Resolution of Supernumerary Rotational Rainbows in Na_2-Ne Scattering

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The resolution of the supernumerary rotational rainbow structure in state-to-state differential cross sections for Na_2-Ne collisions which had been predicted by infinite-order sudden-approximation theory is reported. These data, by proving the existence of such a structure in quantitative agreement with the infinite-order sudden-approximation theory, answer one of the major remaining questions in the physics of rotationally inelastic scattering.

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The advent of a new generation of molecular-beam experiments[1-6] has begun to make available detailed information on the transfer of rotational energy in atom-molecule collisions. Thus, by increasing the resolution of conventional techniques[1-3] or by introducing new methods involving lasers,[4-6] these experiments are providing differential cross sections for transitions between individual rotational states of various molecules.

The results of such experiments show that the dominant features of such cross sections, in systems where the ratio of collision energy E to the average energy transferred is low (small E/B; B is the rotational constant) and the interaction potential anisotropy is small, are diffraction oscillations and normal rainbow structures.[1,6] An example of such a system is Ne+HD,[1] with a collision energy of $E=30$ meV and a rotational constant of $B=60.8$ cm^{-1}. For scattering systems such as Na_2+He, Ne, and Ar ($E=150$ meV, $B=0.15$ cm^{-1})[4-6] or K+N_2, CO ($E=1$ eV, $B=2$ cm^{-1})[2] with large collision energies as compared to the average energy transferred (large E/B) and large potential anisotropies, the dominant features of the differential cross sections are rotational rainbows.[2,7-12] An elegant explanation of rotational rainbows is given by the semiclassical (stationary phase) version of the infinite-order sudden approximation (IOSA) as interference between scattering from different orientation angles which lead to the same final rotational state.[9-11]

While the existence of the main rotational rainbow maximum in Δj distributions at a fixed scattering angle, or equivalently, in angular distributions for particular Δj transitions, has been proven experimentally,[2-5] additional quantum structure on the "bright" side of the rainbow predicted by IOSA and coupled-state (CS) calculations[9] has not yet been resolved in any of the experiments. Because of the centrifugal decoupling approximation made in the theory,[13] some doubts have arisen as to whether or not such *supernumerary rotational rainbows* are real or an artifact of the approximations. One can speculate that this structure would be averaged out in exact close-coupling calculations because of summation of S-matrix elements for different initial and final orbital angular-momentum quantum numbers for fixed total angular momentum. Unfortunately, close-coupling calculations are computationally unmanageable for systems such as Na_2+Ne which have many energetically open channels, strong rotational coupling, and a large number of partial waves contributing to the scattering. Therefore any real proof of the existence of such supernumerary rotational rainbows must be based on comparison with experiment.

The basic features one expects to see in the differential cross sections of Na_2+Ne can be seen from the set of IOSA cross sections for selected $j_i=0\rightarrow j_f$ transitions shown in Fig. 1 versus center-of-mass (c.m.) scattering angles for the experimental collision energy of 175 meV. The scattering calculations, assuming a rigid-rotor Na_2 molecule, are performed on an analytical potential surface based on *ab initio* configuration-interaction (CI) energies[14] calculated to the same level of accuracy as for He-Na_2.[15] All cross sections show the characteristic rotational rainbow structure; a rapid rise out of the classically forbidden region, a broad maximum at $\theta_{max}(j_f)$, and oscillations in the classically allowed angular range. The characteristic features for gradually increasing j_f are (i) the onset of the cross section becomes less steep and $\theta_{max}(j_f)$ shifts to larger angles, (ii) the main rainbow maximum becomes

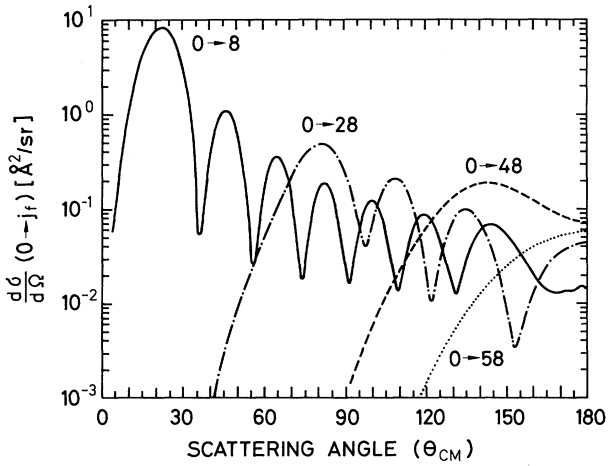

FIG. 1. A set of $j_i = 0 \rightarrow j_f$ cross sections calculated in infinite-order sudden approximation for Na_2-Ne at a collision energy of 175 meV with use of an *ab initio* potential surface (Ref. 14). The primary rotational rainbow and supernumerary rainbow maxima are clearly seen.

