PHYSICAL REVIEW VOLUME 154, NUMBER 1 5 FEBRUARY 1967

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

HOWARD B. LEVINE AND GEORGE BIRNBAUM
North American Aviation Science Center, Thousand Oaks, California

(Received 1 August 1966)

Collision-induced far-infrared absorption has been observed experimentally in several rare-gas mixtures. A theoretical calculation of these spectra is carried out using classical radiation theory to determine the emission spectrum and converting to absorption via Kirchhoff's law. Using a simple empirical form to describe the variation of the collision-induced dipole moment with internuclear separation, and assuming straight-line collision paths, an analytic expression is obtained for the spectrum which agrees well with the experiments. Several elementary integrations allow us to compute analytically the correlation function, relaxation time, static dielectric constant, and other invariants of the spectrum.

1. INTRODUCTION

INFRARED absorption arising from collisions between dissimilar rare-gas atoms in highly compressed mixtures of helium-neon, helium-argon, and neon-argon was discovered by Kiss and Welsh.[1,2] Since this absorption monotonically increased with increasing wavelength, it was clearly the short-wavelength wing of an absorption band. The main band was observed in the far-infrared region by Bosomworth and Gush[3] for helium-argon and neon-argon mixtures, although they failed to observe it for helium-neon mixtures.

This absorption was suggested as arising as a consequence of the distortion of the electron distribution during the collision between two atoms. If the atoms are dissimilar, a net dipole moment will appear in the pair which will last for the duration of the collision. This mechanism accounts for the observed dependence of the absorption upon the product of the densities of the two components. It also suggests that the absorption band has a width of the order of the mean relative velocity divided by the range of interaction. Since the absorption is of the nonresonant variety, the absorption maximum also is expected to be of this order. For reasonable values of these parameters, their ratio predicts an absorption peak in the far-infrared region. These features of the spectrum are characteristic of the translational absorption arising from collision-induced dipole moments, and they also apply in the translational absorption arising from quadrupolar interaction.

It is interesting to contrast collision-induced absorption with absorption in gases with permanent dipole moments. In the latter case, the absorption process goes on undisturbed except for collisions which interrupt the absorption and emission of radiation. This interruption broadens the energy levels of the molecules and leads to spectral lines whose widths depend on the pressure. In most of the line-shape theories dealing with this process, it is assumed that the duration of collision is negligible compared with the mean time between collisions. On the other hand, the duration of collision is the important time interval in collision-induced absorption since there is clearly no dipole moment and consequently no absorption when the molecules are separated. It is the purpose of this paper to develop a theory of such absorption in rare-gas mixtures, and to make detailed comparisons of this theory with experiment.

Some theoretical work on collision-induced absorption has already appeared. Poll and van Kranendonk[4] have presented a theory for the integrated absorption, relating it to the pair distribution function and to the function which describes the variation of the dipole moment of the colliding pair with internuclear separation. Maryott and Birnbaum[5] have considered collision-induced absorption in quadrupolar molecules such as CO_2, and were able to obtain an approximate expression for the line shape for both resonant and nonresonant transitions which could be evaluated by doing one numerical integration. They only applied their result to the microwave wing of the nonresonant line, where an expression in closed form was obtained which agreed well with experiment. Recently, Tanimoto[6] has developed a line-shape theory for collision-induced absorption in rare-gas mixtures. However, he has adopted functional forms for the induced dipole moment $\boldsymbol{\mu}(\mathbf{r})$ and the intermolecular potential which lead to complex expressions which must be evaluated by machine calculation. Furthermore, he unfortunately based the evaluation of parameters in his expression by comparison with the rather inaccurate data in the high-frequency tail, and consequently his results cannot be expected to be accurate for the region of the peak.

In the present work, the line-shape problem is treated classically. A form for the induced dipole moment is adopted which results in a rather simple analytic expression for the absorption coefficient. From this, it is easy to obtain several integrals such as the

---

[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] A. A. Maryott and G. Birnbaum, J. Chem. Phys. 36, 2026 (1962).

