High Rydberg states of methyl iodide perturbed by nitrogen: A mutual cancellation of shift terms

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The dependence of the positions of both prethreshold and autoionizing high Rydberg states of CH_3I on the density ρ of the perturber N_2 was measured at room temperature, using synchrotron radiation. Up to $\rho = 2.2 \times 10^{20}$ cm^{-3} no pressure shift was observed, showing that the scattering shift by the valence electron is compensated by the polarization shift due to the core. From the results, the value $A = (1.9 \pm 0.3) \times 10^{-9}$ cm was found for the scattering length, in good accord with previous pressure shift and swarm results. The wide range of useful applications of the photocurrent excitation spectra to the study of perturbed transitions is stressed.

I. INTRODUCTION

The shift of high Rydberg levels of molecular absorbers caused by rare gas perturbers has received considerable attention within the past few years.[1-3] From such shift data, good estimates can be obtained both for the energy V_0 of a free thermalized electron and for the electron scattering length A in the perturber gas. Like the classical Rydberg shift measurements with alkali metal atom absorbers[4-6] these studies too were pursued by means of absorption spectroscopy: Use of a molecular perturber enabled investigations in a much broader pressure range than previously. Absorption measurements are, however, limited in practice to such spectral ranges, where the perturber gas is transparent. This difficulty has been circumvented recently[7-9] by recording photocurrent excitation spectra instead of absorption spectra. Photocurrent excitation spectra from the absorber can be readily obtained even in such spectral regions, where the perturber absorbs strongly, provided it does not become ionized. Autoionizing high Rydberg levels of the absorber are obvious candidates for useful pressure shift measurements, but high prethreshold Rydberg levels can also readily be used in some cases.[7]

Nitrogen as a perturber is interesting for several reasons. (a) we deal with the interaction of slow electrons with the main constituent of the atmosphere; (b) early data[10] indicate an almost zero pressure shift and therefore the absolute values of the polarization and scattering shifts (see below) are very nearly equal; (c) the only indications for the value and sign of A from momentum transfer cross section measurements[11] are based on the fitting of the cross sections as a function of the electron wave vector to theoretical formulas.[12,13]

During the study of the pressure shift in nitrogen it also turned out that it is a very convenient substance to test sensitively the pressure shift formulas[14,15] and compare the use of the absorption method with the use of the photocurrent method in the study of the pressure shift of high Rydberg levels.

II. EXPERIMENT

The spectra were taken at the HONORMI experimental station[16] at the Hamburger Synchrotronstrahlungslabor HASYLAB. Experimental details were described in previous publications.[8,9] The cell[8,9] served both for photocurrent excitation and photoabsorption measurements. Nitrogen gas by Deutsche L'air Liquide, 99.9992% purity, was used. The absorber gas was CH_3I. Its concentration by volume was in the range 8–48 ppm. The potential difference between the two electrodes was 80–100 V. The spectral resolution was 0.1 nm.

III. RESULTS

Figure 1 shows transmission and photocurrent excitation spectra of the methyl iodide absorber/nitrogen perturber system at two densities. For comparison, the transmission spectrum of pure methyl iodide is also presented. It can be seen that at the positions of the transmission minima of pure methyl iodide [Fig. 1(a)] there appear minima in the transmission [Figs. 1(c) and 1(e)] of the CH_3I/N_2 system as well. Moreover, there are maxima of the photocurrent excitation spectra [Figs. 1(b) and 1(d)] in the autoionization region ($\hbar\omega > 9.538$ eV) at the same positions. At the lower density shown [Figs. 1(b) and 1(c)] the resolution of the transmission and the photocurrent excitation spectra is about the same. At the higher density, the features of both spectra become less prominent, but the deterioration is appreciably stronger in the transmission spectrum. For example, while the CH_3I absorption lines[17] at 9.94 eV ($10d'$), 9.79 eV ($10s'$), and 9.72 eV ($9p'$) are still present in the photocur-

