

Threshold Shapes and Resonances in the Photodetachment Cross Sections of Chloride, Bromide, and Iodide

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The photodetachment curves of Cl^- , Br^- , and I^- have been examined in their threshold regions by absorption spectroscopy of shock-heated alkali halide vapors. The chloride curve appears smooth and normal in terms of threshold laws, but the bromide and iodide curves show maxima about 500 cm^{-1} above the thresholds, with widths of about 200 cm^{-1} at half-height. The threshold positions are not affected by changes in conditions. The anomalously large absorption or resonances seem to be due to the halide ions, but to be influenced to some degree by the alkali atoms or ions. Three explanations, none entirely satisfactory, are put forth for the maxima; these are (1) near-resonant transfer of energy from $\text{X} + e^-$ to M , giving $\text{X}^- + \text{M}^*$; (2) metastable autodetaching states of the halides; and (3) mixing of vacant alkali ion orbitals with continua of the halides. The third is considered most plausible.

I. INTRODUCTION

PHOTODETACHMENT of electrons from gaseous negative ions has proved to be a powerful method for the determination of electron affinities.¹⁻⁴ Moreover cross sections have been determined with considerable accuracy in several cases. The use of light beams of relatively narrow bandwidth has made it possible to study the shape of the photodetachment cross section of I^- in some detail.⁵ We wish to report here a study of the relative photodetachment cross sections of Cl^- , Br^- , and I^- based on photographic spectroscopy of partially dissociated alkali halide vapors.

The work was undertaken initially in order to examine the shapes of photodetachment curves under relatively high resolution in the region of E_0 , the threshold energy for photodetachment, equal to the electron affinity. From these shapes, one could presumably determine the range of validity of the threshold laws governing the energy dependence of the photodetachment cross section σ_{det} .⁶⁻⁸ The experiments

on chloride ion do, in fact, give this information with little or no ambiguity. Near threshold, the Cl^- photodetachment cross section is a smooth monotonic function of energy from which phenomenological constants can be evaluated, in principle. The detachment cross section of I^- in our work, however, shows a distinct maximum at an energy above but very near the threshold. The cross section of Br^- is an intermediate case, displaying a change of slope which can most easily be interpreted as an incipient maximum or resonance.

In the following section the experiments and methods for data handling are described. The third section includes the results of the experiments and a discussion of their interpretation.

II. EXPERIMENTAL

The basic method for obtaining photodetachment cross sections from photographic absorption spectra has been described in some detail previously.⁴ A shock wave in argon is used as a convenient heating device to vaporize and dissociate alkali halide salts. The shock strength is chosen so that the temperature of the gaseous sample of argon and alkali halide is about $2800^\circ\text{--}3300^\circ\text{K}$. The final choice of driver gas (H_2) and of argon pressures had to be made by trial and error because the amount and rate of vaporization of solid salt could not be guessed *a priori*. The useful range of driver pressures was 290–350 psi and of argon pressures 1.4 to 2.0 cm Hg. Typically, the argon temperatures upstream of the solid sample were approximately 8000°K , so that over 60% of the thermal energy of the shocked argon is expended to heat, vaporize, and dissociate the salt if local thermal equilibrium is achieved.

At a temperature of about 3000°K , the vapor of an alkali halide consists of a mixture of monomeric molecules, neutral atoms, alkali positive ions, halide negative

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¹ L. M. Branscomb, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Chap. 4.

² M. L. Seman and L. M. Branscomb, *Phys. Rev.* **126**, 1602 (1962).

³ B. Steiner, M. L. Seman, and L. M. Branscomb, *J. Chem. Phys.* **37**, 1200 (1962).

⁴ R. S. Berry, C. W. Reimann, and G. N. Spokes, *J. Chem. Phys.* **37**, 2278 (1962); R. S. Berry and C. W. Reimann, *ibid.* **38**, 1540 (1963).

⁵ B. Steiner, M. L. Seman, and L. M. Branscomb, in *Atomic Collision Processes*, edited by M. R. C. McDowell (John Wiley & Sons, Inc., New York, 1964), p. 537.

