PHYSICAL REVIEW VOLUME 160, NUMBER 1 5 AUGUST 1967

Quantum Theory of Collision-Induced Absorption in Rare-Gas Mixtures

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(Received 3 January 1967)

A theoretical calculation of the collision-induced far-infrared absorption, which has been observed in rare-gas mixtures, is carried out using the quantum-mechanical expression for the absorption coefficient. Using a simple empirical form to describe the variation of the collision-induced dipole moment with internuclear separation, and using plane-wave eigenstates (i.e., assuming straight-line collision paths), an analytic expression is obtained for the spectrum which agrees well with the experiments. Comparison with a previous classical calculation based upon the same model shows that quantum effects are small at room temperature except in the high-frequency wing of the spectrum. A number of analytic integrations allow us to derive simple expressions for the correlation function, relaxation time, static dielectric constant, and other spectral invariants.

I. INTRODUCTION

COLLISION-INDUCED far-infrared absorption in mixtures of helium-neon, helium-argon, and neon-argon was discovered by Kiss and Welsh,[1,2] who also suggested its physical origin. More recently, the interferometric experiments of Bosomworth and Gush[3] have located the peak of this absorption and measured much of the wings for both helium-argon and neon-argon mixtures, although these experimenters were unable to see the helium-neon spectrum.

Previous work on the theory of these spectra has appeared. Poll and van Kranendonk[4] gave an analytic theory for the integrated absorption, and Tanimoto[5] has carried out a numerical calculation of these spectra. More recently, Levine and Birnbaum[6] presented an analytic theory of these spectra, based upon classical radiation theory. Despite the fact that the observed spectra do not entirely satisfy the apparent criterion $\hbar\omega/kT \ll 1$ for the applicability of a classical approach, the latter authors were able to obtain good agreement with experiment.

It is of interest to see in a clear way what role quantum effects play in these spectra. To do this, it is necessary to carry out a calculation based upon the general expression for the absorption coefficient derived in quantum mechanics. Such a calculation is carried out in this paper, using the same model for the variation of the dipole moment with internuclear separation, and the same assumption of straight-line collision paths as was used by Levine and Birnbaum. It is found that the spectra can be expressed in a simple analytic form. Examination of this form then shows that quantum effects are unimportant at room temperature except in the high-frequency wing. At lower temperatures the range of frequencies over which quantum effects are unimportant diminishes, but possibly except for helium-neon mixtures below about 150°K it appears as if this range is sufficiently broad so that as a practical matter quantum effects can be ignored.

In Sec. II we derive the absorption coefficient. In Sec. III, we derive analytic expressions for several spectral invariants. In Sec. IV we discuss the evaluation of the parameters of the model. In Sec. V, we derive analytic expressions for the correlation function and relaxation time. In Sec. VI, we compare the classical and quantum spectra, and make some concluding comments. A number of mathematical details are contained in four appendices.

II. DERIVATION OF THE LINE SHAPE

An expression for the absorption coefficient may be derived from the quantum-mechanical "golden rule." It reads

$$\alpha(\omega)=\frac{4\pi^2}{\hbar cV}\sum_a\sum_b \omega_{ab}|\langle\mu_z\rangle_{ab}|^2 \times(1-e^{-\hbar\omega_{ab}/kT})P_a\delta(\omega_{ab}-\omega)\,, \qquad (2.1)$$

where V is the volume of the sample, P_a is the statistical probability that the sample is in the initial state a, $\hbar\omega_{ab}=E_b-E_a$ is the energy difference between a final state b and an initial state a, and c is the speed of light. The matrix element $\langle\mu_z\rangle_{ab}$ is for the z component (chosen arbitrarily) of the total dipole moment of the system. By a straightforward procedure, outlined in Appendix I, Eq. (2.1) may be reduced to a form which expresses $\alpha(\omega)$ in terms of transition matrix elements for two-molecule systems. For a system without bound states, or for which the equilibrium population of the bound states is small enough to be neglected, this reduction leads to

$$\alpha(\omega)=\frac{4\pi^2\omega n_An_B}{\hbar c}\left(\frac{\hbar^2}{2\pi mkT}\right)^{3/2}\int d\mathbf{k}\exp(-\beta\hbar^2k^2/2m) \times\int d\mathbf{k}'|\langle\mu_z{}^{(\mathrm{rel})}\rangle_{\mathbf{k}',\mathbf{k}}|^2(1-e^{-\beta\hbar\omega'})\delta(\omega'-\omega)\,, \qquad (2.2)$$

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[1] Z. J. Kiss and H. L. Welsh, Phys. Rev. Letters 2, 166 (1959).
[2] R. Heastie and D. H. Martin, Can. J. Phys. 40, 122 (1962).
[3] D. R. Bosomworth and H. P. Gush, Can. J. Phys. 43, 729 (1965).
[4] J. D. Poll and J. van Kranendonk, Can. J. Phys. 39, 189 (1961).
[5] O. Tanimoto, Progr. Theoret. Phys. (Kyoto) 33, 585 (1965).
[6] H. B. Levine and G. Birnbaum, Phys. Rev. 154, 86 (1967).

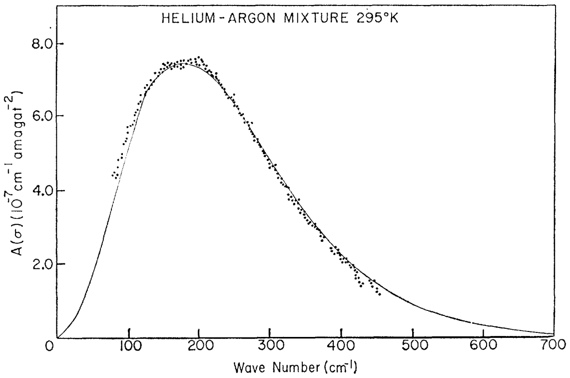

FIG. 1. Absorption coefficient for a helium-argon mixture at 295°K. Points are experimental data of Ref. 3; solid line is theoretical curve based upon Eq. (2.16) and constants of Table I.

where

$$\hbar\omega'=\frac{\hbar^2}{2m}(k'^2-k^2) \tag{2.3}$$

is the energy difference between an initial scattering state of energy $\hbar^2k^2/2m$ and a final scattering state of energy $\hbar^2k'^2/2m$, m is the reduced mass of a colliding pair, $\beta=1/kT$, and n_A, n_B are the number densities of the two species. In Eq. (2.2), the matrix elements are for the dipole moment of a pair of atoms in the relative coordinate system, and these may be written as

$$\langle\mu_z{}^{(\mathrm{rel})}\rangle_{\mathbf{k}',\mathbf{k}}=(8\pi^3)^{-1}\int\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}]\chi_{\mathbf{k}}{}^*(\mathbf{r}) \\ \times\chi_{\mathbf{k}}(\mathbf{r})\mu_z(\mathbf{r})d\mathbf{r}, \tag{2.4}$$

where $(8\pi^3)^{-1/2}\exp(i\mathbf{k}\cdot\mathbf{r})\chi_{\mathbf{k}}(\mathbf{r})$ is the scattering-state wave function in terms of the relative coordinate $\mathbf{r}$ written as a product of a δ-function normalized plane wave and a correlation part $\chi_{\mathbf{k}}(\mathbf{r})$. Equation (2.2) was used by Tanimoto[5] numerically to derive a line shape for rare-gas mixtures. He assumed exponential forms for both $\boldsymbol{\mu}(\mathbf{r})=\mu(r)\mathbf{r}/r$ and for the potential.

In the calculation which follows, we have not used exponential functions, but instead have resorted to a simple model: (1) straight-line collision paths, i.e., zero interatomic potential; and (2) a dipole function of the form $\mu(r)=\mu_0\gamma r\exp(-\gamma^2r^2)$. The reasons for this choice have been pointed out previously.[6] These include mathematical convenience, the provision of a basis from which one might judge the sensitivity of the calculation to the forms assumed for $\mu(r)$ and for the potential, and a simplicity which nonetheless contains all the important physical features. The classical theory based upon this model leads to spectra which are expressible in a simple analytic form and which are in quite good agreement with the measurements. As we shall see, this model, in the quantum case as well as in the classical case, enables us to obtain a simple analytic expression for the spectrum.

