

## Theoretical study of collision-induced far-infrared absorption of dense rare-gas mixtures

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A theory investigating collision-induced absorption in dense rare-gas mixtures is presented. The basic assumption of the theory is that the collision-induced dipole moment of a pair of dissimilar atoms is proportional to the force acting between them. It is then shown that the relevant dynamical variable is the interdiffusion current fluctuation,  $\vec{J} = (1-x) \sum_i^A \vec{v}_i - x \sum_{i'}^B \vec{v}_{i'}$ , in the fluid mixture. The correlation function and absorption spectrum are generated by the Zwanzig-Mori theory of Brownian motion. Two modes are theoretically predicted. A diffusive mode, due to the mutual diffusion of rare-gas atoms, produces a low-frequency dip in the line shape whereas an oscillatory mode, due to the oscillations of atoms in the local structure of the fluid, generates a caging spike in the wing of the spectrum. Spectral behavior is shown to depend on density, concentration, and atomic masses of the two components of the mixture and is discussed in detail.

### I. INTRODUCTION

The far infrared absorption by rare-gas mixtures has been one of the most explored collision-induced processes in the last twenty years. A large number of theories have been proposed, but each deals with restricted aspects of the problem and none of them is applicable in all circumstances.<sup>1</sup>

The theoretical analysis has first been developed for low-density mixtures. Using quantum-mechanical methods, several authors<sup>2-6</sup> have attempted to compute the absorption coefficient; recent work is particularly accurate.<sup>5</sup> Some other authors<sup>7-12</sup> have made classical calculations in which the trajectory of the colliding pair is described on different levels of approximation. The line shape has also been investigated through moment analyses<sup>13-18</sup>; semiempirical expressions for the absorption coefficient have been proposed. However, the number of theoretical studies is much more limited for dense rare-gas mixtures. Four types of theory may be distinguished: (i) Van Kranendonk and Lewis<sup>19-22</sup> have proposed a kinetic theory based on the assumption of the temporal superposition of dipoles induced in successive collisions. This theory has predicted a low-frequency dip in the spectral density produced by the interference

between successive collisions; its validity is restricted to moderate densities. (ii) Lewis and Tijon<sup>23,24</sup> have simulated a two-dimensional Lorentz gas by computer calculations. The system consists of an assembly of fixed scatterers, randomly distributed, through which a light particle moves. The theory generates the line shapes but the limitations of the two-dimensional model are difficult to ascertain. (iii) Buontempo *et al.*<sup>25,26</sup> have interpreted their data on dilute solutions of He, Ne, and Kr in liquid Ar with the help of a model involving an impurity-doped crystal. Alternatively, they applied a memory-function technique to analyze the translational motion of an impurity isolated in the liquid. (iv) Finally, Gray *et al.*<sup>27</sup> have calculated for liquid mixtures the first two classical moments of the absorption spectrum. Their formalism, where only two- and three-body interactions are considered, has led to expressions which have been evaluated with the help of a computer. Although a quantitative theory of the spectrum at low densities is available and a phenomenological one at moderate densities has been advanced, dense rare-gas mixtures require new developments.

The purpose of the present paper is to calculate the collision-induced absorption spectrum in rare-gas mixtures for a wide range of densities, concen-

trations, and masses of the two components. The basic assumption of the theory is that the collision-induced dipole moment of a pair of dissimilar atoms is proportional to the force acting between them. The spectrum is then analyzed by adopting the interdiffusion current fluctuation as the basic dynamical variable and by treating its temporal evolution with the help of the Zwanzig-Mori method. The parameters of this theory are calculated analytically whereas some integrals are estimated by applying a lattice-gas model. A simple interpretation of the spectrum is given and the evolution of the profile with density, concentration, and atomic masses are discussed in detail.

## II. THEORY

### A. Collision-induced absorption

The absorption coefficient  $\alpha(\omega)$  can be obtained either from the golden rule of quantum mechanics or, equivalently, from the linear response theory. One finds

$$\alpha(\omega) = \frac{2\pi}{3\hbar c V} \omega (1 - e^{-\beta\hbar\omega}) \int_{-\infty}^{+\infty} dt e^{-i\omega t} \Phi(t), \quad (1)$$

where  $\Phi(t) = \langle \vec{M}(t) \cdot \vec{M}(0) \rangle$  is the autocorrelation function associated with the total dipole moment of the fluid mixture. In the theory of collision-induced absorption one frequently uses the spectral density  $G(\omega)$  given by

$$G(\omega) = \left[ \frac{4\pi}{3\hbar c V} \omega \tanh \frac{\beta\hbar\omega}{2} \right]^{-1} \alpha(\omega) = \int_{-\infty}^{+\infty} dt e^{-i\omega t} \Phi_+(t). \quad (2)$$