⁶ E. P. Wigner, *Phys. Rev.* **73**, 1002 (1948).

⁷ T. F. O'Malley, L. Spruch, and L. Rosenberg, *J. Math. Phys.* **2**, 491 (1964).

⁸ T. F. O'Malley, Report No. 14, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Colorado (unpublished).

ions, and electrons. Typically, a vapor containing 4×10^{16} total CsI molecules/cm³ will contain about 9×10^{15} undissociated molecules/cm³, about 2.7×10^{16} neutral Cs atoms/cm³, one-tenth this many Cs⁺ ions, and slightly more I⁻ ions than electrons, 1.5×10^{15} /cm³ of the former and 1.2×10^{15} /cm³ of the latter. Under the conditions of our experiments, the total density of the shocked sample gas containing argon and salt was always above 6×10^{17} /cm³. Consequently, the ions represented only a few percent of the total gas sample. (Larger percentages of salt vapor were also obtained in many shocks, but, because the negative-ion concentrations were very high, light absorption by these shocks was so great that their spectra were useless for studying shapes of photodetachment cross sections.) Ion densities were estimated from the alkali linewidths as described previously.⁴ Since no attempt is made in the present discussion to fix absolute cross sections, no more precise method was required.

Solid salts were generally supported on thin aluminum foil, but cleansing tissue was also used in order to eliminate effects of the aluminum on spectra. (It might be noted here that the $^2\Sigma-^2\Sigma$ band system of AlO was found in absorption in some spectra.)

Spectra of I⁻ were taken on a Hilger E474 glass prism spectrograph; spectra of Br⁻ and Cl⁻ were taken on a Bausch & Lomb Medium Quartz spectrograph. Both Eastman Kodak 103-O and 103-F plates were used, to eliminate the possibility of artifacts due to emulsion characteristics. Both kinds of plates were calibrated for the wavelength regions of interest with a Jarrell-Ash seven-step neutral density filter. Plates were developed in Kodak D-19 for 5 min at a temperature of $68 \pm 2^\circ\text{F}$. Plate densities were recorded on a Leeds and Northrop Knorr-Albers recording microdensitometer.

Each plate contained a shock spectrum and at least one comparison spectrum taken through the same optics but without a shock. It had been found previously that calibration of each plate individually was not necessary. The plate densities of the shock and comparison spectra were converted to optical densities. The difference curves of the optical densities of shock and comparison spectra are essentially relative cross section curves for photodetachment; however these will exhibit spectra of any other absorbing species present in the sample but not in the comparison. For this reason it was necessary to use rather extensive checks to eliminate any possible contaminant which could give rise to absorption in the region of the halide ion thresholds.

In addition to the checks just mentioned, namely the use of different supporting materials and of different emulsions, we have used three salts of I⁻ (cesium, rubidium, and sodium) and two salts (cesium and rubidium) of Br⁻ and Cl⁻. We have used salts of various purities from different sources. We have also obtained absorption spectra of molecular CsI (from a

sample heated in a tube furnace in the conventional way).⁹ We have not been able to associate the unusual features of either the I⁻ or Br⁻ photodetachment curves with any contaminant or molecular alkali halide species. The molecular spectrum of CsI shows several diffuse maxima, the well-known fluctuation bands, but these are much too closely spaced to correspond to anything in the spectra from shock-heated CsI; in fact, the absorption spectra of I⁻ exhibit a minimum at the frequency of one of the CsI maxima. The absorption maxima associated with the bromide and iodide curves were not observed in comparison spectra of shocked samples containing none of the appropriate halide.

The plates were taken with a spectral resolution of approximately 0.3 Å. Wavelengths were determined from internal standards and were simply measured on the recording chart paper of the microdensitometer tracings, since the features of interest are all very broad. The estimated accuracy of the wavelength measurements is about 0.5 Å.

