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# Density effects on high-$n$ molecular Rydberg states: $CH_3I$ in argon

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Absorption spectra of the high-$n$ molecular Rydberg states of $CH_3I$, perturbed by varying number densities of argon (up to $\sim 11\times10^{20}$ cm$^{-3}$), are reported. Red shifts, which increase with increasing argon number density, are observed for both discrete and autoionizing states. These red shifts vary linearly with the perturber number density for principal quantum numbers $n\geqslant10$. We explain these results quantitatively on the basis of the electron scattering length in argon, as well as the polarization of the medium by $CH_3I^+$.

The effects of a perturber atmosphere on highly excited (i.e., Rydberg) states of atoms and molecules is a historically important problem, originally treated theoretically by Fermi[1,2] (see also Refs. 3 and 4), which has gained increasing importance recently,[5–13] primarily as a result of a massive renascence of interest in Rydberg-state studies. The earlier molecular work focused on external pressure effects on low-energy Rydberg states[14,15] and, as a result, was unable to draw on the theoretical treatment of Fermi,[1,2] which is strictly applicable only for Rydberg states near their ionization threshold. In contrast, studies of high-$n$ atomic Rydberg states perturbed by an inert atmosphere of up to 4–6 rd (rd = relative density, 1 rd$\simeq2.7\times10^{19}$ cm$^{-3}$),[16–20] for example, cesium perturbed by the rare gases,[20] have shown the applicability of the Fermi theory near threshold, albeit not without raising several questions concerning the limits of this model.

In the present paper we report experimental results on the effect of increasing argon number density on the energy positions of high-$n$ Rydberg states of $CH_3I$, as measured by absorption spectroscopy. In addition, we provide an analysis of these data within the context of the Fermi model,[1,2] and a recent extension[8] of this model which incorporates a linear dependence of the polarization energy on the perturber number density. It is important to note that the number densities of argon considered in the present work are more than one order of magnitude larger than those previously employed in atomic studies.[20]

Our choice of $CH_3I$ for this study was predicated on the existence of extensive assignments[21–27] of those molecular Rydberg states which converge to $I_1\equiv I(^2E_{3/2})=9.538$ eV and $I_2\equiv I(^2E_{1/2})=10.164$ eV. Thus we were able to investigate argon pressure effects on the discrete states ($E_n<I_1$) as well as on the autoionizing states ($I_1<E_n<I_2$), all at energies below the cutoff of the LiF windows used in this study in the vacuum ultraviolet.

The experimental arrangement for the absorption measurements has been described previously;[28] the details of the sample cell[28] and of the gas-handling system[29] have been given. Briefly, monochromatic synchrotron radiation (DORIS storage ring, Deutsches Elektronen-Synchrotron, HONORMI monochromator, and data-acquisition system[30]) is passed through a stainless-steel sample cell capable of sustaining pressures up to $\sim100$ atm. Entrance to and exit from the sample cell is via a pair of optically matched LiF windows, thus permitting the measurement of transmission spectra $T(h\nu)$. These spectra, which are presented here as absorption spectra $A(h\nu)=1-T(h\nu)$, are normalized to both the incident photon flux and the empty-cell transmission.

The $CH_3I$ (99% pure) was from Merck-Schuchardt and was used without further purification. We verified the absence of contaminants in the spectral region of interest by comparison of our pure $CH_3I$ spectrum with previously published spectra.[22–26] The argon (99.997% pure) was from Deutsche l'Air Liquide.

