Rotational Rainbows in Electron-Molecule Scattering

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(Received 18 March 1987)

We report the measurement of state-to-state differential cross sections for rotationally inelastic electron-Na_2 collisions for impact energies from 150 to 300 eV. The data demonstrate for the first time large rotational transitions ($0 \leq \Delta j \leq 30$) for backward scattering. The most surprising result is the observation of pronounced rotational rainbows. These structures are expected to be general features in high-energy electron-molecule scattering.

PACS numbers: 34.80.Gs, 34.50.Ez, 34.50.Pi

Rotational excitation of molecules in their electronic ground state by electron impact is one of the most important energy-transfer processes in low-temperature laboratory gas discharges and in low-lying planetary ionospheric layers. Over the last few years, crossed-beams experiments yielded total and differential cross sections and elucidated the mechanisms through which these processes proceed preferentially.[1,2] Short-living negative-ion states such as shape resonances and nuclear-excited Feshbach resonances as well as direct interaction via a permanent dipole moment and/or the polarization are most effective. The cross section for $|\Delta j| = 1$ rotational excitation can be as large as 10^{-13} cm^2 for molecules with strong dipole moments.[1] Excitation via the other interactions lead to $\Delta j \lesssim 4$ with cross sections ranging from 10^{-15} to 10^{-18} cm^2.[2]

No experimental or theoretical investigations with state selection for other than hydrogen molecules[3] or energies exceeding 100 eV have been reported. In particular, no experimental data under these conditions are available for scattering in the backward direction. This angular range is not accessible in conventional electron scattering spectrometers, except for special configurations and using trochoidal electron spectrometers.[4] At high collision energies, short-living negative-ion states do not contribute to rotational excitation within the electronic ground state. The Born approximation is expected to be valid only for small-angle scattering processes ($\lesssim 50°$). Thus, a model study investigating rotational excitation associated with backward scattering at high collision energy is needed to supplement our knowledge of rotational excitation of molecules by electron impact.

In this paper we present state-to-state differential cross sections for scattering angles in the range $130° < \theta \lesssim 180°$ for collision energies of 150, 225, and 300 eV. We find rotational transitions as large as $\Delta j = 28$ and pronounced rotational rainbow structures.[5] This result is of fundamental importance because it is expected to be generally valid for high-energy electron-molecule scattering.

Rotational rainbows have first been observed in rotationally inelastic heavy-particle collisions.[6] Subsequently, they have been found in many other collision systems, e.g., molecule-surface scattering[7] and photodissociation as well as collisional dissociation.[8] Supernumerary rotational rainbows are more difficult to resolve and only a few measurements have been reported.[9] The dominance of repulsive interaction is a common characteristic of the collision systems discussed in Refs. 6–9. In this paper we report the first observation of rotational rainbows involving attractive interactions.

The experimental setup is shown schematically in Fig. 1. A supersonic sodium beam, consisting of about 85% atoms and 15% dimers, is crossed with a high-current ($\cong 10$ mA) electron beam, the energy of which is varied in the range $150 < E_{coll} < 300$ eV. Strong cooling of the internal degrees of freedom of the sodium dimers in the course of the expansion leads to a rotational temperature of about 30 K.[10] Thus low rotational levels are predominantly populated with the maximum population found near $j = 7$. The scattered dimers cover the angular range $\theta_{lab} < 11°$ in the laboratory frame (for $E_{coll} = 300$ eV). The largest scattering angles correspond to backward scattering in the center-of-mass frame. Because we detect the heavy particle rather than the electron, backward scattering ($\theta_{c.m.} \lesssim 180°$) angles are easily accessi-

