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Density effects on high-n molecular Rydberg states: CH_3I in He, Ne, Ar, and Kr

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Absorption studies of the high-n Rydberg states of CH_3I perturbed by varying number densities of He, Ne, Ar, and Kr (up to 23.0, 24.0, 11.3, and 6.6×10^{20} cm^{-3}, respectively) are reported. Energy shifts, which increase with increasing perturber number density, are observed and analyzed for both discrete $[nd(^2E_{3/2})]$ and autoionizing $[nd'(^2E_{1/2})]$ states. These shifts vary linearly with the perturber number density for principal quantum numbers $n\geq10$. Moreover, depending upon the nature of the perturber, these shifts are to the blue region (He), slightly to the blue region (or nearly zero) (Ne), or the red region (Ar and Kr). We explain these results quantitatively on the basis of the electron scattering length in the various rare gases, as well as on the polarization of the medium by CH_3I^+. For low perturber number densities, it is well known that the Fermi model of perturber effects on high-n Rydberg states is invalid. The present experimental results show, for the first time, that this model also fails at high number densities. On the other hand, the energy shifts can be reproduced quantitatively by extending a model developed by Alekseev and Sobel'man to high number densities.

I. INTRODUCTION

Highly excited (i.e., Rydberg) states of atoms and molecules are extremely sensitive to their surroundings because of the "large orbital" nature of these states. For this reason, Rydberg states have recently received an increasing amount of attention, particularly with regard to external field effects.[1] The interaction of electric and/or magnetic fields with the Coulomb field represents a set of fundamental problems of continuing interest. A no less fundamental problem, however, is posed by the interaction between the Coulomb field and external perturber atoms and/or molecules.

The study of host pressure effects on high-n Rydberg states has a rich, but sporadic, history. After the first experiments were performed on perturbed atomic Rydberg states,[2] Fermi presented a simple model to explain the shift in energy position of these states as a function of the perturber number density.[3,4] In this model, as we will explain in more detail below, the energy shifts were viewed as arising from two independent phenomena: (i) the optical electron, which is far away from the dopant core, scatters off of the perturber atoms, thus leading to a positive or negative energy shift depending upon the sign of the electron scattering length in the host medium; (ii) the monopole on the dopant core polarizes those perturber atoms which are within the "orbital radius" of the optical electron, thus leading to a negative shift. Shift (i), which we label Δ_{sc}, depends linearly upon the perturber-atom number density ρ. Shift (ii), which we label Δ_p, depends upon $\rho^{4/3}$, at least in the original Fermi model.

These pioneering studies[2,3] have been followed by numerous investigations, both experimental and theoretical, of external pressure effects on atomic and molecular Rydberg states.[5–35] One of the most important aspects of these later works has been the extension of the experimental data base to ever increasing host number densities. For example, the high-n Rydberg states of alkali metals perturbed by rare gases have been measured[7–9,11,16–18] for perturber number densities up to 4—6 rd (rd is defined as relative density, 1 rd$=2.7\times10^{19}$ cm^{-3}) for He, Ar, and Kr, and up to 16 rd for Ne. Even though in the original Fermi model the contribution of Δ_p is rather small at such low densities, the experimental results[7–9,11,16–18] have shown the invalidity of this model at these densities.

So far, molecular studies have focused on external atom effects on low-n Rydberg states only.[24,25,31–34] The basic Fermi model breaks down for low-n Rydberg states, however, since in this case one can no longer separate Δ_{sc} and Δ_p. The focus of attention in these works[24,25,31–34] has been on the development of a qualitative criterion for distinguishing molecular Rydberg states from valence states: As the perturber number density increases, the Rydberg states broaden considerably because of their highly polarizable, large orbital nature; valence states, however, remain largely unaffected. Perturber media have ranged from the rare gases[24,25,33–35] to O_2, N_2,[24] SF_6,[31,32] and CF_4.[32] And, depending upon both n and the nature of the perturber medium, the energy shift can be to either the red or the blue region.

The situation at present, then, is as follows. The Fermi model appears not to work well at the low perturber densities for high-n Rydberg states. As will be demonstrated in the present paper, however, at large number densities, where the Fermi model should work,[13,28] discrepancies appear between theory and experiment. And, this is just the region where, in the Fermi model, Δ_p becomes significant. In the case of molecular Rydberg states, external-pressure-effect experiments have been performed only on low-n states, for which the Fermi model is manifestly inapplicable. The effects of perturber media on high-n molecular Rydberg states are currently unknown (see, however, Ref. 35).

In the present work, we study the effects of increasing He, Ne, Ar, and Kr number density on the energy positions of high-n Rydberg states of CH_3I, as measured by absorption spectroscopy. (Our results for CH_3I/Ar have been communicated previously.[35]) In addition, we provide an analysis of these data in terms of a recent extension[13,28] of the Fermi model, which incorporates a linear dependence of Δ_p on perturber number density. It is important to note, however, that the rare-gas number densities considered here are more than one order of magnitude larger than those employed in the earlier atomic studies.[7–9,11,16–18] Thus, one of our purposes is to investigate the validity of the Fermi form for Δ_p at higher perturber densities.