Generally speaking, the function

$$(8\pi^3)^{-1/2}\exp(i\mathbf{k}\cdot\mathbf{r})\chi_{\mathbf{k}}(\mathbf{r})$$

which appears in Eq. (2.4) is the relative coordinate wave function for a pair of colliding atoms. If the system has a nonvanishing central potential, it is natural to rewrite this in polar coordinates. However, in our model, where we take the potential to be zero, we have $\chi_{\mathbf{k}}(\mathbf{r})\equiv1$, the wave functions are plane waves, and it is more convenient to remain in Cartesian coordinates. Introducing the induced-dipole function

$$\mu_z(r)=\mu_0\gamma z\exp(-\gamma^2r^2) \tag{2.5}$$

into Eq. (2.4), the integral is elementary and we have

$$\langle\mu_z{}^{(\mathrm{rel})}\rangle_{\mathbf{k}',\mathbf{k}}=-\frac{i\mu_0}{16\pi^{3/2}\gamma^4}(k_z-k_z')^2 \\ \times\exp\left\{-\frac{(\mathbf{k}-\mathbf{k}')^2}{4\gamma^2}\right\}. \tag{2.6}$$

Then, replacing $|\langle\mu_z{}^{(\mathrm{rel})}\rangle_{\mathbf{k}',\mathbf{k}}|^2$ in Eq. (2.6) by

$$\tfrac{1}{3}\{|\langle\mu_x{}^{(\mathrm{rel})}\rangle_{\mathbf{k}',\mathbf{k}}|^2+|\langle\mu_y{}^{(\mathrm{rel})}\rangle_{\mathbf{k}',\mathbf{k}}|^2+|\langle\mu_z{}^{(\mathrm{rel})}\rangle_{\mathbf{k}',\mathbf{k}}|^2\},$$

which is clearly equivalent, we see that we can write

$$\sum_{\mathbf{k}'}|\langle\mu_z{}^{(\mathrm{rel})}\rangle_{\mathbf{k}',\mathbf{k}}|^2\delta(\omega'-\omega) \\ =-\frac{\mu_0{}^2}{768\gamma^8\pi^3}\frac{\partial}{\partial q}\int e^{-q(k^2-2\mathbf{k}\cdot\mathbf{k}'+k'^2)}\delta(\omega'-\omega)d\mathbf{k}', \tag{2.7}$$

where

$$q\equiv(2\gamma^2)^{-1}. \tag{2.8}$$

Fixing the direction of $\mathbf{k}$ and writing $\mathbf{k}'$ in polar form, the integral in Eq. (2.7) is elementary:

$$\int e^{-q(k^2-2\mathbf{k}\cdot\mathbf{k}'+k'^2)}\delta(\omega'-\omega)d\mathbf{k}' \\ =\frac{m\pi}{\hbar qk}[e^{-q(v-k)^2}-e^{-q(v+k)^2}], \tag{2.9}$$

where

$$v\equiv v(k)=\left(k^2+\frac{2m\omega}{\hbar}\right)^{1/2}. \tag{2.10}$$

Differentiating the right side of Eq. (2.9) with respect to q, as required by Eq. (2.7), and combining these results with Eq. (2.2), we obtain

$$\alpha(\omega)=\frac{\pi\omega n_An_B\mu_0{}^2m}{12\hbar^2c\gamma^4}\left(\frac{\hbar^2}{2\pi mkT}\right)^{3/2}(1-e^{-\hbar\omega/kT})U(\omega), \tag{2.11}$$

where

$$U(\omega)=\int_0^\infty kdk\,e^{-\epsilon^2k^2}\{[1+q(v-k)^2]e^{-q(v-k)^2} \\ -[1+q(v+k)^2]e^{-q(v+k)^2}\}, \tag{2.12}$$

with $\epsilon^2 = \beta\hbar^2/2m$. In Appendix II, we show that

$$U(\omega) = \frac{[\exp(\frac{1}{2}\beta\hbar\omega)]x^2 K_2[x(1+\theta^2)^{1/2}]}{4\epsilon^2(1+\theta^2)}, \qquad (2.13)$$

where

$$x = (\omega/\gamma)(\beta m)^{1/2} \qquad (2.14)$$

is the dimensionless frequency variable of the classical theory, K_2 is a modified Bessel function of the second kind, and

$$\theta = \tfrac{1}{2}\gamma\hbar(\beta/m)^{1/2} \qquad (2.15)$$

is the correction factor for quantum effects. It should be observed that θ is proportional to the ratio of the thermal de Broglie wavelength to the range of the dipole moment, and expresses the dynamical effects of quantum mechanics. Combining Eqs. (2.11) and (2.13), we have

$$\alpha(\omega) = \frac{\mu_0^2 \pi^3 n_A n_B}{6\hbar c\gamma^3}\left(\frac{2}{\pi}\right)^{1/2} \times \sinh\left(\frac{\hbar\omega}{2kT}\right)\frac{x^3 K_2[x(1+\theta^2)^{1/2}]}{1+\theta^2}. \qquad (2.16)$$

In the limit $\hbar \to 0$, this reduces to the classical result[6]

$$\alpha(\omega) \to \alpha_0(\omega) = \frac{\mu_0^2 \pi^3 n_A n_B}{12 c\gamma^2}\left(\frac{2}{\pi m k T}\right)^{1/2} x^4 K_2(x). \qquad (2.17)$$

III. INTEGRALS OF THE ABSORPTION SPECTRUM

Before proceeding with a discussion of the spectrum, Eq. (2.16), it is convenient to write down some integrals of the absorption coefficient, as we did in the classical analysis.[6] It proves possible to obtain these integrals in terms of elementary functions, although the mathematics is somewhat more difficult than in the classical case. We consider the Kramers-Kronig transform

$$\epsilon'(0) - 1 = \frac{2c}{\pi}\int_0^\infty \frac{\alpha(\omega)d\omega}{\omega^2}, \qquad (3.1)$$

and in addition the first two moments of this transform,

$$\beta_1 \equiv c\int_0^\infty \frac{\alpha(\omega)d\omega}{\omega}, \qquad (3.2)$$

and

$$\beta_2 \equiv \frac{1}{2\pi}\int_0^\infty \alpha(\omega)d\omega. \qquad (3.3)$$

The coefficients on the right sides of Eqs. (3.2) and (3.3) have been chosen to conform with definitions used by Poll and van Kranendonk[4] in their work on integrated absorption. In Appendix III, we show that the following hold:

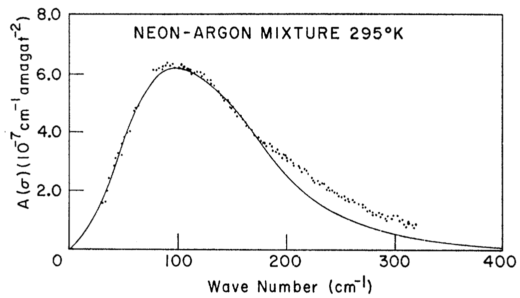

FIG. 2. Absorption coefficient for a neon-argon mixture at 295°K. Points are experimental data of Ref. 3; solid line is theoretical curve based upon Eq. (2.16) and constants of Table I.

$$\epsilon'(0) - 1 = \frac{\mu_0^2 \pi^2 n_A n_B}{2\gamma^3 kT}\left(\frac{\pi}{2}\right)^{1/2} F_0(\theta), \qquad (3.4)$$

$$\beta_1 = \frac{4\mu_0^2 \pi^2 n_A n_B}{3\gamma^2}\left(\frac{\pi}{2mkT}\right)^{1/2} F_1(\theta), \qquad (3.5)$$

and

$$\beta_2 = \frac{5\mu_0^2 \pi^2 n_A n_B}{8\gamma m c}\left(\frac{\pi}{2}\right)^{1/2} F_2(\theta), \qquad (3.6)$$

where

$$F_0(\theta) = (1+\tfrac{1}{3}\theta^2)(1+\theta^2)^{-2}, \qquad (3.7)$$

$$F_1(\theta) = \tfrac{1}{8}[(5+4\theta^2)(1+\theta^2)^{-2} + 3\theta^{-1}\tan^{-1}\theta], \qquad (3.8)$$

and

$$F_2(\theta) = (1+\theta^2)^{1/2} \qquad (3.9)$$

are the quantum correction factors.

