Surface scattering of C_{60}^+: Recoil velocities and yield of C_{60}

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In the impact of a C_{60}^+ beam against solid surfaces, a substantial fraction of the beam is neutralized. By means of a pulsed photoionization experiment, we have detected the neutralized scatterers from a silicon (100) surface, and found that they are mainly intact C_{60}, with little or no fragmentation at impact energies to 200 eV. The neutralization probability is found to increase monotonically with increasing impact energy. This reionization method has been used in a time-of-flight scheme to measure the recoil velocity distributions of scattered C_{60}. Collisions at impact energies above 50 eV are found to be highly inelastic, and the normal recoil distribution changes very little with impact energy over the range from 50 to 200 eV. The peak in the velocity distribution is near 1150 m/s ($\sim$5 eV), with a full width at half-maximum (FWHM) of 350 m/s. By comparison with molecular dynamics simulations, an interpretation of this speed is proposed in terms of a limit to reversible deformation of the fullerene cage. A model of the scattering kinematics, based on treating the fullerene cage as a deformable, hollow sphere, with a harmonic deformation limit (15 eV) as found by theory, predicts the observed speed quantitatively.

I. INTRODUCTION

The recent developments of methods for isolating[1] and purifying[2] macroscopic quantities of C_{60}, C_{70}, and selected higher fullerenes, transferred for the first time a cluster from the high-vacuum and molecular-beam environment into a molecular powder available in gram quantities. This immediately triggered an explosion of experimental and theoretical activities. Particular attention has been focused recently on problems related to surface interactions of fullerenes, their stability in surface collisions,[3] the energetics and dynamics during the collision event,[4,5] and charge-transfer processes[6] as a function of impact energy.

Although a large number of studies on atomic–ion collisions at high collision energies (keV) with a great variety of surfaces exist, only very few have been carried out at lower energies (1–500 eV), and even fewer with molecular projectiles. Furthermore, studies of molecular–ion collisions with surfaces generally focus on fragmentation.[7] The extraordinary resilience and stability of the fullerene molecules coupled with an intense laser-desorption source and a time-of-flight ion-beam surface scattering machine has made it possible to address the question of nondestructive low-energy surface collisions experimentally.

A major difference between molecule–surface collisions and atom–surface collisions is that vibrational excitation opens as a new channel where impact energy can be transferred.[8] Generally this leads to extensive fragmentation. However in the case of C_{60} colliding with a Si(100) Beck *et al.*[3] found no evidence for impact-induced fragmentation at collision energies up to 250 eV.[9] Recently, clear evidence for fragmentation upon surface impact has been reported at energies above 275 eV.[10,11] This surprising result can be explained partly by the structural resilience, with respect to cage-opening processes, found in molecular dynamics (MD) simulations of C_{60} collisions with a hydrogen-terminated diamond (111) surface.[5] Experimentally, the collision process was found to be highly inelastic in the normal as well as in the parallel velocity component.[3] Furthermore, <10% of the incident positive ions were found to be returned in the scattered ion channel. This overall low yield of scattered ions was attributed to neutralization[3,6] and the decrease at higher impact energies to sticking and implantation[12] during the collision event.

In the reionization experiment described below on neutralized and scattered positive molecules, we have (i) measured the velocity distribution of C_{60} scattered from a silicon surface at the incident energies 50, 100, 150, and 200 eV; (ii) extended our previous results on the remarkable resilience of scattered C_{60} ions to the neutrals; and (iii) successfully confirmed the relevance of collision induced neutralization to explain the strong decrease in the scattered ion channel.

II. EXPERIMENTAL METHODS

The methods we have used here include laser-desorption into a supersonic gas jet to obtain an intense cold ion beam, time-of-flight ion beam mass-selection, surface-scattering time-of-flight measurements, and pulsed reionization of the neutralized scatterers. All of these have been described previously in other articles,[13] with the exception of the reionization method, which is introduced below.