Our choice of CH_3I for this study was motivated by the existence of extensive assignments[36–41] 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 rare-gas 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 window used in this study in the vacuum ultraviolet. Finally, since He, Ne, Ar, and Kr are transparent in this spectral region, no interference from atomic resonance lines intruded into our molecular spectra. Xe, however, is not transparent in this region and, therefore, we were unable to investigate CH_3I/Xe mixtures.

II. THE FERMI MODEL

Since the optical electron in a Rydberg state is so far removed from the cationic core, the motion of this electron is governed by the Coulomb interaction with the core, corrected by a short-range potential which reflects the influence of the remaining core electrons.[42] Fermi reasoned[3] that the interactions between a high-n Rydberg state and perturber atoms could be separated into the interaction of the optical electron with the perturber atoms, and the interaction of the cationic core with the perturber atoms.

If n is large enough, the optical electron is very nearly a free electron scattering elastically off of the perturber atoms. Moreover, near threshold the kinetic energy of the electron is approximately zero, so that the scattering will be predominantly s wave. In this case, the shift in energy of the Rydberg state due to the scattering effect is given by[3,4,13,28]

$$\Delta_{sc}(\rho) = (2\pi\hbar^2/m)a\rho \ , \tag{1}$$

where m is the electron mass, a is the electron scattering length in the perturber medium (which may be either positive or negative depending on the nature of the perturber), and ρ is the perturber number density.

Fermi then assumed that the cationic core polarized the neutral perturber atoms via the potential

$$V = -\tfrac{1}{2}\alpha e^2 \sum_N R_N^{-4} \ , \tag{2}$$

where α is the polarizability of the perturber medium and R_N is the distance between the core and the Nth perturber atom, with the sum being over all perturber atoms within the orbital radius of the optical electron. For large n and high density, Fermi replaced the summation in Eq. (2) by an integration to give

$$\Delta_p \equiv V = -\tfrac{1}{2}\alpha e^2 4\pi\rho \int_{R_0}^{\infty} R^{-4} R^2 dR \ , \tag{3}$$

where Δ_p represents the Rydberg-state energy shift due to the polarization effect. In Eq. (3), the upper integration limit is justified by the stipulation that $n \gg 1$ and $\rho \gg 1$ cm^{-3}. The lower integration limit R_0 is problematic, however. Fermi chose the Wigner-Seitz radius

$$R_0 = (3/4\pi\rho)^{1/3} \tag{4}$$

since, at any given density, there can be no perturber atoms at a distance $R < R_0$ from the core. Substituting Eq. (4) into Eq. (3), one finds

$$\Delta_p(\rho) = -(32\pi^4/3)^{1/3}\alpha e^2 \rho^{4/3} \simeq -10\alpha e^2 \rho^{4/3} \ . \tag{5}$$

In the original Fermi model, then, the total energy shift as a function of perturber number density, namely,

$$\Delta(\rho) = \Delta_{sc}(\rho) + \Delta_p(\rho) \tag{6}$$

is given by

$$\Delta(\rho) = (2\pi\hbar^2/m)a\rho - 10\alpha e^2 \rho^{4/3} \ . \tag{7}$$

The basic Fermi model correctly predicts that, for a given perturber number density, the energy shifts of the high-n Rydberg states are constant and depend only on the characteristics of the perturber; it fails, however, in describing the behavior of this shift as a function of the perturber number density, at least at low number densities.[13,17,18] [It has been asserted,[13,28] however, that Eq. (2) is essentially correct at sufficiently high densities.] Within the rare-gas number-density range covered for the alkali metals,[16] the deviation from Eq. (7) is not large. Nevertheless, Alekseev and Sobel'man[13,28] have developed an exact treatment of this shift which differs considerably from the Fermi model, as we will discuss below.

In fact, there is a basic contradiction in the argument which reduces Eq. (2) to Eq. (5), as has been pointed out by Ebding.[43] In the limit of very high perturber number densities, Eq. (2) surely fails since this interaction potential neglects van der Waals effects between the perturber atoms and the core (e.g., cluster formation). In an attempt to account for this, Ebding[43] suggested the use of a *constant* cutoff radius R_0, rather than the density-dependent Wigner-Seitz radius of Eq. (4). In this case, Eq. (3) becomes

$$\Delta_p(\rho) = -2\pi\alpha e^2 \rho / R_0 \tag{8}$$

which, of course, will exhibit a very different behavior from Eq. (5). An *a priori* choice of R_0 for a given perturber medium remains problematic, however. As will be shown below, the linear density dependence of $\Delta_p(\rho)$ which is predicted by Eq. (8) is qualitatively correct, and the various values of R_0 turn out to be 7 Å (He), 11 Å (Ne), 20 Å (Ar), and 27 Å (Kr).

