Theory of line shape in
pressure-induced absorption[1]

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A quantum theory of line shape in pressure-induced absorption giving relatively simple results in closed form is developed. A flexible model correlation function satisfying certain general criteria is chosen and incorporated in a general quantum theory of absorption. Relations are derived for estimating the values of the time parameters in the correlation function in terms of known molecular parameters. The theory is applied to far infrared spectra: the translational spectrum of He–Ar, the well resolved $S(0)$ rotational line of H_2 at 77 K, and the unresolved rotational band of N_2. In all cases, the theory fits the spectra and accounts for the spectral features.

On développe une théorie quantique des profils de raie dans l'absorption induite par pression, fournissant des résultats relativement simples sous une forme compacte. Un modèle flexible avec une fonction de corrélation satisfaisant certains critères généraux est choisi et incorporé dans une théorie quantique générale de l'absorption. On établit des relations pour l'estimation de la valeur des paramètres de temps dans la fonction de corrélation en terme des paramètres moléculaires connus. La théorie est appliquée à des spectres dans l'infrarouge lointain: le spectre de transla-tion de He–Ar, la raie de rotation bien résolue $S(0)$ de H_2 à 77 K, et la bande rotationnelle non résolue de N_2. Dans tous les cas, la théorie est en accord avec les spectres et rend compte des détails de ces spectres.

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1. Introduction

Collision-induced absorption arises from the transient dipole induced by intermolecular forces in colliding molecules (see the references cited in Gray (1971)). It is important that a spectral shape for such absorption be available, not only to interpret the spectra but also to cal-culate the opacity of planetary atomspheres where collision-induced absorption plays an im-portant role (Pollack 1973; Trafton 1967). The first treatment of the line shape problem was due to Maryott and Birnbaum (1962) who dealt with the shape of the translational and rotational bands due to induction by molecular multipoles. Since then the shape of the translational band in rare gas mixtures has attracted a great deal of attention (Tanimoto 1965; Levine and Birnbaum 1967; Levine 1967; Trafton 1966; Okada *et al.* 1968; Sears 1968; McQuarrie and Bernstein 1968; Miller *et al.* 1972). Relatively little work, however, has appeared on the shape of collision-induced ro-tational lines (Maryott and Birnbaum 1967; Van

Kranendonk and Gass 1973). Although a rota-tional shape proposed by Welsh and Hunt (1963) has been used extensively in the analysis of collision-induced spectra in H_2, their shape is empirical apart from having built into it detailed balance.

Despite this considerable effort on the shape of collision-induced lines, a theory encompassing both translational and rotational bands, which is quantum mechanical, and gives relatively simple results in closed form, is still lacking. We under-took this work to fill this need and present such a theory here. It is not a first principles theory since it does not start with the equations of mo-tion governing the interaction between colliding molecules. Rather it is constructed along the lines of our previous work on a classical theory of Debye absorption where a model correlation function is chosen which satisfies certain general criteria and leads to a relatively simple expression for the line shape (Birnbaum and Cohen 1970). The validity of such an approach is tested here by detailed comparison with several experiments.

In Sect. 2a, a number of general relations in-volving the absorption coefficient and spectral moments are summarized. Section 2b presents our model correlation function and the spectrum

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[1] This paper is dedicated to Professor H. L. Welsh on the occasion of his retirement from active teaching at the University of Toronto.

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it yields. The specialization of these results to collision-induced absorption in single component molecular gases where induction is due predominantly to the molecular multipole moments is presented next. This is followed by considering the case of collision-induced absorption by overlap interaction in rare gas mixtures. Relations are derived connecting the time parameters in the correlation function and line shape with molecular parameters thereby allowing theoretical predictions to be made regarding these parameters. These results are applied to far infrared spectra: the well resolved $S(0)$ line of H_2 at 77 K; the unresolved translational–rotational spectrum of N_2 at 300 K; and the translational band in an He–Ar mixture at 300 K. We find that the spectral shapes derived here satisfactorily represent the experimental results and are useful in analyzing collision-induced spectra. In particular, we account for the frequency shift of the $S(0)$ and $S(1)$ lines of H_2 from their respective Raman frequencies, and find a quantum shift in the frequency of maximum absorption in the translational spectrum of rare gas mixtures.

2. Theory of Collision-Induced Line Shape

a. General Relations

The absorption coefficient per unit path length of a substance enclosed in a volume V is given by the formula (Kubo 1959; Huber and Van Vleck 1966)

$$[1] \quad \alpha(\omega) = \frac{2\pi\omega}{3\hbar c V}(1 - e^{-\beta\hbar\omega})$$

$$\times \int_{-\infty}^{\infty} e^{-i\omega t}\langle M(0)\cdot M(t)\rangle \, dt$$

where $\beta = (kT)^{-1}$ and $\langle M(0)\cdot M(t)\rangle$ is the dipole moment correlation function. Here M is the total dipole moment of the system and the brackets denote a thermal average. For a dilute gas one has

$$[2] \quad \begin{aligned}\langle M(0)\cdot M(t)\rangle &= N\langle m(0)\cdot m(t)\rangle \\ &= N\Phi(t)\end{aligned}$$

where N is the number of dipoles and m is the dipole operator. Then [1] and [2] give

$$[3] \quad \alpha(\omega) = (4\pi^2\omega N/3\hbar c V)(1 - e^{-\hbar\omega\beta})\phi(\omega)$$

where

$$[4] \quad \phi(\omega) = (2\pi)^{-1}\int_{-\infty}^{\infty} e^{-i\omega t}\Phi(t) \, dt$$

and N/V is the number of dipoles per unit volume.