[6] O. Tanimoto, Progr. Theoret. Phys. (Kyoto) 33, 585 (1965).

static dielectric constant and the absorption integrals of Poll and van Kranendonk.[4] We also obtain the correlation function and the relaxation time. The parameters describing the variation of the dipole moment with internuclear separation are obtained, for He–Ar and Ne–Ar mixtures, by fitting the theoretical expression to the experimental data at the peak of the absorption.[3] For He–Ar, the theoretical curve then accurately fits the experimental data over the entire spectrum. For Ne–Ar, the fit it not quite as good, the theory predicting the high-frequency wing to be weaker than the observations indicate. Nevertheless, the fit is still good enough so that predictions of integral properties, i.e., static dielectric constant, relaxation time, etc., are quite satisfactory. For He–Ne, the dipole moment parameters have been obtained from data on the high-frequency wing of the absorption,[1] since this is the only data available. Our analysis indicates that the He–Ne spectrum should be considerably weaker than that for the other two gas pairs, in agreement with the experiments.[3]

2. GENERAL RELATIONS

The starting point of our analysis is Kirchhoff's law,[7] which relates the absorption coefficient $\alpha(\omega)$ to the power due to spontaneous emission per unit frequency interval per unit volume of sample $I(\omega)$ by

$$\alpha(\omega)=I(\omega)/cu(\omega)\,, \tag{2.1}$$

where c is the velocity of light, and $u(\omega)$ is the energy density in the black-body radiation field. The latter is given by Planck's law

$$u(\omega)=\frac{\hbar\omega^3}{\pi^2c^3[e^{\hbar\omega/kT}-1]}\,, \tag{2.2}$$

or in the limit of low frequency by the Rayleigh-Jeans law

$$u(\omega)\rightarrow u_0(\omega)=\omega^2kT/\pi^2c^3\,. \tag{2.3}$$

In what follows we shall calculate $I(\omega)$ by means of classical electromagnetic theory. It has been observed, for example by Van Vleck and Margenau,[8] that detailed balance between emission and absorption at all frequencies occurs for classical oscillators provided the radiation field has an energy distribution given by the Rayleigh-Jeans law. Inasmuch as Kirchhoff's law is merely a statement of detailed balancing between emission and absorption, we anticipate that the Rayleigh-Jeans form of the radiation law is appropriate for our calculation, despite the fact that $\hbar\omega/kT$ is *not* $\ll 1$ over a good part of the experimental spectra.[1–3]

The quantity $I(\omega)$ can be written as a statistical average over power from various classes of collisions:

$$I(\omega)=\int\int N(b,v)\hat{I}(b,v,\omega)dbdv\,, \tag{2.4}$$

where $N(b,v)$ is the number of collisions per unit volume per unit time for which the impact parameter is b and the magnitude of the relative velocity is v. In writing Eq. (2.4), we have already averaged over the orientation of $\mathbf{v}$ and the orientation of the angular-momentum vector. This is appropriate since the collision paths are distributed isotropically, and Kirchhoff's law, as stated in Eq. (2.1), requires $I(\omega)$ to be the power radiated into the total solid angle 4π. We have also integrated over the Boltzmann distribution of the center-of-mass velocity $\mathbf{V}$, assuming $\hat{I}$ to be independent of $\mathbf{V}$. This is justified since it can easily be shown that the center-of-mass motion of a radiating atomic pair leads to negligible Doppler broadening for thermal velocities.

The factor $N(b,v)$ is known from the kinetic theory of gases,[9] and is given by

$$N(b,v)=2\pi bn_An_B\left(\frac{m}{kT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2}v^3 \times\exp[-mv^2/2kT]\,, \tag{2.5}$$

where n_A, n_B are the number of molecules per unit volume of the two colliding species, and m is the reduced mass of a colliding pair. The emission intensity $\hat{I}(b,v,\omega)$ can be obtained from classical electromagnetic theory. By Fourier transformation of the Larmor power formula, one has[10]

$$\hat{I}(b,v,\omega)=\frac{2\omega^4}{3c^3\pi}\left|\int_{-\infty}^{\infty}dt\,e^{i\omega t}\boldsymbol{\mu}(b,v,t)\right|^2\,, \tag{2.6}$$

where $\boldsymbol{\mu}(b,v,t)$ is the electric dipole moment of the colliding pair as a function of time for given b and v values.

3. MODEL FOR THE DIPOLE MOMENT AND POTENTIAL

By combining Eqs. (2.1) and (2.3)–(2.6), we have an equation for the absorption spectrum, provided we specify a form for the dipole moment, $\boldsymbol{\mu}(b,v,t)$. We write

$$\boldsymbol{\mu}=\boldsymbol{\mu}(\mathbf{r})=\mu(r)\mathbf{r}/r \tag{3.1}$$

to denote the fact that the dipole moment depends upon the separation of the nuclei $\mathbf{r}$ and

$$\mathbf{r}=\mathbf{r}(b,v,t)\,, \tag{3.2}$$

to specify the collision path, which is fixed by b and v and is a functional of the interatomic potential.

---

[7] F. K. Richtmyer and E. H. Kennard, *Introduction to Modern Physics* (McGraw-Hill Book Company, Inc., New York, 1949), pp. 143, 283.

[8] J. H. Van Vleck and H. Margenau, Phys. Rev. **76**, 1211 (1949).

