## Neutralization of Fast Molecular Ions $H_2^+$ and $N_2^+$ at Surfaces

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Energy spectra of the products of surface scattering of  $H_2^+$  and  $N_2^+$  in the primary-beam energy range from 200 to 600 eV are presented. Large neutral-molecular yields are observed for incident  $N_2^+$ , i.e., beams of neutral molecules can be produced with optical properties similar to that of the incident beam. The results provide a new experimental method to study resonant and Auger-type processes in ion-surface charge-exchange events.

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The charge-exchange processes between particles and solids are of great scientific and technical interest.<sup>1, 2</sup> Among the processes discussed, the resonant charge exchange between valence-electron states and atomic levels and Auger-type processes between the same type of levels are the most relevant. In the present work we demonstrate that molecular-ion scattering may afford a unique possibility to study the dependence on valence-electron momentum and density of the resonant and Auger transition-matrix elements over the complete width of the valence band. Besides this special aspect our results have also some importance for negative-ion sources<sup>3</sup> and atmospheric and astrophysical processes, i.e., the interaction of molecular ions with surfaces.<sup>4,5</sup> The experiments also provide a source of fast neutral molecules (around 100 eV) as a beam with good "ion" optical properties. Beams of this type may prove useful for the study of neutral molecules and atom- or molecule-molecule interactions.<sup>6</sup> Furthermore, the production of exotic neutrals<sup>7</sup> is possible, whenever the ions can be produced in conventional ion sources.

Here we report results of scattering of  $H_2^+$  and  $N_2^+$  from a clean Ni(111) target. The scattered particles, neutrals and ions, are analyzed by the timeof-flight (TOF) mass and velocity spectrometer described earlier.<sup>8</sup> The experiment consists of an UHV system incorporating an electrostatic energy analyzer at 90° to the beam direction for ionscattering spectrometry (ISS),<sup>9</sup> an ion-beam system operating between 100 eV and 20 keV, and a TOF system for particles scattered at grazing angles, i.e., impact (glancing) angles of 0–10° and a fixed scattering angle of 10.5°. TOF spectra are taken with post-acceleration to separate ions and neutrals

The energy spectra produced by  $H_2^+$  at two different primary energies are shown in Fig. 1. Besides surviving  $H_2^+$  and dissociated  $H^+$  (in agreement with previous experiments<sup>10-13</sup>), we observe as expected H, but in addition the neutral spectrum contains a narrow peak, which can be identified as  $H_2$  by comparison with the  $H_2^+$  peak and from estimates of the expected energy spectrum based on conservation of energy and momentum. For binary scattering the energy of the reflected particles is given by  $E = E_0 f(\delta, A)$ , where  $E_0$  = primary energy,  $\delta =$  laboratory scattering angle, and A = mass ratio. For dissociation it is  $E_{\text{lab}} = \frac{1}{2}E_{\text{beam}} + \frac{1}{2}E_{\text{rep}}$  $\pm (E_{\text{beam}}E_{\text{rep}})^{1/2}\cos\theta$ , where  $E_{\text{rep}} = \text{repulsive energy}$  from dissociation,  $\theta = \text{angle of molecular axis}$ with beam.<sup>10</sup> It is not seen with use of primary  $H^+$ beams. The neutral  $H_2$  peak is not predicted by models for the interaction of swift molecular ions with surfaces,<sup>14-16</sup> although recently the production of slow H<sub>2</sub> in ion sources due to ion-wall interactions has been proposed.<sup>3</sup> For dissociation by collisions the elastic energy transfer is too low at the energies and scattering angle discussed here. Desorbed H can also not cause the narrow peak observed here.<sup>17</sup>

With  $N_2^+$  the dominance of neutralization over other processes is even greater (Fig. 2). At about 200 eV the spectrum shows mainly the neutral  $N_2$ peak with a ratio of about 10:1 over N. The experimental errors in the detector sensitivity calibration cause an error of  $\pm 20\%$  of the  $N_2/N$  and  $H_2/H$  ratios.

