Electron scattering in dense He-Ar gas mixtures: A pressure shift study

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The dependence of the energies of high-n Rydberg states of CH_3I on the molar composition of helium-argon mixtures (in the number density range 1.3×10^{20}–5.6×10^{20} cm^{-3}) is reported. The energy shifts, when normalized to a given density value, are found to vary linearly with the mole fraction of either component of the binary, rare-gas mixture. The observed change in sign of the energy shift is attributable to the different signs of the electron scattering lengths for the two rare-gas components. As a result, there exists a mixture composition, at a mole ratio [He]/[Ar] ≈2.0, at which the shift is null. The experimental results for the gas mixture agree with the Fermi formula, as modified to include the Alekseev-Sobel'man polarization term. Effective electron scattering lengths and cross sections, polarizabilities, and thermal velocities are used to characterize the effects of the binary gas perturber system.

Recent attempts to describe the band properties of dense rare gases[1] have revived an interest in pressure shift studies at higher densities. Specifically, when alkali-metal absorbers[2] are replaced by molecular absorbers such as methyl iodide[3] and benzene,[4] an order of magnitude increase in the perturber gas density becomes possible. The shift of the high-n Rydberg states of these absorbers was found to vary linearly with perturber number densities as high as $\sim 2 \times 10^{21}$ cm^{-3}. Electron scattering lengths obtained from shift data for He, Ne, Ar, and Kr (Refs. 3 and 4) agreed with the results of previous pressure shift studies[5,6] and with electron scattering cross sections extrapolated to zero energy.[7-10]

The interaction between a highly excited molecular absorber and the perturbing medium can be decomposed into two independent additive terms according to the Fermi model. These two terms are (i) a scattering term, $\Delta_{sc}(\rho)$, describing the interaction between the optical electron and perturber; and (ii) a polarization term, $\Delta_p(\rho)$, describing the interaction between the cationic core and the perturber. The sum of these two terms gives the total energy shift, $\Delta_t(\rho)$:

$$\Delta_t(\rho) = \Delta_{sc}(\rho) + \Delta_p(\rho) , \qquad (1)$$

where

$$\Delta_{sc}(\rho) = \pm (2\pi\hbar^2/m)a\rho , \qquad (2)$$

$$\Delta_p(\rho) = -10\alpha e^2 \rho^{4/3} , \qquad (3)$$

and m and e are the electronic mass and charge, respectively, a is the electron scattering length, ρ is the number density, and α is the polarizability of the perturber medium. The sign of the scattering term may be either positive or negative depending on the nature of the perturber. Because of the increasing contribution of the nonlinear polarization term at higher densities, the Fermi model cannot describe the observed linear density dependence of the energy shift. The observed linearity can be reproduced,[3] however, by replacing Eq. (3) with the polarization term of Alekseev and Sobel'man,[11] so that the modified Fermi formula now reads

$$\Delta'_t(\rho) = \pm (2\pi\hbar^2/m)a\rho - 9.87(a e^2/2)^{2/3}(h\upsilon)^{1/3}\rho , \qquad (4)$$

where υ is the relative thermal velocity of the colliding partners.