The moments M_n of the spectrum may be defined by (Miller *et al.* 1972)

$$[5a] \quad M_n = \int_{-\infty}^{\infty} \omega^n\phi(\omega) \, d\omega$$

or alternatively by

$$[5b] \quad M_n = \int_0^{\infty} [1 + (-)^n e^{-\beta\hbar\omega}]\omega^n\phi(\omega) \, d\omega$$

since $\phi(\omega)$ satisfies the condition of detailed balance

$$[5c] \quad \phi(-\omega) = e^{-\beta\hbar\omega}\phi(\omega)$$

The moments are related to the absorption coefficient by

$$[6a] \quad M_{2n} = \frac{3cV}{2\pi^2 N\beta}\int_0^{\infty} f\left(\frac{\beta\hbar\omega}{2}\right)\alpha(\omega)\omega^{2n-2} \, d\omega$$

$$[6b] \quad M_{2n+1} = \frac{3\hbar c V}{4\pi^2 N}\int_0^{\infty} \alpha(\omega)\omega^{2n} \, d\omega$$

where

$$f(x) = x \coth x$$

and to the correlation function [2] by

$$[6c] \quad M_n = (-i)^n \frac{d^n\Phi(t)}{dt^n}\bigg|_{t=0}$$

It is convenient to consider the function $\gamma(\omega)$ defined by

$$[7a] \quad \gamma(\omega) = \frac{\beta\hbar}{2}\frac{\alpha(\omega)}{\omega \tanh(\beta\hbar\omega/2)}$$

$$[7b] \quad = \frac{2\pi^2\beta N}{3c V}(1 + e^{-\beta\hbar\omega})\phi(\omega)$$

which is proportional to the transition probability. In terms of $\int\gamma(\omega) \, d\omega$, M_0 is given by

$$[8a] \quad M_0 = \frac{3cV}{2\pi^2\beta N}\int_0^{\infty} \gamma(\omega) \, d\omega$$

According to [6b] we see that M_1 is proportional to the integrated absorption coefficient,

$$[8b] \quad M_1 = \frac{3\hbar c V}{4\pi^2 N}\int_0^{\infty} \alpha(\omega) \, d\omega$$

A useful relation is obtained from [7b] by letting $\omega = 0$, in which case

$$[8c] \quad \gamma(0) = \frac{2\pi^2\beta N}{3c V}\frac{2}{\pi}\int_0^{\infty} \Phi(t) \, dt$$

Thus the limiting value of $\gamma(0)$ at low frequencies is proportional to the time integral of the correlation function.

b. Model Correlation Function and Spectral Shape

The trace in [2] can be written in terms of the orthonormal molecular wave functions as

[9a] $\quad \langle \boldsymbol{m}(0)\cdot \boldsymbol{m}(t)\rangle = \sum_{if\,d_i d_f} \rho_i\, e^{i\omega_{if}t}$

$$\times \langle (i, d_i|\boldsymbol{\mu}(0)\cdot|f, d_f)\rangle \langle (f, d_f|\boldsymbol{\mu}(t)|i, d_i)\rangle_{\text{av}}$$

where i and f are respectively the nondegenerate initial and final states, d_i and d_f represent the sets of quantum numbers which characterize the degeneracies, and

[9b] $\qquad \rho_i = e^{-\beta E_i} \Big/ \sum_i d_i\, e^{-\beta E_i}$

The natural oscillation at angular frequency

[9c] $\qquad \omega_{if} = (E_f - E_i)/\hbar$

has been factored out of the dipole motion in [9a], where $\langle...\rangle_{\text{av}}$ represents an average over all dynamical paths. To obtain [9a] it is assumed that cross relaxing collisions which couple spectral line amplitudes are negligible. This means that the absorption due to a band is just the sum of the absorption due to individual lines.

A normalized relaxation or reduced correlation function $C(t)$ may be defined by

[10a] $\quad \displaystyle\sum_{d_i d_f} \langle (i, d_i|\boldsymbol{\mu}(0)\cdot|f, d_f)\rangle$

$$\times \langle (f, d_f|\boldsymbol{\mu}(t)|i, d_i)\rangle_{\text{av}} = |\boldsymbol{\mu}_{if}|^2 C_{if}(t)$$

where

[10b] $\quad |\boldsymbol{\mu}_{if}|^2 = \displaystyle\sum_{d_i d_f} |(i, d_i|\boldsymbol{\mu}|f, d_f)|^2$

is the dipole matrix element. The correlation function may now be written as

[11a] $\quad \Phi(t) = \displaystyle\sum_{if} \rho_i |\boldsymbol{\mu}_{if}|^2\, e^{i\omega_{if}t} C_{if}(t)$

and the spectral function [4] becomes

[11b] $\quad \phi(\omega) = \displaystyle\sum_{if} \rho_i |\boldsymbol{\mu}_{if}|^2 (2\pi)^{-1}$

$$\times \int_{-\infty}^{\infty} e^{i(\omega_{if}-\omega)t} C_{if}(t)\, dt$$

The detailed balance condition [5c] can be written in the equivalent form

[12] $\qquad \Phi(-t) = \Phi(t + i\beta\hbar)$

In order to achieve this condition, we replace t in $C_{if}(t)$ by the complex time (Egelstaff 1960)

[13] $\qquad y = (t^2 - i\beta\hbar t)^{1/2}$

and require that $C_{if}(y)$ be a real even function of y so that the real part of $C_{if}(y)$ is even in t and the imaginary part is odd in t.