In this equation the correlation function is written in its Hermitian form

$$\Phi_+(t) = \frac{1}{2} \langle \vec{M}(0) \vec{M}(t) + \vec{M}(t) \vec{M}(0) \rangle,$$

and in what follows,  $\Phi_+(t)$  will be calculated within the framework of classical mechanics. For a binary mixture of rare-gas atoms, the macroscopic dipole moment may conveniently be decomposed in pair contributions involving dissimilar atoms, triplet contributions involving similar<sup>28</sup> and dissimilar atoms, and high-order contributions. In this context, it is sufficient to consider only the  $N_A \times N_B$  pair contributions,

$$\vec{M} = \sum_{i,i'}^{N_A, N_B} \vec{\mu}_{ii'},$$

with  $N_A$  atoms of species  $A$  and  $N_B$  atoms of species  $B$ . To each pseudomolecule  $(i, i')$ , corresponds an induced dipole moment

$$\vec{\mu}_{ii'} = \mu(r_{ii'}) \vec{r}_{ii'} / |\vec{r}_{ii'}|,$$

where  $\vec{r}_i$  is the position vector of atom  $i$ ,  $\vec{r}_{i'}$  that of atom  $i'$ , and  $\vec{r}_{ii'} = \vec{r}_i - \vec{r}_{i'}$ . It has been recognized earlier that the dipole moment  $\vec{\mu}(\vec{r}_{ii'})$  is basically a short-range function of  $r$  (Ref. 29) due to the existence of overlap forces during collisions.<sup>30</sup> However, further investigations based on quantum-chemical calculations<sup>5,31-33</sup> have shown that the dispersions forces play some role too and contribute to the long-range part of the induced dipole. One thus adopts the analytical form  $\mu(r) = \mu_0 e^{-r/\lambda} + c_7/r^7$ , where  $\mu_0$ ,  $\lambda$ , and  $c_7$  are constants which may be evaluated by a moment or line-shape analysis of low-density data, or, obtained from *ab initio* quantum calculations. Alternatively, one may assume that the induced dipole moment associated with a pair of dissimilar atoms is proportional to the force acting between them, namely,  $\vec{\mu}_{ii'} = c \vec{f}_{ii'}$ ,  $c$  being a constant. This assumption is roughly supported by comparisons in the gas phase between the expression of  $\mu(r)$  and that of the force derived from commonly used potential,<sup>34</sup> and the observation that the range of the overlap induced dipole and the force are approximately proportional.<sup>17</sup> It is nevertheless useful to assume this proportionality, in which case the expression of the total dipole moment  $\vec{M}$  may be deduced in the following way. The equations of motion of the atom  $i$  of species  $A$  and the atom  $i'$  of species  $B$  are, respectively,

$$\frac{d\vec{v}_i}{dt} = \frac{1}{m_A} \left[ \sum_{j \neq i}^{N_A} \vec{f}_{ij} + \sum_{i'}^{N_B} \vec{f}_{ii'} \right], \quad (3a)$$

$$\frac{d\vec{v}_{i'}}{dt} = \frac{1}{m_B} \left[ \sum_{j' \neq i'}^{N_B} \vec{f}_{i'j'} + \sum_{i}^{N_A} \vec{f}_{i'i} \right], \quad (3b)$$

where  $m_A$  and  $m_B$  represent the mass of the atoms and the indices  $i, j$  run over all atoms of species  $A$  and  $i', j'$  run over all atoms of species  $B$ . Then, using the action-reaction law  $\vec{f}_{ii'} = -\vec{f}_{i'i}$ , letting  $x = N_A / (N_A + N_B)$  be the concentration of species  $A$ , introducing the interdiffusion current density fluctuation  $\vec{j}(\vec{r}, t)$  as well as its zero  $\vec{k}$  Fourier component  $\vec{J}(t)$  (Refs. 35 and 36), and writing

$$\vec{M} = c \sum_{i,i'}^{N_A, N_B} \vec{f}_{ii'}$$

one finds

$$\vec{j}(\vec{r}, t) = (1-x) \sum_i^{N_A} \vec{v}_i(t) \delta(\vec{r} - \vec{r}_i(t)) - x \sum_{i'}^{N_B} \vec{v}_{i'}(t) \delta(\vec{r} - \vec{r}_{i'}(t)), \quad (4)$$

$$\vec{J}(t) = \vec{j}_{\vec{k}=0}(t) = (1-x) \sum_i^{N_A} \vec{v}_i(t) - x \sum_{i'}^{N_B} \vec{v}_{i'}(t), \quad (5)$$

$$\vec{M} = c \left[ \frac{1-x}{m_A} + \frac{x}{m_B} \right]^{-1} \frac{d\vec{J}(t)}{dt}. \quad (6)$$

The presence of the interdiffusion current fluctuation  $\vec{J}$  in this problem emphasizes that collision-induced absorption spectra of rare-gas mixtures describe the mutual diffusion of atoms in these mixtures.