IV. EVALUATION OF PARAMETERS

As was done in the classical analysis,[6] we have determined the parameters μ_0 and γ for He-Ar and Ne-Ar by fitting the theoretical expression, Eq. (2.16), to the height and frequency of the experimental peaks observed by Bosomworth and Gush.[3] For He-Ne, the

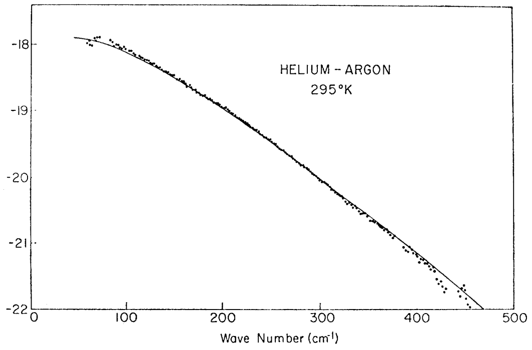

FIG. 3. Initial-state averaged transition probability for a helium-argon mixture at 295°K. Points are experimental data of Ref. 3; solid line is theoretical curve based upon Eq. (2.16) and constants of Table I.

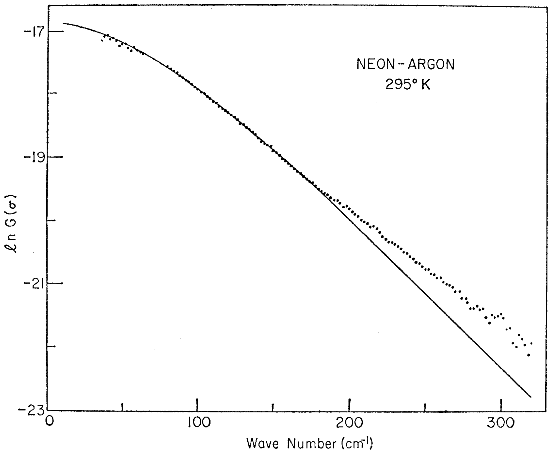

FIG. 4. Initial-state averaged transition probability for a neon-argon mixture at 295°K. Points are experimental data of Ref. 3; solid line is theoretical curve based upon Eq. (2.16) and constants of Table I.

determination of parameters is more difficult because the only available data are those for the high-frequency wing of the spectrum, as seen by Kiss and Welsh.[1] Figures 1 and 2 show $A(\sigma)=\alpha(\sigma)(n_Bn_A)^{-1}(N_0/V_0)^2$ (N_0= Avogadro's number, $V_0=22413.6$ cm^3; $\sigma=\omega/2\pi c$) for He-Ar and Ne-Ar, respectively. Figures 3 and 4 show the quantity $G(\sigma)=\sigma^{-1}A(\sigma)[1-\exp(-hc\sigma/kT)]^{-1}$, which falls off exponentially with σ, as observed by Bosomworth and Gush.[3] Figure 5 shows $A(\sigma)$ for He-Ne, with the parameters chosen to fit the experimental data at two points: 500 cm^{-1} and 575 cm^{-1}. As was discussed previously,[6] the data below 475 cm^{-1} are probably not reliable; above 575 cm^{-1}, the absorption has become so weak that the accuracy of the data prohibits a very meaningful fit. The derived parameters, and hence the over-all spectrum, for He-Ne, is therefore to be thought of as only roughly correct. In Table I, we list the parameter values we have obtained from the quantum line-shape formula Eq. (2.16). We also give the values obtained previously using the classical formula, Eq. (2.17). The small differences between these values indicate the relative unimportance of the quantum effects at the temperature of the experiments. This will be discussed further in Sec. VI.

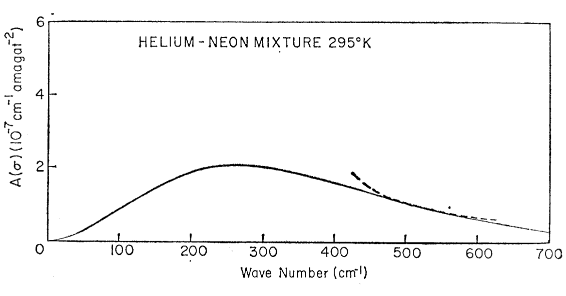

FIG. 5. Absorption coefficient of a helium-neon mixture at 295°K. Dashed line is experimental data of Ref. 1; solid line is theoretical curve based upon Eq. (2.16) and constants of Table I.

TABLE I. Dipole moment parameters (γ in Å^{-1}; μ_0 in debyes).

Formula used		He-Ne	He-Ar	Ne-Ar
$\alpha(\omega)$ [Eq. (2.16)]	γ	1.870	1.338	1.443
	μ_0	0.121	0.166	0.223
$\alpha_0(\omega)$ [Eq. (2.17)]	γ	1.920	1.357	1.446
	μ_0	0.121	0.166	0.223

V. CORRELATION FUNCTION AND RELAXATION TIME

According to the theory of Kubo,[7] the imaginary part of the complex dielectric constant $\epsilon=\epsilon'-i\epsilon''$ is given by

$$\epsilon''(\omega)=\frac{1}{2\hbar}\tanh\left(\frac{\hbar\omega}{2kT}\right)\times\int_{-\infty}^{\infty}\cos\omega t\langle\mathbf{P}(0)\cdot\mathbf{P}(t)+\mathbf{P}(t)\cdot\mathbf{P}(0)\rangle, \quad (5.1)$$

where $\langle\ \rangle$ denotes a Boltzmann average and $\mathbf{P}(t)$ is the Heisenberg representation of the total moment of the system. Combining this equation with our expression, Eq. (2.16), for the absorption coefficient, and using the relation $\epsilon''(\omega)=c\alpha(\omega)/\omega$, we can obtain the correlation function $B(t)\equiv\frac{1}{2}\langle\mathbf{P}(0)\cdot\mathbf{P}(t)+\mathbf{P}(t)\cdot\mathbf{P}(0)\rangle$ by a Fourier inversion:

$$B(t)=\frac{\mu_0^2\pi n_An_B}{6\gamma^4(1+\theta^2)}\left(\frac{2\pi m}{kT}\right)^{1/2}\times\int_0^{\infty}\cosh\left(\frac{\hbar\omega}{2kT}\right)x^2K_2[x(1+\theta^2)^{1/2}]\cos\omega t d\omega, \quad (5.2)$$

where x is given by Eq. (2.14). Since $K_2(y)$ is asymptotic to $(\pi/2y)^{1/2}\exp(-y)$ at large y, the integral in Eq. (5.2) is always convergent. It is evaluated in Appendix IV, where we obtain

$$B(t)=\frac{\mu_0^2n_An_B}{32\gamma^8}\left(\frac{2\pi m}{kT}\right)^{5/2}\times\{(C^2+t^2+2iCt\theta)^{-5/2}+(C^2+t^2-2iCt\theta)^{-5/2}\}, \quad (5.3)$$

with

$$C=\gamma^{-1}(m/kT)^{1/2}. \quad (5.4)$$

This function behaves like a Gaussian at small times and falls off as t^{-5} at long times. We have previously derived the classical limit of this function.[6] Because of the excellent agreement between the theoretical and computed spectra, the correlation function at 295°K is for all practical purposes a Fourier inversion of the experimental spectrum, and hence is the true correlation function for He-Ar. In Appendix IV, we also derive

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[7] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).

the relaxation time, defined by

$$\tau = \int_0^\infty B(t)dt/B(0), \tag{5.5}$$

and find

$$\tau = (2/3\gamma)\left(\frac{m}{kT}\right)^{1/2} \frac{1}{(1+\theta^2)^2}. \tag{5.6}$$

This result goes over to the previously derived classical result[6] as $\hbar \rightarrow 0$. Equation (5.6) shows that the effect of quantum mechanics is to reduce the relaxation time, which is to be expected since the spreading of wave packets clearly must speed up the washing out of correlations.

