Role of Negative-Molecular-Ion Resonances in Collisional Detachment: $Cl^- + N_2$

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Double-differential studies of the fast neutrals (Cl) resulting from collisional detachment of Cl^- on N_2 ($E_{lab} \lesssim 300$ eV) show energy-loss peaks at 6 and 12 eV. It is noteworthy that a high-loss peak is dominant at low $E\theta$. Similar studies of the inelastically scattered Cl^- reveal significant vibrational-rotational excitation of N_2 but no electronic excitation of the N_2 is observed. Arguments are presented which support the hypothesis that the known negative-ion resonances of N_2 are involved in the detachment processes.

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Electron detachment in collisions of halogen negative ions with the rare gases has recently received considerable attention.[1-3] At low energies, total detachment and various differential cross sections have been measured[1] and the results have been analyzed with a complex-potential model to account for the discrete-continuum coupling which gives rise to "direct" detachment. As the relative collision energy is increased above about 100 eV, the complex-potential model fails and Fayeton, Dhuica, and Barat[2] propose that a quasimolecular negative-ion resonance may be involved in the collisional dynamics. For molecular targets, e.g., $Cl^- + H_2$,[4] time-of-flight spectra for the Cl reaction product indicate that H_2^- resonances may play an important role in the detachment mechanism even at relative collision energies as low as 20 eV. Risley[5] has also demonstrated the importance of the $N_2^-(^2\Pi_g)$ resonance in the collisional detachment of H^- by N_2.

The purpose of this Letter is to present the results of doubly differential cross-section measurements for

$$Cl^- + N_2 \rightarrow Cl + N_2 + e^- \quad (1a)$$

$$Cl^- + N_2 \rightarrow Cl^- + N_2 \quad (1b)$$

over the energy range $100 \lesssim E \lesssim 300$ eV which show evidence that the N_2^- resonances play a dominant role in the collisional dynamics for reaction (1). In fact, the present studies indicate that detachment occurs almost uniquely via charge transfer to N_2: Direct detachment is found to be a minor mechanism.

For the detachment studies (1a), a previously described time-of-flight (TOF) apparatus[4] was modified to permit angular measurements. A beam of Cl^- ions formed from CCl_4 which is incident upon a thoriated iridium filament is pulsed at 25–60 kHz [~ 0.5 μsec full width at half maximum (FWHM)] and passed through a scattering cell containing N_2. The ion beam is then deflected and the fast Cl atoms are detected by a channel-plate multiplier located ~ 1 m from the scattering center.

Typical TOF spectra for Cl formed via (1a) at a laboratory collision energy of 198 eV are shown in Fig. 1 for scattering angles of 1.6, 3.0, and 4.5 deg. The abcissae indicate the inelasticity, Q, for the reaction (the minimum inelasticity is 3.6 eV, the electron affinity of Cl). In order to illustrate the apparatus energy resolution, the TOF spectra for the elastic scattering of Cl^- by argon are also indicated in the figure as the dashed lines. The solid curve in the lowest figure shows a TOF spectrum for $Cl^- + Ar \rightarrow Cl + Ar + e$; this spectrum has a peak at $Q \simeq 4$ eV which is typical of direct detachment and it exhibits a high energy-loss tail as found by Fayeton, Dhuica, and Barat[2] and as manifested by the e^- energy spectra measured by de Vreugd *et al.*[3]

In the data shown for detachment on N_2, two energy-loss peaks are clearly resolved corresponding to energy losses of approximately 6 and 12 eV. Figure 2 shows the most probable Q for each peak as a function of τ ($= E\theta$) taken at laboratory energies of 148, 198, and 297 eV. For both peaks the most probable energy loss is almost independent of τ which would be expected if the inelasticity resides in electronically, rather than vibrational-rotational, excited states of the target.

A remarkable feature in the data is the dominance of the high-energy-loss channel at low τ. As indicated in Fig. 2, the high-energy-loss

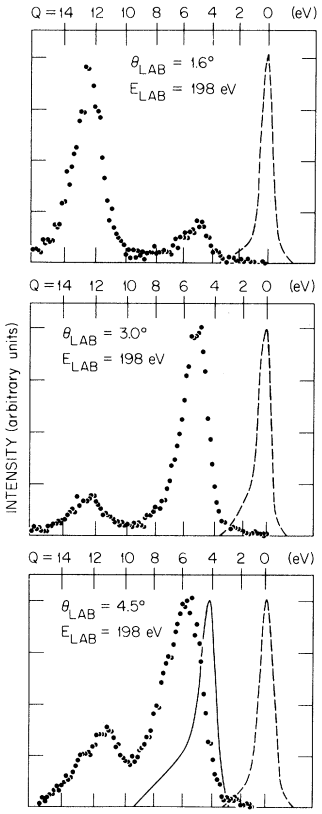

FIG. 1. Time-of-flight energy-loss spectra of Cl^0 formed by detachment in Cl^- (E_{lab} = 198 eV) + N_2 collisions. Also shown are spectra for elastic scattering from Ar (dashed lines) and collisional detachment from Ar (solid lines).

