Density effects on highn molecular Rydberg states: CH3I and C6H6 in H2 and Ar

U. Asaf, W. S. Felps, K. Rupnik, S. P. McGlynn, and G. Ascarelli

---

Articles you may be interested in

Softening of C—H Symmetric Stretching Vibrational Modes for CH2 and CH3 Radicals Adsorbed on Cu n (n=1–6) Clusters
Chin. J. Chem. Phys. **25**, 649 (2012); 10.1088/1674-0068/25/06/649-653

Solvation effects on reactive intermediates: The benzyl radical and its clusters with Ar, N2, CH4, C2H6, and C3H8
J. Chem. Phys. **98**, 4339 (1993); 10.1063/1.464996

Predissociation of H3 n=2 Rydberg states: Product branching and isotope effects
J. Chem. Phys. **96**, 8128 (1992); 10.1063/1.462315

Molecular highRydberg fragments from CH4 and C2H6 by electron impact dissociation
J. Chem. Phys. **79**, 213 (1983); 10.1063/1.445560

Molecular beam measurements of inelastic cross sections for transitions between defined rotational states (j,m) of CsF in collisions with He, Ne, Ar, Kr, CH4, CF4, SF6, C2H6, N2, CO, CO2, N2O, CH3Cl, CH3Br, CF3H, and CF3Br
J. Chem. Phys. **71**, 1722 (1979); 10.1063/1.438524

Density effects on high-n molecular Rydberg states: CH$_3$I and C$_6$H$_6$ in H$_2$ and Ar

U. Asaf,[a] W. S. Felps, K. Rupnik, and S. P. McGlynn
Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, 70803

G. Ascarelli
Department of Physics, Purdue University, W. Lafayette, Indiana 47907

The absorption spectra of high-n Rydberg states of methyl iodide and benzene perturbed by varying number densities of hydrogen or argon, range 0.9×10^{20}–10.5×10^{20} cm^{-3} for H$_2$ and 0.6×10^{20}–7.5×10^{20} cm^{-3} for Ar, have been investigated. The high-n molecular states of both absorbers were found to shift linearly with the number density of atomic Ar and molecular H$_2$ scatterers. The Fermi formula modified by the Alekseev–Sobel'man polarization term provides an excellent fit of the shift data. The electron scattering lengths obtained are: $0.93 \, a_0$ for H$_2$ and $-1.63 \, a_0$ for Ar using the CH$_3$I absorber; and $0.99 \, a_0$ for H$_2$ and $-1.57 \, a_0$ for Ar using the C$_6$H$_6$ absorber. The electron scattering lengths for H$_2$ and Ar agree with the results of an empirical model that correlates scattering lengths and the polarizabilities α (spherical) for inert atoms and α_2 (nonspherical) for H$_2$ molecule.

INTRODUCTION

Pressure induced shifts and broadenings of the spectral lines of alkali metal absorbers have been measured for at least 50 years. The shifts of the high-n Ryberg states of alkali metals perturbed by foreign atomic gases have been analyzed by Fermi.[1] These Rydberg electrons behave as if they are "free" and relatively "slow," and, as a result, it is possible to relate the shift data to the elastic scattering of low-energy electrons by foreign gas atoms.

The use of molecular absorbers such as methyl iodide[2] and benzene[3] has permitted an extension of the perturber density range up to $\sim 2 \times 10^{21}$ cm^{-3}. Within this large number density range, the shift of the high-n Rydberg states of these absorbers has been found to vary linearly for He, Ne, Ar, and Kr perturbers[2,3] and these linearities can be reproduced accurately[2] by the Fermi model modified by the Alekseev–Sobel'man polarization term.[4]

The present study is the first attempt to investigate the effects of a molecular perturber on the high-n Rydberg states of molecular absorbers. The aim is to generate information about the scattering potential barrier[5] for electrons in dense H$_2$ gas by measuring the electron scattering length for this medium.

An empirical correlation[6] of electron scattering lengths and polarizabilities, one that accords in principle with effective range theory,[7] has been tested for atomic and simple molecular scatterers.

