

Surface-Molecule Electron Transfer: I₂-Diamond Scattering at 1–12 eV

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(Received 12 September 1988)

We have observed surface-molecule electron transfer from the semiconductor diamond (111) surface to the iodine molecule, following hyperthermal molecular-beam scattering. The negative-ion mass spectrum was dominated by undissociated molecular ions. No positive ions were observed. The threshold kinetic energy was ≈ 3 eV and an absolute yield of $\approx 1\%$ was measured at 10-eV incident kinetic energy. The surface temperature effect on the yield was small. The ions' energy distribution was broad and the angular distribution was shifted towards the surface.

PACS numbers: 79.20.Rf, 34.50.Gb, 35.20.Wg

Hyperthermal molecular and atomic surface scattering is of considerable interest and importance as this energy range contains the thresholds for various physical and chemical phenomena.^{1–11} Electronic excitation of both the surface⁵ or the scattered molecule^{6,11} can occur.

Litvak, Gersh, and Bernstein⁷ have found alkali-ion ejection from a conventional surface ionization detector as a result of hyperthermal scattering of organic molecules. They have noted an interesting correlation between the alkali emission yield and the ionization potential of the organic molecules. Amirav and Cardillo⁴ have measured xenon-induced ion ejection from semiconductor surfaces such as InP(100), GaAs(110), and Ge(100). This phenomenon marks the onset of fast atom bombardment and secondary-ion-mass spectrometry ionization processes. Transient ionization of xenon near the surface was invoked in order to explain the ion emission.

Recently we have reported on the phenomenon of molecular dissociative ionization of 1-iodopropane following scattering from diamond. This process was characterized by an angular shift of both the collision-induced neutral atomic iodine and propyl and iodine ions.¹¹

The dissociation dynamics of molecular iodine upon scattering from sapphire (0001),² MgO(100),^{12–14} and diamond (111)¹⁵ was studied both experimentally^{1,12–15} and theoretically.^{14–16} The results could be well accounted for by the rotational predissociation mechanism following an efficient translational-rotational energy transfer.^{14,16,17} On the other hand, Gadzuk and Holloway^{18–20} have argued about the possible important role of transient charge transfer or “harpoon” processes during the molecular scattering from the surface. Basically they invoked a transient formation of negatively charged molecular iodine near the surface which when reneutralized is formed with a large amount of vibrational energy, possibly resulting in vibrational predissociation.

Electron transfer processes in medium-energy ion scattering from metallic surfaces have been measured for atomic hydrogen and oxygen,^{21,22} and recently for

molecular oxygen by Kleyn and co-workers.²³ Here we present experimental evidence for the existence of this harpoon electron transfer from the semiconductor diamond surface to the neutral iodine molecule at near-threshold energies.

Our experimental apparatus is described in detail elsewhere.¹¹ Iodine (I₂) molecules were seeded in a hydrogen or helium supersonic beam and accelerated to kinetic energy in the range of 1–10 eV.²⁴ Iodine was placed in a sampling chamber 50 mm behind the nozzle at room temperature. The nozzle was an 80- μ m thin hole in a small ruby disk mounted on a 2-mm alumina tube.²⁵ The ceramic nozzle could be differentially heated²⁵ with a heated volume of 10^{-3} cm³. Another nozzle which was used at room temperature alone was a conical nozzle. The beam was skimmed and collimated through two differentially pumped chambers into an ultrahigh-vacuum chamber (UHV) (base pressure of 5×10^{-10} Torr). The accelerated beam was either square-wave modulated for phase-sensitive detection or mechanically chopped for time-of-flight (TOF) kinetic energy measurements. In the UHV chamber the beam (3.2×1.2 mm² cross section) collided with a single-crystal diamond (111) surface (10×10 mm² exposed area). This surface was chemically treated and vacuum annealed at 850°C to give the helium diffraction shown in Ref. 11. The specular reflection was somewhat broader than our angular resolution, reflecting some surface imperfections, and we also suspect that the surface may be at least partially covered with hydrogen. Two quadrupole mass spectrometer (QMS) heads (UTI 100C) served as detectors: the first for the direct unscattered beam, and the second, which was mounted at 45° to the molecular-beam axis, for the scattered beam 2.5 cm from the surface. The QMS heads were modified for external ion collection and negative-ion detection (reversed channeltron voltage biasing). Absolute probability calibration was performed by measurement of the total ion current from the surface. The iodine flux to the UHV chamber was measured with use of an effusive beam as a calibrat-

ed flux source. The estimated uncertainty in the absolute calibration is a factor of 3. The relative precision was 20% with use of current and relative iodine flux measurements. An Auger-electron spectrometer (VG Instruments Inc. model CLAM 100 hemispherical analyzer) served for the ion energy analysis and for ion-angular-distribution measurements.

