

Vibrationally enhanced dissociative scattering of $\text{NO}^+(E_{\text{trans}}, v=0-6)$ on GaAs(110)

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I. INTRODUCTION

The use of molecular ions in electronic device fabrication is wide spread. Fundamental to many of these important industrial applications (e.g., reactive ion etching, oxide/nitride growth, ion enhanced deposition) is an electron transfer even near the substrate which forms energetic molecular and atomic intermediates. In spite of the extensive use of ion beams for surface modification, the detailed dynamics of molecular ion-surface processes remain largely unexplored.

Dissociation from collisions (at hyperthermal energies) of small molecular ions with well-characterized surfaces has been investigated by a limited number of groups. Rabalais and co-workers have measured the translational energy threshold for molecular and dissociative chemisorption of CO^+ and N_2^+ on various metals.^{1,2} In a similar vein, Akazawa and Murata have observed a resonance-like phenomena in the activated dissociative adsorption for N_2^+ on Ni(100) and Ni(111).³ The same authors explored the dissociative scattering of N_2^+ , CO^+ , and CO_2^+ on Pt(100) and measured the angular distribution of the resulting positively charged fragments.⁴ Snowdon, Kleyn, and co-workers have utilized keV molecular ion beams at glancing angles to simulate low "normal" energy collisions of ions and neutrals with surfaces. They have observed neutral fragments from the charge transfer and dissociation of $\text{O}_2^+/\text{Ag}(111)$,⁵⁻⁸ $\text{O}_2^+/\text{Pt}(111)$,⁸ $\text{NO}^+/\text{Ag}(111)$,^{5,8} $\text{CO}^+/\text{Ag}(111)$, $\text{H}_2^+/\text{Ag}(111)$,⁵ $\text{O}_2^+/\text{Si}(001)$,⁹ $\text{O}_2^+/\text{Ni}(110)$, $\text{CO}^+/\text{Ni}(110)$, $\text{CO}_2^+/\text{Ni}(110)$, $\text{N}_2^+/\text{Ni}(110)$,^{10,6} $\text{H}_2^+/\text{Ni}(111)$, $\text{N}_2^+/\text{Ni}(111)$,^{11,12,16} $\text{N}_2^+/\text{Cu}(111)$,^{13,14} and $\text{H}_2^+/\text{Cu}(111)$.^{13,15,16} In all but the last five cases, Snowdon and Kleyn were able to detect negatively charged fragments as well.

An uncontrolled, but potentially important parameter in all of the aforementioned ion/surface scattering experiments is the internal energy of the incident molecular ion. In conventional ion beam sources, the distribution of internal energies often includes multiple quantum states of the ion, and control over state selectivity is limited.⁵ In contrast, resonance-enhanced multiphoton ionization (REMPI)¹⁷ offers a high degree of selectivity ($\sim 90\%$)^{18,19} for producing molecular ions in specific vibronic levels. Hence, by combining the state-selectivity of REMPI with conventional ion optics and negative ion detection, we can directly interrogate the individual roles of vibrational and translational energy on the reaction



II. EXPERIMENT

The experimental apparatus, shown in Fig. 1, utilizes a pulsed laser ionization source, electrostatic optics for ion transport, a surface sample manipulator, an ion sputtering gun for surface cleaning, Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and detectors sensitive to scattered ionic and neutral products. A cryopump, ion pump and titanium sublimation pump establish a main chamber pressure of 3×10^{-10} Torr. A pulsed, collimated, supersonic expansion of gas enters the main chamber through a skimmer and two stages of differential pumping. Because the molecular beam is directed into the cryopump, a pressure rise of only 1×10^{-11} Torr occurs in the main chamber. The frequency-doubled output of a Nd:YAG pumped dye laser (Continuum 682-20/TDL 60) is focused into the chamber with a spherical lens ($f=15$ cm). At the intersection of the free jet and the 6 ns uv laser pulse, 2+1 REMPI through the $C^2\Pi(v=3-6)$ or $E^2\Sigma^+(v=0-2)$ Rydberg levels form a localized packet of $\text{NO}^+ X^1\Sigma^+(v=0-6)$ ions. These state-selected ions are extracted with an electric field, accelerated to ~ 200 eV, mass selected with a Wien filter, and finally decelerated and focused with a Menzinger lens. The packet of incident ions has a measured energy spread (FWHM) of 1.5 eV. In order to stabilize the ion beam intensity, we have developed a feedback wavelength stabilization device²⁰ which markedly reduces the dye laser's wavelength drift.

