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Scattering of CsF by Electrons*

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(Received 8 May 1972)

Absolute differential and total cross sections for the scattering of CsF by 0.6- to 6.5-eV electrons have been measured using the molecular-beam recoil technique. The first-Born-approximation differential cross section is used as the theoretical model to fit the data. The experimental differential cross sections rise more sharply near 0° than predicted. Total cross sections derived from our measurements are a factor of 1.5 to 4 smaller than the first-approximation results.

We report absolute total and differential cross sections for the scattering of CsF by 0.6- to 6.5-eV electrons, measured by the molecular-beam recoil technique. To our knowledge these are the first absolute, single-collision measurements on a molecule of significant polarity, and therefore a first test for features of the theory.

Given the 7.9-D dipole moment of the CsF molecule, one expects the scattering to be described by an electron-permanent-dipole interaction. For a $^1\Sigma$ diatomic with a point dipole moment and a set of rigid-rotor internal energy levels, the first Born approximation (FBA) to the differential cross section is[1]

$$\frac{d^2\sigma}{d\omega^2}=\begin{cases}\frac{4}{3}\left(\frac{me\mu}{\hbar^2}\right)^2\frac{k'}{k}\,\frac{J_>}{2J+1}|\vec{\mathrm{k}}'-\vec{\mathrm{k}}|^{-2} & \text{for } J\to J\pm1,\\ 0 \text{ for } J\not\to J\pm1. & \end{cases}$$

Note the extraordinary prediction that the scattering is entirely inelastic. More exact theories have not been evaluated for CsF, so this form is used in our analysis.

When the electron energy greatly exceeds the rotational spacing, the angle dependence can be approximated,

$$|\vec{\mathrm{k}}'-\vec{\mathrm{k}}|^{-2}\approx\tfrac{1}{2}k^{-2}(1-\cos\theta+\delta)^{-1}.$$

For CsF, $\delta=2.6\times10^{-10}(J_>/E)^2$. The differential cross section is extremely sharply forward peaked. Averaging over the J distribution (1000° K) and integrating over all angles,

$$\sigma(\text{Å}^2)=7024/E+(930/E)\ln E.$$

An interaction of this magnitude should dominate the scattering.

The many-to-one nature of the laboratory to center-of-mass transformation in our experiment prevents a direct inversion of lab measurements to produce a c.m. differential cross section. Instead, the molecular scattering is compared with theory by assuming a c.m. differential cross section with an undetermined constant as a factor, transforming the form into lab coordinates, and then fitting the constant by least squares to best match the experimental lab differential cross section at all angles. Thus our experimental total cross section is simply the theoretical total cross section multiplied by the matched constant. Total cross sections determined in this fashion do not depend on the apparatus angular resolution, but do depend on the differential-cross-section form chosen. Should a FBA result of several thousand Å^2 be trusted?

Despite the large magnitude of the total cross section, it has been felt that the answer is a qualified yes.[2] An expansion in electron partial waves shows that σ_l is proportional to $1/l$. Most of σ comes from small contributions from distant, and presumably only slightly perturbed, electrons.[2] Close-coupled calculations,[3] available for dipole moments up to ~2.5 D, yield total cross sections ~80% of FBA with the defect in low partial waves. Over 90% of the scattering is in the $\Delta J = \pm 1$ channels whose differential behavior mimics that given by the FBA. The remainder, in $\Delta J = 0, \pm 2, \cdots$ channels, is, by comparison, nearly isotropic. Thus an experiment should see any $\Delta J \neq \pm 1$ contribution as an unexpected tail at large angles.

The 7.9-D dipole moment in CsF exceeds the first critical moment for electron binding in rotating or nonrotating molecules.[4] Therefore resonant processes could contribute to electron-CsF scattering. Any individual resonant structures will be averaged out of our measurements. A more isotropic differential cross section, due to long-lived complexes, or a nonmonotonic energy dependence, due to clustering of unresolved structure, remains possible.

In the beam recoil technique[5] the molecular collision partner is observed. Advantages of the method are the determination of absolute cross sections, since the electron number density is known, and the possibility of state selecting the molecular beam. The latter technique, using electrostatic quadrupoles, offers the only way to measure molecular J-state changes, and we will shortly begin such experiments. The major disadvantage is the sophisticated kinematic analysis required to compare c.m. theory and lab observations.