Of the various sources of uncertainty in the optical density of individual plates, the most important was plate noise. This was least severe in the chloride spectra, in the region 0–700 cm⁻¹ above threshold. The iodide curve in the region of the absorption maximum was not as reproducible as the remainder of the iodide curve; the bromide curve suffered the same problem to a lesser degree. The areas under observed maxima in the iodide curves were large enough to be measured approximately when the underlying photodetachment curve was subtracted. These areas correlated at least in a qualitative way with the halide continuum intensity. The chloride curves appeared to be quite reproducible in shape from shock to shock. The threshold positions of all three ions, Cl⁻, Br⁻, and I⁻, were completely reproducible from spectrum to spectrum and were in agreement with the values reported previously.⁴

III. RESULTS AND DISCUSSION

Typical optical density curves of Cl⁻, Br⁻, and I⁻ continua are shown in Figs. 1, 2, and 3, for the regions immediately above threshold. All the cesium iodide spectra show approximately the same sort of maximum as that of Fig. 3(a); with rubidium replacing cesium, the maximum is smaller relative to the height of the main continuum, and is shifted about 75 cm⁻¹ to lower energies. With sodium, the maximum is smaller still and occurs at about the same frequency as that of rubidium iodide. The regions studied are 0–700 cm⁻¹ above threshold for chloride and 0–2000 cm⁻¹ for bromide and iodide.

Phenomenological curves of the form $\sigma(\nu) = \text{const.} (\nu + \nu_0)\nu^3 (1 + \alpha_1\nu^2 + \dots)$ were fitted to the experimental

⁹ K. Sommermeyer, *Z. Physik* **56**, 548 (1929).

data by the method of least squares. (The threshold frequency is ν_0 .) A curve of the form $\sigma \propto (\nu + \nu_0)\nu^3 [1 + \alpha\nu \ln(\beta\nu^3)]$ was examined also. In no way could the bromide and iodide data be matched over the entire observed ranges with such representations. The experimental curves based on error limits of both sets of data points were well beyond even the best three-constant curves. The chloride curve, on the other hand, could fit quite closely, particularly if less weight was given to the intensity values within about 150 cm^{-1} of threshold, where the signal/noise ratio is small. The chloride data did not justify the use of more than one term in the series representation. Two sets of data for Cl^- , virtually superimposable, gave rise to constants α_1 having different signs. Following this observation, we attempted to fit the bromide and iodide curves with the regions of anomalous intensity omitted. This meant fitting the regions 0–600 and 900–2200 for Br^- and 0–150 and 600–1800 cm^{-1} for I^- . As with chloride, the

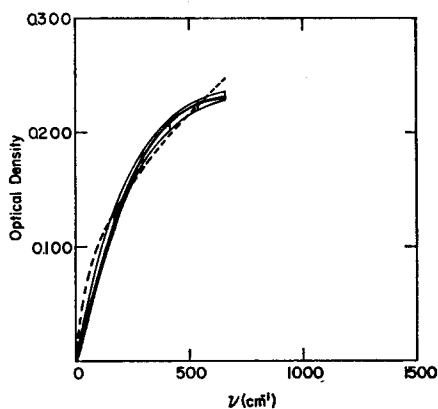


FIG. 1. Threshold region of typical photodetachment curve of Cl^- in CsCl vapor. Probable error is shown by light curves parallel to experimental (solid) curve. Dotted curve is based on one- or two-constant fit to data; they are superimposed on this scale.

photodetachment curves of the heavier halides could easily be fit to within the uncertainty of the data with a single term, provided the anomalous region was omitted. In fact the fit for I^- over its range was somewhat better than that for Cl^- (with all points included) over a much shorter range.

The immediate implication of the success of the one-term fits is a little disappointing; apparently the shapes of photodetachment curves near their thresholds will probably not yield information about atomic polarizabilities or quadrupole moments. Such information is in principle contained in the second and higher terms.⁸ The iodide curve has been measured by Steiner, Seman, and Branscomb⁵ to energies almost 1 eV above threshold, and appears to be quite horizontal over the range beyond the threshold rise. From these results and ours, it seems quite possible that the region of validity of the threshold expansion for σ is just the region in which the first term of the expansion suffices to represent the data.