EXPERIMENTAL

The experimental apparatus consisted of a 1 m McPherson Model 225 normal incidence monochromator equipped with a 1200ℓ/ mm grating, Hinteregger hydrogen lamp and double beam chamber. The experimental bandwidth was 5.7 meV. An oscillating mirror alternately directed the light through a reference cell and a sample cell. Both cells had MgF$_2$ windows. The sample cell, 3.5 cm long, was a stainless steel manifold, the mini-ConFlat ports of which were sealed by the two pressure tight MgF$_2$ windows, the gas inlet tube and an alignment arm. The two latter items provided a simple mounting of the cell along the Wilson seals of the double beam chamber. Absorbances of the room temperature gaseous mixtures were recorded using a McPherson Model 782 logarithmic ratiometer, using scan speeds of 5 Å/min. Research grade Ar and H$_2$(Liquid Carbonic, 99.999%) gases were purified by liquid nitrogen traps to eliminate any trace accumulation of water in the sample cell. The CH$_3$I (Aldrich, 99%) or benzene (J. T. Baker, reagent) were purified by a multiple freeze/thaw procedure in the evacuated gas handling system. High pressures were monitored using a calibrated Model 205-2 Setra pressure transducer. Absorber sample pressures of 0.2–0.4 Torr of CH$_3$I and 0.6–0.7 Torr of benzene were used.

RESULTS AND DISCUSSION

Results for the effect of H$_2$ and Ar gases on the energy of the high-n Rydberg states of CH$_3$I and C$_6$H$_6$ are reported. The highest H$_2$ gas density used with methyl iodide was 1.05×10^{21} cm^{-3}, and with benzene was 7×10^{20} cm^{-3}. These perturber number densities exceeded those of the earlier studies of alkali metal/H$_2$ systems[8,9] by an order of magnitude. The density range for the Ar perturber extended up to 7.5×10^{20} cm^{-3} for CH$_3$I and 6.2×10^{20} cm^{-3} for C$_6$H$_6$ absorbers.

The two lowest ionization potentials to which the transitions[10] of CH$_3$I converge are $I_1 = I(^2E_{3/2}) = 9.538$ eV and $I_2 = I(^2E_{1/2}) = 10.164$ eV. Pressure effects were studied for
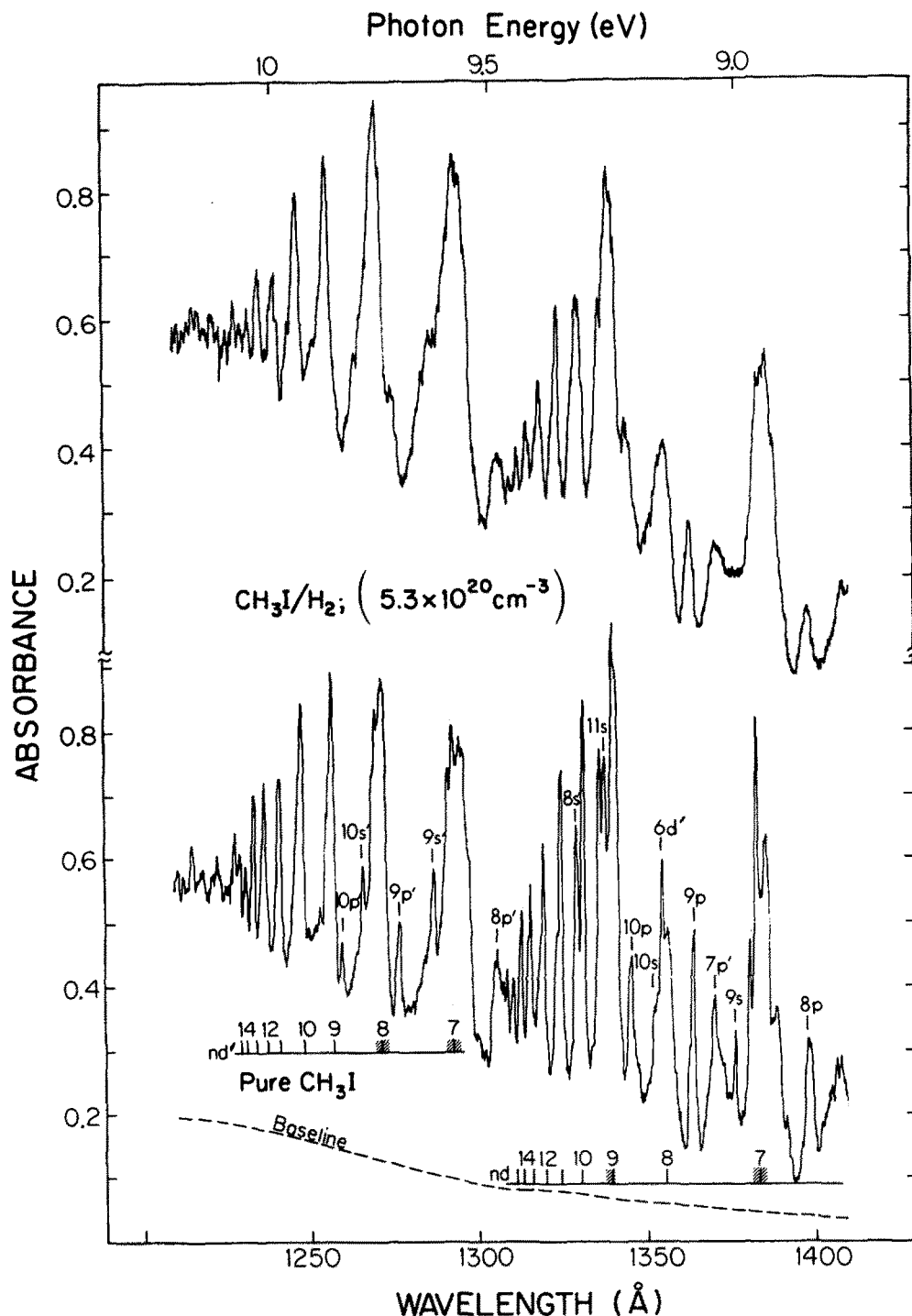
FIG. 1. Room temperature absorption spectra of pure CH_3I vapors before and after the addition of hydrogen gas at high pressure. The nd and nd' Rydberg series are identified at the bottom of figure for $n \geqslant 7$, other transitions of s, p, and d series are marked at the line peaks of the pure CH_3I.