To obtain an explicit function for the line shape, we assume the following model for $C(y)$ which satisfies [12],

[14] $\quad C_{if}(y) = \exp\{\tau_1^{-1}[\tau_2 - (\tau_2^2 + y^2)^{1/2}]\}$

where the parameters τ_1 and τ_2 depend in general on initial and final state. This correlation function is not expected to take into account the intercollisional interference effect discussed by Van Kranendonk (1968) which produces a dip in the translational spectra of rare gas mixtures at low frequencies and at high pressures. The short time expansion of [14] is

[15a] $\quad C_{if}(y) = 1 + it\dfrac{\beta\hbar}{2\tau_1\tau_2} - \dfrac{t^2}{2\tau_1\tau_2}$

$$\times \left[1 + \dfrac{\beta^2\hbar^2(\tau_1 + \tau_2)}{4\tau_1\tau_2^2}\right] + \dots$$

At long times [14] has the asymptotic expansion

[15b] $\quad C_{if}(y) = \exp\left(\tau_2 \pm \dfrac{i\beta\hbar}{2} - |t|\right)\Big/ \tau_1$

$$t \to \pm\infty$$

Although other model correlation functions could be chosen, [14] has been shown to represent in the classical limit the translational band shape in rare gas mixtures.[3]

The spectral function obtained from [11b] and [14] is

[16a] $\quad \phi(\omega) = \displaystyle\sum_{if} \rho_i |\boldsymbol{\mu}_{if}|^2 \Gamma_{if}(\omega_-)$

[16b] $\quad \Gamma_{if}(\omega_-) =$

$$(2\pi)^{-1} \int_{-\infty}^{\infty} e^{i(\omega_{if}-\omega)t} C_{if}(y)\, dt$$

where

[17] $\quad \Gamma_{if}(\omega_-) = \dfrac{\tau_1}{\pi}\, e^{\tau_2/\tau_1}\, e^{\beta\hbar\omega_-/2}\, \dfrac{z_- K_1(z_-)}{1 + \omega_-^{2}\tau_1^{2}}$

$$\omega_\pm = \omega \pm \omega_{if}$$

$$z_\pm = [1 + \omega_\pm^{2}\tau_1^{2}]^{1/2}[\tau_2^{2} + (\beta\hbar/2)^2]^{1/2}/\tau_1$$

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[3]Birnbaum, G. and Levine, H. B. Unpublished notes.

The function $K_1(z)$ is the modified Bessel function of the second kind with the properties,

[18a] $\qquad zK_1(z) \to 1, \quad z \to 0$

[18b] $\qquad K_1(z) \to (\pi/2z)^{1/2}e^{-z}, \quad |z| \gg 1$

If the unrestricted sum in [16]a is written as a restricted sum with $i < f$, then we have

[19] $\quad \phi(\omega) = \sum_i \rho_i |\mu_{ii}|^2 \Gamma_{ii}(\omega)$

$$+ \sum_{i<f} |\mu_{if}|^2 [\rho_i \Gamma_{if}(\omega) + \rho_f \Gamma_{if}(\omega_+)]$$

The first term in [19] gives the nonresonant $(i \to i)$ contribution and the second term gives the resonant $(i \to f)$ contributions. It is clear from the symmetry of $[\rho_i\Gamma_{if}(\omega_-) + \rho_f\Gamma_{if}(\omega_+)]$ and $\Gamma_{ii}(\omega)$ that $\phi(\omega)$ obeys detailed balancing, as it must. In addition, $\Gamma_{if}(\omega_-)$, the dominant contribution to a resonant line, satisfies detailed balance with respect to displacements from resonance, δ,

[20] $\quad \Gamma_{if}(\omega_{if} - \delta) = e^{-\beta\hbar\delta}\Gamma_{if}(\omega_{if} + \delta)$

In the vicinity of a line, $\alpha(\omega)$ has approximately the Van Vleck – Weisskopf shape (Van Vleck and Weisskopf 1945) if $\tau_1 \gg \tau_2$. In the wings where [18b] holds, $\alpha(\omega)$ exhibits an exponential-like frequency dependence.

c. Collision-Induced Absorption in a One Component Gas

Consider now collision-induced absorption in dilute gases where bimolecular collisions predominate. Then μ becomes the induced dipole operator in an interacting pair of molecules, and N the number of dipoles becomes $N_0^2/2$, the number of pairs, where N_0 is the number of molecules, namely,

[21a] $\quad N|\mu_{if}|^2 =$

$$\frac{N_0^2}{2} V^{-1} \int_0^\infty g(R)|\mu_{if}(R)|^2 4\pi R^2 \, dR$$

The pair correlation function, $g(R)$, is given by

[21b] $\qquad g(R) = \exp[-\beta V(R)]$

where the intermolecular potential, $V(R)$, is spherically symmetric.

Since we shall be concerned with rotational transitions, we replace i and f respectively by J, K, M, and J', K', M'. For diatomic molecules $K = K' = 0$, whereas for spherical molecules K and K' are regarded as degenerate quantum numbers.

It has been shown for linear molecules that (Frost 1973)

[22a] $\quad |\mu_{JJ'}(l)|^2 =$
$$2\overline{\alpha^2}(l + 1)(Q_l^2/R^{2l+4})(2J + 1)C(JlJ';00)^2$$

where the relevant Clebsch–Gordon coefficients are listed in Table 1. For tetrahedral molecules, one has

[22b] $\quad |\mu_{JJ'}(l)|^2 =$

$$2\alpha^2 \frac{l + 1}{2l + 1} \frac{Q_l^2}{R^{2l+4}} (2J + 1)(2J' + 1)$$

In [22b] α is the molecular polarizability. In [22a], for linear molecules with an anisotropic polarizability, the mean square polarizability $\overline{\alpha^2} = (1/3)(\alpha_\parallel^2 + 2\alpha_\perp^2)$ must be used. The quantity l is the order of the multipole and Q_l its tensor magnitude. It is related to the usual scalar magnitude (Stogryn and Stogryn 1966) by the relations (Gray 1971)

[23a] $\quad \Theta = Q_2 \quad$ (quadrupole)

[23b] $\quad \Omega = (5/12)^{1/2}Q_3$

$\qquad$ (octupole, tetrahedral molecule)

[23c] $\quad \Phi = Q_4$

$\qquad$ (hexadecapole, linear molecule)

[23d] $\quad \Phi = (7/12)^{1/2}Q_4$

$\qquad$ (hexadecapole, tetrahedral molecule)

A single scalar is sufficient to specify these multipoles for linear (Θ, Φ) and spherical (Ω, Φ) molecules. The factor of 2 in [22] accounts for the fact that either one of two molecules of the pair may undergo the transition $J \to J'$. In obtaining [22] the relevant matrix elements have