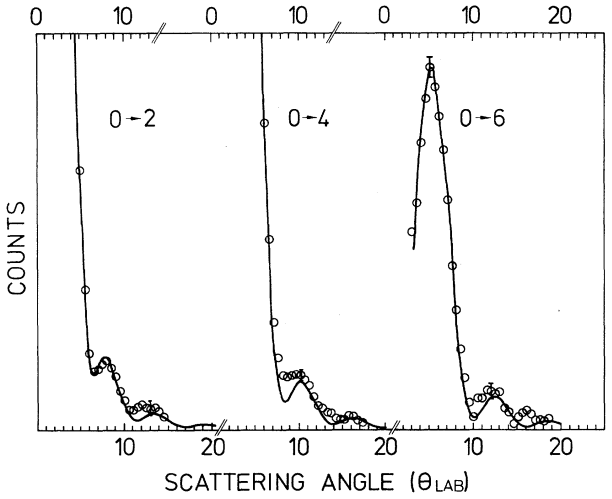

FIG. 2. Experimental state-to-state cross sections (open circles) for Na_2-Ne ($E_{coll} = 175$ meV) for various $0 \rightarrow j_f$ transitions. Infinite-order sudden-approximation cross sections (solid lines) transformed to the laboratory angular scale are also shown. The sets of experimental and calculated cross sections are normalized relative to each other at the main rotational rainbow for the $0 \rightarrow 6$ transition.

broader while the cross section at $\theta_{max}(j_f)$ decreases, and (iii) the frequency of the supernumerary oscillation decreases. Transitions with $j_f > 50$ are classically inaccessible over the entire range of scattering angles.

The experimental technique used to obtain the cross sections reported here has been described in detail earlier.[3] Briefly, a supersonic sodium beam with a relative velocity spread of $\Delta v/v = 0.2$ [16] crosses a supersonic Ne beam ($\Delta v/v = 0.07$). The flux of molecules in the level j_f, scattered at the laboratory angle θ_{lab}, is measured in the detector by laser-induced fluorescence.[17] The probe laser is coupled into the detector with a single optical fiber, while the fluorescence is collected and transferred to the photomultiplier with a fiber bundle. The observed signal is proportional to *the sum of the cross sections* $\sigma_{i \rightarrow f}(\theta_{lab})$ for transitions out of thermally populated levels j_i to a final level j_f weighted by the population n_i of level j_i. *A single state-to-state cross section* is isolated by optically pumping molecules out of the state j_i with a second laser. Modulation of the pump laser modulates the observed fluorescence intensity from the molecules in the level j_f. The modulation is proportional to the $j_i \rightarrow j_f$ differential cross section: $\Delta I_f^i(\theta_{lab}) = D n_i \sigma_{i \rightarrow f}(\theta_{lab})$, where D summarizes factors such as detector efficiency and relative particle velocities.

The experimental results for several $j_i \rightarrow j_f$ transitions (Figs. 2 and 3) reproduce nicely the trends expected on the basis of the IOSA calculations. Each data point shown in the figures is, including background subtractions, the difference of four individual count rates.[4] A $2\sqrt{N}$ statistical error based upon the largest count rate in the sequence of the four data-collection intervals is taken as the error in the measurement. This overestimates the standard deviation of the data. The angular resolution is $\Delta\theta_{lab} \lesssim 2^\circ$ over the interval $0 \leq \theta_{lab} \leq 30^\circ$, based upon a Monte Carlo analysis of the detector system, which employed the experimentally determined Na_2 and Ne beam parameters and the known collimation conditions.

The differential cross sections for inelastic scattering out of the rotationless level into the rotational levels $j_f = 2$, 4, and 6 are shown in Fig. 2. The experimental curves show clearly resolved first supernumerary rotational rainbows at $\theta_{lab} = 8^\circ$, 10°, and 12° for the $\Delta j = 2$, 4, and 6 transitions, respectively. In comparison with the IOSA calculation (solid lines) a marginal indication of a second supernumerary maximum is present. The set of theoretical curves, after being transformed into the laboratory frame and averaged over the kinematic conditions, has been normalized to the set of experimental ones by normalizing the $0 \rightarrow 6$ cross sections at the peak of the primary rainbow.

As expected on the basis of the calculations (see Fig. 1) the data show that the ratio of the value of the cross section at the peak of the primary rotational rainbow as compared to that at the first supernumerary maximum is approximately ten for these Δj transitions; the cross section for the $\Delta j = 2$ transition has its maximum value at an angle which lies within the Na_2 beam profile and therefore cannot be measured while the $\Delta j = 4$ transition peaks at slightly greater than twice the value of the $\Delta j = 6$ transition.

The experimental and theoretical curves show remarkable agreement. The predicted and observed rainbow maxima, both primary and supernumerary, agree in position and relative magnitude to within the resolution of the experiment. This would seem to provide strong support for the accuracy of the *ab initio* scattering surface[14] and the applicability of the IOSA assumptions to the Na_2 + Ne collision system.