The undoped GaAs wafer (Liton Airtron) is oriented to the (110) plane within 0.25° . Cleaning in UHV consists of sputtering with 500 eV Ar^+ at a surface temperature of 425 K, followed by annealing to 625 K.²¹ Cleanliness and surface order are checked by AES and LEED, respectively. For all experiments reported here, the temperature of the crystal was kept at 298 K.

Ions are collected with a novel two-dimensional velocity image detector, described in detail elsewhere.²² Briefly, a CCD camera records an instantaneous image of the ions' spatial distribution, in a plane orthogonal to the ions' velocity vector. In order to quantify the number of ions impinging on the surface, the detector is positioned along the surface normal. Throughout the experiment, the computer switches the electronics to alternate between detection of incident positive ions (mass ~ 30 amu) and scattered negative ions (mass ~ 16 amu).²³ Because the same detector is

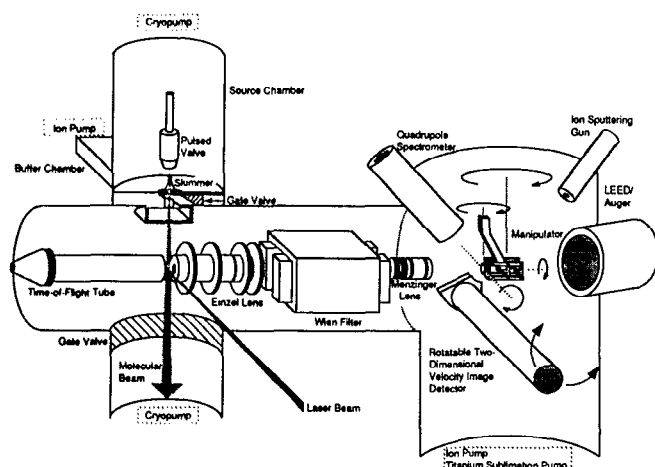


FIG. 1. Experimental apparatus.

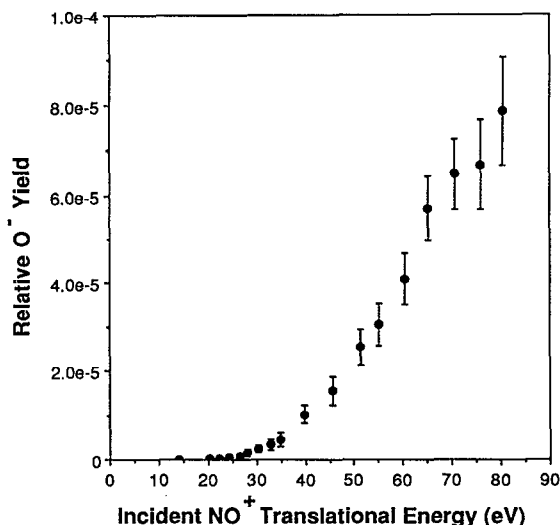
used for both incident and scattered ions, product yields are expressed in terms of the fraction of incident ions.

The ion beam is directed along the surface normal to within 0.5° . The azimuthal orientation of the surface is adjusted so that the [001] direction of the lattice and the surface normal define the detection plane of the two-dimensional velocity image detector. The velocity distribution of O^- products is reduced from the spatial distributions of scattered ions, measured at a series of time delays between the repeller and laser pulses.²² Average energies reported here are obtained by integrating over all speeds and the range of angles ($\pm 21^\circ$ along the detector plane and $\pm 6^\circ$ out-of-plane) accessed by the two-dimensional velocity image detector, centered along the surface normal. The reported relative yields represent the number of scattered O^- ions, collected in the aforementioned detector solid angle, divided by the number of NO^+ ions incident on the surface. This provides a lower limit to the fraction of incident NO^+ ions which form O^- fragments, because the scattering distribution extends beyond the acceptance angles of the detector.

III. RESULTS

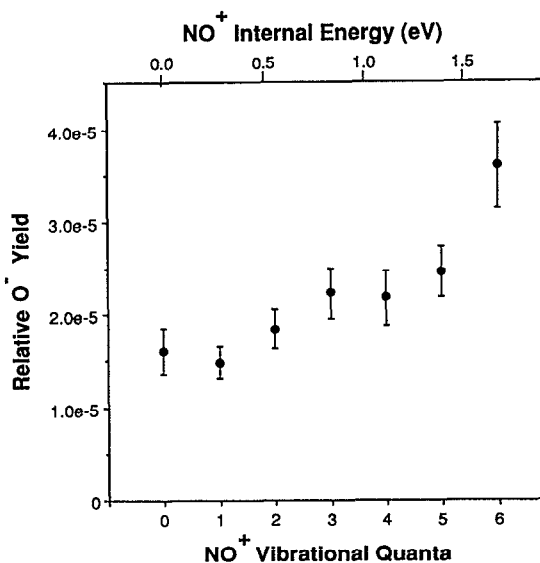
In order to assess the relative influence of translational and vibrational energies on the yield of reaction (1), two separate experiments were conducted. First, NO^+ ($v=1$) was reacted with GaAs(110) at a series of collision energies. Figure 2 shows the relative O^- yield as a function of incident NO^+ translational energy. Below a collision energy of 22 eV, no scattered O^- ions were observed. An extrapolated threshold for the appearance of O^- occurs at 25 ± 1 eV. Beyond this point, the measured O^- yield steadily increases with increasing NO^+ energy, approaching a relative yield of 10^{-4} near 80 eV.