the discrete states $E_n < I_1$ and the autoionizing states $I_1 < E_n < I_2$, all at energies well below the MgF_2 cutoff. Systematic shift studies were restricted to nd and nd' Rydberg states. The spectra of pure CH_3I (lower) and CH_3I plus H_2 (upper) are shown in Fig. 1. While somewhat broadened, most of the high-n members of both series are clearly resolved. The evaluation of the line shifts was facilitated by a simultaneous recording of the line spectrum of the hydrogen lamp and the use of these lines for calibration. Differences of $\geqslant 0.1$ Å of line positions were measureable by this tactic.

Energy shifts were reproducible within of ± 1.5 meV. The results for the CH_3I/Ar system agree with previous work[2] and provided a check of the experimental and data evaluation systems.

Some results are shown in Fig. 2. Positive (CH_3I/H_2) and negative energy shifts (CH_3I/Ar) are plotted as a function of n. For all $n \geqslant 10$, the energy shifts are found to be the same (i.e., constant) for a fixed perturber density.

Spectra of benzene are shown in Fig. 3. Pressure studies of benzene were restricted to the R' series (IP = 9.247 eV)[11]
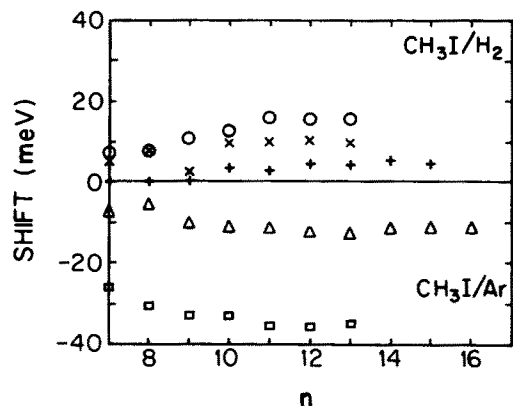