### B. Equation of motion

The calculation of the autocorrelation function associated with the total dipole moment is thus reduced to that of the correlation function which describes the interdiffusion current fluctuation in the mixture. To obtain a theoretical expression for this function which is not well known in the literature, we use the Zwanzig-Mori theory of Brownian motion. The correlation matrix  $\Theta(t)$  constructed on an appropriate set of basic dynamical variables thus satisfies the generalized Langevin equation

$$\frac{d\Theta(t)}{dt} = i\Omega\Theta(t) - \int_0^t ds K(s)\Theta(t-s), \quad (7)$$

$$\langle \vec{M}(t) \cdot \vec{M}(0) \rangle = c^2 \left[ \frac{1-x}{m_A} + \frac{x}{m_B} \right]^{-2} \langle \vec{J}^{(1)}(t) \cdot \vec{J}^{(1)}(0) \rangle,$$

$$\frac{\langle \vec{M}(t) \cdot \vec{M}(0) \rangle}{\langle \vec{M}(0) \cdot \vec{M}(0) \rangle} = - \frac{2\lambda_1\lambda_2 e^{-\lambda_1 t}}{(\lambda_1 - \lambda_2)^2 + \lambda_3^2} + \frac{e^{-\lambda_2 t}}{(\lambda_1 - \lambda_2)^2 + \lambda_3^2} \times \left[ \frac{\lambda_2}{\lambda_3} (\lambda_2^2 + \lambda_3^2 - \lambda_1^2) \sin\lambda_3 t + (\lambda_1^2 + \lambda_2^2 + \lambda_3^2) \cos\lambda_3 t \right].$$

In this expression  $\lambda_1$ ,  $\lambda_2 + i\lambda_3$ ,  $\lambda_2 - i\lambda_3$  represent the real and complex conjugate roots, respectively, of the transport matrix  $\Gamma$ . They satisfy the secular equation depending on three parameters,

$$\lambda^3 - \lambda^2 \tau^{-1} \left[ \frac{\omega_1^4}{(\omega_0^2)^2} - 1 \right] + \lambda \frac{\omega_1^4}{\omega_0^2} - \omega_0^2 \tau^{-1} \left[ \frac{\omega_1^4}{(\omega_0^2)^2} - 1 \right] = 0,$$

where  $\Omega$  and  $K(s)$  represent the frequency and memory matrix, respectively. When the mechanism involved is essentially diffusive, a convenient way to solve this equation is to use the Kivelson-Keyes successive approximation procedure,<sup>37</sup> which is briefly discussed in the Appendix. This procedure consists in generating, from a relevant dynamical variable, a basic set of correlated dynamical variables which have similar time scales. Then the generalized Langevin equation is solved in the subspace described by the basic set which contains these so-called slow variables. The usefulness of the method is insured when the dimension of the basic set required by the phenomenon is not too high, which is the case for diffusive-type motion (see Ref. 38).

In the present case, the method is used as follows. The basic set of dynamical variables is formed by the interdiffusion current fluctuation  $\vec{J}$  and by its first and second time derivatives at time  $t=0$ , i.e.,  $\vec{J}^{(1)}$  and  $\vec{J}^{(2)}$ . No significant improvement is obtained by including  $\vec{J}^{(3)}$  to the basic set. In the Kivelson-Keyes approximation, the memory matrix  $K(t)$  is written  $K(t) = K\delta(t)$ , with

$$K = 2 \lim_{z \rightarrow 0} \int_0^\infty dt e^{-zK(t)}.$$

The projected Liouville operator  $(1-P)L$  is eliminated from the transport matrix  $\Gamma = -i\Omega + K$ , a step which is accomplished in a rigorous way without approximation. Once Eq. (7) has been solved by applying the procedure outlined above, the correlation function  $\langle \vec{M}(t) \cdot \vec{M}(0) \rangle$  may be determined. One obtains

$$\tau = \int_0^\infty dt \frac{\langle \vec{J}(t) \cdot \vec{J}(0) \rangle}{\langle \vec{J}(0) \cdot \vec{J}(0) \rangle}, \quad \omega_0^2 = \frac{\langle \vec{J}^{(1)}(0) \cdot \vec{J}^{(1)}(0) \rangle}{\langle \vec{J}(0) \cdot \vec{J}(0) \rangle},$$

$$\omega_1^4 = \frac{\langle \vec{J}^{(2)}(0) \cdot \vec{J}^{(2)}(0) \rangle}{\langle \vec{J}(0) \cdot \vec{J}(0) \rangle}.$$

The spectral density  $G(\omega)$ , given by Eq. (2), may

then be derived by Fourier transforming Eq. (7). This result does not need the solution of the secular equation, which is required to obtain the correlation function, and may be directly expressed with the help of the three parameters just mentioned. By either method one readily obtains

$$G(\omega) = \frac{\left(\frac{\omega^2}{\omega_0^2}\right) \tau \Phi(0)}{\left[1 - \frac{\omega^2}{\omega_0^2}\right]^2 + \omega^2 \tau^2 \left[1 - \frac{\omega^2}{\omega_0^2} - \frac{\omega_1^4}{(\omega_0^2)^2}\right]} \quad (9)$$

The problem which remains is to estimate the parameters  $\tau$ ,  $\omega_0^2$ , and  $\omega_1^4$ .

