suppose the energy levels a and b to be non-degenerate. This statement is accurate to the extent that $\Delta\omega=1/\tau\ll\omega_{mn}$. The simultaneous equations (28) then reduce to

$$P_{ab}^{(+)}=-\frac{V_{ab}}{2\hbar(\omega-\omega_0+i/\tau)}\left[\frac{\omega}{\omega_0}(\rho_a^{(0)}-\rho_b^{(0)})+(R_{aa}-R_{bb})\right],$$

$$P_{ba}^{(-)}=-\frac{V_{ba}}{2\hbar(\omega-\omega_0-i/\tau)}\left[\frac{\omega}{\omega_0}(\rho_a^{(0)}-\rho_b^{(0)})+(R_{aa}-R_{bb})\right],\quad(29)$$

$$R_{aa}-R_{bb}=-i(\tau/\hbar)[V_{ab}P_{ba}^{(-)}-P_{ab}^{(+)}V_{ba}],$$

$$R_{aa}+R_{bb}=0.$$

The solution of these equations is

$$R_{aa}-R_{bb}=-\frac{\omega}{\omega_0}\frac{|V_{ab}|^2/\hbar^2}{(\omega-\omega_0)^2+1/\tau^2+|V_{ab}|^2/\hbar^2}\times(\rho_a^{(0)}-\rho_b^{(0)}),$$

$$P_{ab}^{(+)}=P_{ba}^{(-)*}=-\frac{V_{ab}}{2\hbar}\frac{\omega}{\omega_0}\frac{\omega-\omega_0-i/\tau}{(\omega-\omega_0)^2+1/\tau^2+|V_{ab}|^2/\hbar^2}\times(\rho_a^{(0)}-\rho_b^{(0)}).\quad(30)$$

In computing the average dipole moment,

$$\mathbf{p}(t)=Sp\mathbf{p}\bar{\rho}(t)=Sp\mathbf{p}\rho_0(t)+Sp\mathbf{p}D(t),\quad(31)$$

we may ignore the time-dependent contribution of ρ_0, for this is neither resonant nor contributes to the absorption. Hence

$$\mathbf{p}(t)=Sp\mathbf{p}D(t)=2Re\mathbf{p}_{ba}P_{ab}^{(+)}e^{-i\omega t}=Re\frac{1}{\hbar}\mathbf{p}_{ba}\mathbf{p}_{ab}\cdot\mathbf{F}e^{-i\omega t}\times\frac{\omega}{\omega_0}\frac{\omega-\omega_0-i/\tau}{(\omega-\omega_0)^2+1/\tau^2+|V_{ab}|^2/\hbar^2}\times(\rho_a^{(0)}-\rho_b^{(0)}).\quad(32)$$

The assumption of non-degeneracy must be relinquished at this point, for orientation degeneracy, at least, is necessarily present. However, our theory is easily extended if the component of the dipole moment in the direction of the field has vanishing matrix elements between different degenerate states. This is indeed realized in the most important situation of orientation degeneracy since the magnetic quantum number relative to the direction of the field is unaltered in any transition induced by the radiation. Under these circumstances the appropriate generalization of Eq. (32) is

$$\mathbf{p}(t)=Re\frac{1}{\hbar}\sum_\kappa|p_{ab}^\kappa|^2\mathbf{F}e^{-i\omega t}\times\frac{\omega}{\omega_0}\frac{\omega-\omega_0-i/\tau}{(\omega-\omega_0)^2+1/\tau^2+|p_{ab}^\kappa|^2F^2/\hbar^2}\times(\rho_a^{(0)}-\rho_b^{(0)}),\quad(33)$$

where p_{ab}^κ designates a non-vanishing matrix element of the component of the dipole moment in the field direction, and κ is a degeneracy index. This is of the desired form (2), with

$$Im\chi=\frac{1}{\hbar}\sum_\kappa|p_{ab}^\kappa|^2\times\frac{\omega}{\omega_0}\frac{1/\tau}{(\omega-\omega_0)^2+1/\tau^2+|p_{ab}^\kappa|^2F^2/\hbar^2}\times(\rho_b^{(0)}-\rho_a^{(0)}),\quad(34)$$

