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Pressure shifts and electron scattering lengths in atomic and molecular gases

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Photoabsorption or photoionization spectra of CH_3I are discussed as a function of perturber pressure for 11 different binary gas mixtures consisting of CH_3I and each one of 11 different gaseous perturbers. Five of the perturbers were rare gases and six were nondipolar molecules. The energy shifts of CH_3I Rydberg states become independent of n, the principal quantum number, for $n \geqslant 10$. The energy shifts for $n \geqslant 10$ vary in a linear fashion with perturber number density. The electron scattering lengths for the perturbers are extracted from the shifts using Fermi theory in which the polarization term is that of Alekseev and Sobel'man. These scattering lengths are compared with those from swarm and time-of-flight experiments. It is found that the uncorrected shift scattering lengths correspond to the zero energy or near-zero energy scattering lengths obtained from extrapolated swarm and time-of-flight data. It is found that plots of scattering length vs polarizability α ($\bar{\alpha}$ for molecules) define two linearities, one for the rare gases and one for molecules, CO_2 being an exception to the latter linearity (presumably because of its large quadrupole moment). For a given polarizability, it is also found that molecules exhibit a larger scattering length than the rare gases. These results are discussed and consequences for scattering cross sections are elaborated.

INTRODUCTION AND OVERVIEW OF RESULTS

Highly excited Rydberg states, because of their "large orbital" nature, are very sensitive to surrounding medium. Following Amaldi and Segré,[1] who used gaseous perturbers to modify the excited states of Na and K atoms, Fermi presented a simple model[2] of the observed energy shifts. According to Fermi, the interaction between a highly excited absorber and a perturbing medium can be decomposed into two independent, additive terms. These are the scattering term, $\Delta_{sc}(\rho)$ of Eq. (1), describing the interaction between the optical electron and perturber, and a polarization term, $\Delta_p(\rho)$ of Eq. (2), describing the interaction between the cationic core and perturber. The sum of these two terms is the total energy shift, $\Delta_t(\rho)$ of Eq. (3), of the high-n Rydberg state,

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

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

$$\Delta_t(\rho) = \Delta_{sc}(\rho) + \Delta_p(\rho), \tag{3}$$

where m and e are electronic mass and charge, respectively; A is the electron scattering length of the perturber atom or molecule; ρ is the number density of the perturber gas; α is the polarizability of the perturber medium; and v is the relative velocity of the absorber–perturber pairs.

Equation (2) is the Alekseev–Sobel'man expression[3] which follows from the impact approximation to line-broadening theory and which is discussed in detail in Köhler et al.[4] The linear dependence of $\Delta_t(\rho)$ on ρ, which has been observed by a number of authors,[4,5,6,7] is verified here in extenso. In addition, the null dependence on nitrogen number density observed in the CH_3I/N_2 system, also shown in Fig. 1, provides a further corroboration[8] of the ρ-dependence of Eq. (2). Since $\Delta_t(\rho) = \Delta_t = 0$ for N_2 we find $-\Delta_p = \Delta_{sc}$, which yields a scattering length $A = 1.9 \times 10^{-9}$ cm for N_2, in good agreement with results from swarm experiments (vide infra).