Alekseev and Sobel'man[13,28] have provided a generalization of the Fermi model which, in large measure, overcomes the very approximate nature of the original treatment. These authors[13,28] still assume that, for high-n Rydberg states, the interactions of the optical electron and the core with the perturber atoms are independent. They then show that the energy shift due to elastic scattering of the optical electron is[13,28]

$$\Delta_{sc}(\rho)=(2\pi\hbar^2/m)\rho \times\int\left[\pi k^{-1}\sum_l(2l+1)\sin(2\delta_l)\right]W(k)dk \, , \tag{9}$$

where $\hbar k$ is the momentum of the scattered electron, δ_l is the l-wave phase shift of the scattered electron, and $W(k)$ is a (momentum-dependent) excited-state distribution function. In addition, for Rydberg states near threshold, where the scattering is predominantly s wave, Eq. (9) reduces to Eq. (1).

For the polarization effect, Alekseev and Sobel'man assume an interaction potential of the form of Eq. (2). They are then able to show[13,28] that, within the impact approximation of line-broadening theory,

$$\Delta_p(\rho)=-9.87(\alpha e^2/2)^{2/3}(\hbar v)^{1/3}\rho \, , \tag{10}$$

where v is the thermal velocity of the perturber atoms.

Both Eq. (9) [and, consequently, Eq. (1)] as well as Eq. (10) require the validity of the impact approximation, which is a requirement that the time between collisions be long in comparison to the interaction time, for all scattering events. Quantitatively, this means that[13,28]

$$r_i \ll n^2 a_0 \text{ and } X_i = r_i^3\rho \ll 1 \, , \tag{11}$$

where r_i, the Weisskopf radius of the cationic core (i.e., the impact parameter for core-perturber scattering), is $r_i=(\pi\alpha e^2/4\hbar v)^{1/3}$, a_0 is the Bohr radius, and X_i is a dimensionless parameter which represents the fraction of the core interaction volume sampled by a single perturber.

For the case in which $X_i \gg 1$ (i.e., the high-density limit) the impact approximation fails for the core-perturber scattering. Alekseev and Sobel'man[13,28] invoke a quasistatic approximation at this point, and claim that the polarization shift at very high densities goes over to the form given by Fermi [i.e., Eq. (5)].

Thus, the present situation is as follows. For low perturber number densities, the Alekseev-Sobel'man model works well, with the energy shift being given by

$$\Delta(\rho)=(2\pi\hbar^2/m)[a-9.87(m/2\pi\hbar^2)(\alpha e^2/2)^{2/3}(\hbar v)^{1/3}]\rho$$
$$=(2\pi\hbar^2/m)a_{\text{eff}}\rho \, . \tag{12}$$

For high perturber number densities, the energy shifts are expected[13,28] to be given by the Fermi model [i.e., Eq. (7)]. As has been noted by Allard and Kielkopf,[29] however, a test of the validity of the Fermi model in the high-density limit awaits further experimentation.

In the present paper, we provide data which show that

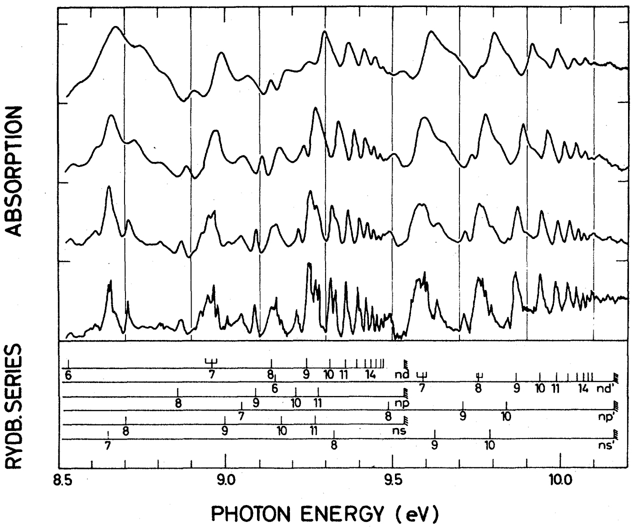

FIG. 1. Absorption spectra of CH_3I in varying number densities of He. The bottom-most spectrum is pure CH_3I at $p=0.1$ Torr. (The assignment given at the bottom refers to this spectrum.) Thereafter, proceeding to the top of the figure, the number density of He is 3.05, 10.8, and 23.0×10^{20} cm^{-3}, respectively, with the CH_3I being present at less than 10 ppm. Spectral resolution is 6 meV.

