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

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A measurement of the infrared collision-induced absorption spectrum of collisional pairs of Ar and Xe atoms is reported. An improved empirical collision-induced dipole model is obtained, which, if combined with quantum line-shape computations, permits an accurate reproduction of the measured spectrum. [S1050-2947(98)01412-7]

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I. ABSORPTION SPECTRA

Pure monatomic gases do not absorb electromagnetic radiation, except at photon energies exceeding 10 eV or so. 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, e.g., individual Ar and Xe atoms in collisional interaction [3–5]. The interaction-induced dipole moments are generated by mechanisms that are familiar from the studies of interatomic forces: the exchange, overlap, and dispersion type interactions. The dipole surfaces of specific systems are thus potentially as interesting as the interaction potentials. In this paper we present a measurement of the absorption spectrum in the far infrared of argon-xenon gas mixtures at room temperature (292 K). The gas densities were kept as small as possible so that essentially the pure spectrum of Ar-Xe pairs (unaffected by contributions from ternary or higher-order complexes of atoms) is obtained. Based on an analysis of the spectral line shape and a refined interaction potential, an empirical dipole model is determined that permits the reproduction and prediction of spectroscopic measurements from line-shape calculations.

A Fourier-transform spectrometer was used with a resolution of 2 cm^{-1} in the 20–300 cm^{-1} region, with two beam splitters of 20 and 6 μm. The multireflection White cell has a base distance of 17.8 cm and is equipped with silicon windows. It is capable of withstanding pressures of 200 atm and permits temperature variations from 77 to 400 K. Our measurement was carried out at 292 K, with a path length of 358 cm, at partial gas densities from about 35 to 100 amagat.

The partial densities of the gases were determined in two steps. One gas was introduced into the cell of known volume (1.228 l). The pressure was measured with an accuracy of 0.4% and the density was calculated using the known second virial coefficient in the equation of state. Then the cell was cooled to liquid nitrogen temperature and the other gas was added. The quantity of this gas was found from the pressure decrease in another vessel of known volume (1.85 l). After that the gases were mixed for one day using convection enhanced by temperature gradients. We estimate the accuracy of the product of gas densities to be better than 5%.

Water impurities were removed with the help of P_2O_5 powder. The main difficulty was the removal of water from the inner surfaces of the cell. This was attempted by ‘‘washing’’ the heated cell many times with dry gas. After this procedure no traces of H_2O lines were found, so that the water concentration was lower than 1 part in 10^5.

The absorption coefficient is obtained according to

$$\alpha(\omega)=\ln[I_0/I(\omega)]/(L\rho_{\mathrm{Ar}}\rho_{\mathrm{Xe}}); \tag{1}$$

units are cm^{-1} amagat^{-2}. I_0 and $I(\omega)$ are incident and transmitted intensity, $\omega=2\pi c\nu$ is the angular frequency, ν is the frequency in units of cm^{-1}, c is the speed of light in vacuum, L is the absorption path length, and the ρ represent the densities of argon and xenon in units of Loschmidt's number, $N_L=2.68675\times10^{19}$ particles per cm^3, which very nearly amounts to the use of Amagat units. Special care was taken to measure the far wing of the spectrum where absorption is weak. Figure 1 shows the measured absorption of Ar-Xe pairs at room temperature (solid trace).

The absorption coefficient $\alpha(\omega)$ is related to the product of volume V and the so-called spectral function, $G(\omega)$, according to [5]

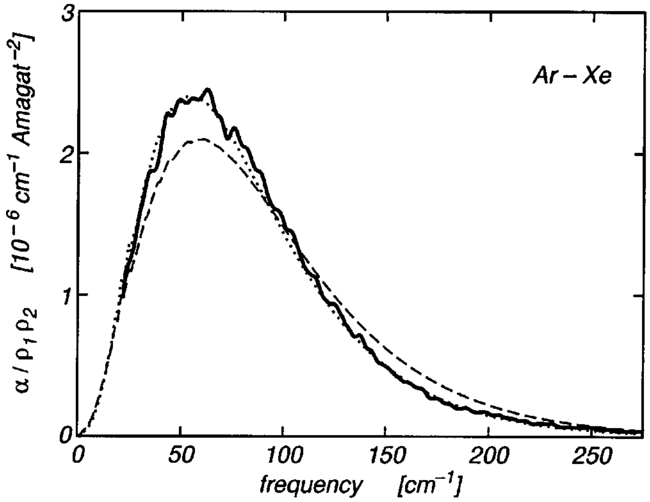

FIG. 1. The absorption spectrum at 292 K; experiment: solid; calculations: pure exponential dipole (dashed) and exp+D_7 dipole best fit model (dotted).