[9] R. D. Present, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1958), p. 145.

[10] J. D. Jackson, *Classical Electrodynamics* (John Wiley & Sons, Inc., New York, 1962), Chap. 14.

The interatomic potential for rare-gas atoms is not well known. The subject has been well reviewed by Abrahamson[11,12] in his papers on Thomas-Fermi-Dirac potential calculations. It is also possible to carry out potential calculations based upon the Hartree-Fock approximation,[13] and Nesbet and Matcha[14] recently have done this for He–Ne. In the present work, we neglect the potential and assume straight-line molecular paths, i.e.

$$x=vt,\quad y=b,\quad z=0. \tag{3.3}$$

Although this is certainly not correct, particularly for small b values, nevertheless it has two virtues. The first is that it leads to simple mathematics; in particular, we do not have to compute trajectories, and the subsequent derivation of the lineshape is easy; and second, the comparison of the results of such a calculation with experiment helps us to assess the importance of the potential in fixing the line shape, i.e., helps us decide whether or not line-shape measurements can be expected to yield useful information about the potential function.

The dipole moment function $\mu(r)$ of Eq. (3.1) is not accessible by any experiment other than measurement of far-infrared absorption (the effect of collision-induced dipoles upon the static dielectric constant, e.g., would be much too small to be observable). However, it may be calculated as part of the same Thomas-Fermi, Thomas-Fermi-Dirac,[12] or Hartree-Fock computations that yield the potential curve. The dipole moments corresponding to the former calculations[12] apparently have not been published. As to the latter, Nesbet and Matcha[14] have now computed the dipole moment for He–Ne, and expect to do other pairs in the near future. It is difficult to place limits upon the accuracy of such calculations, and we regard them as having their greatest value in suggesting the functional form of $\mu(r)$. They have found[14] that for the r values of interest in line shape calculations, the dipole moment can be represented by an exponential function $\mu(r)=\mu_0\exp(-\gamma r)$. This form was used by Poll and van Kranendonk[4] and by Tanimoto[6] in their work on collision-induced absorption, on the idea that the dipole moment would be related to overlap matrix elements.

In the present calculation, we have not used an exponential but instead have chosen a form which leads to simple mathematics. A Gaussian function is an obvious choice, but it must be modified for a reason related to neglect of the interatomic potential and hence straight-line collision paths. Thus, if one combines Eq. (3.3) with any functional form for $\mu(r)$ which does not go to zero as $r\rightarrow 0$, then the Fourier transformation of Eq. (2.6) leads to a spectrum whose intensity does not go to zero as $\omega\rightarrow\infty$. Briefly, the idea is this: If we consider those collisions for which $b\rightarrow 0$, then at $t=0$ there is a very rapid change in the x component of the dipole moment (a discontinuity in the limit $b=0$). The Fourier transformation of this jump gives rise to a constant term independent of ω, the statistical average of which does not vanish. Because of this, any empirical function $\mu(r)$ used in conjunction with straight-line collisions must go smoothly to zero as $r\rightarrow 0$ if it is to yield a sensible spectrum. We also seek a functional form which describes the general characteristics of the physical dipole function, i.e., one which has a short range.

The form we have chosen is

$$\mu(r)=\mu_0\gamma r\exp(-\gamma^2r^2), \tag{3.4}$$

where γ^{-1} is the range of the dipole moment, and μ_0 characterizes its strength. The factor γr may be looked upon from another point of view: If one considers a realistic potential, then its repulsive part prevents two atoms from approaching too close to one another, i.e., the distance of closest approach is of the order of the range of the repulsive component of the potential. In a manner of speaking, the potential function "shuts off" the dipole moment for very small r values. Similarly, in Eq. (3.4), the factor γr "shuts off" the dipole moment when $r\lesssim\gamma^{-1}$. Thus, roughly speaking, the absence of a repulsive potential has been corrected for in the form used for $\mu(r)$. It may be noted that this also roughly corresponds to choosing a dipole function whose range is about equal to the range of the repulsive part of the potential. Since both the dipole moment and the real potential arise from overlap distortion effects on the electronic shells, it is not unreasonable that their ranges should be similar.