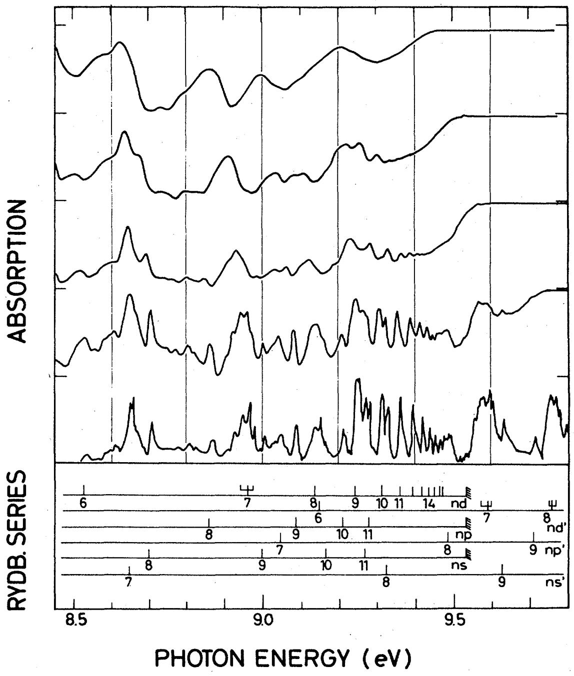

FIG. 2. Absorption spectra of CH_3I in varying number densities of Kr. The bottom-most spectrum is pure CH_3I at $p=0.1$ Torr. (The assignment given at the bottom refers to this spectrum.) Thereafter, proceeding to the top of the figure, the number density of Kr is 0.63, 3.4, 6.6, and 13.0×10^{20} cm^{-3}, respectively, with the CH_3I being present at less than 10 ppm. Spectral resolution is 6 meV.

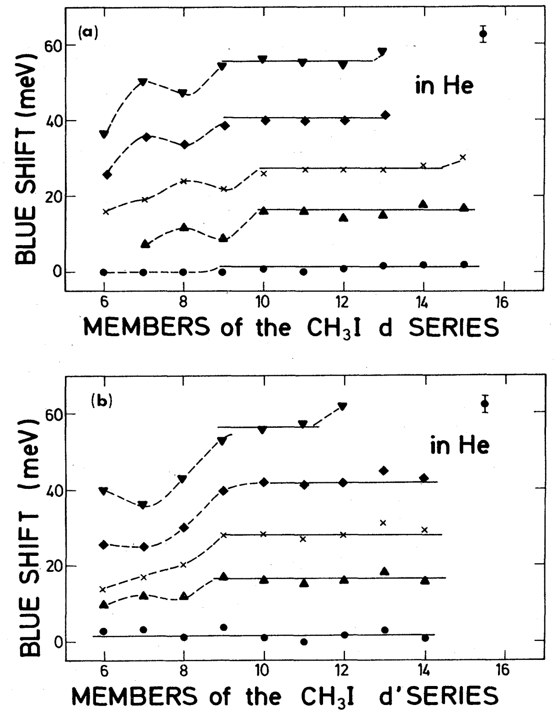

FIG. 3. (a) Energy shifts of the CH_3I $nd(^2E_{3/2})$ series in varying He number densities (10^{20} cm^{-3}): ●, 0.67; ▲, 6.1; ×, 10.8; ◆, 16.8; ▼, 23.0. (b) As in (a), but for the CH_3I $nd'(^2E_{1/2})$ series.

the Fermi model fails in the high-density limit as well, but that an extrapolation of the Alekseev-Sobel'man model to high densities quantitatively describes the density-dependent energy shifts.

III. EXPERIMENTAL DETAILS

The experimental arrangement for the absorption measurements has been described previously;[44] the details of the sample cell,[44] and of the gas-handling system,[45] have been given. Briefly, monochromatic synchrotron radiation (DORIS storage ring, DESY; HONORMI monochromator and data-acquisition system[46]) is passed through a stainless-steel sample cell capable of sustaining pressures up to ~100 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

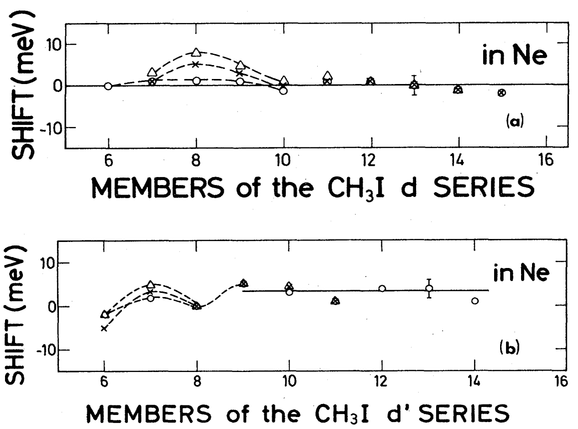

FIG. 4. (a) Energy shifts of the CH_3I $nd(^2E_{3/2})$ series in varying Ne number densities (10^{20} cm^{-3}): ○, 4.0; ×, 11.0; △, 24.0. (b) As in (a), but for the CH_3I $nd'(^2E_{1/2})$ series.