A. Ion source

A 3 mm diam steel rod is coated with pure C_{60} and placed in a short nozzle assembly that is mounted in a high vacuum chamber. The assembly is fixed on the faceplate of a pulsed gas valve. The rod is continuously rotated ($\frac{1}{2}$ turn/min) and translated ($\sim$10 mm/h) in order to continually

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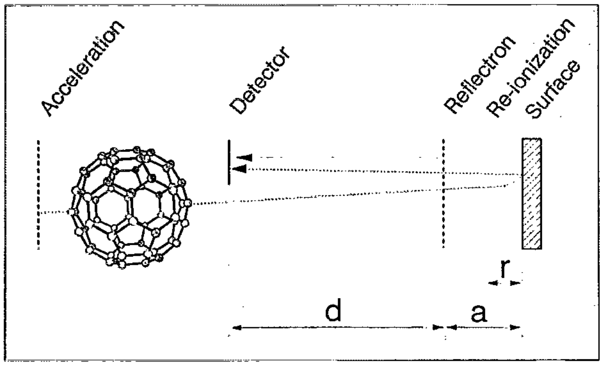

FIG. 1. Schematic representation of the pulsed reionization experiment for surface impact/neutralized C_{60}. Charged C_{60}^{+} ions, coming from a He-seeded laser desorption source are extracted perpendicular to the molecular beam axis by a pulsed field toward the surface. At a, entering the retarding field of the reflectron, they are slowed down to a controlled impact energy and collide with the Si(100) surface. Scattered ions are accelerated in the same field toward the detector. A significant fraction of the incident ion beam is neutralized at the surface and rebounds as neutral $C_{60}^{(0)}$. At a fixed distance r from the surface but a variable time delay with respect to the impact, the neutral $C_{60}^{(0)}$ is reionized with the pulsed output of an ArF excimer laser (193 nm) and accelerated over the remaining reflectron field region $a-r$. Given the applied potential on the surface U_0, the distances a and d, the arrival times of the scattered ions t_{ion}, and reionized $C_{60}^{(0)}$ molecules t_n, as well as the reionization time t_r, the velocity of the scattered/neutralized C_{60} between impact and reionization can be calculated. Varying the reionization delay and monitoring the intensity of the reionized C_{60}, the velocity distribution for this specific impact energy is measured.

expose fresh surface to the laser. The lightly focused fourth harmonic radiation from a Nd:YAG laser (266 nm; <1 mJ/pulse on a 1 mm^2 area) was used for desorption. The laser, fired into the 10 bar helium gas pulse, desorbs charged and neutral molecules. These are swept along by the helium pulse as the jet expands through a 0.5 mm valve orifice into vacuum. After passing the skimmer, the beam enters the ion-extraction region of a reflectron time-of-flight mass spectrometer.

B. Ion beam

The charged molecules are extracted perpendicular to the helium beam by a two-stage Wiley–McLaren-type pulsed high-voltage extraction field, focused by an einzel lens and mass selected in a high resolution temporal mass gate. After 35 cm of free flight the monodisperse C_{60}^{+} beam enters a 1.4 cm decelerating field where it is retarded to the desired momentum of impact before collision with the surface, as shown schematically in Fig. 1. The surface is heated in vacuum to drive off molecular adsorbates; however the scattering results reported here are from the native-oxide passivation layer.[14] The scattered, charged particles are accelerated in the same field toward the detector. Further details on the ion-beam scattering experiment can be found in Refs. 3 and 13.

C. Reionization of neutralized scatterers

The fraction of the ion-beam that is neutralized in the collision is not accelerated toward the detector following impact. In order to detect the neutralized C_{60}, the pulsed output of an ArF excimer laser (~15 ns, 193 nm, 6.4 eV), focused by a 30 cm cylindrical lens to a line parallel to the surface within the retarding field region, is fired shortly after the ion beam has collided with the surface. The delay between impact and the laser pulse is long enough to separate ions and neutrals completely. At this wavelength, resonant two-photon ionization of fullerenes is very efficient,[15] making it possible to detect all the scattered molecules within this well defined spatial region. By varying the delay of the ionizing laser while keeping the distance from the surface fixed, one can determine the surface-normal component of the velocity distribution of the reionized neutral C_{60} molecules.

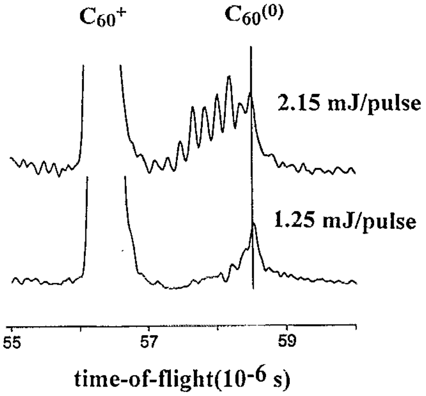

FIG. 2. Fluence dependence of the reionized C_{60} signal at 150 eV impact energy. To reionize $C_{60}^{(0)}$ with our ArF (193 nm) radiation, at least two photons are required. At high laser fluence multiphoton ionization processes lead to important internal excitation and subsequent fragmentation of the molecule (a). Lowering the fluence from 2.15 mJ/pulse (a) to 1.25 mJ/pulse (b) makes a multiphoton absorption/fragmentation event less efficient, compared to the two-photon ionization.