TABLE 1. Clebsch–Gordan coefficients for transitions governed by the triangular relation $\Delta(JlJ')$ for $l = 2$ and 4

$$C(J, 2, J; 00)^2 = \frac{J(J + 1)}{(2J - 1)(2J + 3)}$$

$$C(J, 2, J+2; 00)^2 = \frac{3}{2} \frac{(J + 1)(J + 2)}{(2J + 1)(2J + 3)}$$

$$C(J, 4, J; 00)^2 = \frac{9}{4} \frac{(J - 1)J(J + 1)(J + 2)}{(2J - 3)(2J - 1)(2J + 3)(2J + 5)}$$

$$C(J, 4, J+2; 00)^2 = \frac{5}{2} \frac{J(J + 1)(J + 2)(J + 3)}{(2J - 1)(2J + 1)(2J + 3)(2J + 7)}$$

$$C(J, 4, J+4; 00)^2 = \frac{35}{8} \frac{(J + 1)(J + 2)(J + 3)(J + 4)}{(2J + 1)(2J + 3)(2J + 5)(2J + 7)}$$

been summed over all degenerate quantum numbers as indicated in [10b].

The integral in [21a] with [21b] may be written in the form

$$[24] \quad \int_0^\infty g(R)|\mu_{JJ'}(l)|^2 4\pi R^2 \, dR =$$

$$L_{JJ'}(l)I_{2l+4}/\sigma^{2l+1}$$

where

$$I_k = \int_0^\infty g(x)x^{-k}4\pi x^2 \, dx$$

$x = R/\sigma$, and σ is the Lennard–Jones molecular diameter. The $L_{JJ'}(l)$ functions are from [22a]

$$[25a] \quad L_{JJ'}(l) =$$

$$2\overline{\alpha^2}(l + 1)Q_l^2(2J + 1)C(JlJ';00)^2$$

for diatomic molecules, and from [22b]

$$[25b] \quad L_{JJ'}(l) =$$

$$2\alpha^2 \frac{l + 1}{2l + 1} Q_l^2(2J + 1)(2J' + 1)$$

for tetrahedral molecules. With these results the correlation function [11a] becomes

$$[26] \quad \Phi(t) = V^{-1} \sum_{lJJ'} \rho_J \frac{L_{JJ'}(l)}{\sigma^{2l+1}} I_{2l+4} \, e^{i\omega_{JJ'}t}C(y)$$

where τ_1 and τ_2 in $C(y)$ (eq. 14) in general depend on l, J, and J', but for simplicity the J and J' dependence is ignored. From [3], [4], and [26] the absorption coefficient becomes

$$[27a] \quad \alpha(\omega) = \frac{2\pi^2 n^2}{3\hbar c} \omega(1 - e^{-\beta\hbar\omega})$$

$$\times \left\{ \sum_{l,J} \rho_J \frac{L_{JJ}(l)}{\sigma^{2l+1}} I_{2l+4}\Gamma_{JJ}(\omega) \right.$$

$$+ \sum_{l,J<J'} \frac{L_{JJ'}(l)}{\sigma^{2l+1}} I_{2l+4}$$

$$\left. \times [\rho_J\Gamma_{JJ'}(\omega_-) + \rho_{J'}\Gamma_{JJ'}(\omega_+)] \right\}$$

where the spectral functions Γ are defined by [17], and $n = N_0/V$ is the number of molecules per unit volume. From [7a] the transition probability $\gamma(\omega)$ is given by

$$[27b] \quad \gamma(\omega) = \frac{\pi^2 n^2 \beta}{3c} (1 + e^{-\beta\hbar\omega})\{...\}$$

where the function within the braces is the same as in [27a].

d. Spectral Invariants and Relations for Evaluating τ_1 and τ_2

It is convenient to define the spectral invariants α_1 and γ_1 which are the first coefficients in the density expansions

$$[28a] \quad \alpha = \int_0^\infty \alpha(\omega) \, d\omega = \alpha_1 n^2 + \alpha_2 n^3 + ...$$

$$[28b] \quad \gamma = \int_0^\infty \gamma(\omega) \, d\omega = \gamma_1 n^2 + \gamma_2 n^3 + ...$$

Then from [6c], [8a], [8b], and [26] we obtain

$$[29] \quad \gamma_1 = \frac{\pi^2\beta}{3c} \sum_{lJJ'} \rho_J \frac{L_{JJ'}(l)}{\sigma^{2l+1}} I_{2l+4}$$

$$[30] \quad \alpha_1 = \frac{2\pi^2}{3\hbar c} \sum_{lJJ'} \rho_J \frac{L_{JJ'}(l)}{\sigma^{2l+1}} I_{2l+4}$$

$$\times [\omega_{JJ'} - i\dot{C}_l(0)]$$

where $\dot{C}_l(0)$ is the derivative of $C(y)$ with respect to t evaluated at $t = 0$. From the properties of $C(y)$, [12] and [13], we see that $-i\dot{C}_l(0)$ is a real positive quantity. The first term in [30], α_{1r}, is due to rotational transitions, and the second term, α_{1t}, is due to the translational band ($\Delta J = 0$ transitions) and the translational broadening of the rotational band ($\Delta J \neq 0$ transitions). We can see from [30] that in order to obtain a finite α_{1t}, it is necessary that the reduced correlation function have a finite first time derivative. Equations 29 and 30 give

$$[31a] \quad \frac{\alpha_{1t}}{\gamma_1(l)} = -i\dot{C}_l(0)\frac{2}{\beta\hbar}$$

which for the model correlation function [14] becomes with [15a]

$$[31b] \quad \frac{\alpha_{1t}(l)}{\gamma_1(l)} = \frac{1}{\tau_1(l)\tau_2(l)}$$

We find for either linear or tetrahedral molecules that

$$[32] \quad \sum_{JJ'} \rho_J L_{JJ'}(l) = 2\overline{\alpha^2}(l + 1)Q_l^2$$

Of course, for a tetrahedral molecule, $\overline{\alpha^2} = \alpha^2$. With this result, [29] becomes

$$[33] \quad \gamma_1 = \frac{2\pi^2\overline{\alpha^2}}{3ckT} \sum_l \frac{(l + 1)Q_l^2 I_{2l+4}}{\sigma^{2l+1}}$$

which agrees with the expression given by Gray (1971).