Absorption spectra for pure $CH_3I$ ($p=0.1$ Torr, trace a) and for $CH_3I$ in Ar ($<10$ ppm $CH_3I$, traces b–e) are shown in Fig. 1. The spectral resolution in all cases is 2 meV. There is an obvious red shift of both the discrete and autoionizing structure as the argon number density is increased. The energy positions of the high-$n$ Rydberg states belonging to the $d$ and $d'$ series ($n\geqslant10$) are plotted versus argon number density in Fig. 2. (Zero argon number density corresponds to pure $CH_3I$ at $p=0.1$ Torr.) The energy shift is clearly linear over the large density range investigated. Moreover, this shift is independent of $n$, for $n\geqslant10$, as is shown in Fig. 3 for the $d$ series. (Our evaluation is limited to $nd,nd'$ states with $10\leqslant n\leqslant16$ because of the strong overlap and perturbation by members of other series for $n<10$, as well as the rapid line broadening with increasing argon number density for $n>16$.)

According to the Fermi model,[1,2] the energy shift $\Delta(\rho)\equiv E_n(\rho)-E_n(\rho=0)$ ($\rho$ is the perturber number density) for high-$n$ Rydberg states is comprised of two effects:

$$\Delta(\rho)=\Delta_{sc}(\rho)+\Delta_p(\rho)\quad. \tag{1}$$

Since, in a high-$n$ Rydberg state, the optical electron is far removed from the cationic core, this electron scatters off the perturber atoms as essentially a free electron, thereby inducing a shift in excitation energy which is given by[1,2]

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

where $m$ is the electron mass and $a$ is the scattering length

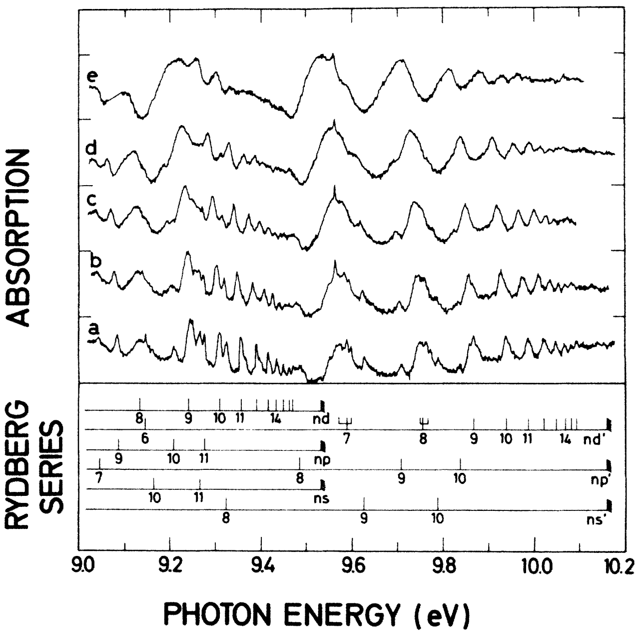

FIG. 1. Absorption spectra (room temperature) of pure $CH_3I$ (a, $p = 0.1$ Torr) and $CH_3I$ ( < 10 ppm) in argon. The argon number density is b, 1.5; c, 3.4; d, 5.7; e, $11.3 \times 10^{20}$ $cm^{-3}$. The spectral resolution is 2 meV. The assignments given in the lower frame refer to pure $CH_3I$.

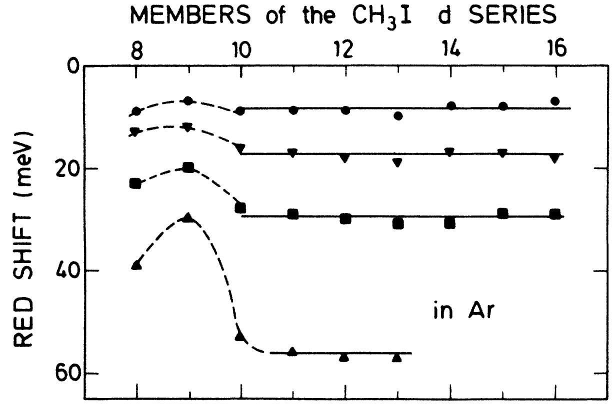

FIG. 3. $CH_3I$ $d$ series energy shifts vs principal quantum number for four argon number densities: ●, 1.5; ▼, 3.4; ■, 5.7; ▲, $11.3 \times 10^{20}$ $cm^{-3}$.