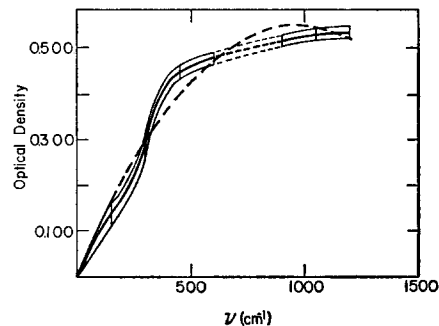


FIG. 2. Threshold region of typical photodetachment curve of Br^- in RbBr vapor. Dotted curve is a two-constant least-squares fit (terms linear and quadratic in k) to the data. Probable-error curves are indicated above and below the experimental curve.

The result derived by O'Malley⁸ for the relationship between the first two terms is this: in atomic units,

$$\sigma \propto k \left[1 - \left(\frac{5.9}{3.50} Q_{Av}^2 + \frac{4}{3} \alpha_{Av} \right) k^2 \ln k + \text{const.} k^2 + \dots \right], \quad (1)$$

where Q is the atomic quadrupole moment and α is the atomic polarizability. At the upper limit of our energy

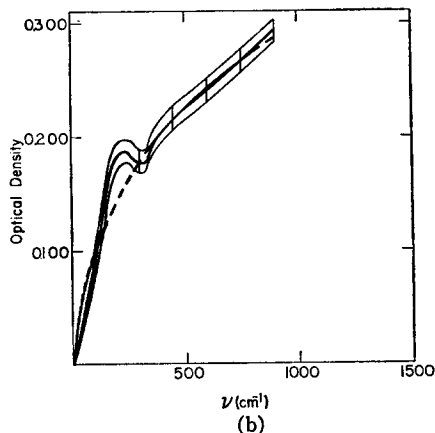
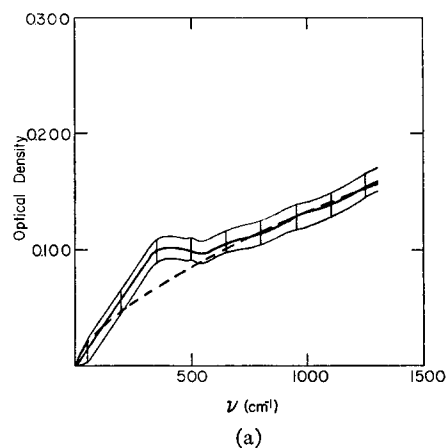


FIG. 3. (a) Threshold region for photodetachment from I^- in CsI vapor, with two-constant fit (dotted curve). (b) Similar region for I^- in RbI vapor with two-constant fit included, taken from a spectrum somewhat more intense than those of Figs. 1, 2, or 3(a). "Bump" region was omitted in calculation of dotted curve.

range, k is much less than 1 a.u., so that the sign of the second term is positive. The least-squares fits to our data gave both signs. The magnitude of atomic quadrupole moments and polarizabilities make it appear that the second term could be a large fraction of the first over the range of our observations. We may presume $Q \approx 4a_0^2$ ($a_0 =$ Bohr radius) and $\alpha \approx 10a_0^3$, so that the second term in (1) is about $\frac{1}{3}$ of the first at $k \approx 0.1$ a.u. or about 1000 cm^{-1} above threshold. The size of the third term is unknown; we have assumed that it is small compared with the second term if k is in atomic units.

Steiner, Seman, and Branscomb⁵ have used a three-term polynomial expansion for the I^- curve. They found that the second term is positive and is about half the first at an energy about 1000 cm^{-1} above threshold. This is in close accord with those of our calculated two-term fits for the I^- curve which have a positive second term. Whenever the second term is positive, it is smaller in magnitude by a factor of about 5 than the positive coefficient. The two sets of experimental curves leading to positive and negative second terms look to be indistinguishable, so that the explanation of the negative constants is probably an accidentally close but physically meaningless solution of the least-squares equations. The fact that the one-term fit is as successful as the two-term expression suggests these possibilities. It may be that the intensity data from photographic measurements are not precise enough to justify the use of a second term, that the shock tube experiments have artifacts, as yet undetermined, which limit their validity to threshold measurements, or that the threshold expansion for the cross section is a rapidly converging series only over the range in which the first term is dominant.