The second experiment examines collisions of NO^+ (v) with GaAs(110) at a constant translational energy of 45 eV. Here, the relative O^- yield is measured as a function of the number of vibrational quanta in the incident NO^+ molecule. Figure 3 shows that the scattered O^- yield from NO^+ ($v=6$) is a factor of 2.4 greater than the corre-

FIG. 2. Relative yield of scattered O^- as a function of incident translational energy for NO^+ ($v=1$) colliding at normal incidence.

sponding yield from vibrationally cold incident ions. A comparison of Figs. 2 and 3 reveals an intriguing result: Only 1.7 eV of vibrational energy produces an enhancement of 140% in the negative ion fragmentation channel; yet, if the same amount of initial energy were instead to be deposited as translational energy, an enhancement of merely 14% would be expected. Under these conditions, this result suggests that vibrational energy is roughly ten times more effective than translational energy in producing scattered O^- ions.

In each of the experimental runs comprising Fig. 2, an angle-resolved velocity distribution is recorded. This information is most simply shown as a plot of the average translational energy measured in the O^- fragment versus the incident NO^+ translational energy. Figure 4 suggests that

FIG. 3. Relative yield of scattered O^- as a function of vibrational quanta in NO^+ (45 eV collision energy, normal incidence).

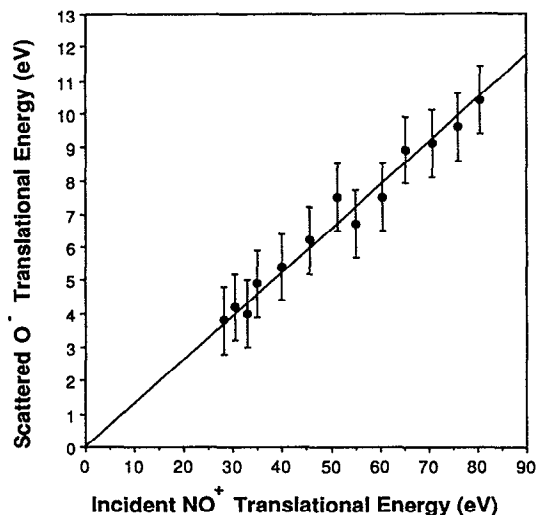


FIG. 4. Average kinetic energy of O^- fragment vs incident translational energy for NO^+ ($v=1$) colliding at normal incidence. The linear fit is constrained to pass through the origin.

the relationship between these two quantities is linear. Approximately 13% of the incident translational energy appears in the form of O^- kinetic energy.

IV. DISCUSSION

The observed 25 eV threshold for O^- emergence in dissociative collisions of NO^+ with GaAs(110) is in excess of any reasonable thermodynamic energy barrier. The endoergicity of reaction (1) is 4.6 eV,²⁴ if one assumes the NO^+ reactant is in the first excited vibrational level of the ground electronic state, the nitrogen and oxygen fragments scatter in their ground electronic states, and the two holes created in the surface are generated at the Fermi level. The experiment indicates that an additional 20 eV of translational energy is required to drive this reaction. Nevertheless, this observation is consistent with appearance threshold measured for similar ion/surface scattering systems: $O_2^+ \rightarrow O^-/Ag(111)$ [15 eV],⁷ $N_2^+ \rightarrow N^+/Pt(100)$ [40 eV], $CO_2^+ \rightarrow CO^+/Pt(100)$ [25 eV], and $CO^+ \rightarrow C^+/Pt(100)$ [70 eV].⁴ In each of these cases, the authors implicate a collision-induced dissociation (CID) mechanism. This classical mechanism assumes that dissociation occurs as a result of an impulsive transfer of incident translational energy to rovibrational energy.^{25–28}

A simple model calculation was performed to simulate our experimental results. Classical trajectories were carried out on a system consisting of a rotating, vibrating NO diatom colliding with a single Ga surface atom, bound harmonically to its equilibrium position. The repulsive interaction between the surface atom and each of the molecular nuclei was modeled by a Born–Mayer potential, and the molecule was bound by a Morse potential. For cases where the incident molecule was described by the Morse parameters corresponding to isolated NO^+ , NO , and NO^- , the thresholds for appearance of scattered fragments occurred at 31, 17, and 13 eV, respectively. These values bracket the experimentally determined threshold of 25 eV.