We observed the generation of a large current of negatively charged ions ($I > 10^{-9}$ A) upon scattering of hyperthermal molecular iodine on diamond. In Fig. 1 we show the mass spectrum of these ions. The dominant feature is at mass 254 of the negative molecular ion. An additional small peak of 2% at 127 amu is of atomic iodine. Based on Fig. 1 we conclude that (a) surface-molecule electron transfer occurs at hyperthermal scattering and (b) the generated I_2^- ions mostly do not dissociate. The relative I^- intensity ranges up to 3% depending on the molecular kinetic energy. Upon heating the nozzle to $\approx 650^\circ\text{C}$ the mass spectrum is totally dominated by negative atomic iodine ions (at even higher yield) on account of thermal dissociation behind the nozzle. In Fig. 2 we plot the kinetic-energy dependence of the absolute production yield of negatively charged molecular iodine versus its kinetic energy. A practical threshold of 2.8 ± 0.3 eV is observed. The kinetic energy was measured with use of TOF of the molecules to the QMS detector as I_2^- ions, and this TOF was corrected for the ion TOF from the surface by extrapolation of the ion energy to ∞ . Thus the threshold value is inherently corrected for the velocity distribution width ($\Delta v/v < 8\%$). This threshold is somewhat lower than the expected 3.5-eV threshold based on the difference between the surface work function and the molecular electron affinity. We attribute this lower threshold to surface impurities or imperfections that lower the diamond work function to ~ 5.4 eV. Another possibility exists that the diamond surface contains small graphitized islands and

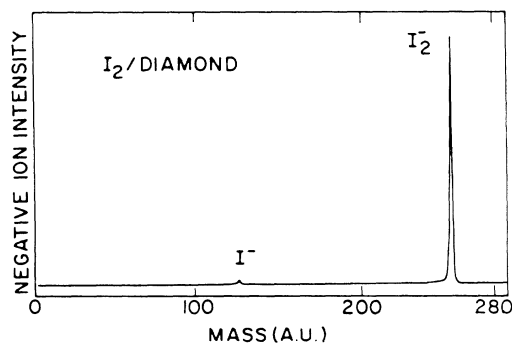


FIG. 1. Mass spectrum of negative ions formed after I_2 -diamond scattering at 8.8-eV iodine kinetic energy. Surface temperature was 380°C and the incident angle was 20° . The ceramic nozzle temperature was 220°C and the hydrogen backing pressure was 1040 Torr. Iodine sample temperature was 40°C . (Identical spectrum is obtained with use of a nozzle at room temperature.)

that these islands are responsible for the threshold behavior.

We note that we could not measure any production of positive atomic or molecular iodine and the positive mass spectrum exhibits mostly trace amount of alkali (K^+ , Na^+) ions ejected from the surface as is described in detail for other "clean" surfaces.⁴ When the surface height or position was scanned, we found that the production yield of the negative ions was negligibly small on the technical "dirty" tantalum and molybdenum metals that served as a holding support for the diamond. We believe that this observation is due to an efficient reneutralization process on these dirty metals.

In Fig. 3 we show the kinetic-energy distribution of the negative ions as measured using our Auger-energy analyzer. As expected from the existence of the image potential, the ions scattered at supraspecular angles. These angular shifts to the grazing of the surface were

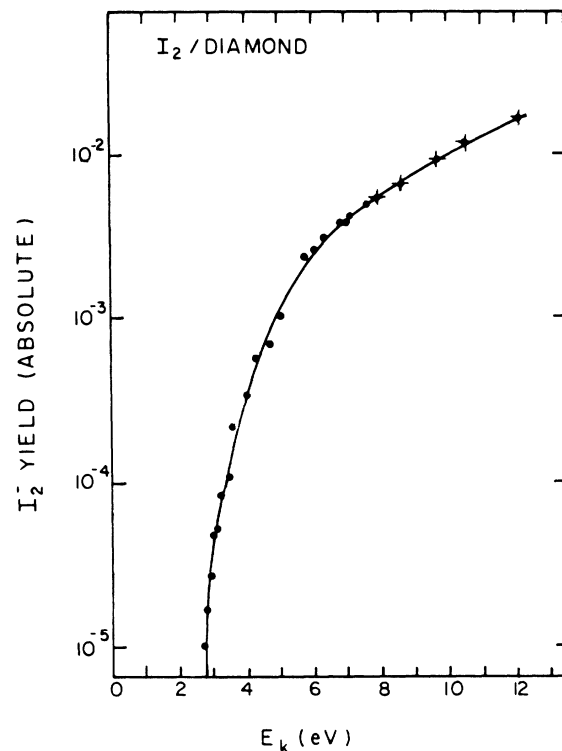


FIG. 2. Absolute I_2^- formation yield vs the average molecular iodine incident kinetic energy. The circles represent measurements using the ceramic nozzle at room temperature and hydrogen-argon gas mixture as a carrier gas at variable argon concentrations in the range 0%-12% gas mixture. The pluses represent measurements using the ceramic nozzle at variable nozzle temperature in the range 30 - 300°C , and pure hydrogen as a carrier gas. The nozzle backing pressure was ≈ 1400 Torr. Practically identical results were obtained with use of helium as a carrier gas or stainless-steel conical nozzle. The diamond surface temperature was 450°C and the incident angle was 35° .