We can return now to the more provoking problem raised by the results presented here, the origin of the "bumps," the anomalously high intensities in the bromide and iodide photodetachment curves. We cannot pretend here to give a full or even definitive identification of these maxima, but we are able to eliminate some possibilities on the basis of experimental evidence and to specify certain others which may be responsible for the "resonances."

The possibilities which we feel can be eliminated are absorption by impurities, by molecules, and by neutral atoms or alkali ions. That is to say, the anomalous absorption is primarily a property of the halide ions themselves. The blank and comparison experiments make the possibility of an impurity spectrum very slight. The principal molecular constituents of the gas are alkali halides, whose known spectra have been compared with the anomalous maxima and have been found completely different. The alkali ionic and halogen atomic excited states are much too high lying to be responsible, either via ground-excited or excited-excited transitions. The alkali neutral-atom states can

be ruled out definitely not only by their known positions (which is not necessarily strong evidence because they are relatively dense and Stark broadened) but also because the absorption maximum which we observe above the iodide threshold, for example, is not present when CsBr is shock heated. Finally, the integrated intensity of the anomalous region has been estimated by subtracting the smooth-fitting parabolic curve. The intensity of the anomaly for a given salt is roughly proportional to the intensity of the normal photodetachment absorption. The range of conditions over which meaningful intensity measurements can be made is narrow, so that this proportionality has only been examined over about a factor of 2 in the photodetachment absorption intensity. Therefore the intensity correlation is only weak supporting evidence for the halides as the responsible species.

Three possible explanations suggest themselves:

- (1) enhancement due to slightly nonresonant transfer of energy from excited halide to a passing metal atom, according to the scheme $M + X^- + h\nu \rightarrow (M + X + e^-) \rightarrow M^* + X^-$, with the nonresonant part of the energy taken up in kinetic energy;
- (2) absorption by the halide ions to give metastable excited states buried in the continuum, which decay by autodetachment; and
- (3) enhancement of the normal photodetachment cross section due to mixing of halide continuum states with empty bound states of passing ions.

Let us examine all three of these.

The first process is the least likely, and is attractive only on the grounds that the appropriate collisions are very frequent and that it would provide a mechanism which would depend both on alkali and on k . The frequency of Cs^0-I^- collisions is typically about $8 \times 10^8 \text{ sec}^{-1}$. The alkalis, particularly Cs and Rb, have states which might be excited by direct energy transfer in a colliding system $M^0 + X^- + h\nu$. For example the Cs levels $8s$ ($24\,317 \text{ cm}^{-1}$) and $4f$ ($24\,472 \text{ cm}^{-1}$) and possibly the $8p$ resonance level at $25\,709 \text{ cm}^{-1}$ could be excited by an electron just photodetached from an I^- ion since the minimum energy of the photodetachment process is approximately $24\,680 \text{ cm}^{-1}$. Rubidium has an orbital at $25\,700$, and a resonance state below at $23\,715$. Sodium, however, has only a $4s$ state at $25\,740 \text{ cm}^{-1}$, so that it is difficult to understand how shocked NaI could have an intensity anomaly. It is true that the anomaly is much smaller for NaI than for rubidium and cesium iodides and that perhaps it is either an artifact or a result of some contaminant.

The energy transfer process (1) requires that the nuclei exchange some kinetic energy with the electronic system. This in itself is reasonable, insofar as the polarization potential holds the electron in question close to the M and X atoms for a time long compared

with a Bohr period. This means that it is probably meaningful to speak of a compound MX^- system; in other systems, which may be analogous, the presence of two crossing potential curves has been shown to lend to very effective interchange of electronic and vibrational energy.^{10,11} Nevertheless this process seems less likely than either of the other two.

The second process would be analogous to the absorption processes which produce the lowest autoionizing states of the isoelectronic inert gases.^{12,13} The $(np^5 \ ^2P)n'd$ would be more intense than the $(np^5, \ ^2P)n's$ according to Beutler's analysis¹³ of the rare-gas spectra, and it is attractive to suppose the bromide and iodide ions might have short-lived $np^5 nd$ states. The widths of the maxima in the observed spectra imply that these states would have lifetimes about 10^{-12} sec, if the anomalous intensity were due to autodetachment alone.