(determined by the nature of the perturber). Moreover, the cationic core polarizes the neighboring perturber atoms, thus leading to an additional shift in excitation energy which, in the Fermi model, is given by[1,2]

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

where $\alpha$ is the polarizability of the perturber.

It follows from the Fermi model that, for argon (scattering length $a = -1.70a_0$ and polarizability $\alpha = 1.63 \times 10^{-24}$ $cm^3$),[31] the energy shift $\Delta$ should not depend linearly upon $\rho$, at least for the high number densities reported in this Rapid Communication, where Eq. (3) predicts a strongly nonlinear behavior. This prediction is contradicted by the present results, as is shown in Fig. 4. In this figure we have plotted the average experimental shift of the $n \geq 10$ $d'$ Rydberg states (closed circles), $\Delta_{sc}$ (dotted line), and $\Delta_{sc} + \Delta_p$ (dot-dashed line), each as a function of increasing argon number density. The experimental data exhibit a linear dependence on $\rho$ which is not fully accounted for by $\Delta_{sc}$. Clearly, the treatment of $\Delta_p$ given by the Fermi model does

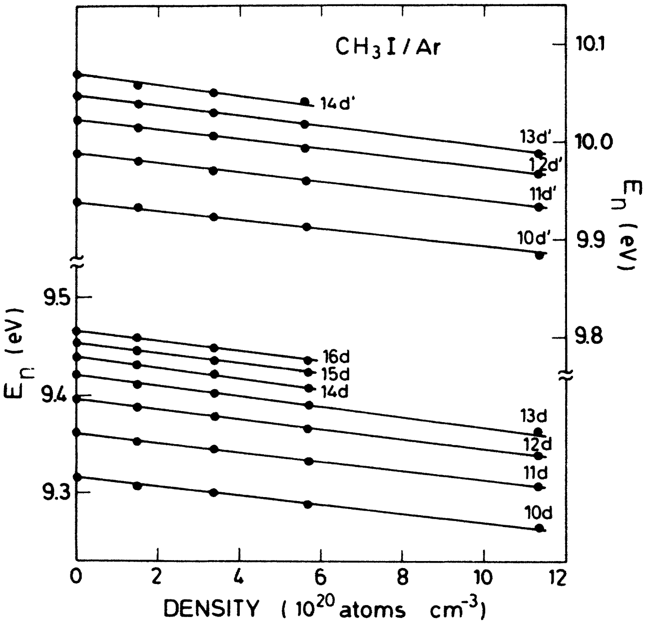

FIG. 2. Excitation energy positions of members of the $CH_3I$ $nd$, $nd'$ series as a function of argon number density. The lines are least-squares fits.

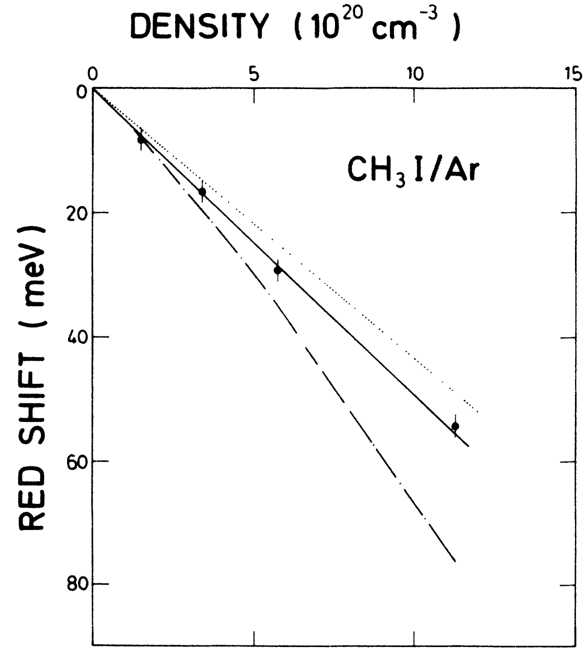

FIG. 4. $CH_3I$ $d'$ series energy shift vs argon number density. The experimental points, with error bars, represent the average (for $n \geq 10$) $d'$ energy shift. · · · , $\Delta_{sc}$ from Eq. (2) of text. — · — · , $\Delta$ from Eqs. (1)–(3) of text. ——, $\Delta$ from Eq. (5) of text.

not adequately describe the observed polarization effect.