VI. CONCLUSIONS

The spectra computed above are in good agreement with the experimental results. This is not surprising, since a previous classical calculation using the same model also was in good agreement with the experiments, and the additional refinement of quantum mechanics should only serve to improve the situation. Of greater interest is the relation between the theoretical classical and quantum expressions for a fixed set of parameters, since such a comparison serves to delineate the importance, or lack thereof, of quantum-mechanical effects in determining the character of this spectrum.

Whatever comparisons we make, of course, are between the two theoretical spectra, Eqs. (2.16) and (2.17), and are therefore not independent of our model. Calculations based upon a more precise model would lead to differences between classical and quantum spectra somewhat different than we will find here. This is particularly true when we consider the temperature dependence of our spectra, since the parameters we have used can only be optimum at 295°K, the temperature at which they were fit to experimental data. Nevertheless, the relative behavior of $\alpha(\omega)$ [Eq. (2.16)] and $\alpha_0(\omega)$ [Eq. (2.17)] should be fairly independent of the model, and least provide a good general idea of the importance of quantum effects. Ideally, we should directly compare the analytic forms of the spectra, Eqs. (2.16) and (2.17). However, because of the transcendental nature of the Bessel function, it is somewhat simpler to compare numerical calculations of the spectra at various temperatures.

As shown in Table I, fitting the two theoretical expressions, Eqs. (2.16) and (2.17), to the experimental data yields nearly identical parameters for the dipole moment. The small differences are an indication, for He-Ar and Ne-Ar, that quantum effects are unimportant at the peak frequency at $T = 295$°K. For He-Ne, where the fit was made at 500 cm^{-1} and 575 cm^{-1}, the results indicate that the quantum effects are still small at about twice the computed peak frequency, although this statement is less firm in view of the uncertainty in the experimental data. To obtain a better idea of the importance of quantum effects over the entire frequency range, we have in Figs. 6, 7, and 8 plotted spectra at $T = 295$°K using both Eqs. (2.16) and (2.17), but now with a single set of parameters common to both curves in each of these figures. The small difference over the bulk of the strong absorption region is striking. The scale of these figures does not allow a comparison in the high-frequency wing. We therefore show in Figs. 9, 10, and 11 a plot of the ratio $\alpha(\sigma)/\alpha_0(\sigma)$ of the spectra at 295°K computed by the two formulas versus wave number $\sigma = \omega/2\pi c$. We see that as $\sigma \rightarrow 0$, this ratio is <1, and in fact from Eqs. (2.16) and (2.17) it is easy to show that

$$\lim_{\sigma \to 0} [\alpha(\sigma)/\alpha_0(\sigma)] = (1+\theta^2)^{-2} < 1 \tag{6.1}$$

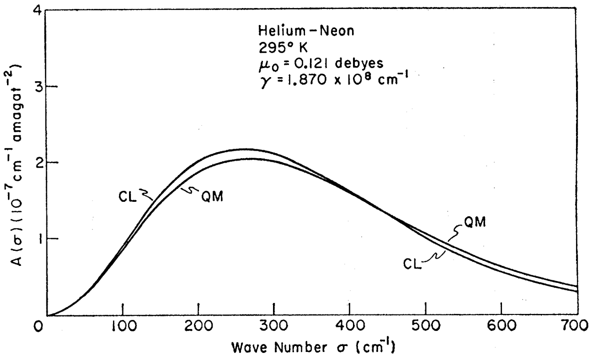

FIG. 6. Theoretical absorption coefficients for a helium-neon mixture at 295°K. The curve labeled QM is based upon Eq. (2.16); the curve labeled CL is based upon Eq. (2.17).

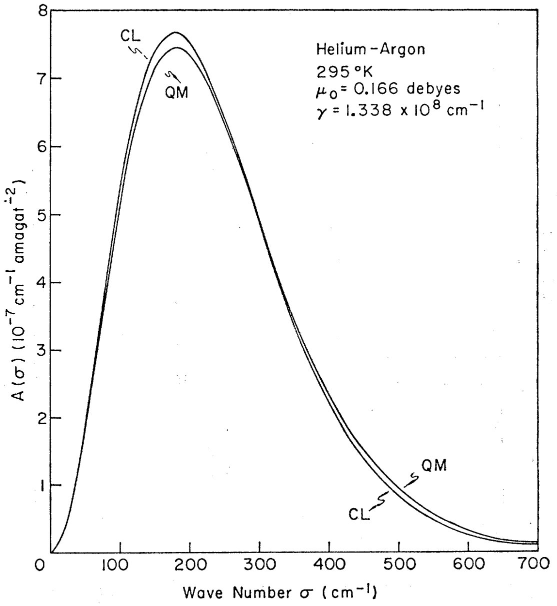

FIG. 7. Theoretical absorption coefficients for a helium-argon mixture at 295°K. The curve labeled QM is based upon Eq. (2.16); the curve labeled CL is based upon Eq. (2.17).

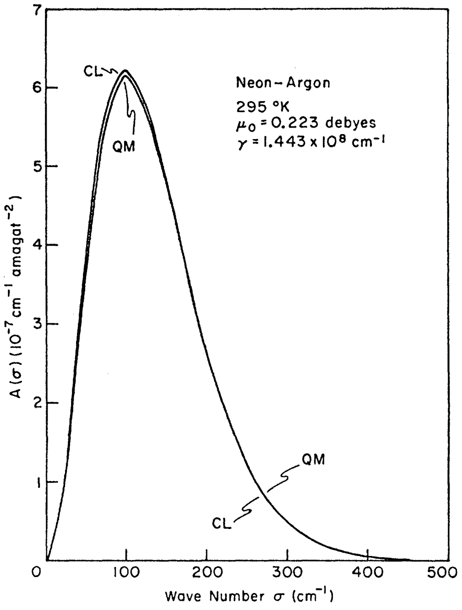

FIG. 8. Theoretical absorption coefficients for a neon-argon mixture at 295°K. The curve labeled QM is based upon Eq. (2.16); the curve labeled CL is based upon Eq. (2.17).

for all temperatures. The ratio then decreases through a shallow minimum, after which it increases monotonically, passing through unity and ultimately diverging exponentially to infinity. The latter divergence also can be seen by using the asymptotic representation of the Bessel function,[8] which leads to

$$(\alpha(\sigma)/\alpha_0(\sigma)) \xrightarrow[\sigma\to\infty]{} \frac{\exp\{x[1+\theta-(1+\theta^2)^{1/2}]\}}{2x\theta(1+\theta^2)^{5/4}}, \qquad (6.2)$$

with the dimensionless frequency variable x given by Eq. (2.14). A similar situation occurs at other temperatures, and in Figs. 9, 10, and 11 we also show $\alpha(\sigma)/\alpha_0(\sigma)$ versus σ at $T=75°$, $150°$, and $600°$K. Examination of these three figures shows that quantum mechanics affects the intensity the most at very low and at very high frequencies, and less at intermediate frequencies. On the other hand, the range of frequencies over which this effect is small diminishes with decreasing temperature, as is to be expected.

In addition to the relative intensity changes, other parameters of interest include peak frequency, and the integrals $\epsilon'(0)-1$, β_1, and β_2 formulated in Sec. III. The latter are readily evaluated from the formulas in Sec. III. In Table II, we give values of the quantum correction factors $F_0(\theta)$, $F_1(\theta)$, and $F_2(\theta)$, which measure the ratio of the quantum to the classical values for $\epsilon'(0)-1$, β_1, and β_2, respectively.