Simple and attractive as the autodetachment interpretation is, it unfortunately cannot provide the complete explanation, if it is a contributing factor at all, because the anomalous absorption clearly depends on the alkali species. Furthermore Steiner, Seman, and Branscomb found no evidence for any absorption maximum in I^- . The bandpass of the slit in their apparatus was 18 \AA , corresponding to about 110 cm^{-1} , so that it is conceivable that a weak feature having a width of about 100 cm^{-1} (like that of Fig. 3) might have been obscured in their work. This is a possibility which must be left open. On the other hand the effect of different metals makes it seem just as reasonable that the maxima are absent in the spectra of the free ions.

The third possibility is the most attractive, but cannot be established on present evidence alone. It is indicated schematically in Fig. 4. We can interpret this process either as an ionizing electronic transition between states of the alkali halide molecule which lie in the vibrational continuum or as a photodetachment process in which the electronic continuum states contain some alkali Rydberg state component. In either case the two dominating factors are the size of transition dipoles connecting the alkali Rydberg orbitals with halide bound p orbitals and the dependence on electron energy of the mixing coefficient of the alkali orbitals with halide continuum functions. A calculation of the strength of such transitions can be performed within the framework of the adiabatic classical path approximation of time-dependent perturbation theory and will be presented in a later publication. Here, we only make a casual comparison of the size and shape of the appropriate orbitals to see that the process is reasonable.

The iodide ion wavefunction is not yet available. A

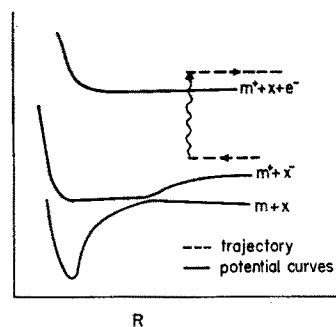


FIG. 4. Excitation process for absorption by halide ion in collision with an alkali ion. Dotted lines show the trajectory of the incoming ions and outgoing alkali ion and halogen atom for Type (3) process.

wavefunction for $I^0 5p$ orbital has been calculated¹⁴; its outermost zero is at 0.5 \AA and its outer maximum is at about 1.1 \AA . We may expect the corresponding I^- orbital to have corresponding dimensions larger by no more than a factor of about 3. Then its valence p orbital will be concentrated in a shell with inner radius of about 1 \AA and significant amplitude to a distance of 6 or 7 \AA . The Rydberg orbital sizes of the alkali can be estimated from their quantum defects¹⁵ by comparison with hydrogenic orbitals. The $7s$ and p orbitals of cesium are quite similar in radial character to our guessed orbital of I^- . This is at least consistent with the notion that there can be a sizeable dipole matrix element connecting them when the two nuclei are less than about 12 \AA apart. The higher metal orbitals rapidly become more diffuse and must give smaller transition dipoles with the iodide $5p$ orbitals. At the same time their statistical weight increases with increasing alkali-halide separation, so that the contributing Rydberg orbitals need not be limited to the lowest-lying one or two.

The mixing coefficients of alkali Rydberg orbitals with halide continuum functions will, like the transition dipole values, depend on momentum matching. The halide continuum functions are determined over most of the range important to us by the atomic polarization potential. That is, most of the space in which the halide continuum function may mix with an alkali Rydberg orbital lies at distances outside the valence shell of the alkali. Therefore one may be able to compute meaningful continuum wavefunctions from the known solutions of the Schrödinger equation with an r^{-4} potential and an empirical scattering length.⁷ For present purposes, we only need note that the deBroglie wavelength of an electron with $k=0$, in the polarization well of an iodine atom, varies from 7.7 to 50 \AA as the electron-nucleus

¹⁰ G. J. Schulz, *Phys. Rev.* **116**, 1141 (1959).

¹¹ J. C. Y. Chen, *Ref. 5*, p. 428 and references therein.

¹² H. E. White, *Phys. Rev.* **38**, 2016 (1931).