A thermal beam of CsF is crossed at 90° by a 100% square-wave-modulated electron beam. The modulated component of the molecular beam is detected at a surface ionization detector which can be reproducibly positioned to 5×10^{-6} rad lab angle. CsF dimer concentrations[6] are reduced to ~ 3% by 150°K superheat in the second oven chamber, and the beam is considered pure monomer in the analysis. Electrons are produced by a planar, gridded, magnetically confined gun closely patterned after the one described by Collins *et al.*[7] Measured electron energy widths are <300 mV full width at half-maximum at all energies. Electron currents are held to <150 μA/cm^2 so that scattering is linear in electron flux. Electron energies are fully corrected for contact potentials, space charge, and leakage potentials, the last two by numerically solving Poisson's equation.

A typical laboratory differential cross section and straight-through beam profile are shown in Fig. 1. With respect to this diagram, electrons traveling from left to right strike a molecular beam moving out of the plane of the paper. The negative sign for scattering at small angles means that fewer molecules reach these detector positions with the electrons on than with the electrons off (scattering out). The positive sign to the left (backscattering) and the right of the center indicates net scattering in.

The kinematic analysis extends the theory successfully applied to molecule-molecule scattering[8] to include the angular divergences in both the molecular and electron beams. The molecular divergence describes the straight-through beam profile, whose width is not small when compared with a typical deflection produced by scattering. The need for explicit averages over the electron angles is demonstrated by the existence of backscattering. For 90° electron-molecule collisions, backward molecular deflections are im-

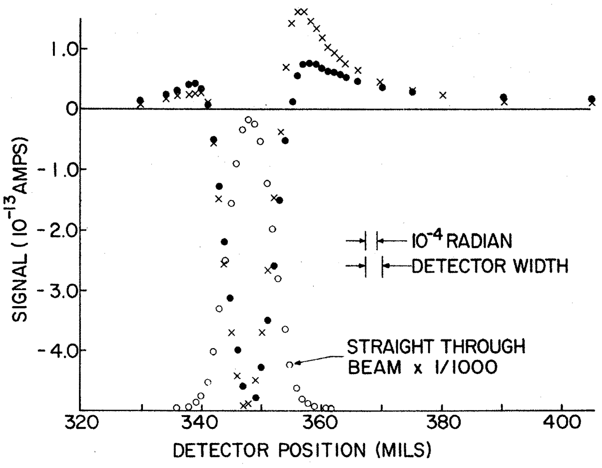

FIG. 1. Typical laboratory differential cross section (crosses) and best fit of theory (closed circles) at a corrected electron energy of 2.73 eV.

possible. Nonperpendicular meetings produce such events and reinforce them with a kinematic singularity.

Note the absence of a c.m. angle scale in Fig. 1. As the precollision conditions change over their experimental ranges, many c.m. angles are observed at one detector position. For example, consider molecules with the most probable molecular velocity which are scattered from the center of the straight-through beam into a detector at the scattering in maximum. Variation of only the two angles which orient the electron velocity sweeps the detector over c.m. angles from 9° to 46°. Despite this width, the detector appears narrow to any given set of initial conditions (i.e., to any given incident molecule), typically subtending 3° c.m. The process of transforming a c.m. differential cross section into the lab system involves integration over initial conditions (detector height, molecular J state, detector width, electron velocity and angles, molecular velocity, and the straight-through beam profile), each weighted by its distribution. The first two integrals are analytic, the next five are performed numerically at ~8000 points per lab deflection, and the last is a numerical convolution at ~100 points per lab point. Considerable cancelation of scattering in and scattering out takes place in the averaging, particularly at small c.m. angles. This means that scattering at c.m. angles less than ~10° is under-represented in the determination of the constants that we report below. The reader is cautioned to keep this in mind. Details of the kinematics will be presented in a later publication.

The least-squares fit of the theoretical lab differential cross section (FBA in the c.m. multiplied by a constant) at an electron energy of 2.73 eV is shown in Fig. 1. The constant is determined by least squares as 0.449 in this case. Similar curves are found at all energies. Theory and experiment are not well matched.

Since the constant adjusts the theory to the same apparent total cross section as the experiment, differences in the shapes of the two curves indicate relative errors in the c.m. differential cross section. The calculated values underestimate the scattering in at small and intermediate angles. In other words, at fixed total cross section, the true differential cross section must rise towards $\theta = 0$ considerably more sharply than the already sharply peaked FBA cross section. On the other hand, 0° scattering out and large-angle scattering in are adequately represented. These points would be increased in absolute magnitude by any attempt to add low partial waves to the fit. The FBA, if anything, already overestimates the large-angle scattering and we find no evidence for $\Delta J \neq 1$ or resonant processes. The conclusions hold at all electron energies studied.