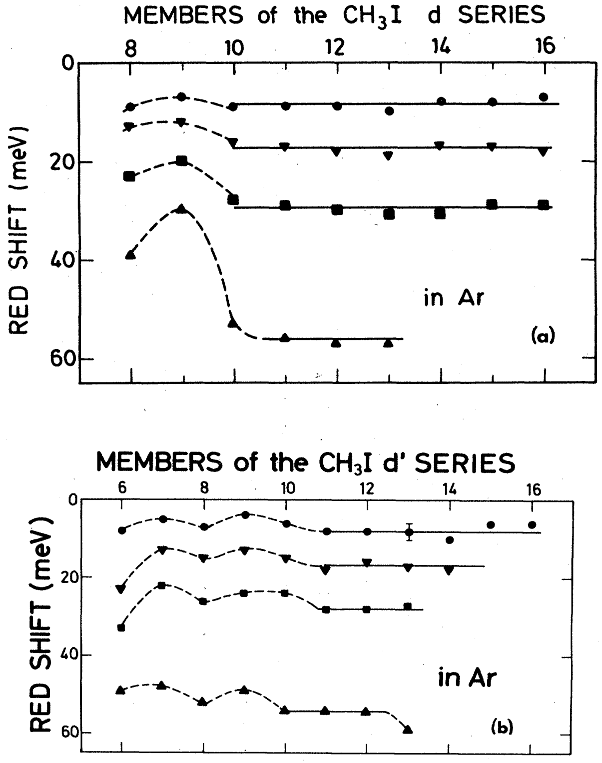

FIG. 5. (a) Energy shifts of the CH_3I $nd(^2E_{3/2})$ series in varying Ar number densities (10^{20} cm^{-3}): ●, 1.5; ▼ 3.4; ■, 5.7; ▲, 11.3. (b) As in (a), but for the CH_3I $nd'(^2E_{1/2})$ series.

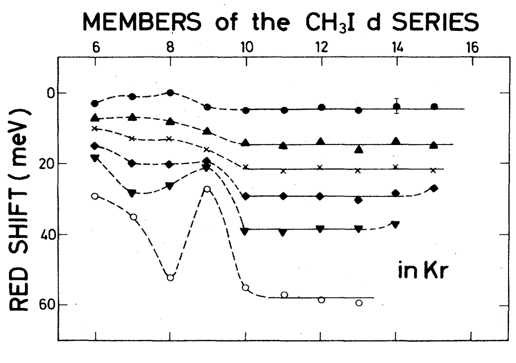

FIG. 6. (a) Energy shifts of the CH_3I $nd(^2E_{3/2})$ series in varying Kr number densities (10^{20} cm^{-3}): ●, 0.63; ▲, 1.6; ×, 2.5; ◆, 3.4; ▼, 4.4; ○, 6.6.

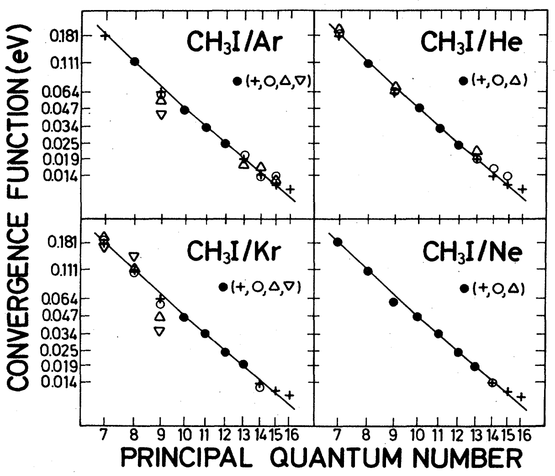

FIG. 7. A plot of the convergence function $F(n)=E_{n+1}-E_n$ vs n for the CH_3I $nd(^2E_{3/2})$ series perturbed by Ar, Kr, He, and Ne. (See text for details.) The rare-gas number densities are as follows (10^{20} cm^{-3}). Ar: ○, 1.5; △, 5.7; ▽, 11.3. Kr: ○, 2.5; △, 4.4; ▽, 6.6. He: ○, 4.8; △, 23.0. Ne: ○, 4.0; △, 24.0. (+) represents pure CH_3I while ● indicates that the values of the convergence function for both pure and perturbed CH_3I are identical.

both the incident photon flux and the empty cell transmission.

The CH_3I (99%) was from Merck-Schuchardt and was run 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.[37–41] The rare gases (He, Ne, Ar, and Kr; 99.997%) were from Deutsche l'Air Liquide.

IV. RESULTS AND DISCUSSION

Representative absorption spectra of CH_3I in He and Kr, for various rare-gas number densities, are presented in Figs. 1 and 2, respectively. (The CH_3I/Ar spectra have been reported previously;[35] the CH_3I/Ne spectra are similar to those shown here and, for that reason, we have not reproduced them.) The spectral resolution is, in all cases, 6 meV. (However, selected spectra were remeasured at 2 meV, with no additional structure being observed.) The bottom-most spectrum in both figures is that of 0.1-Torr CH_3I in the absence of any rare gas; the assignment given at the bottom pertains to this spectrum. Proceeding to the top in both figures, the additional spectra represent less than 10 ppm CH_3I in increasing number densities of rare gas.

For CH_3I in all of the rare gases, as the perturber number density increases, all spectral features, both discrete and autoionizing, broaden and shift. We were able to follow, and to analyze, these trends up to 23×10^{20} cm^{-3} for He, 24×10^{20} cm^{-3} for Ne, 11.3×10^{20} cm^{-3} for Ar, and 6.6×10^{20} cm^{-3} for Kr. At rare-gas number densities higher than these, the perturber produces such a broadening and overlapping of CH_3I Rydberg states as to render impossible any spectral assignment.