TABLE I. The experimental spectral moments.

T (K)	M_0 (erg cm^6)	M_1 (erg cm^6 s^{-1})	M_2 (erg cm^6 s^{-2})
292	1.69×10^{-61}	1.44×10^{-49}	1.12×10^{-35}

$$\alpha(\omega)=\frac{4\pi^2}{3\hbar c}N_L^2\rho_{\mathrm{Ar}}\rho_{\mathrm{Xe}}\omega[1-\exp(-\hbar\omega/kT)]VG(\omega). \tag{2}$$

That expression $VG(\omega)$ (which is actually independent of volume V) is readily computed from theory if models of the interaction potential and the collision-induced dipole function are available.

Important quantities are certain integrals of the measured spectra, the so-called spectral moments of the absorption coefficient α,

$$\gamma_1=\frac{1}{\rho_{\mathrm{Ar}}\rho_{\mathrm{Xe}}}\int_0^\infty\alpha(\nu)d\nu,$$
$$\gamma_0=\frac{1}{\rho_{\mathrm{Ar}}\rho_{\mathrm{Xe}}}\int_0^\infty\coth(hc\nu/2kT)\alpha(\nu)\frac{d\nu}{\nu}. \tag{3}$$

These are related to the moments

$$M_n=\int_0^\infty\left[1+(-1)^n\exp\left(-\frac{\hbar\omega}{kT}\right)\right]VG(\omega)\omega^n d\omega \tag{4}$$

of the spectral function $G(\omega)$ according to

$$\gamma_0=\frac{4\pi^2N_L^2}{3\hbar c}M_0,$$
$$\gamma_1=\frac{2\pi N_L^2}{3\hbar c^2}M_1. \tag{5}$$

For nearly classical systems such as Ar-Xe at 292 K, Planck's constant may be reduced to zero ($\hbar\rightarrow0$), so that $M_1\rightarrow0$ and

$$M_2\rightarrow\frac{2kT}{\hbar}M_1. \tag{6}$$

In this case, the number of spectral moments available for the analysis is reduced from three to two (M_0 and M_2). It is evident from the experimental results given in Table I that the ratio of M_1 and M_2 agrees within roughly 1% with $\hbar/2kT$.

Since an accurate determination of these spectral integrals requires knowledge of the absorption coefficient $\alpha(\nu)$ at low and high frequencies ($\nu\rightarrow0$, $\nu\rightarrow\infty$), which does not exist, it is best to approximate the spectral function $VG(\omega)$ by an analytical model profile with three parameters, the so-called K_0 model [5], which was shown to provide a remarkably close representation of virtually all line shapes arising from exchange and dispersion force induction [5–7]. These parameters have been determined by fitting the experimental spectrum, using a least mean squares procedure. From the fit the three lowest spectral moments of the measurement are readily obtained, Table I.

II. THE DIPOLE MODEL

The collision-induced dipole of two dissimilar rare gas atoms is of the form [5]

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

Here, R designates the separation of the collisional pair; μ_0 and a are adjustable strength and range parameters; $R_0=7.10$ a.u. is the approximate root of the potential; and the D_7 is another adjustable parameter. Equation (7) may be viewed as the sum of an exponential exchange term and the lowest-order dispersion term, but the numerical values obtainable in such fittings do not necessarily represent the accurate, pure exchange and dispersion contributions because of oversimplification of Eq. (7), e.g., the neglect of damping near the range of the dispersion term and the absence of higher-order dispersion force terms, D_9/R^9, etc.