Alekseev and Sobel'man[8] have presented an analysis of the polarization shift which is more general than that provided by the Fermi model. These authors find[8]

$$\Delta_p(\rho) = -9.87(\alpha e^2/2)^{2/3}(\hbar v)^{1/3}\rho \ , \qquad (4)$$

where $v$ is the average thermal velocity of the perturber atoms. They also show[8] that the scattering shift $\Delta_{sc}$ remains the same in their model as in the Fermi theory. Combining Eqs. (1), (2), and (4), then, we find

$$\Delta(\rho) = (2\pi\hbar^2/m)a_{\text{eff}}\rho \ , \qquad (5)$$

where the effective scattering length is given by

$$a_{\text{eff}} = a - 9.87(m/2\pi\hbar^2)(\alpha e^2/2)^{2/3}(\hbar v)^{1/3} \ . \qquad (6)$$

We have calculated $\Delta(\rho)$ from Eq. (5) using the values of $a$ and $\alpha$ given above, with $v = 4.3\times10^4$ cm/s. ($v$ was calculated from the Maxwell-Boltzmann distribution at $T = 300$ K.) This is plotted as a function of argon number density in Fig. 4 (solid line), and the agreement with experiment is excellent. Moreover, our value of $(2\pi\hbar^2/m)a_{\text{eff}} = 4.93\times10^{-23}$ eV cm$^3$ compares favorably with that reported previously[20] for (lower density) measurements of the high-$n$ Rydberg states of cesium in argon, namely, $4.63\times10^{-23}$ eV cm$^3$.

The validity of Eqs. (4)–(6) for high-$n$ Rydberg states in the presence of perturber atoms requires (i) that $n$ be so large that the perturber interacts independently with the optical electron and the cationic core, and (ii) that the impact approximation be valid (i.e., the time between collisions must be long in comparison to the interaction time for both electron-perturber and core-perturber scattering). Quantitatively, this means that[8]

$$r_i << n^2 a_0 \qquad (7)$$

and

$$\chi_i = r_i^3 \rho << 1 \ , \qquad (8)$$

where $r_i$, the Weisskopf radius of the cationic core, is $r_i = (\pi\alpha e^2/4\hbar v)^{1/3}$, while $\chi_i$ is a dimensionless parameter which represents the fraction of the core interaction volume sampled by a single perturber. Alekseev and Sobel'man[8] have shown an example, however, where even in the case when $\chi_i \simeq 1$, Eq. (4) remains valid for $\Delta_p$ as long as the inequality of Eq. (7) is satisfied. And, for the data of Figs. 3 and 4, Eq. (7) holds and $\chi_i \simeq 1$–$7$.

In summary, we have reported experimental results on the effect of argon perturbers on the high-$n$ Rydberg states of $CH_3I$. The perturber-induced energy shift of these states is constant for $n \geqslant 10$ and exhibits a linear dependence on the argon number density, which is in agreement with theory.[8] We find quite close agreement between our molecular measurements and similar measurements made on atoms even though, to our knowledge, this is the first study of high-$n$ Rydberg states made at such large perturber number densities. Finally, we note that we have performed similar measurements on $CH_3I$ perturbed by He, Ne, and Kr. These results will be reported in the near future.

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[1] E. Fermi, Nuovo Cimento **11**, 157 (1934).

[2] See, for example, H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford Univ. Press, 1952), p. 178.

[3] C. Reinsberg, Z. Phys. **105**, 460 (1937).