### C. Estimation of parameters

In the Zwanzig-Mori method, the physics is contained in the parameters of the transport matrix  $\Gamma$ . Thus, any *ad hoc* approximation or fitting procedure employed to estimate these parameters can hide the reality of the physical processes involved. Fortunately, analytical expressions for  $\tau$ ,  $\omega_0^2$ , and  $\omega_1^4$  may be established in classical mechanics without approximation, namely,

$$\tau = \frac{D_{AB}}{kT} \left[ \frac{1-x}{m_A} + \frac{x}{m_B} \right]^{-1}, \quad (10a)$$

$$\omega_0^2 = \frac{4\pi\rho}{3} \left[ \frac{1-x}{m_A} + \frac{x}{m_B} \right] \int dr_{11'} g_{AB}(r_{11'}) \frac{d}{dr_{11'}} \left[ r_{11'}^2 \frac{\partial u_{11'}}{\partial r_{11'}} \right], \quad (10b)$$

$$\begin{aligned} \omega_1^4 = & \frac{4\pi\rho}{3m_{AB}} \left[ \frac{1-x}{m_A} + \frac{x}{m_B} \right] \int dr_{11'} g_{AB}(r_{11'}) \left[ 2 \left[ \frac{\partial u_{11'}}{\partial r_{11'}} \right]^2 + r_{11'}^2 \left[ \frac{\partial^2 u_{11'}}{\partial r_{11'}^2} \right]^2 \right] \\ & + \frac{(1-x)\rho^2}{3m_A} \left[ \frac{1-x}{m_A} + \frac{x}{m_B} \right] \int d\vec{r}_{11'} d\vec{r}_{12'} g_{ABB}(\vec{r}_1, \vec{r}_1', \vec{r}_2') \\ & \times \left[ \frac{1}{r_{11'} r_{12'}} \frac{\partial u_{11'}}{\partial r_{11'}} \frac{\partial u_{12'}}{\partial r_{12'}} + \frac{1}{r_{11'}} \frac{\partial u_{11'}}{\partial r_{11'}} \frac{\partial^2 u_{12'}}{\partial r_{12'}^2} + \frac{1}{r_{12'}} \frac{\partial u_{12'}}{\partial r_{12'}} \frac{\partial^2 u_{11'}}{\partial r_{11'}^2} \right. \\ & \left. + \frac{(\vec{r}_{11'} \vec{r}_{12'})^2}{r_{11'}^2 r_{12'}^2} \left[ \frac{1}{r_{11'}} \frac{\partial u_{11'}}{\partial r_{11'}} - \frac{\partial^2 u_{11'}}{\partial r_{11'}^2} \right] \left[ \frac{1}{r_{12'}} \frac{\partial u_{12'}}{\partial r_{12'}} - \frac{\partial^2 u_{12'}}{\partial r_{12'}^2} \right] \right] \\ & + \frac{x\rho^2}{3m_B} \left[ \frac{1-x}{m_A} + \frac{x}{m_B} \right] \int d\vec{r}_{11'} d\vec{r}_{21'} g_{AAB}(\vec{r}_1, \vec{r}_2, \vec{r}_1') \\ & \times \left[ \frac{1}{r_{11'} r_{21'}} \frac{\partial u_{11'}}{\partial r_{11'}} \frac{\partial u_{21'}}{\partial r_{21'}} + \frac{1}{r_{11'}} \frac{\partial u_{11'}}{\partial r_{11'}} \frac{\partial^2 u_{21'}}{\partial r_{21'}^2} + \frac{1}{r_{21'}} \frac{\partial u_{21'}}{\partial r_{21'}} \frac{\partial^2 u_{11'}}{\partial r_{11'}^2} \right. \\ & \left. + \frac{(\vec{r}_{11'} \vec{r}_{21'})^2}{r_{11'}^2 r_{21'}^2} \left[ \frac{1}{r_{11'}} \frac{\partial u_{11'}}{\partial r_{11'}} - \frac{\partial^2 u_{11'}}{\partial r_{11'}^2} \right] \left[ \frac{1}{r_{21'}} \frac{\partial u_{21'}}{\partial r_{21'}} - \frac{\partial^2 u_{21'}}{\partial r_{21'}^2} \right] \right]. \quad (10c) \end{aligned}$$

Here  $D_{AB}$  represents the mutual diffusion coefficient,  $\rho$  the number density of the fluid mixture,  $m_{AB}$  the reduced mass of a colliding pair and  $u_{11'} = u(r_{11'})$  the pair potential between the two dissimilar atoms (11').