4. CALCULATION OF THE LINE SHAPE

With the model given in Eqs. (3.3) and (3.4) the algebra is quite simple. We give it in outline. The Fourier integral of Eq. (2.6) has two nonvanishing components, which by elementary integration we find to be

$$\tilde{\mu}_x(b,v,\omega)=\frac{\mu_0\omega\pi^{1/2}}{2\gamma^2v^2}\exp\left\{-\gamma^2b^2-\frac{\omega^2}{4\gamma^2v^2}\right\}, \tag{4.1}$$

and

$$\tilde{\mu}_y(b,v,\omega)=\frac{\mu_0 b\pi^{1/2}}{v}\exp\left\{-\gamma^2b^2-\frac{\omega^2}{4\gamma^2v^2}\right\}, \tag{4.2}$$

where now

$$\hat{I}(b,v,\omega)=(2\omega^4/3c^3\pi)(\tilde{\mu}_x^2+\tilde{\mu}_y^2). \tag{4.3}$$

After multiplying $\hat{I}(b,v,\omega)$ by $N(b,v)$, Eq. (2.5), we perform the elementary integration over b. We then are left with two integrals over v, of the form

$$\int_0^\infty v^n\exp\left\{-\frac{mv^2}{2kT}-\frac{\omega^2}{2\gamma^2v^2}\right\}dv, \tag{4.4}$$

---

[11] A. A. Abrahamson, Phys. Rev. **130**, 693 (1963).

[12] A. A. Abrahamson, Phys. Rev. **133**, A990 (1964).

[13] R. K. Nesbet, J. Chem. Phys. **43**, S30 (1965).

[14] R. K. Nesbet and R. Y. Matcha (private communication).

with $n=-1$ for the x component and $n=1$ for the y component. The substitution $v^2=w$ in Eq. (4.4) then leads to two integrals over w which may be expressed as modified Bessel functions of the second kind and derivatives of such functions.[15] Finally, using the recurrence relations for Bessel functions and their derivatives,[16] we obtain an expression for $I(\omega)$, which when substituted into Eq. (2.1) gives the absorption spectrum. Using the Rayleigh-Jeans radiation law, Eq. (2.3), we find

$$\alpha(\omega)=\frac{\mu_0{}^2\pi^3 n_A n_B}{12c\gamma^2}\left(\frac{2}{\pi mkT}\right)^{1/2} x^4 K_2(x)\,, \tag{4.5}$$

where

$$x=\frac{\omega}{\gamma}\left(\frac{m}{kT}\right)^{1/2}=\frac{2\pi c\sigma}{\gamma}\left(\frac{m}{kT}\right)^{1/2} \tag{4.6}$$

is a dimensionless frequency variable, and σ is the frequency in wave numbers. K_2 is a modified Bessel function of the second kind.[15] Using the $x\rightarrow 0$ limiting form for $K_2(x)$, it is easy to show that $\alpha(\omega)\sim\omega^2$ as $\omega\rightarrow 0$ as is required by the fact that $\alpha(\omega)$ is an even function of frequency. Similarly, we can study the high-frequency limit of $\alpha(\omega)$ by using the asymptotic representation of $K_2(x)$. If we consider not $\alpha(\omega)$, but instead the initial-state-averaged transition probability

$$g(\omega)=\frac{\alpha(\omega)}{\omega}\left[1-e^{-\hbar\omega/kT}\right]^{-1} \tag{4.7}$$

plotted by Bosomworth and Gush,[3] then we easily find[16]

$$g(\omega)\sim\omega^{3/2}\exp\left\{-\frac{\omega}{\gamma}\left(\frac{m}{kT}\right)^{1/2}\right\}. \tag{4.8}$$

Thus, in the limit of high frequency, $\ln g(\omega)$ is linear in ω, in agreement with the experimental results.[3] More completely, using elementary representations or tables[16] of the function $K_2(x)$, we can easily compute the entire spectrum.

5. EVALUATION OF μ_0 AND γ

To complete our calculations, we must specify values for the parameters μ_0 and γ. For He–Ar and Ne–Ar, we have chosen these values such that the data of Bosomworth and Gush is fitted at the peak of the spectrum. For He–Ar, the experimental peak is rather broad, but our fit indicates that it occurs at 180 cm^{-1} and has a height of 7.46×10^{-7} cm^{-1} amagat^{-2}. In Figs. 1 and 2, we plot our results for $A(\sigma)=\alpha(\sigma)(n_A n_B)^{-1}\times(N_0/V_0)^2$ (N_0=Avogadro's number, $V_0=22413.6$ cm^3), which is the absorption coefficient normalized to standard partial densities following Bosomworth and Gush.[3] In Figs. 3 and 4, we plot our results for $G(\sigma)=\sigma^{-1}A(\sigma)\{1-\exp(-hc\sigma/kT)\}^{-1}$, which is the normalized initial-state-averaged transition probability plotted by Bosomworth and Gush.

