Interaction-induced dipole and absorption spectra of collisional He-Ar pairs

Lothar Frommhold[1] and Michael V. Tonkov[2]

[1]*Physics Department, University of Texas at Austin, Texas 78712-1081*
[2]*Physics Department, St. Petersburg University, St. Petersburg, Russia*

We compute the absorption coefficient in the far infrared of collisional He-Ar pairs for comparison with measurements at four temperatures (140, 165, 200, and 240 K) in mixtures of helium and argon. An accurate *ab initio* dipole surface and an advanced model of the He-Ar interaction potential are input. The comparison with the measured absorption spectra shows agreement, generally within the accuracy of the measurement of roughly 10%. This fact suggests that this *ab initio* dipole surface of He-Ar pairs is probably as accurate as it was claimed to be (± 3–5 %) in the range where the optical interactions take place at the above temperatures. Three types of line profiles are considered: classical, quantal, and a ''symmetrized'' quantal profile, which has been believed to approximate the classical profile. Classical and symmetrized profiles diverge, however, with increasing frequency. This fact suggests that analyses of measured spectra based on symmetrized profiles should be reconsidered. [S1050-2947(96)04112-1]

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I. ABSORPTION SPECTRA

Pure monatomic gases do not absorb electromagnetic radiation, except at photon energies of several eV and higher. Mixtures of rare gases, on the other hand, absorb in the microwave and far infrared regions of the spectrum [1,2] due to dipoles induced in dissimilar pairs, such as He-Ar atomic pairs in collisional interaction [3–5]. The processes which generate the induced dipole moments are related to the interaction mechanisms familiar from the study of van der Waals forces: exchange, overlap, and dispersion. The dipole surfaces of specific systems are thus potentially as interesting as the interaction potentials. Interaction-induced dipoles are small, but perturbation techniques cannot be used for their computation, because of the well known problems of accounting for exchange at short range. In recent years accurate quantum chemical calculations have appeared which account nearly fully for the effects of configuration interaction [5]. Absorption spectra,

$$\alpha(\omega) = \frac{4\pi^2}{3\hbar c} N_L^2 \rho_1 \rho_2 \omega [1 - \exp(-\hbar\omega/kT)] V G(\omega), \quad (1)$$

calculated from such *ab initio* dipole surfaces were generally found to be in remarkably close agreement with the measurements of collision-induced absorption spectra [6,7]. In Eq. (1) α designates the absorption coefficient, which is a function of frequency ω and temperature T; $\hbar$ is Planck's constant; c is the speed of light in vacuum; $N_L = 2.7 \times 10^{19}$ particles per cm^3 is Loschmidt's number; ρ_1, ρ_2 are the densities of helium and argon in amagats; and $VG(\omega)$ is the so-called spectral density or spectral function, which is also a function of frequency and temperature. We note that the product $VG(\omega)$ does not depend on the sample volume V [5]. Quantum mechanical computer codes exist which permit the calculation of $VG(\omega)$ if the dipole and potential functions are known [5].

One advanced calculation of interaction-induced dipole surfaces exists for rare gas pairs. The He-Ar *ab initio* dipole surface may be represented by the analytical expression [8]

$$\mu(R) = \mu_0 \exp[-a(R - R_0) - b(R - R_0)^2] - \frac{D_7}{R^7}. \quad (2)$$

Here, R designates the separation of the collisional pair (in atomic length units); $\mu_0 = 0.0386$ a.u.; $R_0 = 4.50$ a.u.; $D_7 = 290$ a.u.; $a = 1.37$ a.u.; and $b = 0.04\,832$ a.u. Equation (2) may be viewed as the sum of an exponential exchange term and the lowest-order dispersion term, but the numerical values given do not necessarily represent the accurate, pure exchange and dispersion contributions because of the oversimplified form of the equation, e.g., the neglect of damping at near range of the dispersion term and the absence of higher-order dispersion terms, $D_9/R^9 \ldots$. The numerical values specified above were obtained by a fit of the calculated data and represent these well over a range of separations from 4.5 to 7.5 bohrs. The dipole function (2) was used in conjunction with a good potential model to compute absorption spectra for comparison with existing measurements [8]. Reasonable agreement was observed. However, when the spectral function $VG(\omega)$ obtained from Bosomworth and Gush's celebrated measurement of the absorption spectrum of helium-argon gas mixtures [1] is plotted in a semilogarithmic grid, it shows a slight convex (arclike) curvature at low and high frequencies (where the absorption is small and thus difficult to measure accurately), which was not reproduced by the fundamental theory [8]. In other words, as far as this measurement at 298 K is concerned, a question remained whether the observed, slight inconsistencies in the wings of the spectral function are artifacts of the theory or of the measurement. Moreover, only one other measurement of the absorption spectrum [9] at 165 K was then considered, which apparently was not scaled correctly [8]; the comparison with the theory is not valid in that case.