The value of the correlation time  $\tau$  depends on that of the mutual diffusion coefficient which at

the present time is not accurately known (see Ref. 39). It is worth noticing that  $\tau$  is nothing but the correlation time of the interdiffusion current fluctuation  $\vec{J}$  (see Ref. 36).

The calculation of  $\omega_0^2$  and  $\omega_1^4$  involves the two- and three-particle distributions functions  $g_{AB}$ ,  $g_{AAB}$ , and  $g_{ABB}$ , whose evaluation for fluid mixtures is a

problem in itself and has only been investigated in the last few years.<sup>40-43</sup> The molecular-dynamic results, based on different type of approximations in simulating the rare-gas mixture, are as yet qualitative. Nevertheless, the integrals involved in Eqs. (9b) and (9c) may be estimated by emphasizing the following points. The short-range contributions to the integrals are largely dominant due to the overlap character of the induced dipole.  $g_{AB}(r)$  may then be replaced by its limit  $e^{-\beta u_{AB}(r)}$ , which is valid for small  $r$  or very low densities. When the calculations are performed with the help of computer generated  $g_{AB}(r)$ , the results are only changed

$$\omega_1^4 = \frac{4\pi}{3} \rho \left( \frac{1-x}{m_A} + \frac{x}{m_B} \right) \left[ \frac{1}{m_{AB}} - \frac{(1-x)\rho}{m_A \rho_0} - \frac{x\rho}{m_B \rho_0} \right] \int dr_{11'} g_{AB}(r_{11'}) \left[ 2 \left[ \frac{\partial^2 u_{11'}}{\partial r_{11'}^2} \right]^2 + r_{11'}^2 \left[ \frac{\partial^2 u_{11'}}{\partial r_{11'}^2} \right]^2 \right]. \quad (11)$$

It must be pointed out that the value of  $\rho_0$  is not entirely fixed by the lattice-gas model.  $\rho_0$  may conveniently be identified with the close-packing density, namely,  $\rho_0 = \sqrt{2}/\sigma_0^3$ , where  $\sigma_0$  is the effective diameter in the substituted fluid, given by the van der Waals mixing rule (see Ref. 40). Actually, one would expect the value of  $\rho_0$  to be contained between the close-packing density and the solid density of the mixture.

The quantum corrections to these results can be evaluated by using the method given in Ref. 18. The lowest-order quantum corrections of  $\omega_0^2$  and  $\omega_1^4$  amount to less than 10% for the heavy mixtures like Kr-Ar but are greater in the lighter mixtures. A further investigation indicates that the contribution for heavy mixtures of these corrections to the spectra obtained by the theory is small and leads to no essential improvement of the results.

### III. ABSORPTION SPECTRA

Contrary to the low-pressure gas phase where extensive experimental data are available, systematic investigations at higher densities, and, particularly at liquid densities, have only been undertaken recently. Although some discrepancies appear by comparing different experimental data, due to the intrinsic difficulties of experiment, the following conclusions may be reached: (i) At liquid densities, and for dilute solution of He, Ne, and Kr in liquid Ar,<sup>25,26,45,46</sup> the profile  $G(\omega)$  presents a low-frequency dip ( $\Delta_{1/2} \geq 10 \text{ cm}^{-1}$ ) as well as a high-

frequency wing. Although not yet experimentally detectable,  $G(0)$ , the minimum of the dip, could be close to zero. (ii) At lower densities, e.g., in highly or moderately compressed mixtures of noble gases,<sup>47-53</sup> the dip narrows ( $\Delta_{1/2} < 10 \text{ cm}^{-1}$ ) and eventually escapes experimental detection. (iii) At high frequencies the band shape is non-Lorentzian and is weakly density dependent. (iv) In dilute solutions, the maximum of  $G(\omega)$  shifts to lower frequencies and the width of the high-frequency wing decreases when the mass of the dissolved atom increases.