In order to assess the trends in Rydberg energy shifts as a function of perturber number density, we followed two series of states, namely, the discrete series nd, which converges to I_1, and the autoionizing series nd', which converges to I_2. These results are shown in Figs. 3–6 for He, Ne, Ar, and Kr, respectively. For the lighter rare gases, we were able to assign a large number of the nd and nd' states at every perturber number density; for Kr, however, the nd' states were broadened into the host background absorption even at the lowest number density studied (cf. Fig. 2). Two trends are immediately apparent: (i) The energy shift is to the blue region for He, nearly zero (to within experimental error) for Ne, and to the red region for Ar and Kr. As we will discuss below, this trend can be explained, both qualitatively and quantitatively, by the sign of the electron scattering length in the various rare gases. (ii) For $n\geq10$, the energy shifts are very nearly constant for a given perturber number density. This result, of course, provides confirmation of the basic hypothesis of the Fermi model, namely, that the optical electron scattering and core polarization effects can be treated independently for high-n Rydberg states.

In addition to following the shift in energy of Rydberg states as a function of perturber number density, we also were interested in assessing perturber effects on I_1 and I_2. In order to determine these ionization energies at the various rare-gas number densities studied, we employed the following tactic. Starting from the Rydberg equation

$$E_{n\alpha}=I_\alpha-\mathcal{R}/(n-\delta_\alpha)^2\ , \tag{13}$$

where $E_{n\alpha}$ is the excitation energy of the nth d Rydberg state converging to either the $\alpha=1$ or $\alpha=2$ limit, $\mathcal{R}$ is the Rydberg constant, and δ_α is a constant quantum defect

TABLE I. First and second ionization energies [$I_1\equiv I(^2E_{3/2})$, $I_2\equiv I(^2E_{1/2})$] (eV) of CH_3I in various number densities ρ (10^{20} cm^{-3}) of He, Ne, Ar, and Kr.

He			Ne			Ar			Kr	
ρ	I_1	I_2	ρ	I_1	I_2	ρ	I_1	I_2	ρ	I_1
0.67	9.5395	10.1655	4.0	9.538	10.167	1.5	9.529	10.156	0.63	9.533
3.05	9.5465		8.0	9.539		3.4	9.520	10.148	0.77	9.531
6.15	9.5545	10.1805	11.4	9.539	10.168	5.7	9.508	10.136	1.6	9.523
10.76	9.565	10.192	17.9	9.540		11.3	9.481	10.110	2.5	9.517
11.56	9.567		23.7	9.540	10.168				3.4	9.509
16.83	9.579	10.205							4.4	9.500
19.20	9.585								6.6	9.481
23.00	9.593	10.220								

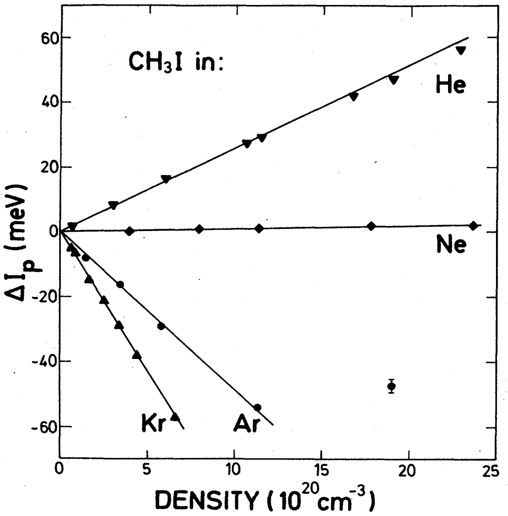

FIG. 8. Shift of the ionization energy of CH$_3$I in He, Ne, Ar, and Kr as a function of the rare-gas number density. Either I_1 or I_2 was used to determine ΔI_p, with the choice being dictated by the particular convergence characteristics at each perturber number density.

pertaining to either the *nd* ($\alpha=1$) or *nd'* ($\alpha=2$) series, we defined a convergence function $F_\alpha(n)$ as follows:

$$F_\alpha(n)=E_{n+1,\alpha}-E_{n\alpha}$$

$$=\mathscr{R}(2n+1-2\delta_\alpha)/(n-\delta_\alpha)^2(n+1-\delta_\alpha)^2 \; . \qquad (14)$$

This convergence function, which is essentially the inverse density of states, has the property that

$$\lim_{n\to\infty} F_\alpha(n)=0 \; .$$

In order to determine I_α, we first plotted $F_\alpha^{\text{expt}}(n)$, which is defined via the experimental excitation energies in the first equality of Eq. (14), versus n, and thereafter adjusted δ_α in the second equality of Eq. (14) in order to achieve a best fit to experiment. This is shown in Fig. 7 for the *nd* series of pure CH$_3$I, and for CH$_3$I—rare-gas systems at various perturber number densities. Similar plots were made for the *nd'* series. What is immediately apparent from Fig. 7 is that the series convergence is both uniform and identical for all of the rare gases and for all of the perturber number densities investigated. (The deviations at $n=9$ for Ar and Kr are due to the 11*s* interloper state.) Thus, δ_α is the same for all of the rare-gas perturbed series, as well as for pure CH$_3$I.