On performing the sum over J and J' in the

first term in [30] (Rosenberg 1974), one obtains α_{1r} obtained previously (Gray 1971). The complete expression for $\alpha_1 = \alpha_{1r} + \alpha_{1t}$ obtained by a general method involving the evaluation of the commutator formed by the kinetic energy and the induced dipole is given by (Gray 1971)

$$[34] \quad \alpha_1 = \frac{2\pi^2 \overline{\alpha^2}}{3Ic} \sum_l \frac{(l+1)Q_l^2}{\sigma^{2l+1}}$$

$$\times \left[(l+2)(2l+3)\frac{I}{m\sigma^2}I_{2l+6} \right.$$

$$\left. + l(l+1)I_{2l+4} \right]$$

where I is the moment of inertia. We obtain from [33] and [34]

$$[35] \quad \frac{\alpha_{1r}(l)}{\gamma_1(l)} = \frac{l(l+1)kT}{I}$$

where the right side of [35] may be identified as a classical mean squared rotational frequency. This increases with l since the frequency of the transitions permitted by the triangular relation $\Delta(JlJ')$ increase with l.

The time parameters in [33b] may be related to molecular quantities by evaluating $\alpha_{1r}(l)/\gamma_1(l)$ from [33] and [34] and using [31b], namely,

$$[36] \quad \tau_1(l)\tau_2(l) = \frac{\beta m\sigma^2}{(l+2)(2l+3)}\frac{I_{2l+4}}{I_{2l+6}}$$

The quantity $[\tau_1(l)\tau_2(l)]^{1/2}$ is clearly a duration of collision parameter since $(\beta m)^{-1/2}$ is a characteristic velocity and $\sigma/[l+2)(2l+3)]^{1/2}$ represents an interaction range which as expected decreases with increasing order of the multipole. The ratio I_{2l+4}/I_{2l+6} is the order of unity.

Other relations between $\tau_1(l)$ and $\tau_2(l)$ and molecular parameters may be obtained by using higher spectral invariants, for example, M_3/M_0, or M_4/M_0. A more empirical approach is to make use of the experimentally determined spectrum. For example, one may use [27b] in the limit $\omega \to 0$ where $\gamma(0)$ is obtained from the spectrum at sufficiently low frequencies. We see from [8c] that $\gamma(0)$ may also be determined by integrating the experimentally evaluated correlation function.

It should be emphasized that the methods for obtaining $\tau_1(l)$ and $\tau_2(l)$ outlined here are essentially for the translational band. We shall as a first approximation assume that these values

are appropriate for the rotational lines provided the same type of interaction is involved.

e. Collision-Induced Absorption in Rare Gas Mixtures

In rare gas mixtures the induced dipole is assumed to depend primarily on an overlap interaction represented by (Poll and Van Kranendonk 1961)

$$[37] \quad \mu(R) = \mu_0 \exp\left[-(R-\sigma)/\rho\right]$$

where ρ is a range parameter and μ_0 is the induced dipole at molecular contact. The correlation function becomes

$$[38a] \quad \Phi(t) = V^{-1}C(y)\int_0^\infty \mu^2(R)g(R)4\pi R^2 \, dR$$

$$[38b] \quad = V^{-1}C(y)\sigma^3\mu_0^2 I_R$$

where

$$[38c] \quad I_R =$$

$$4\pi \int_0^\infty \exp\left[-\frac{2\sigma}{\rho}(x-1)\right]g(x)x^2 \, dx$$

With [38] the expression for $\alpha(\omega)$ (eq. 3) becomes

$$[39] \quad \alpha(\omega) = \frac{4\pi^2 n_A n_B}{3\hbar c}\omega(1 - e^{-\beta\hbar\omega})\sigma^3\mu_0^2 I_R\Gamma(\omega)$$

where $\Gamma(\omega)$ is given by [17] with $\omega_{if} = 0$. The number of dipoles N in [3] is now given by $N_A N_B$, the number of pairs containing an induced dipole, where N_A and N_B are, respectively, the number of species A and B. The quantities $n_A = N_A/V$ and $n_B = N_B/V$ are, respectively, the density of species A and B.

The spectral invariants α_1 and γ_1 obtained from [6c], [8a], [8b], and the correlation function [38b] are

$$[40a] \quad \gamma_1 = (2\pi^2\beta/3c)\sigma^3\mu_0^2 I_R$$

$$[40b] \quad \alpha_1 = (4\pi^2/3\hbar c)[-i\dot{C}(0)]\sigma^3\mu_0^2 I_R$$

where from the general properties of $C(y)$, $-i\dot{C}(0)$ is a real positive quantity. For our model correlation function

$$[41a] \quad -i\dot{C}(0) = \beta\hbar/2\tau_1\tau_2$$

and from [40a] and [40b] one obtains

$$[41b] \quad \alpha_1/\gamma_1 = (\tau_1\tau_2)^{-1}$$

which is similar to [31b].