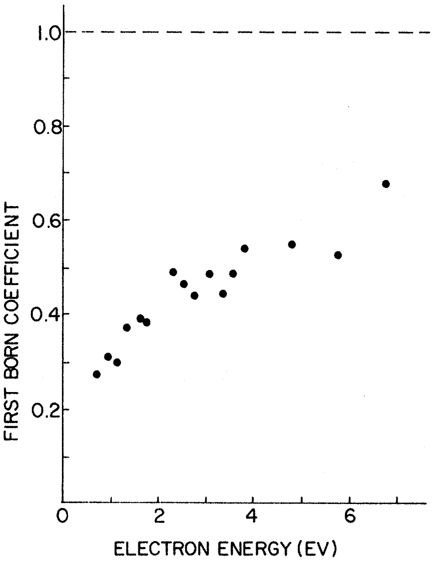

FIG. 2. First–Born-approximation coefficients versus electron energy.

The constants determined at each electron energy are displayed in Fig. 2. Were the FBA total cross sections correct, these values would all be 1. The observed constants are dramatically smaller, rising roughly linearly from 0.3 at 0.5 eV to >0.6 at 7 eV. Predicted and observed total cross sections are shown in Fig. 3. The curve through the experimental points is the peak value of the scattering out. This relative measurement has been scaled to match the absolute cross sections at one point. The smoothness of the curve is strong evidence that any apparent structure in the absolute total cross-section points is artifactual (and therefore a measure of the aggregate error in the measurements and data reduction). There is no clear-cut evidence for resonant behavior.

The most reasonable way for the FBA to fail is by overestimating the scattering from low electron partial waves, making the differential cross section more isotropic than it should be. Such an an error would qualitatively explain the discrepencies in both differential and total cross sections. We are testing simple modifications of the theory at present, and we are definitely in the market for a close-coupled calculation on

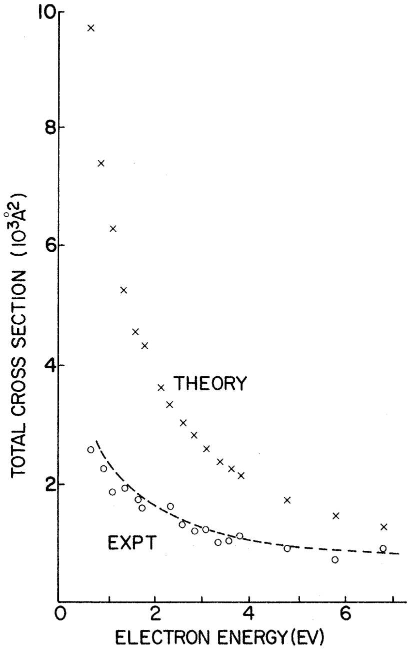

FIG. 3. Total cross sections: crosses, first Born approximation; circles, experimental fit with FBA; dashed curve, scaled maximum scattering out.

CsF.

We wish to thank Professor Benjamin Bederson and his students for generous experimental advice, Professor Philip Pechukas for valuable discussions on theory, and William Becker for help with the experiments.

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*Work supported by the National Science Foundation (under Grant No. GP-11631) and the Petroleum Research Fund of the American Chemical Society (under Grant No. 1656-G2).

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Pressure Shift of the Magnetic Resonance Line of Neon in a He-Ne Laser

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(Received 2 June 1972)

A pressure shift of the magnetic resonance line of the $3s_2$ level of neon in a He-Ne laser operating at 0.633-μm π transitions was observed by varying the partial pressure of helium. The shift in the resonant angular frequency was $(2.8\pm 0.5)\times 10^7$ sec^{-1} Torr^{-1}, and the ratio a of the shift to the pressure broadening (half width at half-maximum) was 0.78 ± 0.14.

Pressure shifts of lines in the optical region have been reported by many authors, and such shifts have been explained primarily by the adiabatic collision theory, in which the atomic collisions change the atomic wave functions and do not induce transitions between the atomic energy levels. However, in the rf or microwave region, the mean kinetic energies of the colliding atoms exceed greatly the energy splitting, so that diabatic collisions have been considered to be important for the collisional broadening of the lines, and hence the pressure shifts have been expected to be very small. Although in the microwave region experiments have been reported on the shifts of the inversion spectrum of ammonia,[1,2] and on the hyperfine spectra of atomic hydrogen,[3,4] deuterium,[4] tritium,[4] sodium,[5] potasium,[6] rubidium,[7] and cesium,[8] the investigation of pressure shifts of lines in the rf region has not been reported.

In this Letter, we report on the experimental