Given the convergence function, one can determine I_α in the following way. $F_\alpha(n)$ can be calculated for every n, up to $\bar{n}$, say, beyond which $I_\alpha-E_{n\alpha}$ becomes negligibly small. Then,

$$I_\alpha=E_{k\alpha}+\sum_{n=k}^{\bar{n}} F_\alpha(n) \; . \qquad (15)$$

This may be performed at the various perturber number densities to give $I_\alpha(\rho)$.

In Eq. (15), k must be chosen to be a principal quantum number beyond which, for a given perturber number density, the energy shifts are constant ($k\geq 10$; cf. Figs. 3—6). Thus $\sum_{n=k}^{\bar{n}} F_\alpha(n)$ is the same for every rare gas and for every perturber number density since the convergence function is the same in all of these cases (cf. Fig. 7). And, since we know the ionization energies and excitation energies for pure CH$_3$I, which we denote $I_\alpha(\rho=0)$ and $E_{n\alpha}(\rho=0)$, respectively, it follows that, for $\alpha=1$ or 2,

$$E_{k\alpha}(\rho)-E_{k\alpha}(\rho=0)=I_\alpha(\rho)-I_\alpha(\rho=0)\equiv\Delta I_p \; . \qquad (16)$$

This is, of course, equivalent to the prediction from the Fermi model that, at a particular perturber number density, the energy shifts for high-n Rydberg states, and consequently the ionization limits of these states, are constant (cf. Figs. 3—6).

With the aid of Fig. 7 we were able to choose those members of the Rydberg series which converge properly to the ionization limit I_α and to exclude others, such as $n=8,9$ for CH$_3$I in Ar and Kr, which were perturbed by interloper states. (Indeed, the main reason why some states cannot be used for the evaluation of the ionization energy is that with increasing perturber density the lines broaden and very close-lying lines merge into each other.) An accurate determination of I_α is then very simple: All absorption lines with the property that $F(n-1)$, $F(n)$, and $F(n+1)$ fall onto the convergence lines of Fig. 7 are used to calculate ΔI_p according to Eq. (16). The resultant ionization energies are collected in Table I.

In Fig. 8, we have plotted ΔI_p versus ρ, where the choice of $\alpha=1$ or 2 in defining ΔI_p was dictated, for a given perturber number density, by the accuracy of the convergence function. Figure 8 contains the main result

TABLE II. Parameters used in Eqs. (7) and (12).

	Polarizability α [a] (10^{-24} cm^3)	Electron scattering length a [b] (Bohr radii, a_0)	Perturber thermal velocity v [c] (10^4 cm/s)
He	0.20	1.15	12.6
Ne	0.396[d]	0.21[d]	5.6
Ar	1.63	−1.69	4.0
Kr	2.46	−3.2	2.8

[a] From J. H. Van Vleck, *The Theory of Electronic and Magnetic Susceptibilities* (Clarendon, Oxford, 1932).

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

[c] Calculated from the Boltzmann distribution at $T=300$ K, $\bar{v}=(8kT/m)^{1/2}$.

[d] From T. F. O'Malley and R. W. Crompton, J. Phys. B **13**, 3451 (1980).

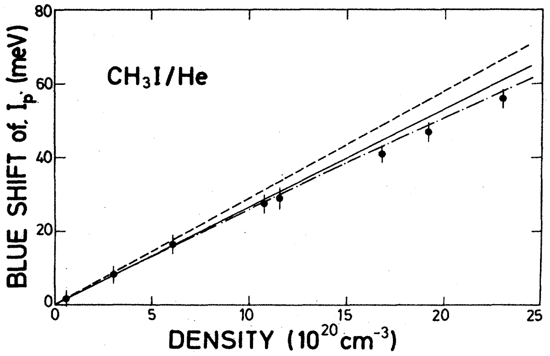

FIG. 9. Shift of the ionization energy of CH_3I in He as a function of the rare-gas number density. Either I_1 or I_2 was used to determine ΔI_p, with the choice being dictated by the particular convergence characteristics at each perturber number density. ●, experimental shifts, including errors bars. —·—·—·, shift predicted by the original Fermi model [Eq. (7) of text]. ——, shift predicted by the Alekseev-Sobel'man modification of the Fermi model [Eq. (12) of text]. — — —, scattering shift Δ_{sc} [Eq. (1) of text].

of this paper: The energy shifts of high-*n* Rydberg states, and their ionization limits, vary linearly with the perturber number density. This result clearly demonstrates that the shifts remain linear in density even at very high densities, in contradiction to the Fermi model.