Three sets of scattering length data are compared in this work, one from density effects on high-n Rydberg states of CH_3I, a second from time-of-flight (TOF) data, and a third based on the drift of electron swarms. The latter two data sets yield A only after extrapolation to zero energy using modified effective range theory (MERT). MERT (Ref. 9) pertains to the phase shifts of the partial waves of a scattering system consisting of an electron and a neutral polarizable atom or molecule, and can be used for extrapolation to otherwise experimentally inaccessible low electron energies. The primary adjustable parameter in MERT is the electron scattering length. Comparisons of scattering lengths from pressure shift data for the CH_3I Rydberg states $n = 10$–16 with those from TOF and swarm measurements are given in Table I. The values of A from both the TOF and swarm sources were extrapolated by MERT to zero energy; those from shift data were not. The
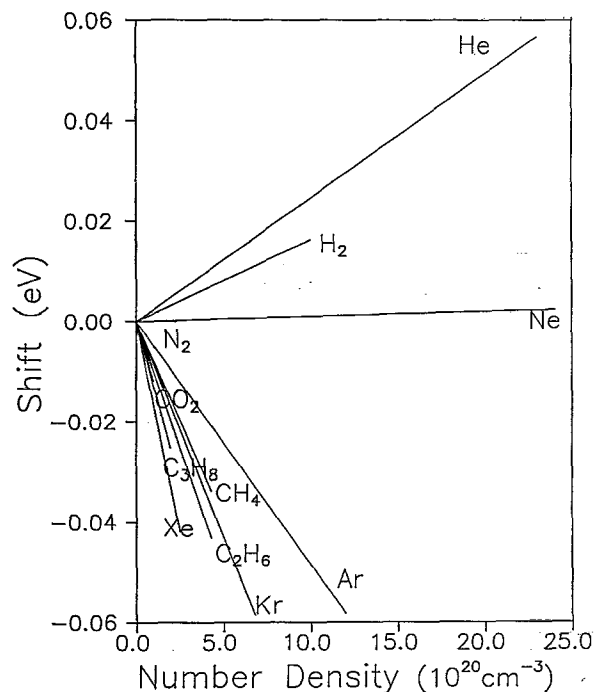
FIG. 1. Total energy shift averaged over the $\tilde{X} \to nd$, $n = 10\text{–}16$, Rydberg transitions of CH_3I for 11 perturber gases. Pertinent references are given in Table II. The total energy shift usually goes asymptotic at $n = 10$.
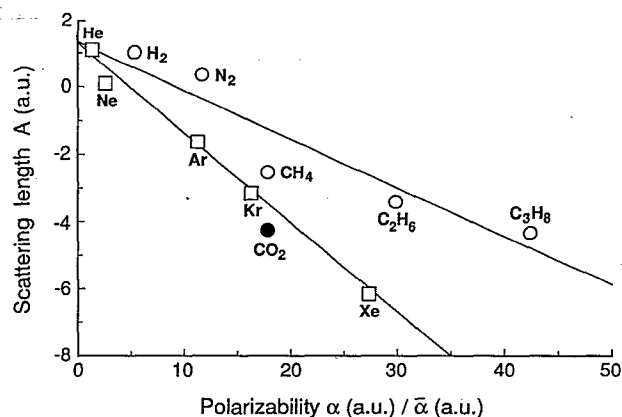

FIG. 2. Scattering lengths of rare gases (denoted by open squares) and molecules (denoted by open circles) are shown plotted against perturber polarizabilities. The best straight line fits are the solid lines which have a slope$= -0.265$ for the rare gases and a slope$= -0.144$ for the molecules. The point for CO_2 is shown as a solid circle; it is not included in either correlation for reasons cited in the text. The equations for the lines are given in Eqs. (7) and (8).

agreement of the three data sets, as will be discussed later, is good.

All available models for the electron scattering length, A, of atomic and molecular systems contain some kind of polarizability dependence. Certainly, scattering cross sections appear to increase monotonically with polarizability. Consequently, we have investigated the effect of polarizabilities on the value of A. We find, as previously,[5] that a linear correlation exists between the electron scattering length, A, and the polarizability α for He, Ne, Ar, Kr, and Xe gases. This correlation is shown in Fig. 2. This simple correlation is considerably different in intent and complex-

ity from the modified effective-range models which have been developed for rare gases. In specific, it makes use of only one parameter, the polarizability, and it presumes to yield scattering lengths at the low-energy limit. In addition, the nature of the scattering potential (whether repulsive or attractive) and the shift (whether blue or red) are contained in the correlative behavior, which predicts both the size and sign of the electron scattering length.

Much of this work is concerned with molecular scatterers. In fact, we will present data for H_2, N_2, CO_2, CH_4, C_2H_6, and C_3H_8. If we exclude CO_2 from the molecular set because of its very large quadrupole moment of -14.8×10^{-14} C m², we find that the two sets

$$\{\text{He,Ne,Ar,Kr,Xe}\}$$

and

TABLE I. Electron scattering lengths (in units of bohr radius, a_0) from pressure shift (A), from MERT extrapolation of both TOF (A_{tof}) cross sections and swarm (A_{sw}) cross sections. References for all data sources are given in the brackets.