Applying the theory described in this paper, the experimental data [Fig. 1(a)], may be interpreted as follows [Fig. 1(b)]. (i) Two modes are theoretically predicted, a dissipative mode due to the mutual diffusion of atoms and an oscillatory mode associated with their oscillations around a given site in the fluid. These two modes correspond to the real root  $\lambda_1$  and to the complex conjugate root  $\lambda_2 \pm i\lambda_3$ , respectively, of the transport matrix  $\Gamma$ . (ii) Their spectral behavior may conveniently be illustrated by Fourier transforming the first and the second terms of the correlation function (8) (Fig. 2). The oscillatory mode, obtained from the second term, generates the wing at medium and high frequencies. At liquid densities its spectral behavior is governed essentially by  $\omega_0^2$ , a quantity similar to the Einstein frequency

$$\omega_E^2 = \rho/3m \int d\vec{r} g(r) \partial^2 u(r) / \partial r^2,$$

of an atom in a cell of a solid and which characterizes the rattling motion between dissimilar atoms. In turn, the dissipative mode, obtained

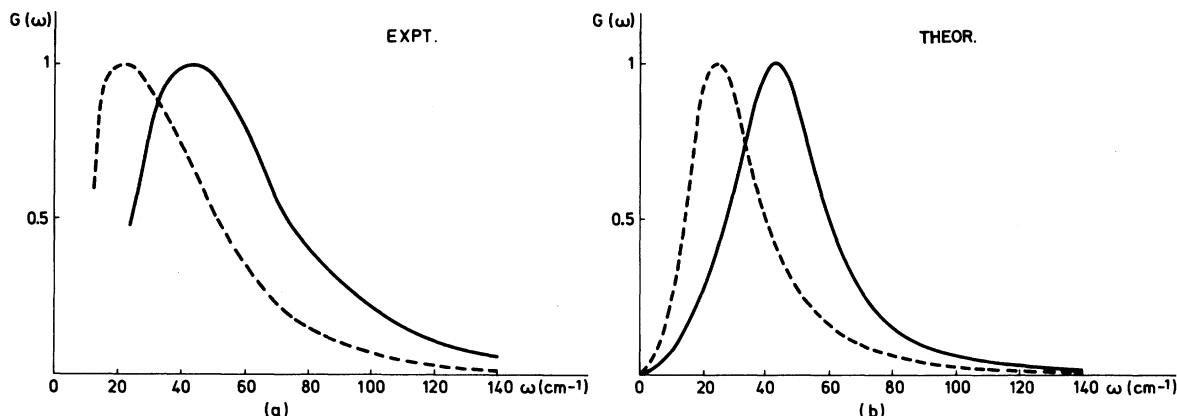


FIG. 1. (a) The experimental reduced line shapes are those given in Refs. 26 and 46; —, neon in liquid argon with  $x_{Ar}=0.989$ ,  $T=90$  K,  $\rho=728$  amagat; ----, krypton in liquid argon with  $x_{Ar}=0.85$ ,  $T=135$  K. (b) Theoretical spectra; —, Ne-Ar with  $x_{Ar}=0.989$ ,  $T=90$  K,  $\rho=728$  amagat; ----, Kr-Ar with  $x_{Ar}=0.85$ ,  $T=135$  K,  $\rho=380$  amagat. All spectra are normalized. (See Ref. 56.)

from the first term, generates an inverted Lorentzian which, when coupled to the oscillatory mode, produces the low-frequency dip in the profile  $G(\omega)$ . Its half-width is of the order of  $1/\tau$ , the correlation time of the interdiffusion current fluctuation. Correspondingly, the correlation function exhibits a damped oscillation (Fig. 3), which is readily understood by considering the physical nature of the two modes. (iii) The evolution of the profile with density, concentration, and atomic masses of the two components is explicitly

described by the theory. In a dilute solution, the shift of  $G_{max}(\omega)$  is proportional to the square root of the mass of the dilute atom as expected from the expression of  $\omega_0^2$ . At lower densities (Figs. 4 and 5), the low-frequency dip narrows, due essentially to the density dependence of the mutual diffusion coefficient, to a point where for weakly compressed mixtures its half-width no longer remains detectable. The two modes then are decoupled and the diffusive mode only is respon-

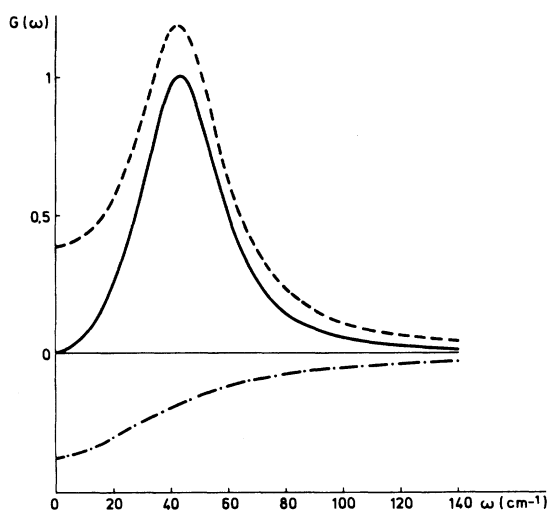


FIG. 2. Spectral contributions to the profile. For neon in liquid argon: —, total spectrum; ----, spectral intensity associated with the diffusive mode; - · - · -, spectral intensity associated with the oscillatory mode.