Figure 3 shows the variation of the cross section for a series of $\Delta j = 8$ transitions with differing j_i. These data cannot be compared directly to the IOSA calculations of Fig. 1. Within the IOSA, however, the cross sections for $j_i \rightarrow j_f$ transitions are related to a set of $j_i = 0 \rightarrow j_f$ transitions by the following factorization formula,[13,18]

$$\frac{d\sigma(j_i \rightarrow j_f; \theta)}{d\Omega} = \left(\frac{k_0}{k_{j_i}}\right)^2 \sum_{j''} C^2(j_i, j'', j_f;\ 0,0,0) \times \frac{d\sigma(0 \rightarrow j''; \theta)}{d\Omega}. \quad (1)$$

The Clebsch-Gordan coefficients are nonvanishing for $|j_i - j_f| \leq j'' \leq |j_i + j_f|$. The theoretical cross sections shown in Fig. 3 have been calculated from the set of $0 \rightarrow j_f$ cross sections with use of Eq. (1) before they are transformed into the laboratory system. Averaging over the experimental resolution is also included. As a direct consequence of Eq. (1) the position of the rotational rainbow is expected to be nearly independent of j_i for a given Δj. This prediction is supported by the experimental results, since from the experimental curves it is evident that the angular position of the rotational rainbow for all four $\Delta j = 8$ transitions is identical to within the experimental resolution. Although the amount of energy transferred in $9 \rightarrow 1$ and $9 \rightarrow 17$ transitions increases by about a factor of 3 from 1.5 to 4.3 meV, the position of the rainbow remains unchanged. This underlines the dominant role of *angular momentum transfer* over *energy transfer* in rotational energy transfer for this system.

Finer details of the shape of the cross sections on the bright side of the main rotational rainbow (see Fig. 3), however, do change with j_i. In general, the supernumerary oscillations are damped with increasing initial rotation j_i of the molecule[9,14,15] and increasingly more intensity is found at larger scattering angles. In the light of Eq. (1) this variation is well understood.

In conclusion, the data presented here answer one of the major remaining questions in rotationally inelastic scattering, since they prove the existence of supernumerary rotational rainbows. The agreement between the experimental differential cross sections and those calculated in IOSA with use of a recently completed *ab initio* surface is remarkably good. Given the high-quality surface, these data allow a very sensitive test of the quality of scattering approximations.

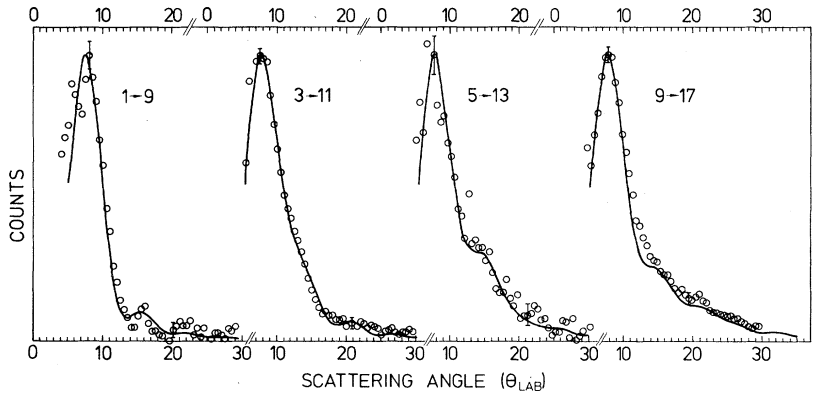

FIG. 3. Experimental state-to-state cross sections (open circles) for Na_2-Ne for various $j_i \rightarrow j_f$ transitions with $\Delta j = 8$. The infinite-order sudden-approximation cross sections (solid lines) are calculated according to Eq. (1). All curves are individually normalized to the same heights at the peak of the main rainbow.

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Ab Initio Study of Dissociative Attachment of Low-Energy Electrons to F_2

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Adiabatic-nuclei resonance theory has been applied to the study of dissociative attachment of low-energy electrons to F_2. Stieltjes moment theory was used to derive fixed-nuclei electronic resonance parameters from large-scale configuration-interaction calculations on F_2 and F_2^-. Dissociative attachment cross sections for the four lowest vibrational levels of F_2 are reported and compared with available experimental data.

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Recent interest in rare-gas fluoride molecules in e-beam and discharge-excited laser devices has prompted a large number of experimental investigations[1-7] of electron attachment in low-energy $e^- + F_2$ collisions. A knowledge of the energy dependence of the cross section for the process

$$e^- + F_2 \rightarrow F + F^- \quad (1)$$

is important for the kinetic modeling of these lasers. There is also much current interest in the dependence of the attachment rate on the vibrational temperature of F_2, since recent experiments[8] have reported a substantial improvement in fluorescence efficiency with heated gas mixtures.

There have been three previous theoretical studies of dissociative attachment in F_2,[9-11] all semiempirical treatments employing parameters determined by a best fit to a portion of experimental attachment data. Drukarev and Pozdneev[10] used the Faddeev equations to calculate the cross section with a simple, separable potential describing the electron-fluorine interaction.