An explanation for these observations may be given by an extension of the present charge-exchange models between solids and  $atoms^{1,2}$  to the case of molecules, and is analogous to that explaining atom-molecular-ion dissociative charge-capture experiments.<sup>18</sup> With atoms the most important processes are resonant and Auger-type processes. The ionization energies of the molecular states in question as a function of the internuclear distance,<sup>18, 19</sup> and a simplified band structure of Ni, are shown in Fig. 3. (Level broadening and shifting<sup>1, 2</sup> of the order of 0.5 eV will not change the following discussion.) With H<sub>2</sub> as the final product mainly the ground state  $X^1\Sigma_g^+$  and the nonbonding triplet



FIG. 1. Energy spectra of 260- and 590-eV  $H_2^+$  backscattered from Ni(111); glancing angle 5°, scattering angle 10°. The spectra of neutral molecules (solid triangles) were obtained by subtraction.

state  $b^3 \Sigma_u^+$  will be important for charge capture. The  $c^3 \Pi_u$  state, which is known to decay radiatively and to predissociate rotationally, or the  $a^3 \Sigma_g^+$  state (almost energetically equal to  $c^3 \Pi_u$ ), which dissociates radiatively, are rather high-lying states compared to the edge of the occupied Ni band. Therefore the electron transitions into  $b^3 \Sigma_u^+$  and  $X^1 \Sigma_g^+$ are expected to dominate. Since the spatial extents of the wavefunctions of  ${}^3 \Sigma_u$  and  ${}^1 \Sigma_g$  are essentially identical, electronic interactions with each state will occur in the same spatial region, so that a sequential model, e.g., resonant filling of  ${}^3 \Sigma_u$  first followed by Auger capture into  ${}^1 \Sigma_g$ , as recently proposed<sup>3</sup> for H<sub>2</sub>, cannot be applied. The electron capture into  ${}^3 \Sigma_u$  will therefore be the main cause of dissociation, and Auger capture into  ${}^1 \Sigma_g$  the primary mechanism for neutral H<sub>2</sub> formation.

On the other hand N<sub>2</sub> allows no electron capture into an antibonding state under the assumption of conservation of the core-electron configuration. Only if during the particle-solid interaction one of four  $1\pi_u$  electrons is excited are the dissociative states  ${}^5\Sigma_g^+$  and  ${}^7\Sigma_u^+$  accessible. With the assumption that the N<sub>2</sub><sup>+</sup> is in the  $X^2\Sigma_g^+$  state, the binding states accessible by single-electron capture are the ground state  $X^1\Sigma_g^+$ ,  $B^3\Pi_g$ ,  $a^1\Pi_g$ , and Rydberg states like  $E^{3}\Sigma_{g}^{+}$ . The latter has an ionization energy of 3.7 eV, i.e., it lies above the Ni band. The  $B^3\Pi_g$ and  $a^{1}\Pi_{g}$  states may dissociate if sufficiently vibrationally and rotationally excited (v = 12 and 6, respectively).<sup>20</sup> Some of the observed atomic particles may also be due to dissociation of long-lived excited molecular ions. We know from spectroscopic studies<sup>21</sup> that the  $N_2^+ A^2 \Pi_u$  exists in the beam, but on the assumption that one third of the  $N_2^+$  are generated in the  $A^2\Pi_u$  state in the source, only 2% are left at the target. Other excited ions, e.g.,  $N_2^+ B^2 \Sigma_u^+$ , are negligible components in the beam as a result of the length of the flight path from the source to the target (1.48 m). Primary excited neutrals are not present as a result of 90° magnetic deflection of the primary beam. Combined together, the above arguments explain the formation of neutral atoms and molecules and the striking difference between  $N_2^+$  and  $H_2^+$ .

As Fig. 3 suggests, the dissociative scattering of molecular ions gives the possibility of studying how the probability for transitions between the metal band and a molecular state depends on the valence-electron momentum and density in the band. The atomic energy spectra of Figs. 1 and 2 contain direct information about the transition-matrix ele-



FIG. 2. Energy spectra of 195- and 295-eV  $N_2^+$  backscattered from Ni(111); glancing angle 5°, scattering angle 10°. The spectra of neutral molecules were obtained by subtraction.

ment in a way not accessible with primary atomic ions.<sup>1</sup> From conversion of the laboratory-energy spectra to the center-of-mass repulsive-energy distributions we can extract essentially the square of the matrix element. The probability for a given repulsive energy to occur is essentially dependent on the primary vibrational population of the molecular ion state, on the shape of the antibonding potential curve, and on the square of the matrix element in question.<sup>18</sup> A second interesting aspect is the comparison of neutral atomic and neutral molecular yields. If the survival of once-formed neutral molecules is not changed by elastic or inelastic effects, the yield ratio ought to provide information on the ratio of the transition probabilities into a state facing the band of the solid and to a



FIG. 3. Simplified band structure of Ni, and ionization energies vs internuclear distance for the most important states of  $H_2$  and  $N_2$ , neglecting level shifts in the near-surface region.

state lying below the band (Auger-type transition). At the present stage of our analysis we can exclude the elastic effects<sup>15</sup> as a result of the low energies and small scattering angles used; inelastic effects,<sup>14</sup> however, are difficult to exclude, as is whether the molecules appear to scatter as one or as two particles.<sup>22</sup>

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