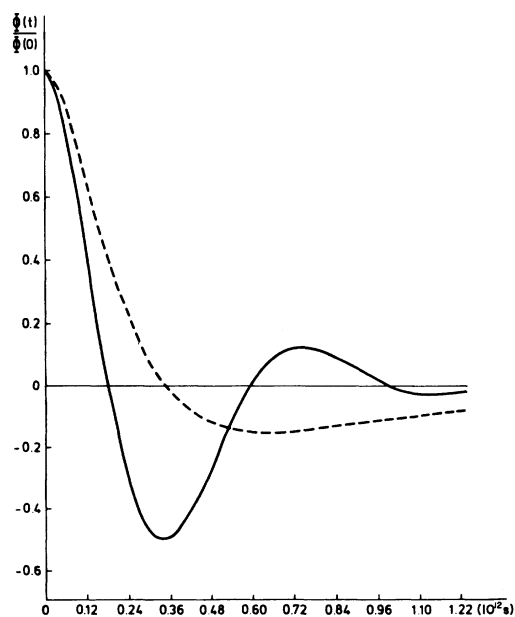


FIG. 3. Theoretical correlation function; —, Ne-Ar with  $x_{Ar}=0.989$ ,  $T=90$  K,  $\rho=728$  amagat; ----, Ne-Ar with  $x_{Ar}=0.989$ ,  $T=130$  K,  $\rho=280$  amagat.

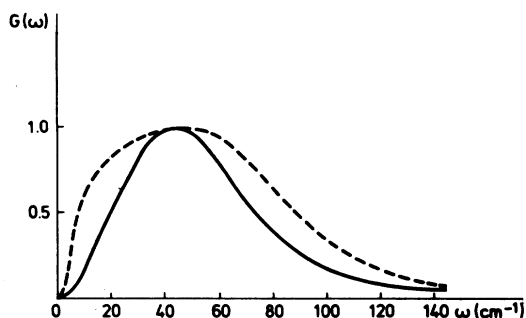


FIG. 4. Theoretical spectra; —, Ne-Ar with  $x_{Ar}=0.989$ ,  $T=130$  K,  $\rho=597$  amagat; ----, Ne-Ar with  $x_{Ar}=0.989$ ,  $T=130$  K,  $\rho=280$  amagat. All spectra are normalized.

sible for the dip. In turn, the caging spike collapses, reflecting the disappearance of the cage effect and only simple binary collisions contribute to the wing of the spectrum. Consequently, the correlation function exhibits an overdamped oscillation (Fig. 3). However, the far wing of the spectrum is only qualitatively given by the theory because the free motion responsible for this far wing is not well described by the method used for solving the generalized Langevin equation (7).

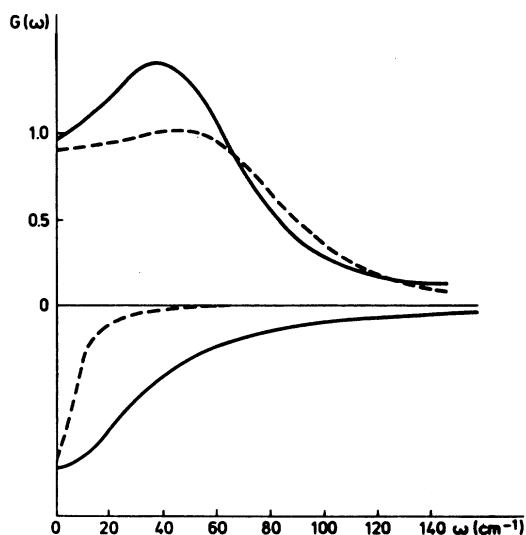


FIG. 5. Spectral contributions to the profile. —, Ne-Ar with  $x_{Ar}=0.989$ ,  $T=130$  K,  $\rho=597$  amagat; ----, Ne-Ar with  $x_{Ar}=0.989$ ,  $T=130$  K,  $\rho=280$  amagat.

#### IV. DISCUSSION

The present theory emphasizes the crucial role played in the description of collision-induced absorption of atomic mixtures at high densities by two modes of atomic motions, the diffusive mode due to the mutual diffusion of atoms, and the oscillatory mode due to oscillations in the local structure of the fluid. This fact had already been recognized in the study of depolarized light scattered by dense rare-gas fluids (see Ref. 44). The three-variable Zwanzig-Mori theory thus appears to be a powerful tool for providing an estimate of the spectrum provided its parameters are available. In this sense, the description of the total dipole moment in terms of the interdiffusion current fluctuation turns out to be a useful element of the interpretation.

The proportionality between the microscopic dipole moment and the microscopic force requires that the dip goes to zero at zero frequency. This latter feature exhibited by the theory seems to be supported by considering the incomplete low-frequency data on atomic mixtures. If this proportionality does not hold, the dip does not go to zero and can have, as found in a previous theoretical investigation (unpublished), several shapes which depend on the relative values of the parameters involved. Clearly, available experimental data at low enough frequencies are crucial for the investigation of this matter.