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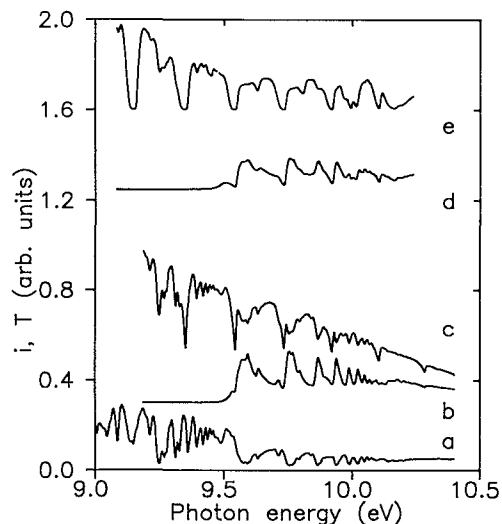
FIG. 1. (a) Transmission spectrum of pure CH_3I ($\rho = 2.5 \times 10^{15}$ cm^{-3}), path length 3.4 cm. (b) Normalized photocurrent excitation spectrum of 48 ppm CH_3I in N_2 ($\rho = 0.27 \times 10^{20}$ cm^{-3}). (c) Transmission spectrum of the sample of "b," path length 3.4 cm. (d) Normalized photocurrent excitation spectrum of 10 ppm CH_3I in N_2 ($\rho = 1.69 \times 10^{20}$ cm^{-3}). (e) Transmission spectrum of the sample of "d," path length 3.4 cm. The spectra are staggered vertically. The transmission spectra are not corrected for reflections at the MgF_2 windows.

rent excitation spectrum Fig. 1(d), they disappeared completely from the transmission spectrum Fig. 1(e).

The dips common to the transmission and photocurrent excitation spectra of Fig. 1 are due[18] to various members of the band systems $a^1\Pi_g \leftarrow X^1\Sigma_g^+$, $a^1\Sigma_g^+ \leftarrow X^1\Sigma_g^+$, $B'^3\Sigma_u^- \leftarrow X^1\Sigma_g^+$, and $w^1\Delta_u \leftarrow X^1\Sigma_g^+$ of N_2. In order to illustrate clearly this point, we show in Fig. 2 the transmission spec-
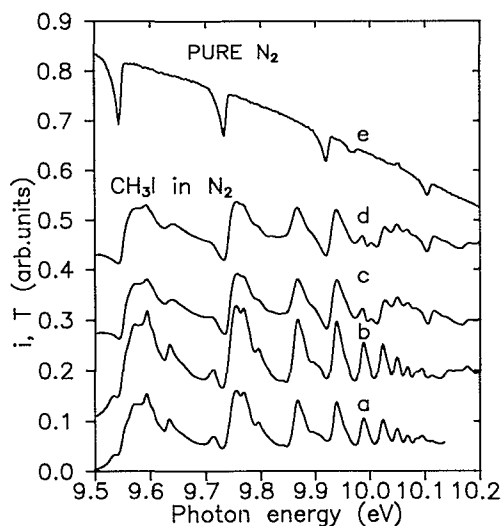
trum of nitrogen along with a set of photocurrent excitation spectra of CH_3I/N_2, obtained at four different densities. The dips of the nitrogen tansmission spectrum appear as dips in the CH_3I/N_2 photocurrent excitation spectra as well, since at the dips absorption by the nitrogen molecules competes with absorption by the methyl iodide molecules, without freeing electrons [the first ionization limit of nitrogen is at 15.576 eV (Ref. 19)]. It should be noted that in Figs. 1 and 2 the positions of the photocurrent peaks do not change with increasing density and they coincide with the absorption lliens of pure methyl iodide.

Figure 3 is an enlarged version of part of spectrum "b" of Fig. 1, along with the transmission spectrum of the same sample obtained simultaneously. Above the $^2E_{1/2}$ series limit a set of further lines appear, barely discernible in the absorption spectrum but well-resolved in the photocurrent excitation spectrum. A similar situation prevails in pure CH_3I as well as in the methyl iodide absorber/argon perturber system.[20] The features discussed are due to the Rydberg lines nd' ($n = 11$–15) of the vibrationally excited state $^2E_{1/2}$ ($v_2^+ = 1$) of the CH_3I molecule ion. Indeed, the distance between the lines of this series and the corresponding Rydberg levels below 10.16 eV is 0.152 eV, in accord with the energy (0.153 eV)[21] of the vibration v_2^+ of the ion.

Figure 4 depicts photocurrent excitation spectra just below the first series limit $I_1 \equiv I(^2E_{3/2})$ of CH_3I at several densities. The current values are multiplied by a factor of ≈ 100 compared with Fig. 1. The photocurrent appears already well below this limit. Superimposed on the increasing slope of the graphs one discerns a series of peaks: these can be identified as the $n = 11$–14 lines of the vibrational autoionizing nd ($v_2' = 1$) Rydberg series originating from the $^1A_1(v'' = 1)$ ground state and converging to the $I_1 \equiv I(^2E_{3/2}(v_2' = 1))$ limit of methyl iodide.[22] Closer scrutiny shows that these lines do not shift with density—they behave similarly to the nd' autoionization lines shown in Figs. 1–3.