FIG. 2. Examples of energy shifts of the CH_3I transitions at several densities ($\rho \times 10^{20}$ cm^{-3}) as a function of principal quantum number. For perturber H_2: $+$, $\rho = 2.23$, nd; $\times$, $\rho = 6.41$, nd; $\bigcirc$, $\rho = 10.5$, nd'. For perturber Ar: $\triangle$, $\rho = 2.3$, nd; $\square$, $\rho = 7.33$, nd'.
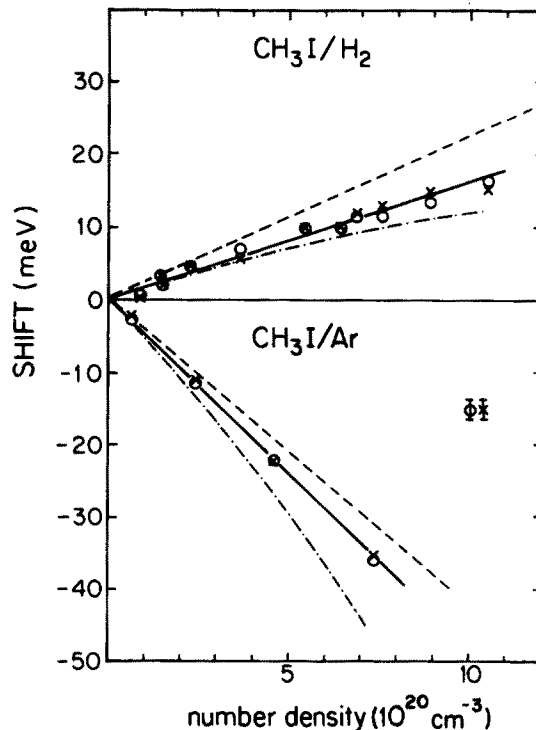
FIG. 4. Energy shifts of CH_3I transitions averaged for $10 \leqslant n \leqslant 16$ members, $\bigcirc$ for nd, $\times$ for nd' series, for both H_2 and Ar. The solid lines are least-squares fits of experiment values. The dashed line is the scattering term, Eq. (2), dot–dashed line is the total shift according to the basic Fermi model [that is, the sum of Eqs. (2) and (3) using the parameters of Table I].
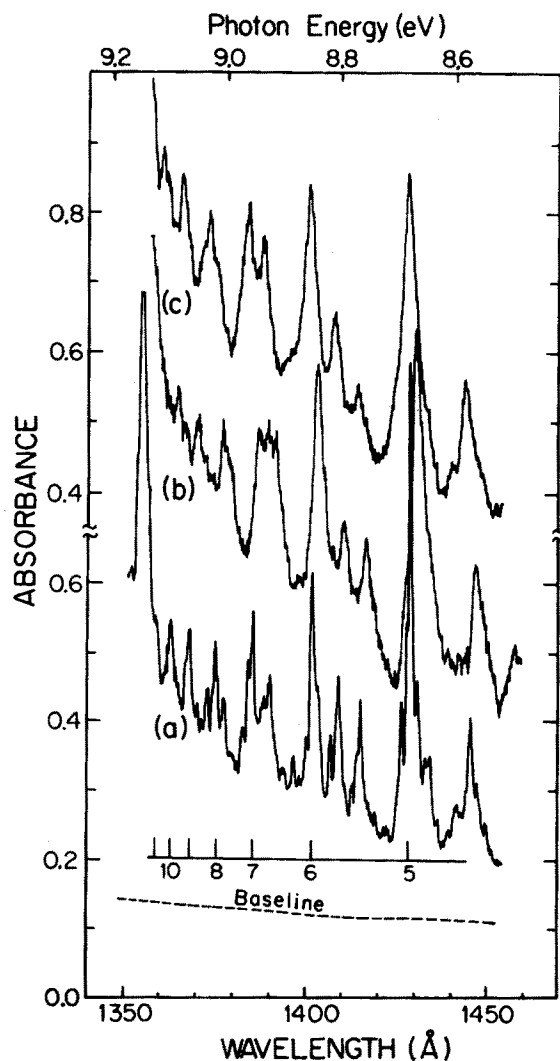

FIG. 3. Room temperature absorption spectra of pure benzene vapors (a); after mixing C_6H_6 with argon gas (3.71×10^{20} cm^{-3}), (b); after mixing C_6H_6 with H_2 gas (4.05×10^{20} cm^{-3}), (c). Members of the R' series are identified at the bottom of the figure. Upper absorbance scale refers to (b) and (c).
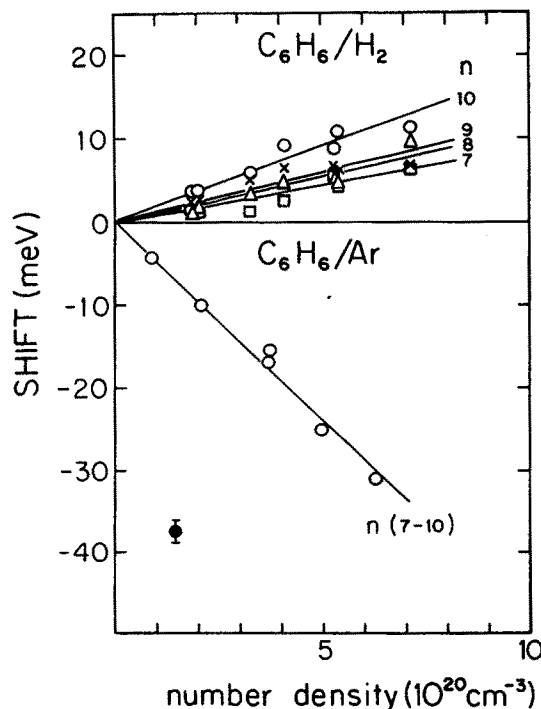