In this paper we consider further measurements of the binary absorption spectra of helium-argon mixtures which are taken at temperatures of 140, 165, 200, and 240 K [10]. We will also reconsider the above mentioned measurement
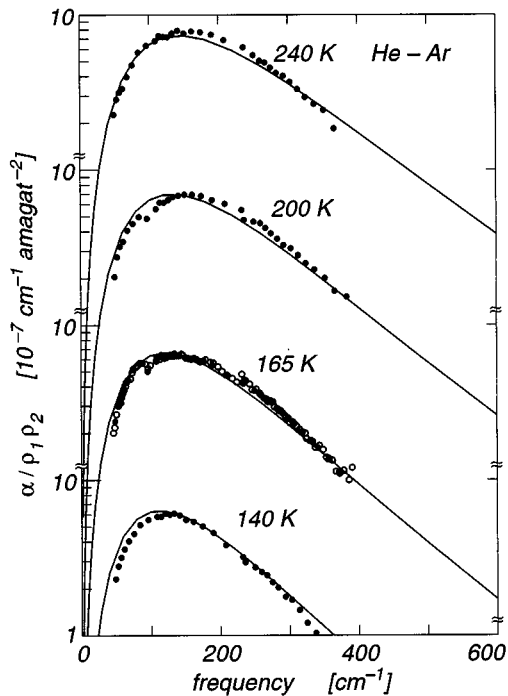
FIG. 1. Comparison of measurements of the absorption coefficient $\alpha(\omega)$, divided by the product of the helium and argon densities, at four temperatures (dots [10]; circles [9]) with spectra computed from the fundamental theory (solid lines).

at 165 K [9]. Absorption spectra are obtained using a quantum mechanical line shape computer code [5] and an advanced, so-called SPFD interaction potential [11], together with the *ab initio* dipole surface [8]. Figure 1 compares the measurements (dots, circles) with the *ab initio* profiles (solid lines). At the four temperatures agreement of theory and measurements is observed, both with regard to spectral shape and absolute intensity. The consistency is generally better than 10 %, the estimated mean uncertainty of the measurement (for not too small absorption; if $\alpha/\rho_1\rho_2$ falls below 10^{-7} cm^{-1} amagat^{-2}, the experimental uncertainties increase rapidly). We note that theory is believed to be slightly more accurate than the measurement: 3 – 5 % for the dipole surface, which amounts to 6 – 10 % for the spectra (which are proportional to dipole squared). No convex curvature (as seen in the 298 K measurement) seems to exist here, certainly not at the three higher temperatures; the hint of such a curvature of the 140 K data may be explained as alluded to above: weak absorption introduces large uncertainties with a fixed absorption length, when higher gas densities cannot be used because three-body contributions are to be avoided. The conclusion is that the *ab initio* dipole surface [8] is in harmony with the measurements at the four temperatures considered. The dipole, Eq. (2), is a reliable representation of the He-Ar dipole moment, at least at a range characteristic of He-Ar interactions at temperatures from roughly 140–300 K. We note that the dipole surface was developed strictly *ab initio*, that is, without resorting to any kind of adjustable parameters in the calculations [8].

We note that the use of another recent He-Ar interaction potential, an HFD-B model [12], in quantum line shape calculations gives profiles which are of a virtually identical

shape (not shown). The calculated integrated intensities are, however, somewhat reduced, namely, by 8 % at 140 K, falling off gradually to 2 % at 300 K. These calculated profiles are not really inconsistent with the measurements shown, even at the lowest temperature. According to the authors, the so-called HFD-B potential model [12] was not intended to supplant earlier models (including that of Ref. [11]) even though it was obtained with some care.