whence, finally

$$\alpha=4\pi\frac{\omega^2}{c}\frac{N}{kT}\sum\nolimits_\kappa|p_{ab}{}^\kappa|^2 \times\frac{1/\tau}{(\omega-\omega_0)^2+1/\tau^2+|p_{ab}{}^\kappa|^2F^2/\hbar^2} \times\frac{1-e^{-\hbar\omega_0/kT}}{\hbar\omega_0/kT}\frac{e^{-E_b/kT}}{\sum_m e^{-E_m/kT}}. \tag{35}$$

In the weak field limit, this result reduces to Eq. (26), as it must, since

$$\tfrac{1}{3}\sum_{\kappa,\lambda}|\mathbf{p}_{a\kappa,\,b\lambda}|^2=\sum_\kappa|p_{ab}{}^\kappa|^2. \tag{36}$$

When, however, $|p_{ab}{}^\kappa|F$ becomes comparable with $\hbar/\tau$, the absorption line begins to widen, and the peak absorption coefficient correspondingly decreases. Indeed, in the limit $|p_{ab}{}^\kappa|F\gg\hbar/\tau$ and $\hbar(\omega-\omega_0)$, but $|p_{ab}{}^\kappa|F\ll\hbar(\omega-\omega_{mn})$, the power absorbed per unit volume exhibits a saturation phenomenon, approaching a value independent of the field strength, namely,

$$P=\alpha cF^2/8\pi \rightarrow\frac{(\hbar\omega)^2}{2\tau}\frac{N}{kT}g\frac{1-e^{-\hbar\omega_0/kT}}{\hbar\omega_0/kT}\frac{e^{-E_b/kT}}{\sum_m e^{-E_m/kT}}. \tag{37}$$

In this formula, g denotes the total number of degenerate transitions contributing to the absorption line.

It is well to note, finally, that our essential results, Eqs. (29) and (30), permit an elementary interpretation. In the immediate vicinity of resonance, ω/ω_0 may be replaced by unity, and the first of Eq. (29) can be written

$$P_{ab}{}^{(+)}=-\frac{V_{ab}}{2\hbar(\omega-\omega_0+i/\tau)}[\bar{\rho}_{aa}-\bar{\rho}_{bb}]. \tag{38}$$

It is apparent from this form that the broadening of the absorption line at high power levels is not to be attributed to any intrinsic modification of the line shape, but rather to a frequency dependent alteration of the populations of the two levels. The net rate of absorption is the difference between the rates of true absorption and stimulated emission, with the common transition probability for the two processes possessing the characteristic frequency dependence $1/[(\omega-\omega_0)^2+1/\tau^2]$. The frequency dependence of the population difference is contained in the first of Eq. (30), which may be written

$$\bar{\rho}_{aa}-\bar{\rho}_{bb}=\frac{1/\tau}{1/\tau+w}(\rho_a{}^{(0)}-\rho_b{}^{(0)}), \tag{39}$$

where

$$w=\frac{1}{\hbar^2}\frac{|V_{ab}|^2/\tau}{(\omega-\omega_0)^2+1/\tau^2}. \tag{40}$$

To interpret this result, we note that $1/\tau$ is the rate at which the population difference tends toward its thermal equilibrium value, as induced by collisions, whence w may be considered the rate at which radiative transitions tend to produce equality in population. That this is a self-consistent interpretation may be seen on computing the power absorbed per unit volume in accordance with the detailed radiative processes:

$$P=\tfrac{1}{2}w\hbar\omega(\bar{\rho}_{aa}-\bar{\rho}_{bb})N =\tfrac{1}{2}\hbar\omega\frac{w(1/\tau)}{w+1/\tau}(\rho_a{}^{(0)}-\rho_b{}^{(0)})N \tag{41}$$

which, with appropriate modifications for degeneracy, agrees precisely with Eq. (35). In writing the last equation, the transition probability for absorption or stimulated emission has been placed equal to $\frac{1}{2}w$, since both processes contribute equally to the rate at which radiative transitions tend to decrease the population difference.