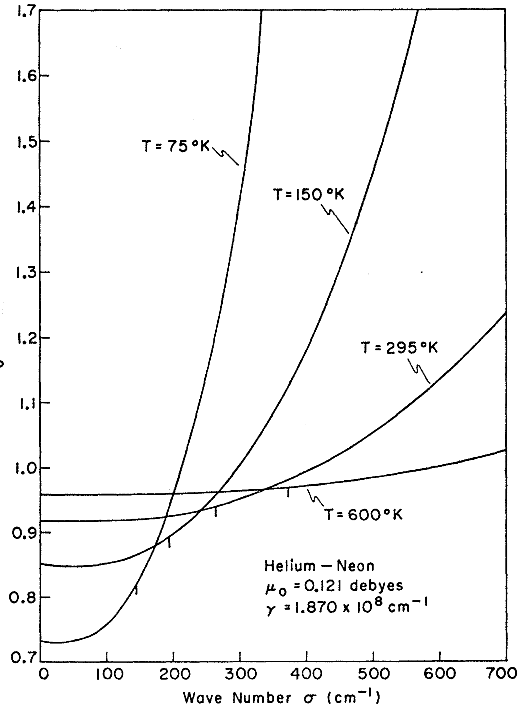

FIG. 9. Ratio of the theoretical absorption coefficients $\alpha(\sigma)$ computed by Eq. (2.16) to the theoretical absorption coefficient $\alpha_0(\sigma)$ computed by Eq. (2.17) versus wave number σ for a helium-neon mixture at various temperatures. The vertical mark on each curve indicates the peak frequency for that temperature.

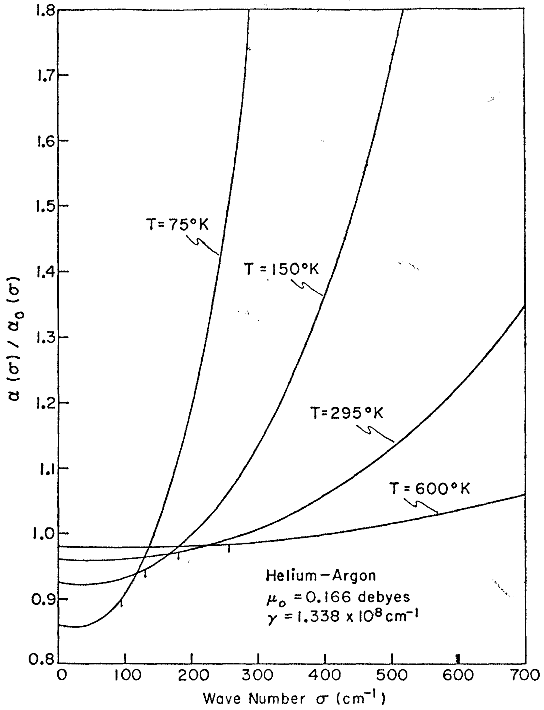

FIG. 10. Ratio of the theoretical absorption coefficient $\alpha(\sigma)$ computed by Eq. (2.16) to the theoretical absorption coefficient $\alpha_0(\sigma)$ computed by Eq. (2.17) versus wave number σ for a helium-argon mixture at various temperatures. The vertical mark on each curve indicates the peak frequency for that temperature.

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[8] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Department of Commerce, National Bureau of Standards, Washington, D.C., 1964), pp. 376–8.

The values in the table show a striking insensitivity to quantum effects at temperatures as low as ≅100°K, particularly for $F_2(\theta)$, the correction factor for β_2. The latter insensitivity is related to the observation of Poll and Van Kranendonk[4] that this integral depends upon quantum effects only via the pair distribution function. At $T\cong 100$°K, the temperature is not yet low enough that diffractive effects of quantum mechanics upon scattering can significantly alter the pair distribution function for rare-gas mixtures.

The peak frequency can be obtained numerically, or via the solution of a transcendental equation. The latter may be expressed as an expansion in powers of θ, which can be shown to be of the form

$$x_0=3.046\{1+0.6362\theta^2+O(\theta^4)\}, \tag{6.3}$$

where $x_0=\omega_0\gamma^{-1}(m/kT)^{1/2}$ is the value of the dimensionless frequency variable x at the peak frequency ω_0. The coefficients in Eq. (6.3) are related to the numerical solution of an equation involving Bessel functions. From Eq. (6.3) we see that quantum mechanics shifts the peak frequency upward, the fractional change approximately being given by $2\theta^2/3$. A 5% shift will thus occur when $\theta\cong(3/40)^{1/2}\cong 0.27$. From Table II, we see that this occurs at $T\cong 100$°K for He-Ar and Ne-Ar, and perhaps at $T\cong 150$°K for He-Ne.

In Fig. 12 we show the correlation function $B(t)/B(0)$ versus reduced time $2t/3\tau_0$, where $\tau_0=\frac{2}{3}\gamma^{-1}(m/kT)^{1/2}$ is the relaxation time in the classical approximation. The curves use the values of θ for He-Ar given in Table II at $T=75$°K, 150°K, 295°K, and 600°K. The curve labeled $\theta=0$ is the classical approximation to the correlation function, and is independent of temperature when plotted versus the reduced time $2t/3\tau_0$. The curves show that the primary effect of quantum mechanics is to introduce a small effective reduction in the relaxation time, as indicated also by Eq. (5.7).

We shall not attempt to analyze other parameters of the spectrum. They can in all cases be studied numerically from Eqs. (2.16) and (2.17), both of which are easy to evaluate. The general conclusion of this analysis is that down to temperatures of the order of 100°K, or perhaps slightly higher for He-Ne (provided the He-Ne parameters of Table I are reasonably accurate), quantum mechanics plays a small role in determining these spectra, except well out in the high-frequency wing. This wing, however, is less readily observable

TABLE II. Quantum correction factors as functions of $\theta\equiv\frac{1}{2}\gamma\hbar\times(\beta/m)^{1/2}$ for various temperatures T and pairs of gases.

T (°K)	Pair	θ	$F_0(\theta)$	$F_1(\theta)$	$F_2(\theta)$
75	He-Ne	0.410	0.774	0.876	1.081
	He-Ar	0.282	0.881	0.934	1.039
	Ne-Ar	0.158	0.960	0.979	1.012
150	He-Ne	0.290	0.875	0.931	1.041
	He-Ar	0.199	0.937	0.968	1.020
	Ne-Ar	0.112	0.979	0.990	1.006
295	He-Ne	0.207	0.933	0.964	1.021
	He-Ar	0.142	0.967	0.983	1.010
	Ne-Ar	0.0799	0.990	0.995	1.003
600	He-Ne	0.145	0.966	0.983	1.010
	He-Ar	0.0996	0.984	0.991	1.005
	Ne-Ar	0.0560	0.995	0.998	1.002

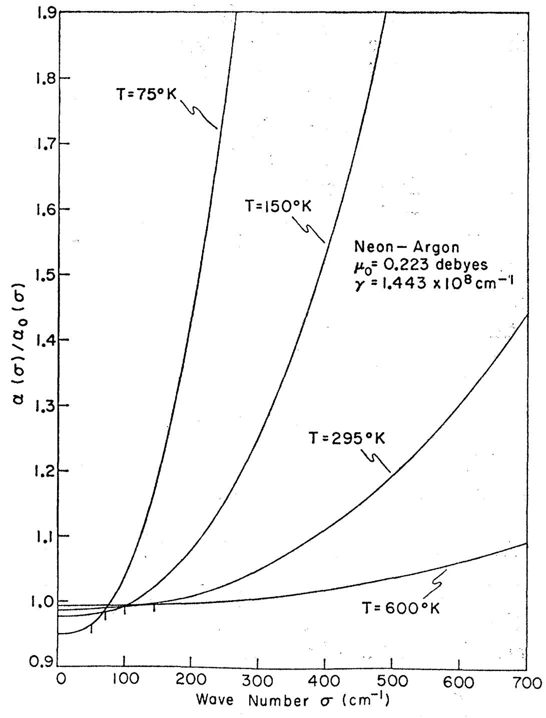

FIG. 11. Ratio of the theoretical absorption coefficient $\alpha(\sigma)$ computed by Eq. (2.16) to the theoretical absorption coefficient $\alpha_0(\sigma)$ computed by Eq. (2.17) versus wave number σ for a neon-argon mixture at various temperatures. The vertical mark on each curve indicates the peak frequency for that temperature.