The quantity α_1, evaluated from the com-

mutator of the induced dipole and the kinetic energy operator, is given by (Poll and Van Kranendonk 1961)

$$[42a] \quad \alpha_1 = \frac{2\pi^2}{3mc}\sigma\mu_0{}^2\left(\frac{\sigma^2}{\rho^2}I_R + 2I_\Omega\right)$$

where m is the reduced mass and

$$[42b] \quad I_\Omega = 4\pi \int_0^\infty \exp\left[-\frac{2\sigma}{\rho}(x - 1)\right]g(x)\,dx$$

The term containing I_Ω is due to the variation of Ω, the direction of R, during a collision, whereas the I_R term is due to the variation of R. The former term is absent in multipolar induction where the induced dipole resides in the molecule. Equations 40a and 42a give the useful result

$$[43] \quad \frac{\alpha_1}{\gamma_1} = \frac{1}{\beta m\sigma^2}\left[\left(\frac{\sigma}{\rho}\right)^2 + 2\frac{I_\Omega}{I_R}\right] = \frac{1}{\tau_1\tau_2}$$

where $(\beta m\rho^2)^{1/2}$ is a duration of collision.

3. Applications of the Theory

a. He–Ar Translational Spectrum

The translational spectrum of He–Ar due primarily to induction by an overlap interaction (Poll and Van Kranendonk 1961; Hartye et al. 1975) is shown in Fig. 1. The experimental points were obtained from the measurements of Bosomworth and Gush (1965) at 295 K. The curve was calculated from [39],

$$[44] \quad \frac{\alpha(\omega)}{\omega n_A n_B} = \frac{2\gamma_1}{\beta\hbar}\left(1 - e^{-\beta\hbar\omega}\right)$$

$$\times \frac{\tau_1}{\pi}e^{\tau_2/\tau_1}\,e^{\beta\hbar\omega/2}\,\frac{zK_1(z)}{1 + \omega^2\tau_1{}^2}$$

where

$$z = [1 + \omega^2\tau_1{}^2]^{1/2}[\tau_2{}^2 + (\beta\hbar/2)^2]^{1/2}\tau_1{}^{-1}$$

and γ_1 is given by [40a]. A least squares fit, minimizing the relative error between [44] and the data, made by adjusting the three parameters τ_1, τ_2, and γ_1, gives $\tau_1 = (2.48 \pm 0.06) \times 10^{-14}$ s, $\tau_2 = (6.80 \pm 0.10) \times 10^{-14}$ s, $\gamma_1 = (6.58 \pm 0.06) \times 10^{-20}$ cm^{-1} s amagat^{-2}. (The uncertainties given here and elsewhere in this section represent one standard deviation in the least squares value of the fitted parameter, but do not include the uncertainty in the values of the assumed molecular parameters, σ and ε/k, nor any contribution from an evaluation of experimental
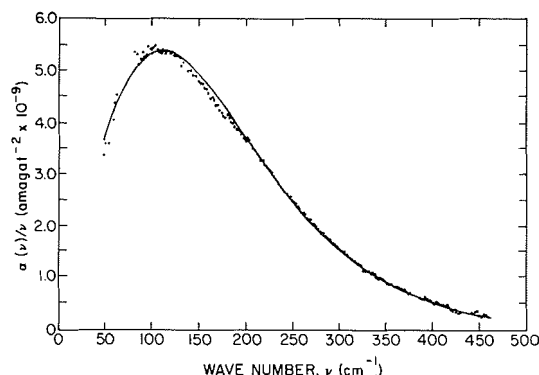

FIG. 1. The translational spectrum of He–Ar at 295 K. $\alpha(\nu)/\nu\rho^2$ is plotted as a function of ν. The experimental points were obtained in Bosomworth and Gush (1965) (the He–Ar data are presented in their Fig. 4) and the curve is computed from [44] with $\tau_1 = 2.49 \times 10^{-14}$ s, $\tau_2 = 6.80 \times 10^{-14}$ s, $\gamma_1 = 6.58 \times 10^{-20}$ cm^{-1} s^{-1} amagat^{-2}, $\sigma = 2.98 \times 10^{-8}$ cm, and $\varepsilon/k = 40.2$ K.

systematic errors.) Using [41b] then gives the integrated absorption, $\alpha_1 = (3.89 \pm 0.03) \times 10^7$ cm^{-1} s^{-1} amagat^{-2}. The quantum time, $\tau_0 = \beta\hbar/2 = 1.29 \times 10^{-14}$, is half of τ_1, indicating that even at room temperature He–Ar should have some quantum character, as has been observed in an analysis of the spectral moments (Hartye et al. 1975).

Using $m = 3.638$ amu, $\sigma = 2.98 \times 10^{-8}$ cm, and $\varepsilon/k = 40.2$ K (Van Heyningen et al. 1968), we obtain $\rho/\sigma = 0.1149 \pm 0.0007$. Our results are close to those obtained by Hartye et al. (1975) (namely $\gamma_1 = 6.61 \times 10^{-20}$ cm^{-1} s amagat^{-2}, $\alpha_1 = 0.395 \times 10^{-8}$ cm^{-1} s^{-1} amagat^{-2}, and $\rho/\sigma = 0.117$), who used the quantum form (Levine 1967) of the Levine–Birnbaum (Levine and Birnbaum 1967) line shape to represent the experimental data. Although this latter shape has been successful in fitting the translational spectrum of rare gas mixtures, the parameters in this equation are purely empirical.

We see from Fig. 1 that except for the region 135–180 cm^{-1} [44] closely fits the data. Even in this region the discrepancy is probably not outside a realistic estimate of the experimental error. We did not use [8c] and [41b] to estimate τ_1 and τ_2 since there is no experimental value for $\gamma(0)$. However, even if such a value were available, this might not have been a satisfactory procedure since we have $\tau_2 > \tau_1$, and $\gamma(0)$ is proportional to $(\tau_1\tau_2)^{1/2}$ when $\tau_2 \gg \tau_1$ and $\tau_2 \gg \tau_0$. In such a situation, an attempt to determine τ_1 and τ_2

separately from $\gamma(0)$ and the ratio α_1/γ_1 is at best a procedure which is extremely sensitive to experimental errors in the data and cannot give a reliable value of the constants. In the least squares fitting of the entire spectrum we avoid this problem as much as is possible but we note that although the geometric mean $(\tau_1\tau_2)^{1/2}$ is determined with a statistical precision of 0.5%, τ_1 and τ_2 individually are determined only with precisions respectively of 2.3 and 1.4%.