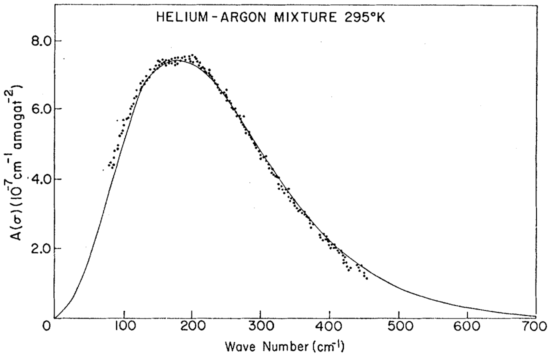

FIG. 1. Absorption coefficient for a helium-argon mixture at 295°K. Points are experimental data of Ref. 3; solid line is theoretical curve based upon Eq. (4.5) and constants of Table I.

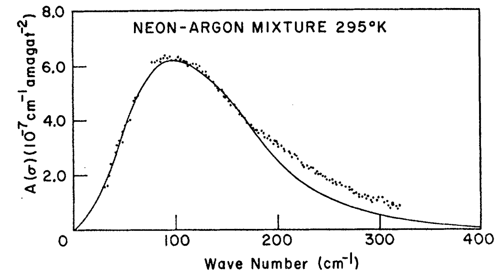

FIG. 2. Absorption coefficient for a neon-argon mixture at 295°K. Points are experimental data of Ref. 3; solid line is theoretical curve based upon Eq. (4.5) and constants of Table I.

We see that for He–Ar, the agreement of our theory with experiment is excellent over the entire frequency range. For Ne–Ar, the agreement is excellent up to a frequency of about 175 cm^{-1}, which is not quite twice

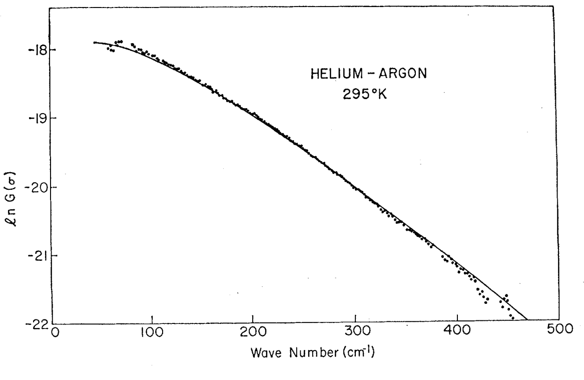

FIG. 3. Initial-state-averaged transition probability for a helium-argon mixture at 295°K. Points are experimental data of Ref. 3; solid line is theoretical curve based upon Eqs. (4.5) and (4.7) and constants of Table I.

---

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

[16] *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), Appl. Math. Ser. 55, pp. 376–9.

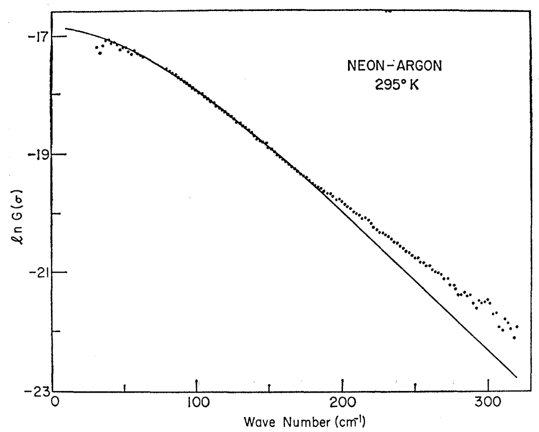

FIG. 4. Initial-state-averaged transition probability for a neon-argon mixture at 295°K. Points are experimental data of Ref. 3; solid line is theoretical curve based upon Eqs. (4.5) and (4.7) and constants of Table I.

the frequency of the peak. Above this frequency, the theory predicts weaker absorption than is observed, e.g., at 300 cm^{-1} the predicted absorption is too low by a factor of 2. This indicates that the simple model we have used is not as suitable for Ne–Ar as for He–Ar. The difference is probably due to the larger collision diameter of the latter pair, which means that the straight-line collision approximation is poorer for a larger range of b values ($0 \leq b \leq b_{\text{max}}$, say) for Ne–Ar. It is just these small-b collisions which can be shown to contribute most strongly to the higher frequencies.