We report here some experimental results on the effects of the molar composition of a binary, rare-gas mixture of helium and argon on the energy positions of the high-n Rydberg states of CH_3I. We have measured the spectral shifts produced by helium-argon mixtures of varying molar compositions as well as by pure helium and argon gases. Research grade (Liquid Carbonic, 99.998%) He and Ar gases, both as single component perturbers and as mixed perturbers, were introduced into a pressure-tight absorption cell containing 0.3–0.5 torr CH_3I (Aldrich, 99%). The CH_3I had previously been purified by freeze-thaw procedures within the evacuated gas handling system. Further details on the experimental arrangement will appear elsewhere.[12] Special care was taken to insure a homogenous mixture of the CH_3I sample and the two high-pressure gases. The two components were alternately introduced into the cell in a series of 10–12 steps. The gas pressure was monitored using a calibrated Model 205-2 Setra pressure transducer. Densities for the pure rare-gas perturbers were $5 \times 10^{19} \leq \rho \leq 7 \times 10^{20}$ cm^{-3}, and for the mixtures they were $1.3 \times 10^{20} \leq \rho \leq 5.6 \times 10^{20}$ cm^{-3}. The spectrometer was a one meter McPherson Model 225 normal incidence monochromator equipped with a Hinteregger hydrogen lamp and a double beam chamber. The experimental bandwidth was 5.7 meV. Absorbance of the room-temperature gaseous mixtures was obtained using a McPherson Model 782 logarithmic ratiometer. Energy shifts were reproducible within an error of ±1.5 meV. Total energy shifts were evaluated for the nd and nd' spectral series of CH_3I for the $10 \leq n \leq 16$ members. In the case of binary mixtures, neither line splitting nor extra line broadening was observed. For the single-component perturbers, the following shift rates were obtained: 2.45×10^{-23} eV cm^3 for helium and -4.86×10^{-23} eV cm^3 for argon. These

values agree with the shift rate values reported in Refs. 3–6.

The absorption spectrum of the pure CH_3I in the high-n Rydberg transition range is shown in Fig. 1. The assignments[13] of the spectral features used in the shift analysis are shown at the top of Fig. 1. The two shaded areas indicate the observed range of the asymptotic line shift. The left-hand side, or "blue limit," of a shaded area represents the perturbation by pure helium and the right-hand side, or "red limit," refers to pure argon. The line positions for binary perturber mixtures fall between these two limits. Shifts due to both pure and binary perturbers are normalized to 1×10^{21} cm^{-3}.

These normalized shift values for helium-argon binary perturbers of different molar compositions are shown in Fig. 2(a) as a function of mole fraction. The experimental points for the binary mixtures lie on the solid line that connects the two shift limits for the pure helium and argon perturbers. Starting from pure He, the shift decreases with increasing Ar content; at a molar ratio [He]/[Ar] $=2$ the shift is zero; and as Ar concentrations increase, the shift changes sign and decreases toward the limiting value for pure Ar. The fact that our experimental points fall on the solid line [Fig. 2(a)] proves the following formula:

$$\Delta'_{tm}(\rho) = X_1 \Delta'_{t1}(\rho) + X_2 \Delta'_{t2}(\rho) . \quad (5)$$

The total shift, $\Delta'_{tm}(\rho)$, produced by the binary rare-gas mixture is a weighted sum of the shifts effected by the
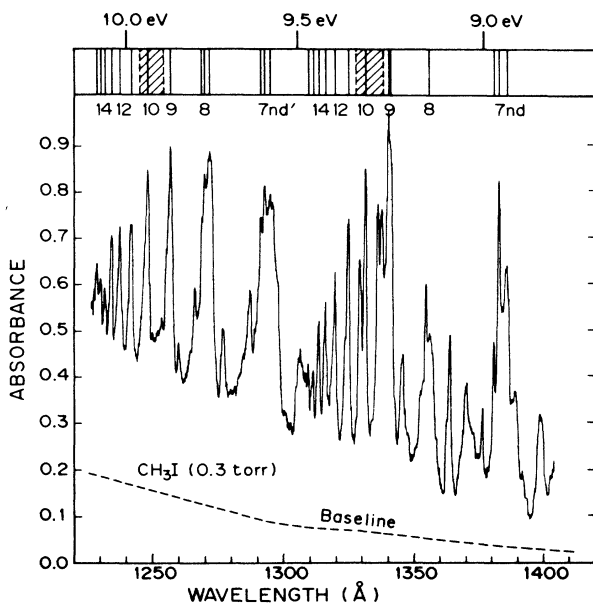