The effect of initial vibrational energy on the dissociative scattering of NO^+ at GaAs(110) is quite surprising because the molecule retains memory of its initial excitation through the vibrational scrambling which accompanies electron transfer processes²⁹ and an impulsive collision with the surface. It is noteworthy that the order of magnitude greater efficacy from vibration vs translation is observed at a collision energy 20 eV above threshold.

There are a few plausible explanations for the vibrational effect. It is reasonable to expect that the classical CID mechanism would predict an enhanced fragment yield with initial vibrational excitation. This is because vibrational excitation represents a direct deposit of energy into the reaction coordinate, i.e., the molecular stretching coordinate. Nevertheless, the classical model, presented above, does not predict the magnitude of the observed vibrational effect. However, our detection of negatively charged fragments requires consideration of the charge transfer processes as well as the mechanism for dissociation. There are two simple reasons why vibration might alter the electron transfer rates: Vibrational excitation can change the Franck–Condon overlaps between the initial and final electron transfer states, and vibrational excitation will shift resonances between molecular energy levels and the density of states at the surface.³⁰ Additionally, the short interaction time between the molecule and the surface may necessitate a time-dependent quantum mechanical description. Specifically, a 45 eV NO molecule moves 1 Å in only 6 fs, while the vibrational period for NO is at least 16 fs. This introduces the possibility of phase coherences arising from the rapid succession of diabatic curve crossings preceding and following the repulsive interaction with the surface.^{31,29}

Figure 4 indicates that the average kinetic energy of the scattered oxygen ion is 13% of the incident NO^+ energy, for all measured incident translational energies. If one assumes that the nitrogen fragment escapes with a comparable kinetic energy, then only one quarter of the available product energy is partitioned into fragment kinetic energy. The remaining three quarters of the available product energy must be distributed between the reaction endoergicity (>4.6 eV), excitation of surface phonons, creation of additional electron-hole pairs, or electronic excitation in the fragments. The classical trajectory simulations predict that $\sim 70\%$ of the incident translational energy is transferred to surface motion. Oxygen ions, observed at collision energies slightly above threshold, scatter with an average translational energy of 3.3 eV. If a CID mechanism is operative, these fragments will be formed with little or no relative energy; therefore, the entire 3.3 eV would correspond to the center-of-mass motion of the diatom, which is neither converted into motion along the reaction coordinate nor absorbed by surface losses.

This study represents the first direct observation of a vibrational effect in ion/surface scattering and complements molecular beam experiments, that have examined the role of vibrational energy in activating dissociative chemisorption.^{32–36} Most notably, vibrational energy is found to be an order of magnitude more effective than

translational energy in producing scattered O^- fragments from $NO^+/GaAs(110)$ collisions at 45 eV. The observed reaction of $NO^+(v=1)$ with $GaAs(110)$ has a translational energy threshold of 25 eV, five times the endoergicity of the reaction. On average, the O^- fragment is produced with a kinetic energy that is 13% of the incident NO^+ energy. These new results begin to reveal the detailed dynamics of electron transfer and dissociation processes for ions at surfaces.