Gas	(A)	(A_{tof})	[Ref.]	(A_{sw})	[Ref.]
He	1.08 ± 0.03	1.95	[39]	1.19	[41]
		1.16	[40]		
Ne	0.17 ± 0.01	⋯	⋯	0.214	[42]
Ar	-1.63 ± 0.09	-1.593	[40]	-1.492	[16]
	-1.55 ± 0.09	-1.492	[43]		
		-1.449	[44]		
Kr	-3.02 ± 0.11	-3.478	[43]	-3.32	[45,46]
		-3.19	[45]		
Xe	-6.12 ± 0.49	-6.527	[43]	-6.0	[9,47]
H_2	0.93 ± 0.04	1.27	[17,18]	1.27	[17,18]
N_2	0.35 ± 0.06	⋯	⋯	0.44	[17,19]
CH_4	-2.61 ± 0.04	-2.475	[21]	-2.755	[22]
C_2H_6	-3.33 ± 0.08	⋯	⋯	⋯	⋯
C_3H_8	-4.31 ± 0.06	⋯	⋯	⋯	⋯
CO_2	-4.23 ± 0.17	⋯	⋯	⋯	⋯

$\{H_2, CH_4, N_2, C_2H_6, C_3H_8\}$
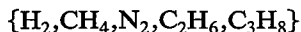
define two reasonable linearities, $A = m\alpha + b$ for atoms and $A = m'\bar{\alpha} + b'$ for molecules, where $\bar{\alpha}$ is the average polarizability. The slopes of these two lines are quite different (i.e., $m \neq m'$) but the intercepts are very similar (i.e., $b \approx b'$). The line for molecules is also shown in Fig. 2. These linearities, one for atoms and one for molecules, represent a very novel finding which will be discussed later.

The purpose of this work, then, is quite straightforward; to collect and discuss pressure shift data; to compare the pressure shift data to TOF and swarm measurements and to assess the consistencies which exist between them; to establish the validity of Eq. (3) for pressure shift analysis; to elaborate the polarizability dependence of the scattering length A for both atoms and molecules; and to discuss the observed linearities of A vs α (or $\bar{\alpha}$) and the consequences for scattering cross sections.

EXPERIMENT

A detailed description of the experimental technique for pressure shift measurements of high-n Rydbergs of CH_3I in various perturber gases is given elsewhere.[4,8]

Deviations from ideal gas behavior are significant, particularly at the higher pressures used in this work. Consequently, number densities were calculated using the Beattie–Bridgeman equation and the parameter sets for the various perturber gases.[10]

A particular advantage of molecular absorbers relative to alkali metal absorbers, is that they may be studied at room temperature. Indeed, the lower temperature limit, being dependent only on the freezing point of the particular absorber/perturber system, can lie considerably below room temperature. That is, molecular perturbers can be studied well below their vibrational thermal excitation thresholds in a molecular absorber system whereas such is not possible with the common alkali metal absorber systems.

Since molecules can rotate and vibrate, the density of states in them is usually much larger than in atoms. Consequently, the bandwidths of molecular absorbers are always considerably broader than those of atoms. There is considerable disadvantage in this because the minimal shift size which can be measured for a molecule is larger than that for an atom, the minimal shift sizes being roughly in the ratio of the Rydberg excitation bandwidths. There is also, however, some advantage; asymptoticity of energy may occur in molecular absorbers at principal quantum number values as low as $n = 10$; and large perturber densities, certainly as large as $\rho = 10^{21}$ cm^{-3}, may be investigated before the effects of pressure on bandwidth and shape begin to confuse the measurements of band shift.

The measurement of pressure shifts from absorption spectra has been restricted to perturbers that do not absorb in the region of Rydberg excitation of the absorber. This restriction may be removed by doing photoionization experiments[11] in which a synchrotron is used to excite the autoionization region of the designated absorber in a narrow sheath in the immediate vicinity of the surface of op-

tical incidence. These energies, however, must be insufficient to ionize the designated perturber. Since the vast majority of potential perturber systems absorb in the vacuum ultraviolet (VUV) region, this technique broadens the scope of the pressure shift technique.