For He–Ne, Bosomworth and Gush did not observe the spectrum, although Kiss and Welsh[1] did see its high-frequency wing. We have used the latter data. It was necessary to exercise some care in doing this, inasmuch as there is a considerable discrepancy between the data of Kiss and Welsh[1] below about 450 cm^{-1} and that of Bosomworth and Gush, as has been pointed out by the latter authors. In addition, the data of Kiss and Welsh above about 600 cm^{-1}, when replotted as a $\ln G(\sigma)$-versus-σ curve, does not appear to be an exponential extrapolation of their data below 600 cm^{-1}. On the arbitrary assumption that the data above 600 cm^{-1} is not valid because it lies in the deep wing of the spectrum, where the absorption is weak, we have limited ourselves to using only that part of their data between 475 and 575 cm^{-1}. After matching the slope of $\ln G(\sigma)$-versus-σ to obtain γ, we then adjusted μ_0 to the measured absorption at 525 cm^{-1}. Fig. 5 shows $A(\sigma)$ as functions of σ, as obtained from our calculations. Our calculation indicates that the He–Ne spectrum has an intensity at its peak which is about one-third of the peak intensities of the other two mixtures. This accounts roughly for the failure of Bosomworth and Gush to observe it, although it is possible that more accurate parameters would predict even weaker absorption. We stress that these results are only rough, considering the limited data upon which they are based. In Table I, we give the parameter values obtained for the three mixtures by the above procedures. In Fig. 6, using the parameters obtained for He–Ar we show its spectrum as a function of temperature, as predicted by Eq. (4.5). The broadening and shift of the peak to higher frequency with increasing T reflect primarily a corresponding shift in the Maxwell-Boltzmann velocity distribution.

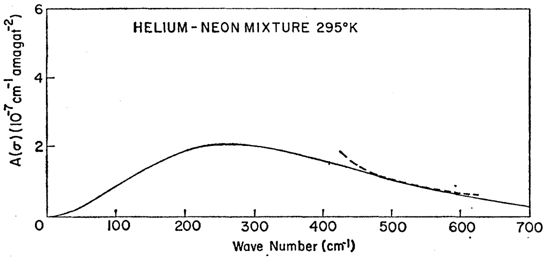

FIG. 5. Absorption coefficient of a helium-neon mixture. Dashed line is data of Ref. 1; solid line is theoretical curve based upon Eq. (4.5) and constants of Table I.

6. INTEGRALS OF THE ABSORPTION SPECTRUM

With the simple analytic form, Eq. (4.5), we can easily evaluate several integrals of the absorption spectrum. The first of these that we consider is the Kramers-Kronig transform

TABLE I. Dipole parameters for rare-gas mixtures.

Mixture	He-Ne	He-Ar	Ne-Ar
γ (Å^{-1})	1.920	1.357	1.446
μ_0 (debyes)	0.121	0.166	0.223

$$\epsilon'(0)-1=\frac{2c}{\pi}\int_0^\infty \frac{\alpha(\omega)d\omega}{\omega^2}. \tag{6.1}$$

The evaluation of this integral with $\alpha(\omega)$ given by Eq. (4.5) is elementary,[17] and we obtain

$$\epsilon'(0)-1=\frac{\pi^2 n_A n_B \mu_0^2}{2kT\gamma^3}(\tfrac{1}{2}\pi)^{1/2}. \tag{6.2}$$

Combining Eqs. (4.5) and (6.2), we can write the shape factor for the absorption:

$$S(\omega)=\frac{c\alpha(\omega)}{\omega[\epsilon'(0)-1]}=\tfrac{1}{3}x^3K_2(x). \tag{6.3}$$

This shape factor is normalized by

$$\int_0^\infty S(\omega)\frac{d\omega}{\omega}=\frac{\pi}{2}. \tag{6.4}$$

---

[17] Reference 15, p. 197.

Equation (6.2) can be verified by evaluating $\epsilon'(0)-1$ by the Langevin-Debye formula for the static dielectric constant. Omitting the terms in the polarizability, which do not contribute to the far-infrared absorption, the latter equation reads

$$\epsilon'(0)-1=\frac{16\pi^2 n_A n_B}{3kT}\int_0^\infty [\mu(r)]^2 g(r) r^2 dr, \qquad (6.5)$$

where $g(r)$ is the pair distribution function. For our model $g(r)=1$, since we have taken the potential to be zero. If we substitute $g(r)=1$ and $\mu(r)=\mu_0\gamma r\exp(-\gamma^2r^2)$ into Eq. (6.5), the integral is elementary, and we easily obtain Eq. (6.2).

Next, we consider the integral

$$\beta_2\equiv\frac{1}{2\pi}\int_0^\infty \alpha(\omega)d\omega \qquad (6.6)$$

considered by Poll and van Kranendonk.[4] This integral also is elementary, and we obtain

$$\beta_2=\frac{5}{8}\frac{\pi^2 n_A n_B \mu_0^2}{\gamma m c}(\tfrac{1}{2}\pi)^{1/2}. \qquad (6.7)$$

TABLE II. Absorption integrals at 295°K.