When $\tau_2 \gg \tau_1$ the correlation function [14] has a Gaussian character except at very long times where $C(y) \ll 1$. The corresponding line shape has a Debye character only at very low frequencies but is dominated by $K_1(z)$ over most of the frequency range. When $\tau_2 \gg \tau_1$, $K_1(z)$ assumes a simple exponential form [18b], and for frequencies such that $\omega\tau_1 \gtrsim 1$, [44] reduces to

[45a] $\quad \dfrac{\alpha(\omega)}{\omega n_A n_B} = \dfrac{2\gamma_1}{\beta\hbar}\left(1 - e^{-\beta\hbar\omega}\right)$

$$\times \left(\frac{\tau_1\tau_3}{\pi}\right)^{1/2} e^{\tau_2/\tau_1} \frac{e^{\omega[(\beta\hbar/2)-\tau_3]}}{(\omega\tau_1)^{3/2}}$$

[45b] $\quad \tau_3 = [\tau_2{}^2 + (\beta\hbar/2)^2]^{1/2}$

A value for τ_2 is conveniently found from the slope of the exponential region.

b. S(0) Line of Equilibrium H₂

The translational band and $S(0)$ line of equilibrium H$_2$ (e-H$_2$) at 77.4 K, due predominantly to dipole induction by the quadrupole moment of H$_2$ (Poll and Van Kranendonk 1961; Van Kranendonk and Kiss 1959; Colpa and Ketelaar 1958), is shown in Fig. 2. The data points[4] were fitted by the curve calculated from [27a]. Data for the $S(1)$ line not shown were also used in order to separate the $S(0)$ line from the background of the low frequency wing of the $S(1)$ line. However, at 77 K these two lines are relatively well separated so that at the peak of the $S(0)$ line (370 cm^{-1}) the $S(1)$ line contributes only about 5% to the absorption coefficient.

Since we are interested here primarily in determining how well the theory fits the shape of an isolated collision-induced rotational line, we adjusted the amplitudes of the translational band and $S(0)$ and $S(1)$ lines independently. Then by allowing different time parameters for the translational band and rotational lines (but the same
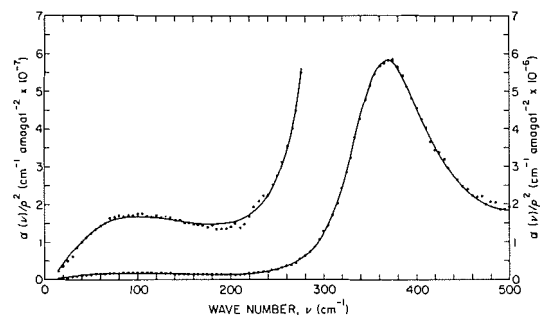
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[4]Birnbaum, G. Unpublished.

FIG. 2. The translational band and $S(0)$ line of equilibrium H$_2$ at 77.4 K. The data, $\alpha(v)$, are given in Van Kranendonk and Kiss (1959) and the curve is computed from [27a] with $\tau_1 = 9.76 \times 10^{-14}$ s and $\tau_2 = 4.94 \times 10^{-14}$ s for the $S(0)$ and $S(1)$ line (not shown), and $\tau_1 = 9.5 \times 10^{-14}$ s and $\tau_2 = 4.1 \times 10^{-14}$ s for the translational band. The amplitudes of this band and the $S(0)$ and $S(1)$ lines were arbitrarily adjusted to obtain a best fit.

parameters for both rotational lines) we obtained the curves shown in Fig. 2. The computed curve contains 9 parameters which were fitted by least squares: the transition frequencies of the two rotational transitions, the amplitudes of the three components, and four time constants.

The values of the time parameters are $\tau_1 = (9.76 \pm 0.09)10^{-14}$ s and $\tau_2 = (4.9 \pm 0.2)10^{-14}$ s for the $S(0)$ line, and $\tau_1 = (9.5 \pm 2.2)10^{-14}$ s and $\tau_2 = (4.1 \pm 1.6)10^{-14}$ s for the translational band. The time $\tau_0 = \beta\hbar/2 = 4.93 \times 10^{-14}$ at 77 K is approximately equal to τ_2 and about one half of τ_1, indicating that the spectrum should be strongly quantum mechanical in character. Unlike the time constants obtained for the overlap-induced spectra in He–Ar collisions, τ_1 is greater than τ_2 for H$_2$–H$_2$ collisions.

To estimate the duration of collision $(\tau_1\tau_2)^{1/2}$, we use [36] with $\sigma = 2.92 \times 10^{-8}$ cm, $\varepsilon/k = 36.8$ K (American Institute of Physics Handbook 1957), $T = 77.4$ K, $l = 2$ for quadrupolar induction, the classical values of I_8 and I_{10}, which may not cause too large an error in the ratio. We find that $(\tau_1\tau_2)^{1/2} = 7.8 \times 10^{-14}$ s, which is larger than the values obtained by using τ_1 and τ_2 from the $S(0)$ line, namely 6.95×10^{-14} s. This difference would be reduced if σ were smaller but it is in the direction to be ascribable to the existence of additional overlap interactions which are of shorter range than the quadrupole interaction and hence reduce the mean effective duration of collision.

The half width of the $S(0)$ line, Δv, calculated

from $\Delta v = (2\pi c \tau_1)^{-1}$ with $\tau_1 = 9.76 \times 10^{-14}$ s
is 54.4 cm^{-1} in comparison with an observed
half width at half height in Fig. 2 (without sub-
tracting any background from the wing of the
$S(1)$ line) of approximately 55 cm^{-1}. This value
cannot be compared directly with the width
parameter given by Kiss and Welsh (1959) and
Welsh and Hunt (1963) (84 cm^{-1}), even after
correcting for their higher temperature (85 K),
because the shape function they used is quite dif-
ferent from ours. Since their shape decreases too
slowly far away from the line center, some dif-
ferent empirical shape factors have been ad-
vanced (Bosomworth and Gush 1965; Mactag-
gert and Hunt 1969).