Photoionization spectra of either pure or perturbed CH_3I can be observed[12,7] at energies less than the lowest ionization limit. These subthreshold photoionization spectra are attributable to nd Rydberg excitations originating in vibrationally-excited ground state levels. These nd Rydberg states may then autoionize to produce a vibrationless CH_3I^+ ion. These spectra, which also may be used to evaluate scattering shifts, also point up the need for low temperatures when working with molecular perturbers/absorbers.

COMPARISON OF PRESSURE SHIFT, TIME-OF-FLIGHT, AND SWARM SCATTERING LENGTHS

The total energy shift of high-n Rydberg states of CH_3I becomes asymptotic at $n \approx 10$. The average asymptotic energy shifts of CH_3I are plotted as a function of perturber number density in Fig. 1. The density dependencies are consistently linear. The typical experimental slope error is ~ 0.1–0.3×10^{-23} eV cm^3 when ρ is of the order of 10^{20} cm^{-3}. The precise individual slope errors are cited in Table II. The accuracy of the shift measurements was approximately ± 0.1 Å, corresponding to ~ 0.7 meV in the spectroscopic range of interest here.

The raw data for total, scattering, and polarization shift rates, Δ_t/ρ, Δ_{sc}/ρ, and Δ_p/ρ, respectively, are given in Table II. These data agree well with both very old[13] and quite recent[14] pressure shift data, the latter of which used "Doppler-free" laser techniques to investigate the Rydbergs of alkali metal absorbers. The scattering shift is obtained by subtracting the calculated polarization shifts of Eq. (2) from the total shift. The polarizabilities and relative thermal velocities required in order to use Eq. (2) to calculate the polarization shifts are also collected in Table II.

The scattering length governs the size and sign of the potential barrier experienced by the optical electron. Electrons of large Rydberg orbitals are quasifree. Close to zero energy, the scattering of these electrons should be governed by the same cross section that is "active" in momentum transfer scattering (σ_m) or TOF experiments (σ_T), and all three types of cross sections should be identical.[15] Indeed, at the zero energy limit, where cross sections are determined by scattering lengths, one may write

$$\sigma_{T,m}(k \to 0) = 4\pi A^2, \tag{4}$$

where k is the wave number of the electron, $k^2 = (2m/\hbar^2)E$. The dependence of the total or the momentum transfer cross sections on electron energy is usually determined from electron attenuation and drift measurements, respectively. These cross section data must be extrapolated to zero energy using a four-parameter MERT expansion,[9] the scattering length being the primary fitting parameter. Scattering lengths, as obtained from the absorptivity of high-n CH_3I Rydbergs (A) and from the MERT extrapolations of

TABLE II. The averaged total, scattering and polarization shift rates for the high-n Rydbergs of CH_3I ($n=10$–16), cited in units of 10^{-23} eV cm^3. Average polarizabilities [Landolt–Börnstein, *Zahlenwerte und Funktionen, I Bd.* (Springer, Berlin, 1951)] and relative thermal velocities (as calculated from the Boltzmann distribution at 300 K) are cited in units of 10^{-24} cm^3 and 10^4 cm/s, respectively. References for pressure shift scattering length measurements are given in the brackets.

Gas	Δ_t/ρ	Δ_{sc}/ρ	Δ_p/ρ	α	v	[Ref.]
He	2.45 ± 0.06	2.73	-0.29	0.20	12.8	[4]
Ne	0.09 ± 0.03	0.45	-0.35	0.40	6.0	[4]
Ar	-4.86 ± 0.4	-4.04	-0.82	1.65	4.5	[4,6,35]
Kr	$-8.6\ \pm0.2$	-7.6	-1.01	2.48	3.5	[4,48]
Xe	$-16.8\ \pm2.0$	-15.5	-1.29	4.04	3.1	[7]
H_2	1.62 ± 0.10	2.35	-0.73	0.81	17.9	[6]
N_2	$0\ \ \ \pm0.15$	0.88	-0.88	1.76	5.2	[8]
CH_4	-7.86 ± 0.15	-6.63	-1.23	2.60	6.7	[11]
C_2H_6	-10.05 ± 0.2	-8.42	-1.63	4.47	5.1	[11]
C_3H_8	-12.93 ± 0.26	-10.99	-1.94	6.29	4.4	[11]
CO_2	$-11.8\ \pm0.5$	-10.71	-1.09	2.65	4.4	[27]