For any given set of parameters μ_0, a, and D_7, the moments M_0, M_1, and M_2 can be computed (using Eqs. 5.41, 5.42, and 5.44 of Ref. [5]) if a reliable model of the interaction potential is known. We choose the so-called HFD-C potential [8], a refined semiempirical model based on a combination of measurement and theory. Starting from some initial guesses of the three parameters, we use again a least-mean-squares procedure to determine suitable parameters μ_0, a, and D_7 so that the lowest three moments M_n, with $n=0$, 1, 2, of Table I are closely matched. That match was always possible with a numerical precision that exceeded the accuracy of the measurement by several orders of magnitude. These parameters define a dipole model that we use to compute a quantum line shape; for details of such calculations see Ref. [5]. We will see here again, as seen previously [5,9], that for an unambiguous definition of an empirical dipole model it is not sufficient that the three lowest spectral moments are matched. Rather the complete spectral profile calculated from such a dipole model must match the measurement. Apparently, if a measurement is reduced to just two or three numbers (the spectral moments), much information is lost, which, however, may be utilized with advantage in a line-shape analysis.

The simplest dipole model is the pure exponential, with $D_7=0$ in Eq. (7). The three experimental moments are then reproduced with the parameter values $\mu_0=0.0124$ a.u. and $a=1.5121$ a.u. The dashed curve, Fig. 1, shows the result of a quantum line-shape calculation based on that dipole model. Despite the fact that the lowest three moments agree with the measurement, the computed profile differs strikingly from the measurement. Similar observations were previously reported for a variety of other gas mixtures [9,5]. We confirm here a previous conclusion that the pure exponential dipole model does not permit an accurate reproduction of the spectral profile.

Improved dipole models possess a nonvanishing D_7 dispersion coefficient that must be of a sign opposite to that of μ_0. We selected initial estimates of D_7 coefficients in the range of 300 a.u. and greater [5] to obtain μ_0 and a values that permit matching the three spectral moments of Table I. The dipole models thus defined were then used to calculate a spectral profile (as in Fig. 1). For small $D_7 \approx 300$ a.u., profiles resembling the dashed curve, Fig. 1, were obtained, but with increasing D_7 the absorption peak of the calculated spectral profiles increased in amplitude and appeared shifted more and more toward that of the measurement. Near perfect agreement was obtained for $D_7 = 14{,}200$ a.u., as shown in Fig. 1 (dotted); the associated values of the other two parameters are $a = 1.225\,22$ a.u. and $\mu_0 = 0.0284$ a.u., which defines our improved (relative to the best existing [10]) dipole model. Larger D_7 values (in excess of 14 200 a.u.) resulted in high-frequency wings that fall off too rapidly below measurement.

We note that an earlier dipole model was proposed for the Ar-Xe pair with $\mu_0 = 0.015$ a.u., $a = 1.416$ a.u., and $D_7 = 0$ [10]. That model was, however, based on a measurement [2] of the absorption coefficient $\alpha(\omega)$, which is consistently 10–20% smaller than our measurement; besides a presumably less refined potential model was used in that analysis. Since that measurement [2] was taken at much higher pressures (1800 bar), we think that it must have been affected by three-body interactions; three-body interactions tend to lower the absorption coefficient. The previous dipole model [10] can, therefore, not be compared with ours, which is based on a low-density measurement, i.e., on a much more purely binary absorption spectrum.

III. PURE XENON

In the course of the work described here, we have had the opportunity to look for absorption in unmixed xenon of high density. Pure rare gases cannot absorb radiation by binary interactions, owing to the inversion symmetry of the diatom, which is inconsistent with the existence of a dipole moment. However, it has long been argued that at high enough densities absorption via three-body and higher interactions should occur. At 200 amagat xenon density, with an absorption pathlength of 358 cm, we found no discernible absorption. In other words, if under those conditions ternary absorption in the far infrared exists, the ternary absorption coefficient α must be smaller than 5×10^{-11} cm^{-1} amagat^{-3}, that is much smaller than the theoretical estimate of 3.6×10^{-9} cm^{-1} amagat^{-3} for krypton suggested previously [11]; for xenon one would have expected an even larger value.

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