Since the scattering apparatus has been designed to achieve low energy spread in the primary beam (5–10 eV at 1700 V extraction potential) and high collection efficiency, if operated at a high extraction potential (1400–2000 V coupled with a large acceptance angle of the detector, ±6°), only very limited angular resolution can be expected. Therefore, no attempt has been made to determine the distribution of the rebound velocity component parallel to the surface, e.g., by spatially resolving the third perpendicular component of the scattering spatial distribution. This is left to a subsequent work. The diameter of the impinging C_{60}^{+} beam on the surface has been measured with a fluorescence screen to be ~5 mm.

III. RESULTS AND ANALYSIS

Figure 2 shows a typical fluence-dependence in the reionized C_{60} channel. Since irradiation of C_{60} with ArF-radiation (6.4 eV) may deposit more than the required two photons [IP (C_{60})$=7.6\pm0.1$ eV (Ref. 16)], a large amount of excess energy is potentially deposited in the reionized C_{60}-molecule, resulting in multiphoton induced fragmentation. If the fragments in Figs. 2(a) and 2(b) are due to the reionization process, rather than impact induced fragmentation, a reduction in fluence should reduce the

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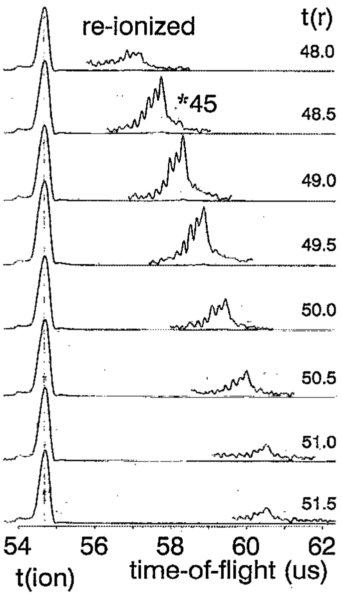

FIG. 3. Time-of-flight data at 200 eV impact energy. Varying the reionization time t_r, the arrival time t_n, and intensity of the reionized $C_{60}^{(0)}$ changes. t_{ion} is the arrival time of the scattered ions.

fragment intensities more strongly than the parent C_{60} intensity. The fragmentation pattern of Fig. 2 clearly supports this interpretation. We find no definite evidence for fragmentation of scattered C_{60} on a 10^{-6} s time scale, at energies to 200 eV. This extends the earlier finding on the outstanding resilience of scattered C_{60} ions to the neutrals.

The reionization spatial region is rather small and the efficiency may be less than unity even at high fluences. Therefore it is not possible to determine the *absolute* probability of neutralization-scattering. However, a rough estimate is consistent with the idea that the entire incoming beam is scattered either as neutrals or as ions in this impact energy range. We have assessed the changes in the relative probability of neutralization by comparing the number of reionized particles detected with the scattered ion beam intensity, and find that it increases monotonically over the range 50–200 eV (see relative intensities in Fig. 4).

The velocity distribution of the scattered/neutralized C_{60} was measured as shown in Fig. 3 by observing the abundance of reionized neutrals as a function of the time delay between surface impact and reionization while keeping the distance of the laser focus from the surface fixed. Given the applied potentials and the geometry of the apparatus, one can convert these time-of-flight data into velocities of the neutrals between impact and reionization. This is done by using measured flight times and calculating separately the distance from the surface to the reionization spot and the flight time between these points.

The position of the reionization spot could be measured directly. However, a much more precise measurement can be made using the time interval, t_1, between the laser pulse and the detection time. Assuming that the velocity of the neutralized molecule emerging from the surface is small compared with the beam velocity of 1.5 keV (verified *a posteriori)*, this time can be expressed as a sum of the time spent in the field, and the free flight time in the following way (see Fig. 1 for notation):

$$t_1=\left[\frac{2a(a-r)m}{qU_0}\right]^{1/2}+d\left\{\frac{2[1-(r/a)]qU_0}{m}\right\}^{-1/2}$$
$$=a\left(\frac{m}{qU_0}\right)^{1/2}\left\{\left[2\left(1-\frac{r}{a}\right)\right]^{1/2}+\left(\frac{d}{a}\right)\left[2\left(1-\frac{r}{a}\right)\right]^{-1/2}\right\}.$$

Solving for $(1-r/a)$ gives the desired distance $(a-r)$.