the electron scattering cross sections of both TOF (A_{tof}) and swarm (A_{sw}) origins are shown in Table I. The TOF and swarm scattering lengths agree well with those measured by the pressure shift method. Inspection suggests that the scattering length obtained from density effects, despite the finite electron energy of $n=10$–16 Rydberg electrons, appear to constitute a "zero energy" scattering length. This, of course, is not surprising; the nondependence of pressure shift on the principal quantum number n beyond $n=10$ implies that the shift at infinite n, where the electron kinetic energy is zero, is the same as that at $n\simeq10$. If this conclusion be correct, it heightens considerably the significance of the pressure shift technique.

O'Malley[9] has also proposed an alternative simplified extrapolation to a zero energy scattering length (A_0). For true "zero energy," one may consider only Rydberg states for which $n\rightarrow\infty$, in which case $k=(na_0)^{-1}\rightarrow0$. Assuming that $\tan\eta_0/k$ is proportional to the energy shift, η_0 being the phase shift, the "extrapolated" value of A, which we designate A_0, may be obtained[9] as

$$A_0=A-(\pi/3a_0)\alpha k \qquad (5)$$

or, more simply, as

$$\pm A_0=\pm A-\alpha\pi/3n. \qquad (6)$$

All of our attempts to extrapolate to near-zero energy by subtraction of the linear k term of Eq. (5) from the experimental value of A gave unsatisfactory results; the values of A_0 exhibited large deviations from the MERT values for A_{tof} and A_{sw}. For example, using the polarizabilities 16.73, 27.29, and $17.54a_0^3$ and $n=13$, we find values of A_0 from Eq. (6) to be $A_0=-4.39a_0$, $-8.16a_0$, and $-3.93a_0$ for Kr, Xe, and methane, respectively. These "zero energy" values differ by $\sim50\%$ from the pressure shift scattering lengths A, as well as from the MERT values of A_{sw} and A_{tof} listed in Table I. It appears that the pressure shift scattering lengths do not require extrapolation to zero energy.

MERT analyses of swarm and TOF data for the rare gases (see Table I) do not always yield the same value for the zero-energy scattering length. Despite this, we find that almost all pressure shift scattering lengths lie within 10%

of A_{sw} or A_{tof}. Indeed, the cross sections of swarm and TOF origins may differ more in themselves than in their deviance from the pressure shift values.

Some further comments on the data of Table I appear to be in order.

(a) Only isotropic long-range potentials need be considered in the MERT extrapolation for electron scattering by rare gases.[9,16] The corresponding extrapolation for molecules, however, requires concern for anisotropic potentials. Chang[17] discussed this problem and found that, for H_2, such effects constitute only $\sim1\%$ of the total cross section. The value $A=0.93a_0$ of Table I for H_2 is 30% lower than the Chang scattering lengths, as Chang derived these from the momentum transfer cross sections of Crompton *et al.*[18] and the TOF data of Ferch *et al.*[19] We have no explanation for this discrepancy.

(b) Chang[17] also evaluated the swarm data of Engelhardt *et al.*[20] for N_2, obtaining $A_{sw}=0.44a_0$. Because of the large anisotropic contribution, $4\pi A^2$ does not, per Eq. (4), yield a true zero energy cross section. Indeed, in order to obtain $\sigma_T(0)$, a factor[17] of 1.58 must be inserted into Eq. (4). This factor originates in the especially high ratio of Q/A for nitrogen, Q being the quadrupole momentum. The scattering length of nitrogen obtained from pressure shifts is then in good agreement with the Chang value. Thus, the nitrogen perturber demonstrates that the parameter obtained from pressure shifts is always the scattering length and not the square root of the cross section [Eq. (4)], two values which, in the Fermi model, are equivalent for atomic scatterers.