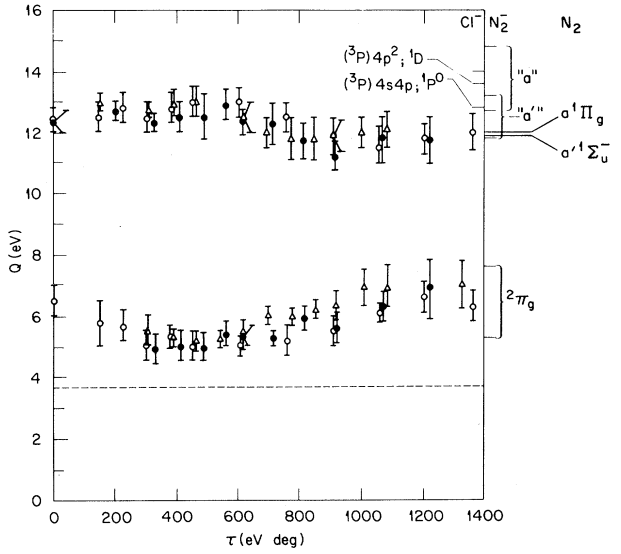

FIG. 2. Energy loss, Q, in $Cl^- + N_2$ detachment collisions vs τ. E_{Cl^-} = 148 eV (open triangles), 198 eV (solid circles), and 297 eV (open circles). Dashed line at 3.6 eV represents the electron affinity of Cl^-. Excitation energies for levels of Cl^-, N_2^-, and N_2 are indicated at the right.

group is commensurate with (1) electron transfer to the a' core-excited shape resonance[6] of N_2^-, (2) simultaneous detachment and excitation of the $a^1\Pi_g$ state of N_2, or (3) excitation of the autodetaching $3p^4(^3P)4s4p;^1P$, and $3p^4(^1D)4s^2;^1D$ states of Cl^- at 9.15 and 9.97 eV, respectively[7] [the $3p^4(^3P)4s^2;^3P$ state at 8.53 eV is forbidden by the Wigner spin-conservation rule].

We discount the formation of Cl^- autodetaching states because the energy losses are a bit too low (Fig. 2). In addition, we carried out some separate experiments in which we substituted F^- for Cl^-. Here we found the same energy-loss spectrum (i.e., Q values commensurate with N_2^- formation) even though the autodetaching states of F^- should lie ~4 eV higher[8] than those for Cl^-. Although this finding does not necessarily eliminate the possibility of autodetaching states when Cl^- is used as the projectile it definitely suggests that negative-molecular-ion states play a role in this detachment process.

The question of a decision between (1) and (2) above may be moot because the lifetime of the a' N_2^- state is approximately 10^{-15} sec,[9] which is comparable to the collision times (~3×10^{-15} sec/Å). However, in another experiment in which we measured the inelastic loss in nondetaching collisions (see below), no evidence for energy loss corresponding to excitation of a $^1\Pi_g$ or $^1\Sigma_u^-$ state of neutral N_2 was observed. From this fact and the fairly large signal observed for the 12-eV loss channel in detachment collisions it may be inferred that the a' N_2^- resonance contributes significantly to the configuration of an $[N_2Cl]^-$ intermediate. The fact that the high-Q channel is dominant at low scattering angle may arise from an attractive region in the scattering potential in the exit channel. It has been suggested that the $Cl^- + N_2$ repulsive state might detach an electron at short distances (as a quasitriatomic molecule) and then exit along strongly attractive ion-pair states ($Cl^- + N_2^+$) which are strongly coupled to excited states [e.g., $Cl + N_2(^1\Pi_g)$] so that little direct ion-pair formation occurs.[10] The observed energy loss is commensurate with such a process. The asymptotic $Cl^- + N_2^+$ curve lies ~4 eV above the $Cl + N_2(^1\Pi_g)$ but a curve crossing should

occur at separations of ~4 Å. Thus the integrated deflection function for such a process could lead to relatively low scattering angles for small-impact-parameter collisions.

The low-energy-loss process is the dominant one in the total detachment cross section (see Fig. 3). The inelastic energy loss scales with τ, is significantly greater than that for simple detachment (compare, e.g., with Ar-target peak in Fig. 1), and is also significantly greater than the vibrational-rotational excitation obtained with K^+ or Ar^+ on N_2.[11,12] The observed Q is, however, entirely consistent with charge transfer to the $^2\Pi_g$ resonance[6] state of N_2^- whose lowest vibrational state lies 1.8 eV above the ground state of N_2. The rise in the inelasticity for $\tau \gtrsim 1000$ eV deg and the asymmetric broadening in the energy spectra toward higher Q seen at the higher τ values indicate that a band of vibrational states with the $^2\Pi_g$ electronic state of N_2^- is involved in the detachment mechanism. The reason for the dominance of this process may involve an attractive well for the $[Cl - N_2(^2\Pi_g)]^-$ system which drops the crossing point at the repulsive wall below that for simple detachment to the continuum.