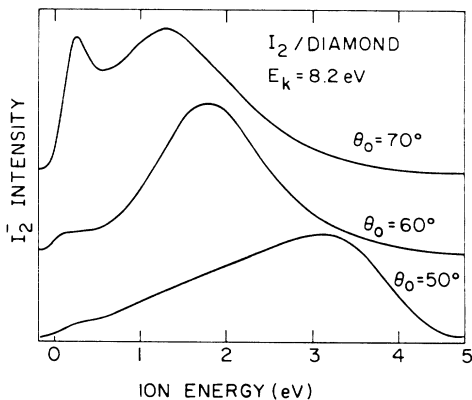


FIG. 3. Kinetic-energy distributions of the negative molecular iodine formed following I_2 -diamond scattering at 8.1-eV incident kinetic energy. The molecular-beam detector angle was fixed at 90° , the outgoing scattering angles are indicated, and the incident angles are $90^\circ - \phi_o$.

especially pronounced for ions having lower kinetic energies. The kinetic-energy distributions are broad and some ions contain almost all the initial kinetic energy minus the difference between the work function and the molecular electron affinity. However, the width of the ion kinetic-energy distribution function also reflects the involvement of the surface in kinetic-surface and/or kinetic-internal-molecular-energy transfer processes.^{1,3,11}

In this Letter we prefer to avoid any speculation about possible origins of the bimodal energy distribution function.

Finally, we note that the surface temperature effect was relatively small and the ion yield increased by less than $\approx 80\%$ over the temperature range $300\text{--}700^\circ\text{C}$ even at near-threshold energies. The electron transfer yield maximized at 0° incident angle (head-on) and decreased with ϕ_i slightly faster than $\cos^2\phi_i$, where ϕ_i is the incident angle.

The production of I_2^- proves the existence of surface-molecule electron transfer or "harpooning" as proposed for I_2 by Gadzuk and Holloway.¹⁸⁻²⁰ This phenomenon is demonstrated on a semiconductor such as diamond with an empty conduction band and a molecular system such as iodine at near-threshold energies.

An important issue that should be addressed concerns the relationship between the production of I_2^- and the relative importance of the proposed harpoon mechanism¹⁸⁻²⁰ versus the rotational-induced dissociation mechanism,^{14,16,17} as a dominant mechanism in the collision-induced dissociation of iodine on diamond.¹⁵ This dissociation process was observed by us to be even more efficient on diamond than on MgO .¹²⁻¹⁴ The mass spectrum shown in Fig. 1 does not preclude the role of harpooning, as atomic iodine, if formed near the surface, has less than half the molecular kinetic energy and thus is expected to be efficiently reneutralized if it forms a negative ion near the surface. However, based on our

Fig. 3 and on our results on 1-iodopropane,¹¹ one expects an angular shift of the atomic iodine if formed after neutralization of negative molecular iodine near the surface because of the combination of image potential and energy transfer. Our observed atomic iodine angular distribution was broad but specular, which gives more weight to the role of the rotational mechanism. It is possible that our observed current of I_2^- may actually represent the total electron transfer probability which is small both in production and in neutralization. Accordingly most ions formed remain charged if formed far enough from the threshold to allow some energy transfer and in this way one can rationalize the curvature in Fig. 2. However, although in I_2 the rotational mechanism is very efficient,^{14,16,17} in polyatomic systems it does not exist and surface-molecule electron transfer processes are of extreme importance.²⁶ These processes can lead to a nonstatistical dissociative ionization as demonstrated in 1-iodopropane.¹¹ We have found kinetic-energy-induced electron transfer in both molecule-surface and surface-molecule processes, with and without dissociation, in over thirty molecules.²⁶ Definitely the proposed harpoon mechanism is of large importance in these ionization processes²⁶ as well as in ion ejection.^{4,7}

We have enjoyed enlightening discussions with Professor W. J. Gadzuk and Professor R. B. Gerber. This work was supported by the U.S.-Israel Binational Science Foundation Grant No. 86-00054 and by the Petroleum Research Fund Grant No. 19307-AC5,6.

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