We have enjoyed several conversations on this subject with J. H. Van Vleck.

APPENDIX I

To simplify the density matrix $\rho_0(t)$, in accordance with the smallness of $\mathbf{p}\cdot\mathbf{F}/kT$, we consider the problem of expanding the operator $\exp(A+B)$ in powers of B. We shall be content with the first two terms of the expansion. It is convenient to introduce

$$F(\lambda)=e^{\lambda(A+B)} \tag{I.1}$$

which satisfies the differential equation

$$d/d\lambda F(\lambda)=(A+B)F(\lambda) \tag{I.2}$$

and the initial condition

$$F(0)=1. \tag{I.3}$$

On performing the transformation

$$F(\lambda)=e^{\lambda A}G(\lambda),\quad G(0)=1, \tag{I.4}$$

we encounter the differential equation

$$d/d\lambda G(\lambda)=e^{-\lambda A}Be^{\lambda A}G(\lambda) \tag{I.5}$$

which is equivalent to the integral equation

$$G(\lambda)=1+\int_0^\lambda e^{-\lambda' A}Be^{\lambda' A}G(\lambda')d\lambda'. \tag{I.6}$$

The latter may be solved by successive substitution, which generates a series of which the first two terms are

$$G(\lambda)=1+\int_0^\lambda e^{-\lambda' A}Be^{\lambda' A}d\lambda'+\cdots. \tag{I.7}$$

Hence

$$e^{(A+B)}=F(1)=e^A+\int_0^1 e^{(1-\lambda)A}Be^{\lambda A}d\lambda+\cdots. \tag{I.8}$$

The matrix elements of $\exp(A+B)$, in a scheme with A diagonal, are

$$[e^{(A+B)}]_{a'a''}=e^{a'}\delta_{a'a''}+\frac{e^{a'}-e^{a''}}{a'-a''}B_{a'a''}+\cdots. \tag{I.9}$$

Thus, with $A=-H_0/kT$, $B=-(V/kT)\cos\omega t$,

$$[e^{-H(t)/kT}]_{mn}=e^{-E_m/kT}\delta_{mn}+\frac{e^{-E_m/kT}-e^{-E_n/kT}}{E_m-E_n}V_{mn}\cos\omega t, \tag{I.10}$$

and

$$1/C=Sp\,e^{-H(t)/kT}=Sp\,e^{-H_0/kT}+\frac{1}{kT}Sp\,e^{-H_0/kT}\mathbf{p}\cdot\mathbf{F}\cos\omega t \tag{I.11}$$
$$=1/C^{(0)}.$$

The latter statement is valid since the average dipole moment of the molecule vanishes, in the absence of an external field. We finally obtain

$$[\rho_0(t)]_{mn}=\rho_m{}^{(0)}\delta_{mn}+(\rho_m{}^{(0)}-\rho_n{}^{(0)})(V_{mn}/\hbar\omega_{mn})\cos\omega t, \tag{I.12}$$

which is Eq. (18) of the text.

APPENDIX II

The situation treated in the text is that of a molecule with widely spaced resonant frequencies. We now treat the opposite extreme, a one-dimensional harmonic oscillator, and we shall show that no saturation effect occurs. The electric dipole moment of a charged particle confined to the x axis, $p=ex$, has the following non-vanishing matrix elements:

$$p_{n,\,n-1}=p_{n-1,\,n}=e\left[\frac{n\hbar}{2m\omega_0}\right]^{\frac{1}{2}},\quad n=1,2,3,\cdots, \tag{II.1}$$

where m and ω_0 are the mass and natural frequency of the particle. According to the third equation of the set (28), only the diagonal elements, R_{nn}, are significant if $\omega_0\gg1/\tau$. The properties of the dipole moment matrix then restrict the other non-vanishing matrix elements of $D(t)$ to