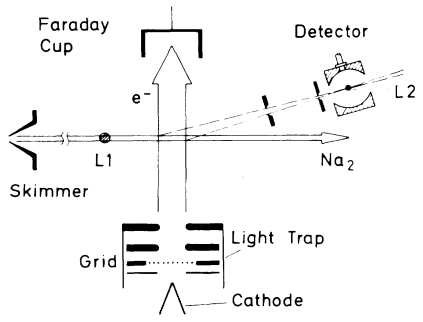

FIG. 1. Schematic experimental setup. A supersonic sodium beam with a flow velocity of $u = 1250$ m/s and a width $\Delta v/u = 0.07$ of the velocity distribution is crossed by an electron beam. The energy spread of the latter is estimated to be 1 eV.

ble. The angular resolution in the laboratory system is $\Delta\theta_{lab} \cong 2°$, which corresponds to about $\Delta\theta_{c.m.} \cong 40°$ in the center-of-mass frame. This angular resolution is adequate for the purpose of this study.

The technique of laser state selection has been used extensively in heavy-particle scattering and is described in detail by Bergmann, Hefter, and Witt[11] and Jones *et al.*[12] Briefly, the flux of molecules scattered under the angle θ_{lab} into a given rotational level j_f is detected by laser-induced fluorescence. Thus the sum of all processes leading from any of the thermally populated levels j into the level j_f under study is measured. The initial state is labeled by depletion of the population of a selected level j_i by optical pumping with a second laser 10 mm upstream of the collision region. The molecules in level j_i are excited to the $A\,^1\Sigma_u$ electronic state of Na_2 and decay by spontaneous emission predominantly to high vibrational levels $v'' \gg 1$ of the electronic ground state. The probability for collisional transfer from these levels back to the level $v''=0$ is expected to be negligible compared with rotational energy transfer within the level $v''=0$. Thus, with the pump laser on, the detector signal decreases because the contribution of the $j_i \rightarrow j_f$ transfer process is missing. As a consequence, the difference of the scattering signal with the pump laser on and off is proportional to the $j_i \rightarrow j_f$ differential scattering cross section.

The scattering signal with the pump laser on and off is measured with the electron beam on and off. Scattered laser light as well as electronic emission following electron-impact excitation contributes to the background signal. Furthermore, despite the small relative velocity distribution of the supersonic beam, Na-Na_2 scattering processes within the beam contribute to the flux at small laboratory scattering angles. This flux is also modulated by optical pumping. By taking appropriate differences of the count rate in the four different channels with pump laser on/off and electron beam on/off, these background signals are eliminated.[11]

The collision processes $j_1=5 \rightarrow j_f$ are originally measured together with the sum of all processes leading to j_f (channel: pump laser off, electron beam on). This is done because the signal-to-noise ratio increases with increasing thermal population of level j_i and decreasing population of level j_f, respectively. The raw data are converted to those shown in Fig. 2 after appropriate normalization and invoking microreversibility. Figure 2 shows the experimentally determined relative cross sections for $j_i \rightarrow j_f=5$ transitions for backward scattering as a function of Δj for a collision energy of 300 eV. The detector, positioned at $\theta_{lab}=9.6°$, samples scattering events from the range $\theta_{c.m.} > 140°$. Obviously, large Δj and a nonmonotonic variation with j_f are observed. Because we are dealing with a homonuclear target molecule in a Σ electronic state, rotational transitions with odd Δj are symmetry forbidden.

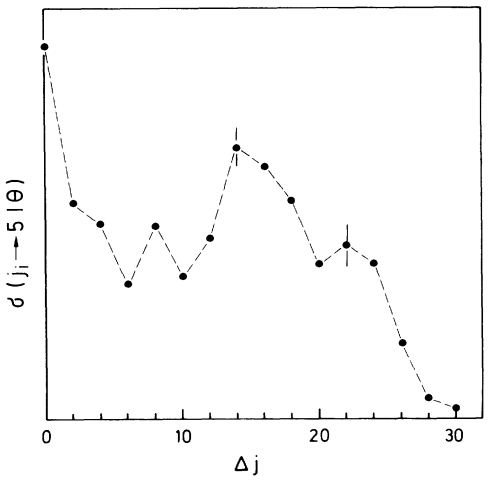

FIG. 2. Experimental relative cross sections $j_i \rightarrow j_f=5$ for scattering into the backward direction in the center-of-mass system at a collision energy of 300 eV.