In order to test the quantitative accuracy of Eq. (12), as compared to Eq. (7) (i.e., the original Fermi model), we have plotted these equations using the parameters of Table II. Our results, including the experimental points, are shown in Figs. 9—12. (In these figures, we have also plotted $\Delta_{sc}(\rho)$ [cf. Eq. (1)] separately as a reference.) Clearly, the slope given by the Alekseev-Sobel'man theory extrapolates to very high densities. In the case of Ne, Ar, and Kr, the fit of Eq. (12) to the experimental data is excellent. For He, the fit is less exact but still quite acceptable. It is important to note that Eq. (12) contains no adjustable parameters. The scattering lengths *a* were taken from the literature and, in order to avoid ambiguities, all *a*'s stem from the same experimental technique, namely, the dc electron swarm method (see also Ref. 47, and references therein). While the low polarizability of He makes a decision between the two models impossible, the results for Ne, Ar, and Kr show unequivocably that the density dependence is linear.

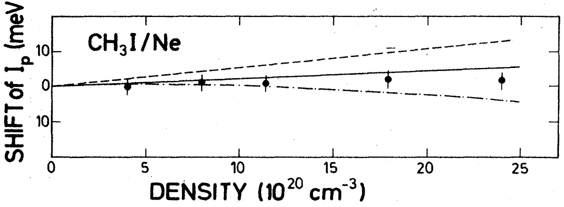

FIG. 10. As in Fig. 9, except that the perturber is Ne.

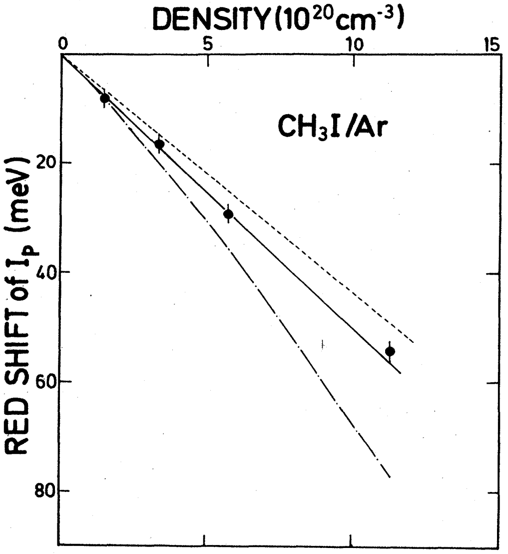

FIG. 11. As in Fig. 9, except that the perturber is Ar.

V. CONCLUSIONS

Our purpose in this paper was to provide, for the first time, experimental data for the energy shifts of high-*n* Rydberg states perturbed by the presence of very high number densities of rare-gas atoms.

We have shown that the energy shifts of high-*n* Rydberg states, and consequently the ionization limits with respect to which these states are defined, depend linearly upon perturber atom number density over the entire densi-

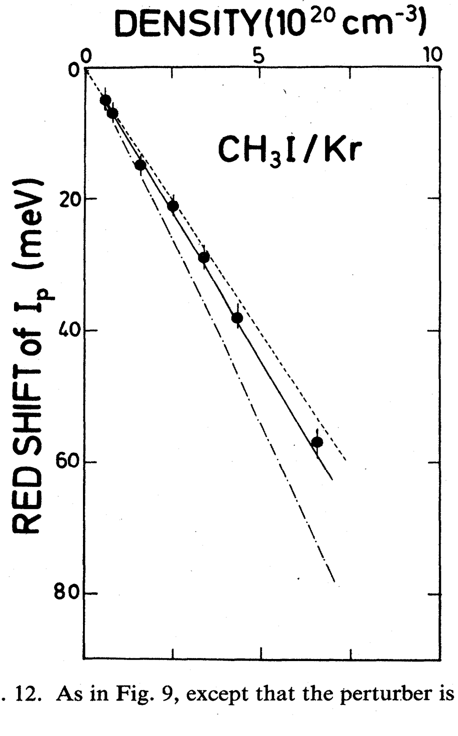

FIG. 12. As in Fig. 9, except that the perturber is Kr.

ty range. The dominant contributor to these shifts, as is apparent in Figs. 9—12, is Δ_{sc}, namely the "free" electron scattering shift, which varies linearly with density. Δ_p, the polarization shift, which becomes significant at higher perturber number densities, also varies linearly with density.

While similar studies have been performed on atomic Rydberg states,[7–9,11,16–18] our measurements represent by far the highest perturber number densities yet investigated for high-n Rydberg states. And, in consequence, one problem immediately arises. The Alekseev-Sobel'man extension of the Fermi model, as expressed in Eq. (12), depends upon the validity of the impact approximation. This, in turn, as discussed in Sec. II, requires that $\chi_i \ll 1$. In the experiments reported here, however, $\chi_i \lesssim 5$. Clearly, the density dependence of the energy shift given by the Alekseev-Sobel'man model remains correct for higher number densities, even though these authors[13,28] argue that the Fermi treatment of Δ_p should hold in the high-density regime. A fundamental theoretical understanding of this result, however, is lacking.

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