(c) Methane is used widely in track detectors and its transport coefficients are important. The application of MERT to such a highly symmetrical molecule as methane has not been fully considered. The scattering length $A=-2.61a_0$, as obtained here from pressure shifts, is intermediate to two recent A values, that of Ferch *et al.*[21] who applied a four parameter MERT (Refs. 9, 16) fit to total scattering cross section data, getting $A=-2.475a_0$; and that of Schmidt,[22] who used a six parameter MERT analysis based on drift velocity and longitudinal and trans-

verse electron diffusion coefficients, and found $A = -2.755a_0$.

(d) Gee and Freeman[23] evaluated momentum transfer cross sections for methane and ethane at very low electron energies. For methane, for which cross sections were followed down to 0.001 eV, the values of σ_m were found to be far higher than any existing data might suggest. No MERT analysis of these σ_m data exist. However, the values of σ_m at $\sim$0.01 eV are comparable to the methane and ethane cross sections obtained from pressure shift studies. For ethane and propane, the TOF cross sections do not extend to low enough electron energies[24] to merit comparison with pressure shift data.

(e) Accurate computed scattering cross sections are available[25] for CO_2 at very low energies. These cross sections increase rapidly with decreasing electron energy, possibly because of a nearly bound $l=0$ state in the e-CO_2 potential. The computations agree well with the TOF measurements of Ferch *et al.*[26] A zero energy extrapolation, however, is not available. Nonetheless, if Eq. (4) is applied at 0.07 eV, the lowest energy for which measurements are available,[26] one finds $A = -4.3a_0$, in good agreement with the pressure shift value of $-4.23a_0$.[27]

THE DEPENDENCE OF SCATTERING LENGTH ON POLARIZABILITY?

A previous work[5] suggested a linear dependence of scattering length on polarizability for the five rare gases He, Ne, Ar, Kr, and Xe. This linearity is quite evident in Fig. 2, in which the scattering lengths, obtained in this work, ones which pertain to zero or near-zero electron kinetic energies, are plotted vs the polarizability α. The linearity covers the range of both negative and positive scattering lengths and is given by

$$A(a_0) = -0.265\alpha + 1.23; \quad d = 0.1a_0, \tag{7}$$

where d is the standard deviation. The linearity is not too surprising since, at least for large atoms, it is well known that the scattering cross section increases monotonically with increasing polarizability. However, the observed linearity indicates, by virtue of the relationship of Eq. (4), and in agreement with Omont,[28] that the monotonicity referred to in the previous sentence does not extend to low atomic masses. The scattering cross sections, as calculated by Eq. (4) from the data of Table I, are shown in Fig. 3. The cross section is parabolic in the polarizability, with the left-hand leg of the parabola being truncated. These results indicate the following: (1) the maximum value of the scattering length (i.e., that for $\alpha=0$) appears to be a natural constant; and (2) scattering cross sections are not monotonic in the polarizability when low atomic masses are considered, whereas the scattering length is.

Rupnik *et al.*[5] attempted to include some nonpolar molecules into the linear correlation which they had obtained for the rare gases. Unfortunately, they had scattering length data for only three molecules, H_2, N_2, and CH_4. Subsequent discussions[29,30] indicated that the molecular sample size was too small. Since the present work includes new data for six molecules, the three extra entries being
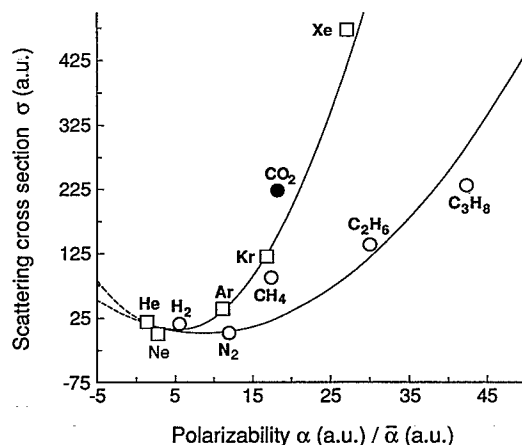

FIG. 3. Scattering cross sections are plotted as a function of polarizability. The two parabolic curves are squares of Eq. (7) for atoms and Eq. (8) for molecules. The fit of the rare gases to the atom curve is excellent, that for molecules to the molecule curve is fair. The minima occur at ($\sigma=0$, $\alpha\approx 5a_0$) for atoms and ($\sigma=0$, $\bar{\alpha}\approx 10a_0$) for molecules. Truncation of the left hand branches of the parabolas occurs at $\alpha=0$. With the exception of CO_2, molecular scattering cross sections for molecules are smaller than for atoms above $\alpha\approx 7a_0$, and larger than for atoms below $\alpha\approx 7a_0$.