FIG. 5. Energy shifts of C_6H_6 transitions (R' series) for $7 \leqslant n \leqslant 10$ for the H_2 perturber and averaged for all $7 \leqslant n \leqslant 10$ memebers for the Ar perturber. Solid lines represent the least-squares fit of the experimental points. Symbols for H_2 perturber are $\bigcirc$, $n = 10$; $\times$ $n = 9$; $\triangle$, $n = 8$; and $\square$, $n = 7$.

for $n \leqslant 10$ because the weaker members of the R and R'' series could not be resolved in the perturbed spectra.

The effects of density on the spectral shift for CH_3I/H_2 and CH_3I/Ar and for C_6H_6/H_2 and C_6H_6/Ar are presented in Figs. 4. and 5, respectively. A linear density dependence was observed for all four systems.

According to Fermi,[1] the total spectral shift $\Delta_t (\rho)$ is a sum of a scattering term $\Delta_{sc} (\rho)$ and a polarization term $\Delta_p (\rho)$

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

The size and sign of the scattering term depends on the electron scattering length, a of the perturber gas and varies linearly with the number density ρ

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

where m is the electron mass. The core of the excited absorber polarizes the perturbers within the orbital radius of the optical electron, resulting in a negative energy shift term

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

where α is the polarizability of the perturber and e the electron charge.

The shift data of Figs. 4 and 5 can not be reproduced using the Fermi model because of the nonlinearity of the polarization term [Eq. (3)]. Alekseev and Sobel'man reevaluated the polarization term [Eq. (3)] using a sophisticated line shape analysis[4] and obtained an energy shift linear in density. The replacement of Eq. (3) with the polarization term $\Delta_p'(\rho)$, of Alekseev and Sobel'man[6]

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

v being the relative thermal velocity of the colliding partners, provides an accurate representation of experiment. In sum, the fitted energy shifts (i.e., the solid lines of Fig. 4) are reproduced by the modified Fermi formula using the a, α, and v parameters given in Table I. The unmodified Fermi model [i.e., Eq. (2) + Eq. (3)] generates the dot–dashed line of Fig. 4 which fails to describe experiment.

The dashed lines of Fig. 4 represent the scattering term of Eq. (2) resulting from the scattering potential experienced by the optical electron. Its density dependence is expressed by the following shift rate: 2.35×10^{-23} eV cm^3 for H_2 and -4.13×10^{-23} eV cm^3 for Ar.

The experimental total shift for H_2 and Ar [Eq. (2) + Eq. (4)] is shown in Table I.

TABLE I. Parameters used with Eqs. (2)–(4) and shift rates.

	Electron scattering length, a	polariz- ability, α	Relative thermal velocity, v	Experimental total shift rate $\Delta_t (\rho)/\rho$
	(Bohr radii, a_0)	(10^{-24} cm^3)	(10^4 cm/s)	(10^{-23} eV cm^3)
CH_3I/H_2	0.93	0.81	17.8	1.62
C_6H_6/H_2	0.99($n = 10$)[a]	0.81	17.8	1.80($n = 10$)
CH_3I/Ar	-1.63	1.66	4.5	-4.86
C_6H_6/Ar	-1.57	1.66	4.8	-4.75

[a] For only one ($n = 10$) Rydberg member of the R' series.

TABLE II. Electron scattering lengths in H_2 gas determined by pressure shift studies.

Scattering length in units of a_0	Absorber	Max. H_2 density used 10^{20} cm^{-3}	Reference
1.16[a]	Na;K	0.5	8
1.22[a]	Na;Cs;Rb	1.3	9
0.93	CH_3I	10.5	present work
0.99	C_6H_6	7.2	present work

[a] As calculated from the experimental results of Refs. 10 and 11 using the modified Fermi formula [Eq. (2) + Eq. (4)].