Extensive experimental tests have been made to prove that the reported scattering signals are in fact related to rotational energy transfer within the $v''=0$ level of the electronic ground state. Because of the relatively high energy of the electrons, many other competing processes, such as vibrational and electronic excitation and ionization, occur in parallel to the rotational excitation. This material will be discussed in more detail elsewhere, together with a more complete set of experimental data. Briefly, the observed signals increase linearly with electron current, excluding multiple collisions, consistent with the estimate of the attenuation of the sodium beam based on measured total cross sections.[13] The scattering signal drops rapidly for laboratory angles that exceed the angular range accessible to molecules deflected by electron scattering. Finally, the rigorous upper limit for the cross section for odd Δj transitions can be set. It is smaller than 5% of the cross sections for transitions to neighboring levels with even Δj. This excludes combined rotational and electronic excitation followed by spontaneous emission back into the level $v''=0$, j_f as an origin of the scattering signals.

Figure 3 shows the relative cross sections for $j_i=0 \rightarrow j_f$ transitions determined from the set of data shown in Fig. 2. Because the interaction time is small compared with the rotational period of the molecule even in the highest levels observed and because the inelasticity is very small, $\Delta E/E_{coll} \ll 1$ [$\Delta E < Bj_f(j_f+1)$], the well-known scaling formula[14,15]

$$\sigma(j_i \rightarrow j_f \mid \theta) - \sum_j C^2(j_i, j, j_f \mid 000)\sigma(0 \rightarrow j \mid \theta)$$

applies, where C is a Clebsch-Gordan coefficient. This equation relates a set of cross sections $j_i \rightarrow j_f$ to transitions $j_i=0 \rightarrow j_f$. This relation between cross sections is widely used in the study of heavy-particle collisions as

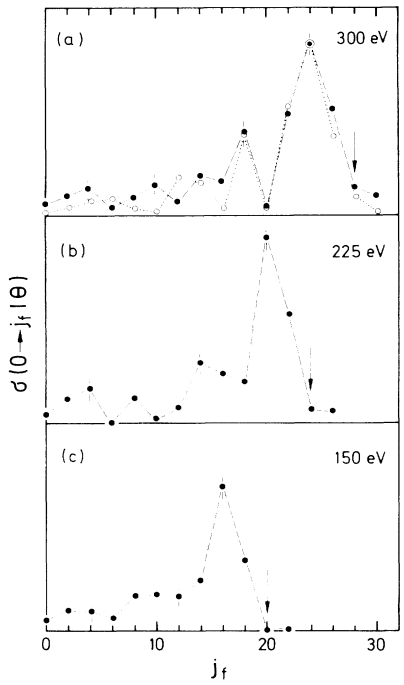

FIG. 3. Relative cross sections for $j_i=0\rightarrow j_f$ scattering into the backward direction ($\theta_{c.m.}\cong 180°$) obtained from the data of Fig. 2 by applying the scaling relation given in the equation. In addition data for $E_{coll}=225$ and 150 eV are also shown. The cross section for transitions with odd Δj are zero because we are dealing with a homonuclear molecule. Pronounced rotational rainbows as well as resolved supernumerary rainbows are observed. The dotted curve in (a) results from the spectator model (Ref. 20).

well as electron scattering. Here we invert the set of equations and determine the relative $j_i=0\rightarrow j_f$ cross sections from a complete set of measured cross sections for $j_i=5\rightarrow j_f$ transitions. As will be discussed in the following, the data of Fig. 3 show a pronounced rotational rainbow and supernumerary rainbow structure.