C_2H_6 (ethane), C_3H_8 (propane), and CO_2 (carbon dioxide), we now proceed to reinvestigate the existence of a molecular correlation line. It is found that five of these molecules exhibit an approximate linearity in $\bar{\alpha}$, the one outlier being CO_2. The best linear fit for the five remaining molecules is

$$A(a_0) = -0.144\bar{\alpha} + 1.304; \quad d = 0.4a_0. \tag{8}$$

This fit is of poorer quality, by a factor of 4 in d, than that for the rare gases. The average polarizability $\bar{\alpha}$, as used in Eq. (8), is defined as $\bar{\alpha} \equiv (\alpha_\parallel + 2\alpha_\perp)/3$.

The following observations concerning Figs. 2 and 3 seem pertinent:

The atom and molecule lines are not even approximately the same.

Both lines, one for atoms and one for molecules, have essentially the same intercepts of $\sim 1.25a_0$, suggesting that the limiting positive scattering length may be a natural constant. Further data, particularly for nonpolar, low quadrupolar molecules are required to establish or invalidate this point.

Scattering lengths for molecules are larger than for rare gases of the same polarizability. That is, molecules attract electrons less than do atoms, which shows up most clearly in the smaller absolute values they exhibit in the negative branch of the scattering length plots. While we do not understand the reasons for this, we surmise that it is a consequence of the larger molecular sizes.

The methane molecule, CH_4, lies closer to the atom line than to the molecular line. Whether or not this is a consequence of the tetrahedral (i.e., near-spherical) symmetry of CH_4 we cannot say. The investigation of other tetrahedral (e.g., SiH_4) and octahedral (e.g., SF_6) molecules would be of considerable interest.

The molecule CO_2 is an outlier. For that reason, we have not included it in our molecular straight-line fitting procedures. This exclusion is a rational use of statistics and, furthermore, is not unexpected because of the large quadrupole moment, -14.8×10^{-14} C m^2, of carbon dioxide. This quadrupole moment is larger by a factor of ~ 3 than that for any other molecule used in Figs. 2 and 3.

The polarizability of radon has been cited as $39.5a_0^3$ by Tuck[31] and $42.5a_0^3$ by Miller,[32] leading to scattering length predictions based on Eq. (7) of -9.05 and $-9.8a_0$, respectively. No experimental value of A seems to be available.

The appropriate molecular polarizability for use in the correlation of scattering length and polarizability is not known to us. We have used $\alpha_\parallel$, $\alpha_\perp$, and $\bar{\alpha}$, and we have obtained linearities of equal or better quality to that of Eq. (8) for both $\alpha_\parallel$ and $\alpha_\perp$. However, since $\bar{\alpha}$ seems to be the more physically-realistic polarizability, we have chosen to use it in the plot of Fig. 2 and in Eq. (8). We also stress that the $\bar{\alpha}$ plot is the only one which provides essentially equal intercepts for both the atom and molecule lines. Whether this be significant or not must await further work.

The linearity of the α or $\bar{\alpha}$ dependence and the existence of both positive and negative scattering lengths suggests, via Eq. (5), a parabolic dependency of scattering cross section on $\alpha/\bar{\alpha}$, the left branch of the parabolas being truncated at $\alpha/\bar{\alpha}=0$. This parabolic dependency has been observed, the minima occurring at $\alpha \approx 5a_0^3$, for atoms and $\bar{\alpha} \approx 10a_0^3$, for molecules.