We find the transition frequency of the $S(0)$
line to be 353.0 ± 0.2 cm^{-1} which compares
favorably with 354.4 cm^{-1} obtained from the
room temperature Raman spectrum of H_2
(Stoicheff 1957). The blue shift of the peak of the
collision-induced spectrum (368.2 cm^{-1}) is due
mainly to the factor $\exp[\beta\hbar(\omega - \omega_0)/2]$ in [27a]
and to a smaller extent, $\omega(1 - e^{-\beta\hbar\omega})$. This
previously unexplained frequency shift is thus
seen to have its origin in the quantum character
of the line shape. A difference between the
collision-induced and the Raman frequencies is
perhaps to be expected because of the perturba-
tions of the molecular energy levels during the
collision, and may be the explanation of at least a
portion of the remaining difference.

c. Translational–Rotational Band of N_2

The far infrared collison-induced absorption
spectrum of N_2 is due mainly to induction by its
quadrupole moment and, to a very much smaller
extent, by its hexadecapole moment (Birnbaum
and Cohen 1976). We have previously used the
data of Buontempo et al. (1975) to determine the
multipole moments from the spectral moments.
We shall now fit [27] to their data to determine
the dynamic parameters τ_1 and τ_2. We use the data
at 300 K, with the extrapolated zero frequency
value, $\gamma_1(0) = 3.54 \times 10^{-32}$ cm^{-1} s^2 amagat^{-2}.
We use the Lennard–Jones parameters (Svehla
1962), $\sigma = 3.789 \times 10^{-8}$ cm, $\varepsilon/k = 71.4$ K,
and find $\Theta^2/\sigma^5 k = 22.4$ K, $\Phi^2/\sigma^9 k = 0.4$ K
from the spectral moments $\alpha_1 = 1.037 \times 10^8$
cm^{-1} s^{-1} amagat^{-2}, $\gamma_1 = 4.78 \times 10^{-19}$ cm^{-1} s
amagat^{-2}. Using these multipole moments, and
[36] to impose a condition on the values of τ_1
and τ_2, allows only one free parameter. This we
fix by choosing values for τ_1 and τ_2 which give

the correct value for $\gamma(0)$, and in this way we ob-
tain the values $\tau_1 = 25.6 \times 10^{-14}$ s, $\tau_2 = 13.6$
$\times 10^{-14}$ s for $l = 2$. The ratio τ_2/τ_1 is 0.53 to be
compared with the value for the $S(0)$ line of H_2,
$\tau_2/\tau_1 = 0.38$. The quantum time constant, $\tau_0 = \beta\hbar/2$, is 1.27×10^{-14} s, an order of magnitude
smaller than either τ_1 or τ_2 so that the room tem-
perature collision-induced spectrum of N_2 is
essentially classical.

The experimental data and the theoretical line
shape calculated from [27b] are shown in Fig. 3.
The results are plotted in terms of the reduced
function $G(v) = \alpha(v)/[v(1 - \exp(-\beta hcv))]$ in or-
der to accentuate the translational band. Except
in the region 30–60 cm^{-1}, where the computed
curve is higher than the data by a few percent, and
in the wing, $\sigma > 200$ cm^{-1}, where our computed
curve is low, the agreement is excellent. When we
recognize that the fitting is carried out using only
three free parameters (the quadrupole and hexa-
decapole moments and the ratio τ_2/τ_1 (the prod-
uct $\tau_1\tau_2$ being fixed by molecular constants)) this
agreement verifies the validity (at least empiri-
cally) of our model correlation function.

4. Summary

A quantum theory of the absorption coefficient
for pressure-induced resonant and nonresonant
spectra has been developed. A relatively simple
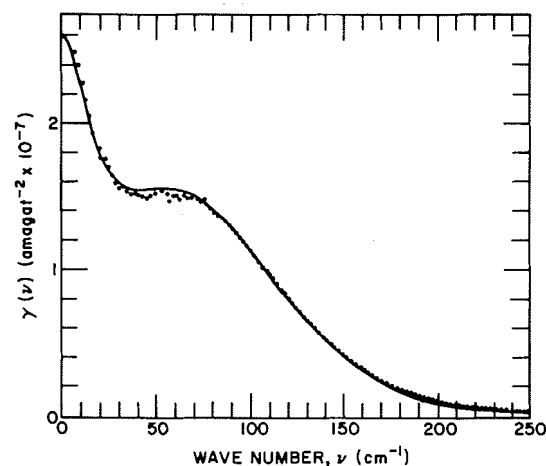analytical expression for the shape function is

FIG. 3. The translational–rotational band of N_2 at
300 K. The ordinate is the function

$$G(v) = \alpha(v)[v(1 - \exp(-\beta\hbar\omega))]^{-1}.$$

The theoretical curve is computed from [27b] using
$\Theta^2/\sigma^5 k = 22.4$ K, $\Phi^2/\sigma^7 k = 0.4$ K, $\sigma = 3.798 \times 10^{-8}$ cm,
$\varepsilon/k = 71.4$ K, $\tau_1 = 25.6 \times 10^{-14}$ s, and $\tau_2 = 13.6 \times 10^{-14}$ s.

obtained from a correlation function represented by a model satisfying certain general criteria. The model function contains two time constants whose geometric mean has the significance of a duration of collision. An equation is derived expressing this time in terms of known molecular parameters. Although the model correlation function is not unique, it is by no means arbitrary. The requirements that the model should satisfy detailed balance (which is met by the introduction of the 'Egelstaff time', y), that it should be an analytic function which admits of a power series expansion in time at the origin (and hence has a Fourier transform which approaches zero exponentially at high frequencies), and that its free parameters are constrained by relations which involve the spectral moments sharply define its character. The resulting line shape expression for translational–rotational spectra in the far infrared region accurately represents various experimental results.

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