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- ¹N. Sharmir, D. A. Baldwin, T. Darko, J. W. Rabalais, and P. Hochmann, *J. Chem. Phys.* **76**, 6417 (1982).
- ²H. Kang, S. R. Kasi, and J. W. Rabalais, *J. Chem. Phys.* **88**, 5882 (1988).
- ³H. Akazawa and Y. Murata, *J. Chem. Phys.* **88**, 3317 (1988).
- ⁴H. Akazawa and Y. Murata, *J. Chem. Phys.* **92**, 5560 (1990).
- ⁵P. H. F. Reijnen and A. W. Kleyn, *Chem. Phys.* **139**, 489 (1989).
- ⁶K. J. Snowdon, *J. Chem. Faraday Trans. 2* **85**, 1347 (1989).
- ⁷P. H. F. Reijnen, P. J. van den Hoek, A. W. Kleyn, U. Imke, and K. J. Snowdon, *Surf. Sci.* **221**, 427 (1989).
- ⁸P. H. F. Reijnen, U. van Slooten, and A. W. Kleyn, *J. Chem. Phys.* **94**, 695 (1991).
- ⁹J.-H. Rechtien, U. Imke, K. J. Snowdon, P. H. F. Reijnen, P. J. van den Hoek, A. W. Kleyn, and A. Namiki, *Surf. Sci.* **227**, 35 (1990).
- ¹⁰S. Schubert, U. Imke, W. Heiland, K. J. Snowdon, P. H. F. Reijnen, and A. W. Kleyn, *Surf. Sci. Lett.* **205**, L793 (1988).
- ¹¹B. Willerding, H. Steininger, K. J. Snowdon, and W. Heiland, *Nucl. Instrum. Meth. Phys. Res. B* **2**, 453 (1984).
- ¹²B. Willerding, W. Heiland, and K. J. Snowdon, *Phys. Rev. Lett.* **21**, 2031 (1984).
- ¹³J.-H. Rechtien, W. Mix, and K. J. Snowdon, *Surf. Sci.* **259**, 26 (1991).
- ¹⁴J.-H. Rechtien, W. Mix, D. Danailov, and K. J. Snowdon, *Surf. Sci.* **271**, 501 (1992).
- ¹⁵J.-H. Rechtien, R. Harder, G. Herrman, C. Röthig, and K. J. Snowdon, *Surf. Sci.* **269/270**, 213 (1992).
- ¹⁶J.-H. Rechtien, R. Harder, G. Herrmann, and K. J. Snowdon, *Surf. Sci.* **272**, 240 (1992).
- ¹⁷For a review of REMPI, see S. L. Anderson in *Advances in Chemical Physics, Vol. LXXXII*, edited by M. Baer and C. Yung (Wiley, New York, 1992).
- ¹⁸T. Ebata and R. N. Zare, *Chem. Phys. Lett.* **130**, 467 (1986).
- ¹⁹C.-H. Kuo, C. G. Beggs, P. R. Kemper, M. T. Bowers, D. J. Leahy, and R. N. Zare, *Chem. Phys. Lett.* **163**, 291 (1989).
- ²⁰P. L. Stricklin and D. C. Jacobs, *Appl. Optics* (in press).
- ²¹V. M. Bermudez, R. J. Williams, J. P. Long, J. C. Rife, R. M. Wilson, A. E. Tuttle, and G. P. Williams, Jr., *J. Vac. Sci. Technol. A* **5**, 541 (1987).
- ²²D. Corr and D. C. Jacobs, *Rev. Sci. Instrum.* **63**, 1969 (1992).
- ²³Scattered NO^- and O^- products are clearly mass resolved. There is no interference in O^- detection from potential N^- products, because if formed, N^- autodetaches prior to entering the detector region.
- ²⁴ $2\Phi[4.8\text{ eV}] - E_{\text{vib}}(NO^+)[0.29\text{ eV}] - I.P.(NO)[9.82\text{ eV}] + D_{O(NO)}[6.57\text{ eV}] - E.A.(O)[1.46\text{ eV}] = 4.6\text{ eV}$.
- ²⁵R. B. Gerber and R. Elber, *Chem. Phys. Lett.* **107**, 141 (1984).
- ²⁶J. S. Bitensky and E. S. Parilis, *Surf. Sci.* **161**, L565 (1985).
- ²⁷P. J. van den Hoek, T. C. M. Horn, and A. W. Kleyn, *Surf. Sci.* **198**, L335 (1988).
- ²⁸E. Spohr and M. Wolfsberg, *Chem. Phys. Lett.* **165**, 221 (1990).
- ²⁹J. W. Gadzuk, *Ann. Rev. Phys. Chem.* **39**, 395 (1988), and references therein.
- ³⁰T. Darko, D. A. Baldwin, N. Shamir, J. W. Rabalais, and P. Hochmann, *J. Chem. Phys.* **76**, 6408 (1982).
- ³¹S. Holloway, M. Karikorpi, and J. W. Gadzuk, *Nucl. Instrum. Meth. B* **27**, 37 (1987).
- ³²C. T. Rettner, *J. Chem. Phys.* **84**, 4163 (1986).
- ³³M. B. Lee, Q. Y. Yang, and S. T. Ceyer, *J. Chem. Phys.* **87**, 2724 (1987).
- ³⁴G. R. Schoofs, C. R. Arumainayagan, M. C. McMaster, and R. J. Madix, *Surf. Sci.* **215**, 1 (1989).
- ³⁵B. E. Hayden and C. L. A. Lamont, *Surf. Sci.* **243**, 31 (1991).
- ³⁶C. T. Rettner, D. J. Auerbach, and H. A. Michelsen, *J. Vac. Sci. Tech. A* **10**, 2282 (1992).