¹³ H. Beutler, *Z. Physik* **93**, 177 (1935).

¹⁴ F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

¹⁵ See, for example, E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1951), pp. 141 ff.

distance increases from 2 to 5 Å, and the polarization energy varies from 20 500 to 525 cm⁻¹. We infer that a few of the low-lying alkali Rydberg orbitals, perhaps the first three or four, can match the wavelength of the halide continuum functions well enough to mix with them and that this mixing can occur for electron positions close enough to the halogen nucleus to make this mixing a possible source of enhancement of the photodetachment cross section. The alkali-halogen distances for which this would be most effective are

about 10–30 Å. A calculation of the total transition probability over the Coulomb trajectories coming into this range will probably give a meaningful test of the hypothesis.

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Molecular Collision Cross Section Due to Quadrupole-Induced Dipole and Dipole-Induced Quadrupole Interactions

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A theory for molecular collision cross section due to quadrupole-induced dipole and dipole-induced quadrupole interactions has been developed following the Anderson-Tsao-Curnutte approach. The OCS-He, OCS-Ar, and HCl-Ar collisions are discussed. For HCl-Ar collisions, $\mu_1 q_1 \alpha_2$ interactions have been found to be important, whereas in OCS-He and OCS-Ar collisions these are negligibly small.

INTRODUCTION

THE collision cross section due to the polarizability interactions, the dipole-induced dipole (Debye induction)^{1,2} and induced dipole-induced dipole (first-order London dispersion forces),³ have already been evaluated following Tsao and Curnutte's exposition¹ of Anderson's theory of pressure broadening of spectral lines.⁴ The next interaction which seems to be fairly important in the spectral linewidth problem is the induction interaction varying as r^{-7} . The aim of this paper is to develop the theory in a calculable form for evaluating the molecular collision cross section due to the quadrupole-induced dipole and dipole-induced quadrupole interactions.

THEORY FOR THE $\mu_1 q_1 \alpha_2$ INTERACTIONS

The interaction Hamiltonian of two molecules, when q_1 interacts with $\alpha_2 \mu_1$ and μ_1 interacts with $\alpha_2 q_1$, where 1 indicates the absorbing molecule and 2 the perturbing

molecule, is given by⁵

$$H_{\mu_1 q_1 \alpha_2} = -(6\mu_1 q_1 \alpha_2 / r_1 \gamma^7) \cos^3 \Theta, \quad (1)$$

where Θ is the polar angle of the Molecule 1 with respect to the intermolecular axis. Changing the coordinate axes as shown earlier,^{1,2} $\cos \Theta$ becomes

$$\cos \Theta = \sin \theta \sin \phi \sin \psi - \cos \theta \cos \psi,$$

where θ , ϕ are the internal coordinates of Molecule 1 and ψ is the angle between the distance of closest approach b and the intermolecular distance at any time. The interaction Hamiltonian of Eq. (1) now becomes

$$H_{\mu_1 q_1 \alpha_2} = -(6\mu_1 q_1 \alpha_2 / r_1 \gamma^7) \times [F_1 \sin \psi + F_2 \cos \psi + F_3 \sin \psi \cos^2 \psi + F_4 \cos^3 \psi], \quad (2)$$

where

$$\begin{aligned} F_1 &= \sin^3 \theta \sin^3 \phi, \\ F_2 &= -3 \sin^2 \theta \cos \theta \sin^2 \phi, \\ F_3 &= 3 \sin \theta \cos^2 \theta \sin \phi - \sin^3 \theta \sin^3 \phi, \\ F_4 &= 3 \sin^2 \theta \cos \theta \sin^2 \phi - \cos^3 \theta. \end{aligned} \quad (3)$$

¹ C. J. Tsao and B. Curnutte, Geophys. Res. Papers (U.S.), No. 69 (1960).

² Research Report No. 3, Microwave Laboratory, Physics Department, University of Allahabad, Allahabad, India (1964).

³ Krishnaji and S. L. Srivastava, J. Chem. Phys. **41**, 2266 (1964).

⁴ P. W. Anderson, Phys. Rev. **76**, 647 (1949).

⁵ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 984.