FIG. 2. (a),(b),(c), and (d); Normalized photocurrent excitation spectrum of CH_3I perturbed by N_2 in the autoionization region ($^2E_{1/2}$ series). CH_3I concentrations in ppm and nitrogen densities in 10^{20} cm^{-3}: (a) 48, 0.138; (b) 48, 0.27; (c) 13, 1.33; (d) 10, 1.69. (e) Transmission spectrum of pure N_2 ($\rho = 1.2 \times 10^{19}$ cm^{-3}). The spectra are staggered vertically.
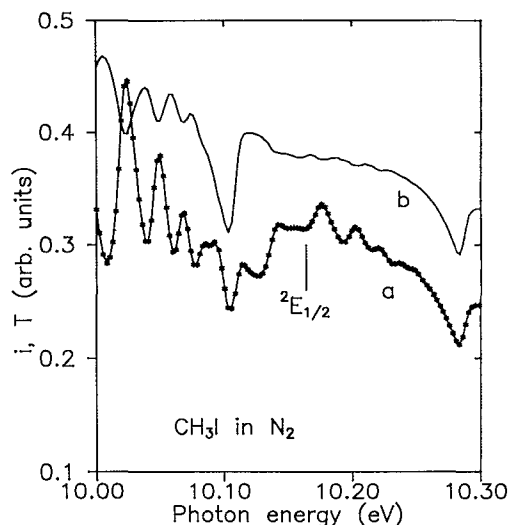

FIG. 3. (a) Normalized photocurrent excitation spectrum; (b) transmission spectrum of 48 ppm CH_3I in 0.53×10^{20} cm^{-3} N_2 above 10 eV.
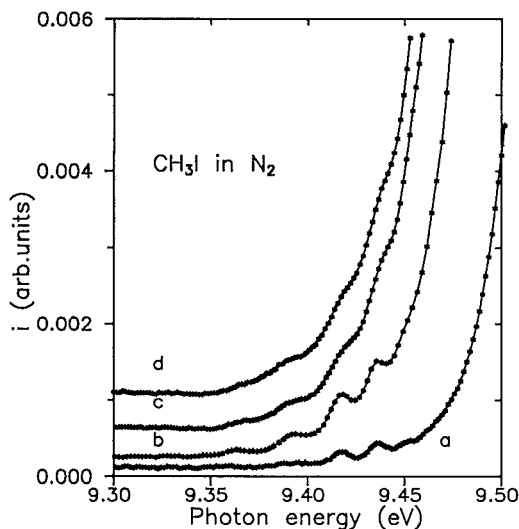
FIG. 4. Normalized photocurrent excitation spectra in the prethreshold region. CH_3I concentrations in ppm and nitrogen densities in $10^{20} cm^{-3}$: (a) 48, 0.138; (b) 48, 0.53; (c) 10, 1.69; (d) 8, 2.2. The currents are multiplied by a factor of about 100 compared with those in Fig. 2.

Peak positions of selected autoionizing Rydberg lines ($n = 9$–15) of the nd' series as a function of density obtained from photocurrent excitation spectra appear in Fig. 5. The lines are linear regression best fits: They look horizontal. Indeed, the fitted slopes vary between -8.2×10^{-5} to 2.6×10^{-3} (in units of 10^{-20} eV cm^3) and the coefficient of correlation from 0.076 to 0.92. We can thus state with confidence that the lines are horizontal; if there is any tilt, it is at most of the order of 10^{-24} eV cm^3.

IV. DISCUSSION

A. Absorption versus photocurrent excitation spectra

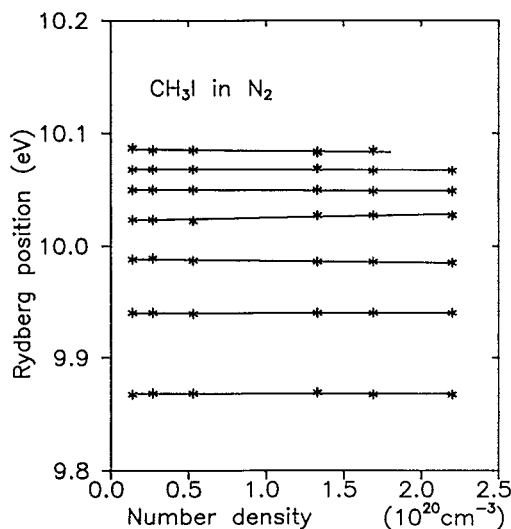The CH_3I/N_2 Rydberg shift data furnish an example, where one can observe high Rydberg states in both the au-