CONCLUSIONS

The systems investigated in this work consisted of binary mixed gases, the VUV absorber in all instances being methyl iodide and the perturber (i.e., the scatterer of the Rydberg electron) being one of either five rare gases or six nonpolar molecules. The scattering lengths derived from Rydberg shifts induced by the perturbers have been compared with both time-of-flight and swarm data which were extrapolated to zero energy. The agreement of the three sets is quite excellent, suggesting that the shift scattering lengths refer to zero or near-zero electron energies.

The shift data presented in this work refer to Rydberg quantum numbers $n=10-16$. The Rydberg absorption bands of molecules are quite broad relative to atoms, the broadening of a given molecular vibronic transition being largely due to rotational excitations. Because of this width, the n-dependence of the shift for a molecular absorber usually settles down between $n=10$ and 12. That is, the shifts that occur beyond $n=12$ are generally much smaller than the rovibronic Rydberg band width and cannot be measured. For one reared on atomic absorbers, for which only at $n > 20$ does the shift become independent of n, it may seem unsettling to work at $n=10$ or, as we have done, to average the $n=10-16$ behavior. Experimentally, however, that is what one is forced to do, at least when using CH_3I. But, the matter need not be altogether that disturbing. Inspection of the atomic absorber shift situations indicates clearly that the bulk of the shift has occurred at $n=12$ and that, beyond $n=12$, the remainder is indeed quite small.

The polarization term, Δ_p of Eq. (2), is smaller for CH_3I than for Li. That is, scattering makes a larger contribution to total shift in methyl iodide, being as large as 85% of Δ_t when argon is the scatterer. Consequently, scattering will dominate the spectroscopic shifts in CH_3I, particularly for heavier scatterers, and the shifts themselves may largely reflect the scattering lengths. This happenstance is a consequence of the high molecular weight of CH_3I and the fact that it is gaseous at 25 °C. For example, for Li which requires a working temperature $T \simeq 600$ K, we find $\Delta_p(\text{Li-Xe})/\Delta_p(\text{CH}_3\text{I-Xe}) \simeq 1.66$ indicative of the larger role played by polarization forces when lithium is the absorber.

The linearity of the A vs α plot for the rare gases may not be too surprising because it does accord with a presumed monotonic increase of scattering cross section with α. It is an observation which may be implicit in a number of computational efforts[28,33,34] but for which, nonetheless, no analytical explanation exists. The situation for molecular scatterers is even worse, at least in the sense that no rationale is available to us for the greater scattering lengths of the molecules compared to rare gases with the same value of α. The situation with respect to cross sections based on Eqs. (4), (7), and (8) is diagrammed in Fig. 3. We are not aware of any representation resembling that of Fig. 3.

The results of Fig. 1, particularly those for nitrogen, establish the Alekseev/Sobel'man density dependence[3] in a very solid way. Thus, there seems no justification for continuance of a nonlinear density dependence of the polarization term.

The density dependence of the scattering shift $\Delta_{sc}(\rho)$ speaks to the evolution of band structure in insulators. The $\Delta_{sc}(\rho) \equiv V_0(\rho)$ equivalence, where V_0 is the electron energy at the bottom of the conduction band, is the crucial connector. Photoelectric injection experiments in both rare and molecular gases[35,36] suggest that "bandlike" behavior occurs well below critical density. The high density limit of the pressure shift experiments reported here depends on the mass of the scatterer and may extend to 2×10^{21} cm^{-3}. In this density range, the accuracy of the photoelectric method[37,38] is low (30–50 meV) because of photocathode surface effects, whereas the accuracy of Δ_{sc}, as obtained from pressure shifts, may well be an order of magnitude higher. Thus, the data of Table II are very relevant to this issue.

The advantages of the molecular methyl iodide absorber for shift studies are threefold (1) it is quite unreactive and can be used with impunity with a great variety of perturbers whereas an alkali metal may not; (2) the polarization term for the heavy methyl iodide is considerably smaller than for either Li or Na and, as a result, the observed shifts consist dominantly of Δ_{sc}, the Δ_p component being much smaller than that for Li; and (3) the methyl iodide systems may be studied at room temperature or lower whereas the alkali metal systems may not...a consideration of some importance for unstable, vibrationally-excitable molecular scatterers.

ACKNOWLEDGMENT

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