Since only a fraction of the molecules are neutralized on the surface, the spectrum thus contains two peaks, one from the molecules that neutralize on the surface and are ionized later, and one from the molecules that do not neutralize. The time from surface impact to ionization can be found using the difference in detection time between these two peaks. This procedure cancels the time-of-flight from the source to the collision with the surface. For the neutralized and reionized molecules, the time from surface impact to detection is

$$t_n=t+t_1,$$

where t is the desired time (i.e., the time from surface impact to reionization) and t_1 is the measured time between reionization and detection. For the ions this time is

$$t_{\mathrm{ions}}=(2a+d)\sqrt{\frac{m}{2qU_0}};$$

The observed difference (t_n-t_{ions}) then gives t in terms of known quantities.

Calculating for each reionization time the corresponding velocity $v=r/t$ and correcting for the time-to-velocity transformation (Jacobian), one obtains the velocity distribution for a specific collision energy. Figure 4 shows velocity distributions for four different collision energies and two different reionization distances from the surface. Not shown are a series of velocity distributions for constant impact energy (50 eV) but varying distance from the surface (3.6, 3.8, 4.1, and 5.1 mm). Apart from a decrease in signal intensity with increasing distance from the surface, the distributions were identical within experimental precision.

IV. DISCUSSION

In C_{60}^{+} surface collision experiments, no more than 10% of the incoming beam intensity is recovered in the positively charged scattered channel. Among other possible explanations, an increasing neutralization efficiency with impact energy has been shown to be an important process to account for this intensity loss.

Previous surface scattering investigations of Beck *et al.*[3] revealed a highly inelastic surface collision of C_{60}, a large fraction of the entire perpendicular momentum component being lost as well as 60±20% of its parallel component. To progress to a more detailed understanding of the energetics and dynamics of the collision event, the dis-

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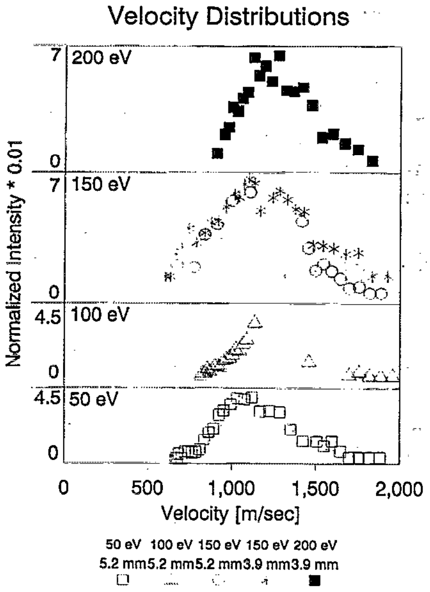

FIG. 4. Velocity distributions of Si(100)-surface scattered/neutralized $C_{60}^{(0)}$ for two different reionization distances from the surface and four different impact energies. The intensities are normalized with respect to incident ion-beam fluctuations by dividing the reionized $C_{60}^{(0)}$ signal intensity by the scattered ion intensity.

tribution of the normal component of the rebound velocities as well as its dependence on the impact energy will now be discussed.

The most prominent feature of the velocity distributions in Fig. 4 is the near-independence of the impact energy, *within the experimental precision of ±100 m/s.* All velocity distributions for impact energies ranging from 50 to 200 eV show a maximum of the scattered intensity distribution between 1100 and 1200 m/s with a full-width at half-maximum (FWHM) of ~350 m/s. This observation is in qualitative agreement with results of Busmann *et al.* for C_{60} scattering from graphite at impact energies from 140 to 450 eV,[11] although they deduced a somewhat higher value for the recoil energy (~40% higher velocity).

Molecular dynamics simulations by Mowrey and coworkers of C_{60} colliding with a hydrogen terminated diamond (111) surface[5] at 100–200 eV show a very strong deformation of C_{60} during the collision event and an impressive resilience of the bonding network, but predict a much larger recoil velocity (50% of the impact velocity), and one which scales approximately with impact energy. This behavior is in clear disagreement with what is found here for C_{60}^{+} scattering from silicon.