Mixture	He-Ne	He-Ar	Ne-Ar
$\epsilon'(0)-1$	0.226×10^{-9}	1.21×10^{-9}	1.80×10^{-9}
β_1 (sec^{-1})	0.956×10^{4}	3.60×10^{4}	2.98×10^{4}
β_2 ($\mathrm{cm}^{-1}\,\mathrm{sec}^{-1}$)	2.55×10^{6}	6.26×10^{6}	2.88×10^{6}

Poll and van Kranendonk have shown that β_2 may be written in terms of $\mu(r)$ and $g(r)$ as

$$\beta_2=\frac{4\pi^2 n_A n_B}{3mc}\int_0^\infty\left[\left(\frac{d\mu}{dr}\right)^2+\frac{2\mu^2}{r^2}\right]g(r)r^2dr. \qquad (6.8)$$

Substituting $g(r)=1$ and $\mu(r)=\mu_0\gamma r\exp(-\gamma^2r^2)$, we indeed obtain Eq. (6.7), verifying their result.

In addition to these integrals, which are obtainable directly from the model, without recourse to a detailed line-shape theory, other integrals are readily computed. We consider here only the integral

$$\beta_1\equiv c\int_0^\infty\frac{\alpha(\omega)d\omega}{\omega}. \qquad (6.9)$$

For this integral, there does not appear to be a simple expression in terms of $\mu(r)$ and $g(r)$.[4] However, given Eq. (4.5), this integral also is elementary,[17] and we obtain

$$\beta_1=\frac{4\pi^3 n_A n_B\mu_0^2}{3\gamma^2}(2\pi mkT)^{-1/2}. \qquad (6.10)$$

Using these formulas, and the parameters of Table I, we have computed $\epsilon'(0)-1$, β_1, and β_2. The values are given in Table II. Here the relative values show again the weakness of the He–Ne spectrum as compared to the other two spectra.

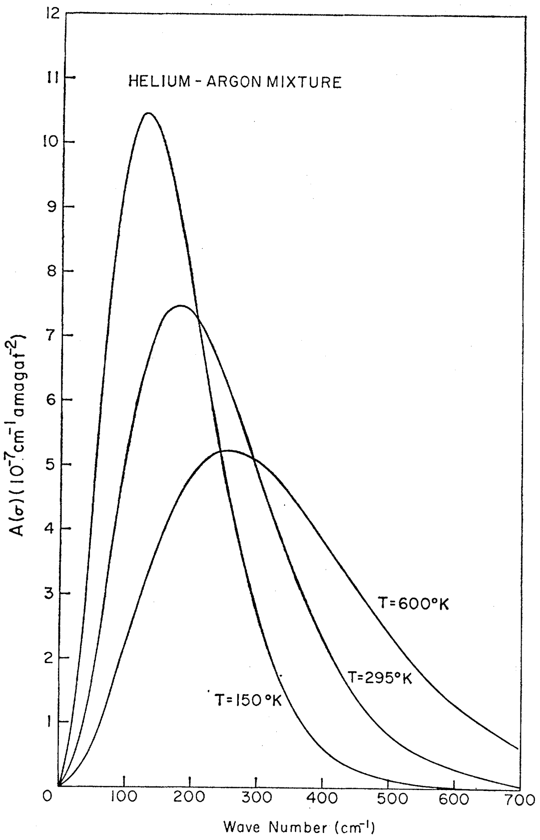

FIG. 6. Theoretical spectra of a helium-argon mixture at various temperatures, based upon Eq. (4.5) and constants of Table I.

7. THE CORRELATION FUNCTION AND THE RELAXATION TIME

According to the work of Kubo,[18] the complex dielectric constant $\epsilon=\epsilon'-i\epsilon''$ is given by

$$\epsilon'(\omega)-1=\Phi(0)-\omega\int_0^\infty \Phi(t)\sin\omega t\,dt, \qquad (7.1)$$

$$\epsilon''(\omega)=\omega\int_0^\infty \Phi(t)\cos\omega t\,dt. \qquad (7.2)$$

The correlation function $\Phi(t)$ is defined for a classical system as

$$\Phi(t)=C\langle\mathbf{M}(0)\cdot\mathbf{M}(t)\rangle, \qquad (7.3)$$

where the brackets represent a statistical average over the equilibrium distribution, $\mathbf{M}$ is the macroscopic moment of the system, and C is a constant, i.e., $\Phi(t)$ is the autocorrelation function of the macroscopic moment.