Measurements[13] of the total detachment cross section for (1a) have shown that the threshold for detachment is $E_{thres} \simeq 7.6$ eV, which does not rule out the possibility that the $^2\Pi_g$ state of N_2^- is involved in detachment at collision energies well below those reported in the present study.

The relative differential cross sections for each of the two detachment channels are given in Fig. 3 for $E = 148$ eV.[14] Local minima were found in the low-loss curve at 650–700 eV deg and in the high-loss curve at approximately 500 eV deg. In the latter case similar minima at the source τ were noted in the data for 200 and 300 eV. It may be seen in Fig. 2 that the nature of the curves for the most probable Q values for each channel also changes in the same τ range. The origin of these features of the data is not presently understood.

The doubly-differential cross sections for the inelastic nondetaching channel, (1b), were measured with an apparatus which utilizes an electrostatic analyzer; this apparatus has been described elsewhere.[1] A summary of the results for several collision energies is seen in Fig. 4. The inelastic component of (1b) is larger than 1(a) for small angles, and the two processes become roughly equal in cross section at $\tau \simeq 1000$ eV deg. Only a single peak is observed in the energy-loss spectrum of (1b), and the most probable Q for (1b) is given in Fig. (4); the results indicate that $Q(\tau)$ is neither constant nor does it scale with τ. Similar vibrational-rotational energy transfer has been observed for the isoelectronic reactants $K^+ + N_2$ (Ref. 11) and for $Ar^+ + N_2$.[12] For all three systems the inelasticity scales reasonably well with $E\theta^2$. However, for the $Ar^+ + N_2$ and the $K^+ + N_2$ systems additional energy-loss peaks corresponding to electronic excitation of N_2 were found. For example, in the $Ar^+ + N_2$ system the energy-loss peak corresponding to electronic excitation of N_2 was more than 0.5 the height of the simple vibrational-rotation excitation peak at $\tau = 2200$ eV deg. The absence of such peaks in the nondetaching channel with

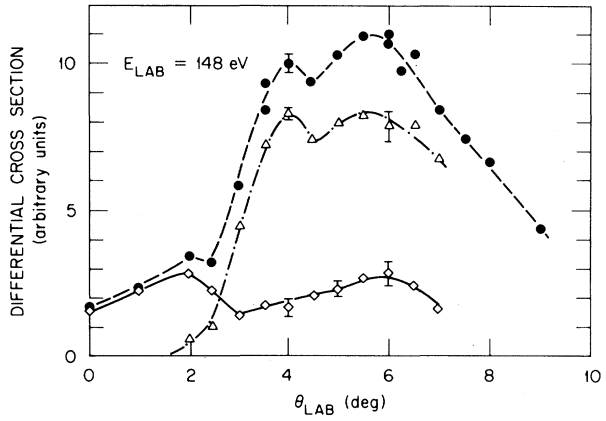

FIG. 3. Relative differential cross sections for Cl^- ($E_{Cl^-} = 148$ eV) detachment in collision with N_2. Solid circles, total cross section; open triangles, partial cross section for low-loss ($\Delta E = 5-7$ eV) peak; open diamonds, partial cross section for high-loss ($\Delta E = 11.5-12.5$ eV).

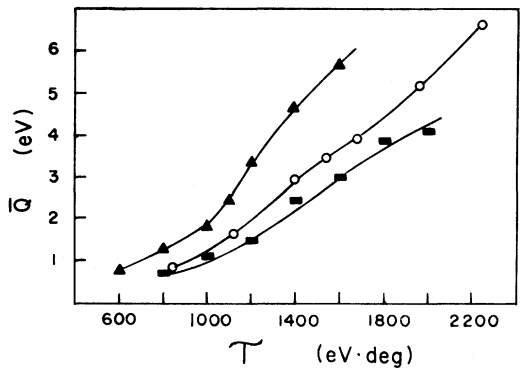

FIG. 4. The most probable energy loss of Cl^- inelastically scattered by N_2 vs τ for the three laboratory energies indicated. $E_{Cl^-} = 100$ eV (solid triangles), 140 eV (open circles), and 200 eV (solid rectangles).

$Cl^- + N_2$ indicates that when electronically excited states of the target molecule are involved, detachment also occurs.

In conclusion, the results discussed here give strong evidence that the negative-molecular-ion resonance states provide the predominant pathway to electron detachment for $Cl^- + N_2$ collisions.

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