FIG. 5. Rydberg peak positions for transitions $nd'(^2E_{1/2})$ with $n = 9,...,15$ of CH_3I as a function of the density of the N_2 perturber. The straight lines are best fit.

toionizing and the prethreshold regions of the absorber. For both regions, absorption spectra and photocurrent excitation spectra may, in principle, equally serve to obtain pressure shift data. However, the transmitted light intensity is proportional (reflections neglected) to $\exp[-(\alpha_1 + \alpha_2)d]$, and the photocurrent (provided there is no perturber photoconduction, the electrode geometry is appropriate, and some further conditions are fulfilled[23]) to $\alpha_1/(\alpha_1 + \alpha_2)$, where d is the sample thickness, α_1 the absorption coefficient of the absorber and α_2 is that of the perturber. Obviously, if $\alpha_1 \ll \alpha_2$, the effect of the absorber on the transmitted light intensity will be very slight. On the other hand, under such circumstances the photocurrent will be proportional to α_1. Accordingly, in regions of strong perturber absorption the photocurrent excitation spectra are preferred. Moreover, the photocurrent excitation spectrum may be the only viable alternative wherever there are rapid variations of the absorption coefficient due to both to the absorber and to the perturber.[7,9] In the case presented the best data were obtained in the autoionization regime; the advantage of the photocurrent excitation spectra is manifested at the highest densities of the experiments presented.

B. Pressure shift in the methyl iodide/nitrogen system

It was shown in the experimental part that the effect of the perturber was the same on all Rydberg levels, independent of the quantum number n: the level positions did not change with density. The independence of n (asymptocity) is in full accord with the literature: according to Kaulakys,[24] the term dependent on n of the pressure shift is roughly proportional to n^{-6} (for the high density expansion) and therefore totally negligible in our case.

The shift of the series limit of high Rydberg levels of a metal atom caused by a monatomic gas is given by the formula[14,15]

$$\Delta = \Delta_{SC} + \Delta_p. \tag{1}$$

Here the scattering shift Δ_{SC} is due to the interaction of the Rydberg electron with the perturber, and the polarization shift Δ_p stems from the interaction between the positive core of the absorber and the surrounding gas.

According to Fermi,[14] for an atomic or a spherically symmetric molecular absorber we have

$$\Delta_{SC} = (2\pi\hbar^2/m)A\rho, \tag{2}$$

$$\Delta_p = -\left(\frac{32\pi^4}{3}\right)^{1/3}\alpha e^2\rho^{4/3}, \tag{3}$$

where $\hbar$ is the reduced Planck constant, m the electron mass, A the scattering length of the Rydberg electron in the perturber, α the atomic polarizability of the perturber, e the electron charge, and ρ the number density. Reinsberg[25] showed that Eq. (2) holds for axially symmetric perturber molecules too. Alekseev and Sobel'man[15] revised the Fermi formula for the polarization shift Δ_p. On the basis of the impact theory for pressure shift and broadening they found that

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

v being the relative thermal velocity of the absorber and per-

turber pair. Koehler *et al.*[1,2] have demonstrated in an experimental study of the pressure shift of high molecular (CH_3I) Rydbergs in rare gases that the linear density dependence, as predicted by Eq. (4), represents correctly the polarization contribution Δ_p to the pressure shift up to densities far beyond the validity range of the impact broadening theory. This is in disagreement with the conclusions by Alekseev and Sobel'man, according to which $|\Delta_p|$ should rise proportionally to $\rho^{4/3}$ at high densities, as in the Fermi theory[14] [Eq. (3)].

For the methyl iodide/nitrogen system we showed above that $\Delta = 0$ and thus, according to Eq. (1), $\Delta_{SC} = -\Delta_p$. If Δ_p were not linear with the density, this would clearly show up: The nonlinearity would be much easier to detect in the present case than most other cases since usually $|\Delta_{SC}|$ is considerably larger than $|\Delta_p|$.

Alekseev and Sobel'man[15] state that the linearity with ρ as predicted by Eq. (4) should hold only as long as

$$\rho \ll \frac{4\hbar v}{\pi \alpha e^2}. \tag{5}$$

With $v = 5.2 \times 10^4$ cm s^{-1} and $\alpha = 1.76 \times 10^{-24}$ cm^3 we find that the right-hand side of Eq. (5) equals 1.7×10^{20} cm^{-3}, while the highest density in our experiments was 2.2×10^{20} cm^{-3}. Thus condition (5) is not satisfied but the linearity still holds, in full accord with Koehler's results[2] on rare gas perturbers. We note that Koehler[2] rewrote Eq. (3) in the following form:

$$\Delta_p = -2\pi\alpha e^2/b_c = -10.78(\alpha e^2/2)^{2/3}(\hbar v)^{1/3}\rho, \tag{4'}$$

here b_c is the Weisskopf radius[1,2] measuring the effective distance of interaction between a perturber and a core. It is defined as

$$b_c \equiv (\pi \alpha e^2/4\hbar v)^{1/3}. \tag{6}$$

The form of (4') is like that of the Fermi polarization term [Eq. (3)], except that b_c appears in Eq. (4') instead of the Wigner–Seitz radius $b_w \equiv (3/4\pi\rho)^{1/3}$. Its physical meaning is immediate: Δ_p is equal to the polarization energy of the medium with the exclusion of a spherical cavity of radius b_c around the core. This form makes the equation plausible even beyond the range of validity of the impact broadening theory.[2]

Returning to the present case we find, according to Eq. (4'), $\Delta_p/\rho = -8.8 \times 10^{-24}$ eV cm^3. From $\Delta_{SC} = -\Delta_p$ and Eq. (2) we find $A = 1.85 \times 10^{-9}$ cm. Allowing an uncertainty of $\pm 1.5 \times 10^{-24}$ eV cm^3 in the slopes of Fig. 5, this implies the error in A is $\pm 0.3 \times 10^{-9}$ cm.

The only previous pressure shift measurements with nitrogen perturber seem to be those performed by Ny and Ch'en.[10] They used Na, Cs, or Rb atoms as absorbers; their measurements extended to $\rho = 10^{20}$ cm^{-3}. From their data using Eqs. (1), (2), and (4') we get $A = 1.9 \times 10^{-9}$ cm, in excellent agreement with our result, obtained in a very different spectral region.

In order to compare the value of A obtained by the pressure shift method with results from swarm data, one needs the relationship between A and the total cross section σ_T for electron scattering (extrapolated to zero energy) by the per-

turber molecules. Chang[13] showed that for homopolar molecules

$$\sigma_T = 4\pi A^2 \left[1 + \frac{4}{45} \frac{1}{e^2 a_0^2} \left(\frac{Q}{A} \right)^2 + f(k) \right]. \tag{7}$$

Q is the quadrupole moment of the molecule and $f(k)$ is a known function that becomes zero when $k = 0$, k being the wave vector of the electron. Equation (7) is based on the effective range theory, modified to deal with electron scattering from molecules. Using the value[26] $Q = -1.13ea_0^2$ and our value of A we obtain $\sigma_T = 8.5 \times 10^{-17}$ cm^2. From the dependence of the momentum transfer cross section on k, obtained by Engelhardt *et al.*[11] in the course of swarm experiments, Chang[13] calculated $A = 2.3 \times 10^{-9}$ cm and $\sigma_T = 10.8 \times 10^{-17}$ cm^2 for $k = 0$. This value for A is just beyond the estimated limit of error from ours $[(1.9 \pm 0.3) \times 10^{-9}$ cm].

In previous papers[3,8,9] we used the simpler expression

$$\sigma_T = 4\pi A^2 \tag{8}$$

instead of Eq. (7), in spite of the fact that the perturbers were molecular gases. This was justified, since for all perturbers investigated $|Q/ea_0A| < 0.5$: Chang showed[13] that if this inequality holds, the difference between the values of σ_T as obtained from the two equations is negligible (less than 2%).

Total cross sections for electrons in nitrogen were measured by single-electron time-of-flight spectrometry.[27,28] Both authors[26,27] report a monotonic decrease of σ_T with decreasing electron energy. At 0.3 eV Baldwin[27] found that $\sigma_T = 7.65 \times 10^{-16}$ cm^2. However, this cannot be compared directly with the pressure shift data, since the measurements did not extend to electron energies below 0.3 eV, while the energies of the Rydberg electrons referred to are about 0.1 eV.

V. CONCLUSIONS

The zero pressure shift observed for high Rydberg states of CH_3I in nitrogen perturber gas demonstrates very clearly the linearity of the polarization contribution to the pressure shift well beyond limit of applicability of the impact theory for spectral shift and broadening. A full theoretical understanding of this fact is still lacking.

The results demonstrate that, using the photocurrent excitation method, pressure shift measurements are possible in many molecular absorber/perturber systems, provided there exist several high Rydberg states of the absorber below the first ionization limit of the perturber and these do not coincide with discrete perturber absorption bands. The results are more accurate, if the Rydberg transitions in question are autoionizing, but if this is not feasible, prethreshold Rydberg transitions can also be used.

ACKNOWLEDGMENT

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