$$\overset{(+)}{P}_{n,\,n-1}=\overset{(-)}{P}_{n-1,\,n}{}^*=\frac{V_{n,\,n-1}}{2\hbar(\omega_0-\omega-i/\tau)}\left[\frac{\omega}{\omega_0}(\rho_n{}^{(0)}-\rho_{n-1}{}^{(0)})+R_{n,\,n}-R_{n-1,\,n-1}\right],$$
$$\overset{(+)}{P}_{n-1,\,n}=\overset{(-)}{P}_{n,\,n-1}{}^*=-\frac{V_{n-1,\,n}}{2\hbar(\omega_0+\omega+i/\tau)}\times\left[\frac{\omega}{\omega_0}(\rho_n{}^{(0)}-\rho_{n-1}{}^{(0)})-R_{n,\,n}+R_{n-1,\,n-1}\right]. \tag{II.2}$$

The average dipole moment may now be computed as

$$p(t)=2Re\sum_{n=1}^{\infty}(p_{n-1,\,n}\overset{(+)}{P}_{n,\,n-1}+p_{n,\,n-1}\overset{(+)}{P}_{n-1,\,n})e^{-i\omega t}$$
$$=Re\sum_{n=1}^{\infty}\frac{|p_{n,\,n-1}|^2}{\hbar(\omega_0-\omega-i/\tau)}Ee^{-i\omega t}\times\left[\frac{\omega}{\omega_0}(\rho_{n-1}{}^{(0)}-\rho_n{}^{(0)})+R_{n-1,\,n-1}-R_{n,\,n}\right]$$
$$-Re\sum_{n=1}^{\infty}\frac{|p_{n,\,n-1}|^2}{\hbar(\omega_0+\omega+i/\tau)}Ee^{-i\omega t}\times\left[\frac{\omega}{\omega_0}(\rho_{n-1}{}^{(0)}-\rho_n{}^{(0)})-R_{n-1,\,n-1}+R_{n,\,n}\right]; \tag{II.3}$$

whence

$$Im\chi=\frac{e^2}{2m\omega_0}\frac{1/\tau}{(\omega-\omega_0)^2+1/\tau^2}\times\sum_{n=1}^{\infty}n\left[\frac{\omega}{\omega_0}(\rho_{n-1}{}^{(0)}-\rho_n{}^{(0)})+R_{n-1,n-1}-R_{n,n}\right]+\frac{e^2}{2m\omega_0}\frac{1/\tau}{(\omega+\omega_0)^2+1/\tau^2}\times\sum_{n=1}^{\infty}n\left[\frac{\omega}{\omega_0}(\rho_{n-1}{}^{(0)}-\rho_n{}^{(0)})-R_{n-1,n-1}+R_{n,n}\right]. \quad (II.4)$$

However

$$\sum_{n=1}^{\infty}n(\rho_{n-1}{}^{(0)}-\rho_n{}^{(0)})=\sum_{n=0}^{\infty}\rho_n{}^{(0)}=Sp\rho^{(0)}=1, \quad (II.5)$$

and

$$\sum_{n=1}^{\infty}n(R_{n-1,n-1}-R_{n,n})=SpD=Sp\bar{\rho}-Sp\rho_0=0. \quad (II.6)$$

We thus obtain

$$Im\chi=\frac{e^2}{2m\omega_0}\frac{\omega}{\omega_0}\left[\frac{1/\tau}{(\omega-\omega_0)^2+1/\tau^2}+\frac{1/\tau}{(\omega+\omega_0)^2+1/\tau^2}\right], \quad (II.7)$$

which leads, finally, to

$$\alpha=2\pi\frac{e^2}{mc}\left(\frac{\omega}{\omega_0}\right)^2N\left[\frac{1/\tau}{(\omega-\omega_0)^2+1/\tau^2}+\frac{1/\tau}{(\omega+\omega_0)^2+1/\tau^2}\right] \quad (II.8)$$

in complete agreement with Eq. (17) of reference (1). It is evident that the absorption coefficient of an oscillator is independent of the distribution of molecules among the states of the system and is therefore unaffected by the redistribution induced by the radiation field.