The differences observed between theory and experiment are due to deficiencies in this theory, which we summarize here. A primary cause is likely to be the truncation of the Zwanzig-Mori expansion. Also, the parameters  $\tau$ ,  $\omega_0^2$  and  $\omega_1^4$  may be inaccurate because of uncertainty in the value of  $\rho_0$  and in the choice of the potential. Finally, a complete quantum treatment important for the far wing, requires a new development outside the scope of this work.

It is interesting to compare this theory with that of Van Kranendonk.<sup>19</sup> The latter is based on kinetic considerations where the temporal superposition of dipoles induced in successive collisions interfere and produce a dip in the spectrum. The function describing the shape of the dip is convoluted with that describing the remainder of the line to obtain an estimate of the complete spectrum. In the present work, the dip results basically from the mutual diffusion of the atoms although its shape is determined, at high densities, by the contribution of the diffusive mode and by the contribution of

the oscillatory mode. The latter is the counterpart at low densities of the binary-collision portion of the van Kranendonk spectral density. The present theory thus extends the calculation of the infrared absorption in rare-gas mixtures to high densities by treating the many-body interactions explicitly, and gives the density dependence of the complete spectrum.

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### APPENDIX

The Zwanzig-Mori theory<sup>54,55</sup> is well known and only a few comments should be sufficient here. According to this theory, the correlation matrix  $\Theta(t) = \langle A(t)A(0) \rangle$  of a dynamical quantity  $A = (A_1, A_2, \dots, A_n)$  obeys the generalized Langevin equation,

$$\frac{d\Theta(t)}{dt} = i\Omega\Theta(t) - \int_0^t ds K(s)\Theta(t-s), \quad (\text{A1})$$

where  $\Omega$  is the  $n \times n$  frequency matrix and  $K$  the corresponding  $n \times n$  memory matrix. This equation can be solved by successive approximations which converge, in principle, to the exact solution.

In the present case, the method involves the following steps. (i) The interdiffusion current fluctuation  $\vec{J}(pq;t)$  is expandable in a Taylor series in  $t$ ,

$$\vec{J}(pq;t) = \sum_{n=0}^{\infty} \frac{t^n}{n!} \vec{J}^{(n)}(pq;0). \quad (\text{A2})$$

This equation is reinterpreted in terms of the Zwanzig-Mori theory by stating that  $\vec{J}(pq;t)$  is contained in that part of the Hilbert space of

dynamical variables generated by  $\{\vec{J}^{(0)}, \vec{J}^{(1)}, \dots, \vec{J}^{(n)}, \dots\}$ . (ii) Successive approximations for  $\langle \vec{J}(t) \cdot \vec{J}(0) \rangle$  are obtained by constructing  $\Theta(t)$  on the successive subspaces  $\{\vec{J}^{(0)}\}$ ,  $\{\vec{J}^{(0)}, \vec{J}^{(1)}\}$ , ...,  $\{\vec{J}^{(0)}, \dots, \vec{J}^{(n)}\}$ , and by assigning to the corresponding  $n \times n$  memory matrix the analytical form  $K^{(n)}(t) = K^{(n)}\delta(t)$  with

$$K^{(n)} = 2 \lim_{z \rightarrow 0} \int_0^{\infty} dt e^{-zt} K^{(n)}(t).$$

The approximations of this sequence are called the one-variable, the two-variables, etc., and the  $n$ -variable theory, respectively. (iii) By eliminating in a rigorous way the projected Liouville operator appearing in the memory matrix, the transport matrix of the  $n$ -variable theory  $\Gamma^{(n)} = -i\Omega^{(n)} + K^{(n)}$ , can be explicitly given in terms of the time integral of  $\langle \vec{J}(t) \vec{J}(0) \rangle$ , and its first  $(2n)$  even time derivatives. Practically, in the frame of the three-variable theory, the transport matrix may be expressed as

$$\Gamma^{(n)} = -i\Omega^{(n)} + K^{(n)} = \begin{pmatrix} 0 & -1 & 0 \\ \omega_0^2 & 0 & -1 \\ 0 & \frac{\omega_1^4}{\omega_0^2} - \omega_0^2 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \left[ \frac{\omega_1^4}{(\omega_0^2)^2} - 1 \right] \tau^{-1} \end{pmatrix}, \quad (\text{A3})$$

where  $\tau$ ,  $\omega_0^2$ , and  $\omega_1^4$  are defined in Sec. II B. By considering the expression (A3), the solution of the Langevin equation (A1) is straightforward and yields the expression (8) for the element of the correlation matrix

$$\Theta_{22}(t) = \langle \vec{J}^{(1)}(t) \cdot \vec{J}^{(1)}(0) \rangle.$$

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