FIG. 1. Room-temperature absorption spectrum of pure CH_3I vapor. The nd and nd' Rydberg series are identified at the top of the figure. The range of spectral shifts produced by He-Ar perturber are indicated at $n=10$ by shaded areas. The high-energy limit of the shaded range refers to the spectral shift effected by pure helium. The low-energy limit refers to pure argon. Both shifts and shift limits are normalized to a number density of 1×10^{21} cm^{-3}.
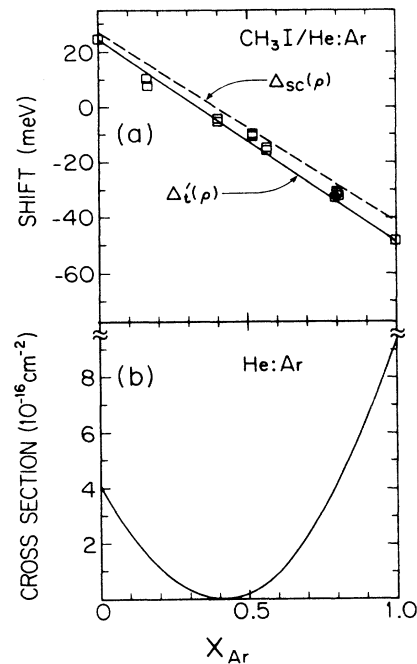

FIG. 2. (a) The "open squares" are averaged total shift values of the CH_3I nd and nd' series in the presence of perturber mixtures of He and Ar gases of varying molar fraction. The solid line, $\Delta'_t(\rho)$ connecting the two experimental shift limits for pure He and Ar perturbers can be reproduced by Eq. (4). The scattering shift is represented by the dashed line, and $\Delta_{sc}(\rho)$ is taken from Eq. (2). All shift values are normalized to number density of 1×10^{21} cm^{-3}. (b) Plot of effective electron scattering cross sections for various He-Ar gas mixture compositions. The cross sections, σ_{eff}-s, were calculated using $a_{eff} = 1.08 a_0 X_{He} - 1.63 a_0 X_{Ar}$ where X_{He} and X_{Ar} are molar fractions.

pure components. X_1 and X_2 are the appropriate molar fractions. The effect of molar ratio on the spectral shift can also be accounted for by inclusion of three effective parameters in Eq. (4). The effective parameters for the binary gas mixtures (i.e., the set $\{a_{eff}, a_{eff}, v_{eff}\}$) were obtained by taking a sum of the component parameters weighted according to their mole fractions. Thus, for example, we define

$$a_{eff} = X_{Ar} a_{Ar} + X_{He} a_{He} , \quad (6)$$

when X_{Ar} and X_{He} are the appropriate molar fractions. The polarizabilities for helium and argon are 0.21×10^{-24} and 1.66×10^{-24} cm^3, respectively; the relative thermal velocities are $v = (8kT/\pi\mu)^{1/2}$, μ is the absorber scatterer reduced mass and the scattering lengths for the single-component perturbers, as derived from our data are $1.08 a_0$ for helium and $-1.63 a_0$ for argon. The dashed line of Fig. 2(a) shows a similar effect on the scattering term, [Eq. (2)] of the He-Ar binary gas mixture. The dashed line [calculated from Eq. (2) using a_{eff}] describes the effect of molar ratio on the potential barrier. The He-rich mixture represents a "repulsive" barrier while the Ar-rich composition is an "attractive" barrier for the optical electron. The scattering shift, $\Delta_{sc}(\rho)$ refers only to the

interaction electron perturber. Therefore, it changes sign at a lower [He]/[Ar] molar ratio than the total shift, $\Delta_t'(\rho)$. The $\Delta_{sc}(\rho)$ becomes null and changes sign at [He]/[Ar] $= 1.5$ molar ratio.

Based on Eq. (6), effective scattering cross sections for high-n Rydberg electrons[14] could be calculated. It is the first attempt to derive cross sections for elastic electron scattering in rare-gas mixtures using pressure shift data. The effective cross sections at the low-velocity limit, $\sigma_{eff} = 4\pi a_{eff}^2$, for gaseous He-Ar mixtures are shown in Fig. 2(b). At a [He]/[Ar] $= 1.5$ molar ratio, σ_{eff} becomes zero.

This study presents new information on the scattering of optical (quasifree) electrons in dense rare-gas mixtures.

The electron scattering properties of rare-gas mixtures of any other combination are predictable and may be "tailored" by variation of the molar composition.

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