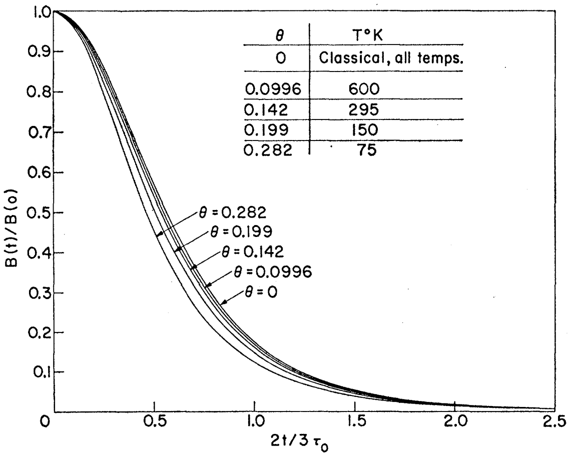

FIG. 12. The reduced correlation function for a helium-argon mixture at various temperatures versus reduced time. The $\theta=0$ curve is the classical result for all temperatures, the classical temperature dependence being contained entirely in the reduction factor for the time.

experimentally since the intensity falls off exponentially. It should also be pointed out that the condensation temperature of Ar being about 87°K, the observation of these spectra in the gas phase below about 100°K is likely to be possible only for He-Ne. Thus, we can conclude as follows: With the possible exception of He-Ne below about 150°K, the use of collision-induced absorption spectra to characterize parameters for the dipole moment, or possibly the interaction potential in more refined calculations, will be satisfactory if done by classical theory, correlated with experimental data at or near the peak intensity, for all temperatures and gas mixtures.

ACKNOWLEDGMENT

I wish to express my appreciation to Dr. George Birnbaum for many valuable discussions.

APPENDIX I: DERIVATION OF EQ. (2.2)

We introduce the Born-Oppenheimer approximation for the wave functions, in terms of which the matrix element in Eq. (2.1) becomes

$$\langle\mu_z\rangle_{ab}=\int\Psi_b^*(\mathbf{R}_1,\cdots,\mathbf{R}_N)\mu_z(\mathbf{R}_1,\cdots,\mathbf{R}_N)\times\Psi_a(\mathbf{R}_1,\cdots,\mathbf{R}_N)d\mathbf{R}_1\cdots d\mathbf{R}_N,\quad(\text{A1.1})$$

where $\mu_z(\mathbf{R}_1,\cdots,\mathbf{R}_N)$ is the total dipole moment of the system expressed as a function of the nuclear positions $\mathbf{R}_1,\cdots,\mathbf{R}_N$, and the Ψ's are wave functions for the nuclear motion. This is the starting point for many analyses of collision induced absorption, including quite general virial expansions.[4,9] In the present paper, only the simplest approach is necessary. Thus, for the dipole moment, we write

$$\mu_z(\mathbf{R}_1,\cdots,\mathbf{R}_N)=\sum_{i=1}^{N_A}\sum_{j=1}^{N_B}\mu_z(\mathbf{R}_{ij}),\quad(\text{A1.2})$$

to indicate that (to the approximation we require) the dipole moment in a rare-gas mixture arises from binary collisions between unlike atoms. We assume N_A atoms of type A and N_B atoms of type B in the volume V. No terms involving like atoms are included, since such binary collisions do not give rise to a dipole moment, and ternary and higher-order terms are omitted, because the experiments have not been done at densities high enough to show ternary absorption. For the wave functions, we write

$$\Psi_a(\mathbf{R}_1,\cdots,\mathbf{R}_N)=\prod_{i=1}^{N_A}\phi_i(\mathbf{R}_i)\prod_{j=1}^{N_B}\phi_j(\mathbf{R}_j)\times\{1+\sum_{i=1}^{N_A}\sum_{j=1}^{N_B}[\chi_{ij}(\mathbf{R}_{ij})-1]\},\quad(\text{A1.3})$$

where the ϕ's are normalized free-particle wave functions

$$\phi_i(\mathbf{R})=V^{-1/2}\exp(i\mathbf{k}_i\cdot\mathbf{R}),\quad(\text{A1.4})$$

with $\mathbf{k}_i$ chosen to satisfy periodic boundary conditions in the volume V, and $\chi_{ij}(\mathbf{R}_{ij})$ is the part of the wave function expressing the correlation between particles i and j. This correlation part depends in general upon the wave vectors $\mathbf{k}_i$ and $\mathbf{k}_j$, but we suppress this dependence in the notation for the sake of brevity. It is clear that $\chi_{ij}(\mathbf{R}_{ij})\rightarrow 1$ as $\mathbf{R}_{ij}\rightarrow\infty$, the range of χ_{ij} being determined by the intermolecular potential. The wave function (A1.3) is not the most general one possible, but it is sufficient to account for all binary effects due to collisions of unlike atoms. Also, we have not symmetrized or antisymmetrized the wave function, because symmetry properties can play no role in a theory of an effect due to collisions between unlike atoms. This wave function is not normalized to unity, but to $O(N_AN_B)$ renormalization would not change the absorption coefficient.

If we combine Eqs. (A1.2), (A1.3), and (A1.4), then to $O(N_AN_B)$, $\langle\mu_z\rangle_{ab}$ reduces to a double sum of terms of the form

$$\langle\mu_z\rangle_{ab}=\sum_{i=1}^{N_A}\sum_{j=1}^{N_B}\langle\mu_z^{(2)}\rangle_{iji'j'}\times[\prod_{m=1\,(m\neq i)}^{N_A}\delta^3(\mathbf{k}_m-\mathbf{k}_m')\prod_{n=1\,(n\neq j)}^{N_B}\delta^3(\mathbf{k}_n-\mathbf{k}_n')],\quad(\text{A1.5})$$

where $\langle\mu_z^{(2)}\rangle_{iji'j'}$ is a matrix element for a transition between two states for a pair of particles, and the δ functions arise from the orthogonality of the free-particle eigenstates (A1.4) with differing wave vectors. The matrix element $\langle\mu_z^{(2)}\rangle_{iji'j'}$ is given by

$$\langle\mu_z^{(2)}\rangle_{i'j'ij}=\int\phi_{i'}^*(\mathbf{R}_1)\phi_{j'}^*(\mathbf{R}_2)\chi_{i'j'}^*(\mathbf{R}_{12})\mu_z(\mathbf{R}_{12})\times\phi_i(\mathbf{R}_1)\phi_j(\mathbf{R}_2)\chi_{ij}(\mathbf{R}_{12})d\mathbf{R}_1d\mathbf{R}_2.\quad(\text{A1.6})$$

In Eqs. (A1.5) and (A1.6), we have used primed indices to indicate eigenvalues and wave vectors in the final state, and unprimed indices to indicate eigenvalues and wave vectors in the initial state.

Following Eq. (2.1), we must square the sum in Eq. (A1.5). When this is done, three classes of terms arise:

(1) Two-particle terms

$$\sum_{i=1}^{N_A}\sum_{j=1}^{N_B}|\langle\mu_z^{(2)}\rangle_{i'j'ij}|^2\times[\prod_{m=1\,(m\neq i)}^{N_A}\delta^3(\mathbf{k}_m-\mathbf{k}_m')\prod_{n=1\,(n\neq j)}^{N_B}\delta^3(\mathbf{k}_n-\mathbf{k}_n')]^2.\quad(\text{A1.7})$$

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[9] J. van Kranendonk, Physica **23**, 825 (1957); **24**, 347 (1958); **25**, 337 (1959).

(2) Three-particle terms, the number of which is $O(N_A{}^2N_B)+O(N_AN_B{}^2)$.