At large e-molecule distances, the interaction is due to the attractive polarization forces. At short distances, in particular inside the charge distribution, Coulomb attraction dominates. At the relatively high collision energies relevant for our experiment, the contribution of exchange forces is small. In fact, preliminary calculations[16] show two steep and deep attractive wells centered at the nuclei of the molecule. Thus, backward scattering is expected to be limited to a small range of orbital angular momenta centered around $l=(kr_e\sin\gamma)/2$ (measured in units of $\hbar$) where k is the wave vector of the incoming electron, r_e is the dimer bond length, and γ is the angle between k and the molecular axis. The angular momentum transferred to the molecule is $\Delta j=2l$. The maximum transfer $\Delta j_{max}=kr_e$ occurs for $\gamma=90°$ and $\theta_{c.m.}=180°$. The value of Δj_{max} is indicated by the arrows in Fig. 3 based on the spectroscopically determined $r_e=0.3079$ nm.[17]

Thus a very simple picture of these processes emerges. The incoming plane wave is scattered from a small region near the nuclei into the backward direction. The angular momentum transferred to the molecule is zero for $\gamma=0$. It increases with γ in the range $\gamma<90°$ before decreasing again to zero at $\gamma=180°$. Thus for $\gamma\neq 90°$ there are two orientations of the molecular axis relative to the direction of the incoming electron that lead to the same $\Delta j<\Delta j_{max}$. The interference of the corresponding scattering amplitudes results in oscillations of the cross sections, the supernumerary rotational rainbows. At $\gamma=90°$ these two orientations coincide, giving rise to the main rotational rainbow.

Processes of this type, characterized by the superposition of independent scattering off two centers (spectator model), have been observed in ion-molecule scattering.[18] They have been treated by Korsch and Eckelt[19] more than a decade ago. According to the spectator model the probability $P_j(\theta)$ for $0\rightarrow j$ excitation varies[20] as $P_j(\theta)=N(2j+1)J_j^2((kr_e\sin\theta)/2)$, where J_j is the spherical Bessel function and θ is the center-of-mass scattering angle. The dotted curve gives this function with r_e taken 3% smaller than the spectroscopic value.[17] The agreement in the range of the rotational rainbow and the first supernumerary rainbow is very good. At smaller Δj, the calculated and measured relative cross sections are of the same order of magnitude but the maxima of the oscillations are not at the same positions. The origin of this discrepancy can be traced back to the fact that the experimental and calculated $j_i=5\rightarrow j_j=5$ cross sections differ by a factor of 2. At the present time it is not clear whether the cause of this discrepancy is due to deficiencies in the experiment or in the theory. The calculated cross sections for $j_i\rightarrow j_f=5$ with $j_i>5$ agree with the experimental results to within the limits of experimental uncertainty.

In summary, application of laser state-selection techniques provided, for the first time, experimental data about rotational rainbows in electron-molecule collisions. In particular, excitation by electron impact leading to scattering angles up to 180° could be investigated. Unlike for the range of scattering angles $\theta_{c.m.}<135°$, covered in conventional electron scattering apparatus, rotational energy transfer is *not* limited to small Δj. Very large rotational quantum jumps, only limited by angular momentum conservation, are observed. The structural features, namely, the rotational main and supernumerary rainbows, are expected to be a general phenomenon in electron-molecule scattering independent of quantitative details of the interaction potential. This finding has important implications for the estimate of the average energy transfer by electron impact.

Experimental and theoretical work to obtain absolute cross sections is in progress.

We thank W. Meyer and H. J. Korsch for valuable

discussions concerning the electron-molecule interaction and the physics of the spectator model for inelastic collisions. We are also grateful to H. D. Meyer for providing his results on e-Na_2 interaction potential prior to publication. We finally thank L. Meyer and R. Walther for skillful technical assistance. This work has been supported by the Deutsche Forschungsgemeinschaft under Sonderforschungsbereich 91 (Energy transfer in atomic and molecular collisions).

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