[4] O. B. Firsov, Zh. Eksp. Teor. Fiz. **21**, 627 (1951); **21**, 634 (1951).

[5] E. E. Nikitin, J. Chem. Phys. **43**, 744 (1965).

[6] B. M. Smirnov, Zh. Eksp. Teor. Fiz. **51**, 466 (1966) [Sov. Phys. JETP, **24**, 314 (1967)].

[7] E. Roueff, Astron. Astrophys. **7**, 4 (1970).

[8] V. A. Alekseev and I. I. Sobel'man, Zh. Eksp. Teor. Fiz. **49**, 1274 (1965) [Sov. Phys. JETP, **22**, 882 (1966)]; see also I. I. Sobel'man, L. A. Vainshtein, and E. A. Yukov, *Excitation of Atoms and Broadening of Spectral Lines* (Sringer-Verlag, Berlin, 1981), Chap. 7.

[9] O. Vallée, P. Ranson, P. Combis, and J. Chapelle, J. Phys. B **10**, L589 (1977).

[10] A. Omont, J. Phys. (Paris) **38**, 1343 (1977).

[11] A. Royer, Phys. Rev. A **22**, 1625 (1980).

[12] H. Allard and J. Kielkopf, Rev. Mod. Phys. **54**, 1103 (1982).

[13] B. Kaulakys, J. Phys. B **17**, 4485 (1984).

[14] M. B. Robin and N. A. Kuebler, J. Mol. Spectrosc. **33**, 274 (1970).

[15] I. Messing, B. Raz, and J. Jortner, Chem. Phys. **23**, 351 (1977); **25**, 55 (1977).

[16] T. Z. Ny and S. Y. Ch'en, Phys. Rev. **51**, 567 (1937); **54**, 1045 (1938).

[17] C. Füchtbauer and W. v. Heesen, Z. Phys. **113**, 323 (1939).

[18] C. Füchtbauer and G. Hansler, Phys. Z. **41**, 555 (1940).

[19] S. Ch'en and M. Takeo, Rev. Mod. Phys. **29**, 20 (1957).

[20] D. K. L. Tan and S. Y. Ch'en, Phys. Rev. A **2**, 1124 (1970).

[21] B. P. Tsai and T. Baer, J. Chem. Phys. **61**, 2047 (1974).

[22] P. Hochmann, P. H. Templet, H.-T. Wang, and S. P. McGlynn, J. Chem. Phys. **62**, 2588 (1975).

[23] S. Felps, P. Hochmann, P. Brint, and S. P. McGlynn, J. Mol. Spectrosc. **59**, 355 (1976).

[24] H.-T. Wang, W. S. Felps, G. L. Findley, A. R. P. Rau, and S. P. McGlynn, J. Chem. Phys. **67**, 3940 (1977).

[25] J. A. Dagata, G. L. Findley, S. P. McGlynn, J. P. Connerade, and M. A. Baig, Phys. Rev. A **24**, 2485 (1981).

[26] M. A. Baig, J. P. Connerade, J. Dagata, and S. P. McGlynn, J. Phys. B **14**, L25 (1981).

[27] G. L. Findley, J. A. Wilder, P. Hochmann, and S. P. McGlynn, in *Photophysics and Photochemistry in the Vacuum Ultraviolet*, edited by S. P. McGlynn, G. L. Findley, and R. H. Huebner (Reidel, Dordrecht, The Netherlands, 1985).

[28] V. Saile, R. Reininger, A. M. Köhler, and G. L. Findley, Nucl. Instrum. Methods A **238**, 558 (1985).

[29] R. Reininger, I. T. Steinberger, S. Bernstorff, V. Saile, and P. Laporte, Chem. Phys. **86**, 189 (1984).

[30] V. Saile, P. Gürtler, E. E. Koch, A. Kozevnikov, M. Skibowski, and W. Steinmann, Appl. Opt. **15**, 2559 (1976).

[31] T. F. O'Malley, Phys. Rev. **130**, 1020 (1963).