(3) Four-particle terms, the number of which is $O(N_A{}^2N_B{}^2)$.

We do not write out the type (2) and (3) terms explicitly here, since they do not contribute to binary absorption.

The type (1) term, Eq. (A1.7), is a sum of N_AN_B terms, each of which contributes identically to the absorption. We therefore take one such term ($i=1, j=2$), multiply it by N_AN_B, and obtain

$$|\langle\mu_z\rangle_{if}|^2 = N_AN_B\Big[\prod_{m=2}^{N_A}\prod_{n=1\,(n\neq2)}^{N_B}\delta^3(\mathbf{k}_m-\mathbf{k}_m{}')\delta^3(\mathbf{k}_n-\mathbf{k}_n{}')\Big] \times\langle\mu_z{}^{(2)}\rangle_{1'2'12}{}^2. \quad \text{(A1.8)}$$

Going over to relative and center-of-mass coordinates, we can write

$$\langle\mu_z{}^{(2)}\rangle_{1'2'12}=\delta^3(\mathbf{k}_1{}'+\mathbf{k}_2{}'-\mathbf{k}_1-\mathbf{k}_2)\langle\mu_z{}^{(\mathrm{rel})}\rangle_{\mathbf{k}',\mathbf{k}}, \quad \text{(A1.9)}$$

where

$$\langle\mu_z{}^{(\mathrm{rel})}\rangle_{\mathbf{k}',\mathbf{k}}=V^{-1}\int\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}] \times\chi_{\mathbf{k}'}{}^*(\mathbf{r})\chi_{\mathbf{k}}(\mathbf{r})\mu_z(\mathbf{r})d\mathbf{r} \quad (\mathbf{r}\equiv\mathbf{r}_{12}) \quad \text{(A1.10)}$$

is the matrix element of the dipole moment of a pair of atoms between states of the relative-coordinate Hamiltonian. Finally, the summation over the center-of-mass velocity distribution and the δ function of Eq. (A1.9) can be ignored, since this amounts to taking the center of mass of each colliding pair as stationary. Inasmuch as the only effect of center-of-mass motion is to give rise to an extremely small Doppler broadening at thermal velocities, the error introduced in this step is negligible. We then obtain

$$\alpha(\omega)=\frac{4\pi^2\omega n_An_B}{\hbar c}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\sum_{\mathbf{k}}\exp\left(-\frac{\beta\hbar^2k^2}{2m}\right) \times\sum_{\mathbf{k}'}|\langle\mu_z{}^{(\mathrm{rel})}\rangle_{\mathbf{k}',\mathbf{k}}|^2(1-e^{-\hbar\omega'/kT})\delta(\omega'-\omega), \quad \text{(A1.11)}$$

where ω' is given by Eq. (2.3). Finally, we can replace the summations of Eq. (A1.11) by integrals, if in the definition of the matrix element, Eq. (A1.10), we replace the plane-wave states Eq. (A1.4) by δ-function normalized states[10] $(8\pi^3)^{-1/2}\exp(i\mathbf{k}\cdot\mathbf{r})$. The result of this step is Eq. (2.2).

APPENDIX II: EVALUATION OF $U(\omega)$

In this appendix, we evaluate the integral $U(\omega)$ in Eq. (2.12). We write

$$U=U_1-U_2, \quad \text{(A2.1)}$$

where

$$U_1=\int_0^\infty dk\, k[1+q(v-k)^2] \times\exp[-\epsilon^2k^2-q(v-k)^2], \quad \text{(A2.2)}$$

$$U_2=\int_0^\infty dk\, k[1+q(v+k)^2] \times\exp[-\epsilon^2k^2-q(v+k)^2], \quad \text{(A2.3)}$$

and $v\equiv v(k)$ is defined by Eq. (2.10).

In Eq. (A2.2), we introduce as a new variable $t=k+v(k)$, which leads to

$$U_1=\frac{1}{4}\int_p^\infty\frac{(t^2+p^2)(t^2-p^2)(1+qt^2)}{t^3} \times\exp\left[-(q+\tfrac{1}{4}\epsilon^2)t^2+\frac{\epsilon^2p^2}{4}-\frac{\epsilon^2p^4}{4t^2}\right]dt, \quad \text{(A2.4)}$$

where

$$p^2=2m\omega/\hbar. \quad \text{(A2.5)}$$

In Eq. (A2.3), we introduce as a new variable

$$t=-k+v(k),$$

which leads to

$$U_2=\frac{1}{4}\int_0^p\frac{(t^2+p^2)(p^2-t^2)(1+qt^2)}{t^3} \times\exp\left[-(q+\tfrac{1}{4}\epsilon^2)t^2+\tfrac{1}{4}\epsilon^2p^2-\frac{\epsilon^2p^4}{4t^2}\right]dt, \quad \text{(A2.6)}$$

with p again given by Eq. (A2.5). Combining Eqs. (A2.4) and (A2.6) gives

$$U=\frac{1}{4}\int_0^\infty\frac{(p^4-t^4)(1+qt^2)}{t^3} \times\exp\{-(q+\tfrac{1}{4}\epsilon^2)t^2+\tfrac{1}{2}\gamma^2p^4-\gamma^2p^4/4t^2\}dt$$

$$=\tfrac{1}{8}\exp(\tfrac{1}{2}\gamma^2p^2)\int_0^\infty\left(\frac{p^4}{u^2}+\frac{qp^4}{u}-1-qu\right) \times\exp\left(-Au-\frac{B}{u}\right)du, \quad \text{(A2.7)}$$

where

$$A=q+\tfrac{1}{4}\gamma^2, \quad \text{(A2.8)}$$

and

$$B=\tfrac{1}{4}\gamma^2p^4. \quad \text{(A2.9)}$$

Starting with the formula[11]

$$\int_0^\infty e^{-(Au+B/u)}\frac{du}{u}=2K_0(2A^{1/2}B^{1/2}), \quad \text{(A2.10)}$$

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[10] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, New York, 1949), p. 51.

[11] W. Grobner and N. Hofreiter, *Integraltafel* (Springer-Verlag, Vienna, 1950), Vol. 2, p. 66.

we can obtain the terms of the integral in Eq. (A2.7) by partial differentations with respect of A and B. Using the recursion relations for the derivatives of the modified Bessel functions of the second kind[8] K_n gives

$$U=\tfrac{1}{8}e^{\frac{1}{2}\gamma^2p^2}\{2p^4A^{1/2}B^{-1/2}K_1(2A^{1/2}B^{1/2})$$
$$+2qp^4K_0(2A^{1/2}B^{1/2})-2B^{1/2}A^{-1/2}K_1(2A^{1/2}B^{1/2})$$
$$-2qBA^{-1}K_2(2A^{1/2}B^{1/2})\}. \quad \text{(A2.11)}$$

Then, using the recursion relation[8] which expresses K_1 in terms of K_0 and K_2, and the definitions Eqs. (A2.5), (A2.8), and (A2.9), we finally obtain Eq. (2.13).

APPENDIX III: EVALUATION OF ABSORPTION INTEGRALS

We compute here the absorption integrals $\epsilon'(0)-1$, β_1 and β_2 defined in Eqs. (3.1), (3.2), and (3.3). Consider first $\epsilon'(0)-1$. Upon substituting Eq. (2.16) into Eq. (3.1), we find that we must compute an integral of the form

$$I_1=\int_0^\infty (e^{a\omega}-e^{-a\omega})\omega K_2(b\omega)d\omega\,, \quad \text{(A3.1)}$$

where $a=\hbar/2kT$ and $b=[\alpha^{-2}(m/kT)+a^2]^{1/2}$. Using the recursion relation[8]

$$K_0(x)-K_2(x)=-2x^{-1}K_1(x) \quad \text{(A3.2)}$$

to write K_2 in terms of K_0 and K_1, and the relation[8] $K_1(x)=-K_0'(x)$, we find that

$$I_1=2\frac{\partial}{\partial a}\int_0^\infty \cosh(a\omega)K_0(b\omega)d\omega$$
$$+\frac{4}{b}\int_0^\infty \sinh(a\omega)K_1(b\omega)d\omega\,. \quad \text{(A3.3)}$$

The two integrals in Eq. (A3.3) can be evaluated in terms of elementary functions,[12] and we find

$$I_1=2\pi\frac{\partial}{\partial a}[(b^2-a^2)^{-1/2}]+\frac{4\pi a}{b^2}(b^2-a^2)^{-1/2}. \quad \text{(A3.4)}$$

Differentiating and substituting the definitions of a and b then leads to Eq. (3.4).