II. ABOUT ANALYSES OF THE SPECTRA

We note that the theoretical treatment above is based on exact quantum mechanical line-shape calculations. The spectral function VG obeys the quantum principle of detailed balance,

$$VG(-\omega)=VG(\omega)\exp(-\hbar\omega/kT). \tag{3}$$

Previous work has often attempted to replace the complex quantum computations by a much simpler classical formalism, for example by substituting the *symmetric* spectral function,

$$S(\omega)=\frac{1}{2}[1+\exp(-\hbar\omega/kT)]VG(\omega) \tag{4}$$

for $VG(\omega)$ if the measurements were done with "nearly classical systems," e.g., He-Ar pairs at the higher temperatures shown. $S(\omega)$, like the classical profile, is symmetric, $S(-\omega)=S(\omega)$, and is often believed to approximate the classical profile. By substituting the symmetric function $S(\omega)$ for the measured $VG(\omega)$, it was thought that the mea-
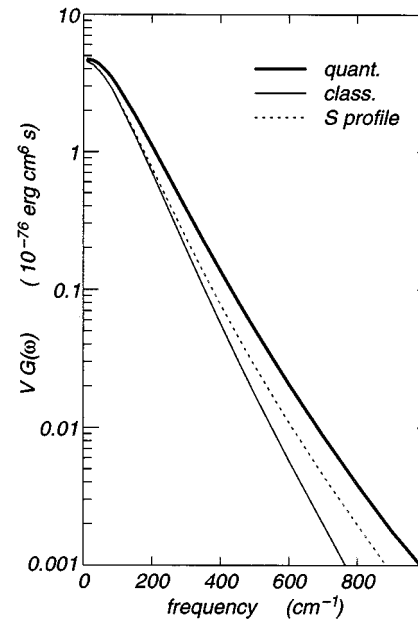

FIG. 2. Comparison of the classical and quantal He-Ar spectral function at 298 K with the "symmetrized" function, $S(\omega)$ of Eq. (4). With increasing frequency the classical and symmetrized functions diverge.

surement could then be analyzed using the much simpler classical expressions for spectral moments and/or line shapes.

The tacit assumption of the symmetrized function $S(\omega)$ representing the classical profile can be tested. Line shapes based on Newtonian mechanics are readily computed [13,5]. Moreover, since we have obtained the above quantal profiles, it is a simple matter to compute the symmetric function, $S(\omega)$ of Eq. (4). Figure 2 compares the classical and symmetric line shapes, the thin solid and the dotted lines, respectively. The quantum profile is also shown for comparison (thick line). The three profiles are computed from the same advanced interaction potential and the *ab initio* dipole function, for absorption by He-Ar pairs at 298 K. While at low frequencies the classical and the symmetrized profiles agree, it is clear that they diverge substantially with increasing frequency. This fact demonstrates that, except at the lowest frequencies, quantum kinetic processes affect the symmetrized function, $S(\omega)$, significantly; $S(\omega)$ does not approximate the classical profile.

Analyses of measured spectra are often based on spectral moments,

$$M_n = \int_{-\infty}^{\infty} VG(\omega)\omega^n d\omega, \qquad (5)$$

with $n = 0, 1, \ldots$. For small n, these are equal to sum formulas that are easily computed from potential and dipole surface; quantal and classical expressions are well known for that purpose [5]. Since all odd moments ($n = 1, 3, \ldots$)

vanish if symmetric or classical profiles are substituted for VG and since generally three lowest-order moments are needed for analyses of measurements, in the symmetrized measurement the zeroth, second, and fourth spectral moments of the function $S(\omega)$ will typically enter the analysis of a measurement. In other words, the deviations of $S(\omega)$ from the classical profile seen in Fig. 2 at high frequencies affect the analysis unfavorably, especially for the higher-order moments. For example, it has been shown elsewhere (p. 219 of Ref. [5]) that for He-Ar pairs at 300 K the second and fourth quantal and classical moments differ by factors of 1.2 and 1.7, respectively, for the reason seen in Fig. 2. (Note that the even-numbered moments of the quantum and the symmetrized functions are the same.) Obviously, if one strives for a precision of a measurement and analysis at the 10 % level, factors like 1.2 and 1.7 cannot be simply ignored. It is preferable not to symmetrize the measurements and use low-order moments for the direct analysis of the spectral function $VG(\omega)$. An analysis based directly on the measured (quantal) function VG the zeroth, first, and second moments of $VG(\omega)$ may be used with advantage. These moments may be computed with the help of classical formulas with low-order quantum corrections (e.g., of the Wigner-Kirkwood type), if the existing quantum moment computer codes are not accessible.

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