The effects of H_2 and Ar on the Rydberg states of benzene are shown in Fig. 5. The upper half of the figure displays the shifts for the $7 \leqslant n \leqslant 10\ R'$ series members, the solid lines being the least-squares fit to a linear density dependence. It is clear that the shifts obtained from the R' members $7 \leqslant n \leqslant 10$ of the benzene/H_2 system are not constant, contrary to what happens, in the case of rare gas perturbers.[3] The shifts averaged for lines $7 \leqslant n \leqslant 10$ in the presence of argon are shown in the lower part of Fig. 5. In this instance, an asymptotic shift value was indeed observed for $7 \leqslant n \leqslant 10$, as is reported in Reininger *et al.*[3]

The gradual increase of the shift rate with n for the system C_6H_6/H_2 is quite unexpected. It seems as if the "high-n character" of the Rydberg electrons is diminished in the presence of the H_2 perturber. Physically speaking the electron–perturber and electron–core interactions appear not to be completely separable. At which value of n the modified Fermi model attains validity is not determinable from our data. However, a comparison of the shift rate for $n = 10$ of C_6H_6/H_2 suggests, by comparison with the CH_3I/H_2 system, that asymptotic behavior might be realized for $n = 10$. A fit of the $n = 10$ data for C_6H_6/H_2 required a slightly higher value of scattering length than was used for the CH_3I/H_2 system (see Table I). The shift rate for the Ar perturber was led nearly to the same electron scattering length for both systems (see Table I).

Scattering lengths obtained from the experimental data are shown again in Table II where they are compared to existing data for pressure shift studies on alkali metal/H_2 systems. The electron scattering lengths obtained in the present study are lower than values from other Rydberg shift studies. However, differences of 30% or more are found between electron beam[12] and swarm[13] cross section data at very low electron energy (~ 0.05 eV) and the scattering lengths derived from Rydberg shifts.

It remains to be understood why the electron scattering length a, measured by pressure shift method differs from the scattering length obtained from the measurement of the scattering cross section ($\sigma \simeq 4\pi a^2$), of low energy electrons in H_2 gas.

A recent empirical model[6] provides a correlation of the electron scattering lengths of He, Ne, Ar, Kr, and Xe gases and the atomic polarizabilities. This correlation is based on the modified atomic effective range formulation[7] for an electron–rare gas atom collision system applied for orbital electrons. According to the empirical model, the electron scattering length, a (in atomic unit) can be calculated using[6]

$$a = -a_1\alpha + a_2, \tag{5}$$

where α is the polarizability in atomic unit and the constants $a_1 = 0.26$ and $a_2 = 1.18$. In the case of molecular perturbers (like H_2 and N_2), the model suggests the use of α_2, the nonspherical polarizability, rather than α. Since the anisotropic polarizability[13] for H_2 is $\alpha_2 = 1.356\, a_0$,[3] the empirical model then predicts a scattering length $a = 0.83\, a_0$, in agreement with experiment. The isotropic polarizability does not generate a value of a even close to the experimental value. In fact, even the sign is wrong. More details concerning the empirical model will be presented elsewhere.[6]

ACKNOWLEDGMENTS

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

[2] A. M. Köhler, R. Reininger, V. Saile, and G. L. Findley, Phys. Rev. A **35**, 79 (1987).

[3] R. Reininger, E. Morikawa, and V. Saile, Chem. Phys. Lett. (to be published).

[4] V. A. Alekseev and I. I. Sobel'man, JETP **22**, 882 (1966); I. I. Sobel'man, L. A. Vainshtein, and E. A. Yukov, *Excitations of Atoms and Broadening of Spectral Lines* (Springer, Berlin, 1981).

[5] J. L. Levine and T. M. Sanders, Jr., Phys. Rev. **154**, 138 (1967).

[6] K. Rupnik, U. Asaf, and S. P. McGlynn (to be published).

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

[8] E. Amaldi and E. Segré, Nuovo Cimento **11**, 145 (1934).

[9] T. Z. Ny and S. Y. Ch'en, Phys. Rev. **54**, 1045 (1938).

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

[11] K. E. Ockenga, P. Gürtler, S. S. Hasnain, V. Saile, and E. E. Koch, *VI International Conference on Vacuum Ultraviolet Radiation Physics*, (Charlottesville, Virginia, 1980) Chap. II, p. 80.

[12] J. Ferch, W. Raith, and K. Schröder, J. Phys. B **13**, 1481 (1980).

[13] M. A. Morrison, R. W. Crompton, Bidhan C. Saha, and Z. Lj. Petrović, Aust. J. Phys. **40**, 239 (1987).