Consider next β_1. Upon substituting Eq. (2.16) into Eq. (3.2), we find that we must evaluate the integral

$$I_2=\int_0^\infty (e^{a\omega}-e^{-a\omega})\omega^2K_2(b\omega)d\omega\,. \quad \text{(A3.5)}$$

First we write

$$I_2=\frac{\partial}{\partial a}\int_0^\infty (e^{a\omega}+e^{-a\omega})\omega K_2(b\omega)d\omega$$
$$=\frac{\partial}{\partial a}\int_0^\infty (e^{a\omega}+e^{-a\omega})\left[K_0(b\omega)+\frac{2}{b\omega}K_1(b\omega)\right]d\omega$$
$$=2\frac{\partial^2}{\partial a^2}\int_0^\infty \sinh(a\omega)K_0(b\omega)d\omega$$
$$-\frac{4}{b}\frac{\partial}{\partial a}\int_0^\infty \cosh(a\omega)K_0'(b\omega)d\omega\,. \quad \text{(A3.6)}$$

To obtain this form, we have used the same relations used in deriving Eq. (3.4). We then can use the limiting form of an elementary relation[12] to evaluate the integral containing K_0 in Eq. (A3.6). In particular

$$\int_0^\infty \sinh(a\omega)K_0(b\omega)d\omega$$
$$=\lim_{\nu\to 0}\tfrac{1}{2}\pi(b^2-a^2)^{-1/2}\frac{\sin[\nu\sin^{-1}(a/b)]}{\sin(\nu\pi/2)}$$
$$=(b^2-a^2)^{-1/2}\sin^{-1}(a/b)\,. \quad \text{(A3.7)}$$

We also use

$$\frac{\partial}{\partial a}\int_0^\infty \cosh(a\omega)K_0'(b\omega)d\omega$$
$$=\frac{\partial}{\partial a}\frac{1}{b}\Big[\cosh(a\omega)K_0(b\omega)\Big]_0^\infty$$
$$-\frac{\partial}{\partial a}\frac{a}{b}\int_0^\infty K_0(b\omega)\sinh(a\omega)d\omega$$
$$=-\frac{1}{b}\frac{\partial}{\partial a}\lim_{\omega\to 0}\cosh(a\omega)K_0(b\omega)$$
$$-\frac{1}{b}\frac{\partial}{\partial a}a\int_0^\infty K_0(b\omega)\sinh(a\omega)d\omega\,. \quad \text{(A3.8)}$$

In the last form in Eq. (A3.8), it is easy to see that the term involving the limit is equal to zero. Thus, expanding $\cosh(a\omega)=1+\frac{1}{2}(a\omega)^2+\cdots$, this term becomes $-(a/b)\lim_{\omega\to 0}[\omega^2K_0(b\omega)]$, which vanishes since $K_0(b\omega)$ diverges only logarithmically as $\omega\to 0$. The integral in Eq. (A3.8) is elementary,[12] and we obtain then

$$I_2=2\frac{\partial^2}{\partial a^2}[(b^2-a^2)^{-1/2}\sin^{-1}(a/b)]$$
$$+\frac{4}{b^2}\frac{\partial}{\partial a}[a(b^2-a^2)^{-1/2}\sin^{-1}(a/b)]. \quad \text{(A3.9)}$$

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[12] I. S. Gradshetyn and I. M. Ryzhik, *Tables of Integrals, Series and Products* (Academic Press Inc., New York, 1965), 4th ed., p. 726.

After carrying out the elementary but tedious differentiations in Eq. (A3.9), and substituting the definitions of a and b, we obtain Eq. (3.5).

Consider finally β_2. Upon substituting Eq. (2.16) into Eq. (3.3), we find that we must evaluate the integral

$$I_3=\int_0^\infty \sinh(a\omega)K_2(b\omega)\omega^3 d\omega$$

$$=\frac{\partial^2}{\partial a^2}\int_0^\infty \sinh(a\omega)K_2(b\omega)\omega d\omega. \qquad \text{(A3.10)}$$

Thus, since we see that $2I_3=\partial^2 I_1/\partial a^2$, the evaluation of I_1 then also leads to the evaluation of I_3. Differentiation of Eq. (A3.4) and substitution of the definitions of a and b thus leads to Eq. (3.6).

APPENDIX IV: EVALUATION OF CORRELATION FUNCTION AND RELAXATION TIME

We evalute here the integral on the right side of Eq. (5.2). We use Eq. (A3.2) to write

$$I(t)\equiv\int_0^\infty \cosh\left(\frac{\hbar\omega}{2kT}\right)x^2K_2[x(1+\theta^2)^{1/2}]\cos\omega t d\omega$$

$$=\int_0^\infty \cosh\left(\frac{\hbar\omega}{2kT}\right)\left[x^2K_0+\frac{2x}{(1+\theta^2)^{1/2}}K_1\right]\cos\omega t d\omega$$

$$=-C^2\frac{\partial^2}{\partial t^2}\int_0^\infty \cosh\left(\frac{\hbar\omega}{2kT}\right)K_0[x(1+\theta^2)^{1/2}]\cos\omega t d\omega$$

$$+\frac{2C}{(1+\theta^2)^{1/2}}\frac{\partial}{\partial t}\int_0^\infty \cosh\left(\frac{\hbar\omega}{2kT}\right)$$

$$\times K_1[x(1+\theta^2)^{1/2}]\sin\omega t d\omega, \qquad \text{(A4.1)}$$

where

$$C\equiv\gamma^{-1}(m/kT)^{1/2}. \qquad \text{(A4.2)}$$

We then use the relations

$$\cosh(a\pm ib)=\cosh a\cos b\mp i\sinh a\sin b \qquad \text{(A4.3)}$$

and

$$\sinh(a\pm ib)=\sinh a\cos b\pm i\cosh a\sin b \qquad \text{(A4.4)}$$

to rewrite Eq. (A4.1) as

$$I(t)=J(t)+J^*(t) \qquad \text{(A4.5)}$$

where

$$J(t)=-\tfrac{1}{2}C^2\frac{\partial^2}{\partial t^2}\int_0^\infty \cosh\left(\frac{\hbar\omega}{2kT}+i\omega t\right)$$

$$\times K_0[C(1+\theta^2)^{1/2}\omega]d\omega$$

$$-\frac{iC}{(1+\theta^2)^{1/2}}\frac{\partial}{\partial t}\int_0^\infty \sinh\left(\frac{\hbar\omega}{2kT}+i\omega t\right)$$

$$\times K_1[C(1+\theta^2)^{1/2}\omega]d\omega. \qquad \text{(A4.6)}$$

The integrals in Eq. (A4.5) are elementary.[12] Substituting their values, and carrying out the differentiations indicated in Eq. (A4.6), we find that

$$I(t)=\tfrac{3}{4}\pi C^4(1+\theta^2)[(C^2+t^2+2iCt\theta)^{-5/2}$$

$$+(C^2+t^2-2iCt\theta)^{-5/2}]. \qquad \text{(A4.7)}$$

When this expression is substituted into Eq. (5.2), the result is that given in Eq. (5.3).

From the definition Eq. (5.7) and from Eq. (5.2), we see that the relaxation time τ is given by

$$\tau=\int_0^\infty I(t)dt/I(0). \qquad \text{(A4.8)}$$

The integral in Eq. (A4.8) is clearly elementary when $I(t)$ is given by Eq. (A4.7). Simple algebra leads to the result given in Eq. (5.7).