---

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

Using the relation between $\epsilon''(\omega)$ and $\alpha(\omega)$

$$\epsilon''(\omega)=c\alpha(\omega)/\omega, \tag{7.4}$$

and inverting the Fourier transform, Eq. (7.2), we obtain

$$\Phi(t)=\frac{\mu_0{}^2\pi^2 n_A n_B}{6\gamma^3 kT}\left(\frac{2}{\pi}\right)^{1/2}\int_0^\infty x^2 K_2(x) \times\cos\left[\left(\frac{kT}{m}\right)^{1/2}\gamma t x\right]dx, \tag{7.5}$$

after substituting Eq. (4.5) for $\alpha(\omega)$. The integral in Eq. (7.5) is elementary,[19] and we obtain

$$\Phi(t)=\frac{\mu_0{}^2\pi^2 n_A n_B}{2\gamma^3 kT}\left(\frac{\pi}{2}\right)^{1/2}\left\{1+\frac{kT\gamma^2 t^2}{m}\right\}^{-5/2}. \tag{7.6}$$

The relaxation time is defined as

$$\tau=\int_0^\infty \Phi(t)dt\bigg/\Phi(0). \tag{7.7}$$

From Eqs. (7.6) and (7.7), an elementary integration gives

$$\tau=\frac{2}{3\gamma}\left(\frac{m}{kT}\right)^{1/2}, \tag{7.8}$$

in terms of which Eq. (7.6) becomes

$$\begin{aligned}\Phi(t)&=\frac{\mu_0{}^2\pi^2 n_A n_B}{2\gamma^3 kT}(\tfrac{1}{2}\pi)^{1/2}\left\{1+\left(\frac{2t}{3\tau}\right)^2\right\}^{-5/2}\\&=[\epsilon'(0)-1]\left\{1+\left(\frac{2t}{3\tau}\right)^2\right\}^{-5/2}.\end{aligned} \tag{7.9}$$

One sees from Eq. (7.9) that $\Phi(t)/[\epsilon'(0)-1]$ goes as $1-(10/9)(t/\tau)^2$ for short times ($t\ll\tau$), but ultimately falls off as $(t/\tau)^{-5}$ for long times ($t\gg\tau$). In view of the excellent agreement between theory and experiment, particularly for He–Ar, this result is an accurate representation of the correlation function in the real physical system. Numerically, with the parameters derived above, the relaxation times are given in Table III.

It is interesting to compare these results for the relaxation time associated with collisions between dissimilar rare-gas atoms with the relaxation time for collisions between molecules containing a quadrupole moment. In the latter case, the relaxation time is given by[5,20]

$$\tau=\frac{3\pi b}{28}\left(\frac{2\pi m}{kT}\right)^{1/2}, \tag{7.10}$$

if one assumes straight-line collision paths, where b is the collision diameter and m is the reduced mass. A determination of the relaxation time, not using Eq. (7.10), but based upon the experimental data[20] for CO_2, gives a complicated temperature dependence quite different from Eq. (7.10), although both theories give the same order of magnitude for τ at room temperature, namely about 2×10^{-12} sec. One sees that the relaxation time for the rare-gas mixtures is less than this by a factor of the order of 30, which is reasonable considering the long range of the quadrupole field of CO_2 as compared to the "collision" field of the rare gases.

TABLE III. Relaxation times at $T=295$°K.

Mixture	He–Ne	He–Ar	Ne–Ar
τ (10^{-14} sec)	4.05	5.99	10.8

8. CONCLUSIONS

A completely classical calculation based on a simple physical picture has been made for the absorption arising from collision-induced dipoles between dissimilar rare-gas atoms. Perhaps the most serious approximation in this calculation is that $\hbar\omega\ll kT$. However, as will be shown in a future paper, a quantum derivation which does not make this approximation gives results in close agreement with those obtained here. Another approximation is the neglect of the intermolecular potential, although the form adopted for the induced dipole moment of the colliding pair in essence corrects for this. The resulting mathematics is straightforward and allows us to obtain simple analytic equations for the absorption coefficient, relaxation time, and several invariants of the absorption. A detailed comparison of theory and experiment demonstrates that the theory is able to account adequately for the experimental results. This comparison provides a determination of the parameters which describes the variation of the dipole moment with internuclear distance. The most serious discrepancy, which is still not great, is in the high-frequency wing. It is expected that some refinement in the theory, or perhaps improvement in the experimental accuracy, may remove this difference. We have predicted how the absorption should vary with temperature, and it would be interesting to check this experimentally. Because of the ability of the theory to describe the observed spectral contours notwithstanding the crude way in which the intermolecular force was handled, it is hard to escape the conclusion that collision-induced absorption by overlap interaction is rather insensitive to the details of the intermolecular potential.

---

[19] I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series, and Products* (Academic Press Inc., New York, 1965), 4th ed., pp. 429, 749.

[20] G. Birnbaum, H. B. Levine, and D. A. McQuarrie, J. Chem. Phys. (to be published).