Recent molecular dynamics simulations of the compression of C_{60} between graphite planes,[4] using empirical many-body potentials, provide important information towards an interpretation of our results. Brenner and coworkers[4] studied the energetics of a C_{60} molecule, as it is compressed between graphite planes. Calculating the restoring force as a function of the compression (see Fig. 2, Ref. 4), they found that C_{60} can be reversibly and nearly harmonically compressed to a diameter that is $\frac{2}{3}$ of the uncompressed molecule (from just under 7 Å in diameter to near 4.5 Å), i.e., the restoring force increase almost linearly throughout this compression. The increase in the potential energy of the molecule at this compression is calculated to be ~15 eV relative to the relaxed C_{60} molecule. Further compression results in a distinct drop of the restoring force, which corresponds to a reversible change of the molecule to a disklike structure. At further compression an increase is again observed.

Combining these experimental and theoretical results, we would suggest the following simple picture of the C_{60}/surface-collision event. As the molecule collides with the surface, 15 eV of the impact energy is consumed to deform the C_{60} molecule harmonically from spherical shape to $\frac{2}{3}$ of its original diameter. Any additional impact energy will deform the molecule into the strongly anharmonic part of the potential curve. It is conjectured that this later stage of deformation will result in strong energy dissipation by way of a strong coupling between the deformation and other vibrational degrees of freedom. Upon rebound, the energy dissipation is effective until the molecule again reaches the harmonic part of the potential curve. At this point the potential energy stored in the harmonic deformation is again ~15 eV. On further expansion, the harmonic potential energy of 15 eV is released partly into a single vibrational motion involving the whole molecule, and partly into translational kinetic energy.

An estimate of this branching ratio has been obtained by assuming that only the quadrupole component of the deformation carries weight, and by approximating the molecule by a spherical shell with constant surface area. In this case, the molecule leaves the surface when the spherical shape is attained, where the deformation energy is converted completely into kinetic energy. In the limit of small quadrupole deformations from spherical symmetry, and assuming the surface area is conserved during deformation, it can be shown (see Appendix) that the ratio of translational energy to the total kinetic energy (translation +quadrupole vibration) at the point where the molecule leaves the surface is 1:3. Taking Brenner *et al.*'s value of 15 eV as the limit, this yields a maximum rebound energy near 5 eV, or a velocity of ~1200 m/s, very close to the experimentally determined mean velocity.

In conclusion, we have succeeded in a laser reionization experiment to detect the scattered neutrals and found that only $C_{60}^{(0)}$ is returned. By measuring the velocity distributions of scattered/neutralized $C_{60}^{(0)}$ we found that they are independent of the impact energy in the range from 50 to 200 eV. Referring to MD simulations of Brenner *et al.*,[4] a simple model to explain the limited elasticity of C_{60}/surface impact has been proposed. This model suggests that larger fullerenes might be capable of storing greater energy for subsequent recoil, and we have verified this prediction in subsequent work, in which we have measured by a different method with increased intensity and resolution the velocity distributions of scattered fullerene *ions.*[17]

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APPENDIX: ENERGY PARTITIONING IN THE RECOIL OF A DEFORMABLE HOLLOW SPHERE

A near-spherical ellipsoid with surface area $4\pi r_0^2$ has one axis of length

$$r_\perp = r_0 + \tfrac{2}{3}\delta_r$$

and two with the length

$$r_\parallel = r_0 - \tfrac{1}{3}\delta_r$$

(where $\delta r = r_\perp - r_\parallel$). In the center of mass (CM) and zero deformation a point on the surface has the velocity

$$v_\perp = \frac{d\delta r}{dt}\frac{2}{3}\cos\theta,$$

$$v_\parallel = \frac{d\delta r}{dt}\frac{1}{3}\sin\theta,$$

where θ is the angle between the line perpendicular to the surface through the CM and the line from the CM to the point under consideration. Since the molecule leaves the surface at zero deformation, the translational velocity is

$$v_{\mathrm{CM}_\perp} = v_0 = \frac{2}{3}\frac{d\delta r}{dt}$$

which gives a translational energy of

$$E_{\mathrm{trans}} = \frac{m}{2}v_0^2.$$

Since the energy is purely kinetic at this point, the total (translational and vibrational) energy can be found by integrating the kinetic energy over the shell

$$E_{\mathrm{tot}} = \frac{m}{2}\int_0^\pi d\theta \cdot \sin\theta [v_0^2(1+\cos\theta)^2 + v_0^2(\tfrac{1}{2}\sin\theta)]^2$$
$$= 3\left(\frac{m}{2}v_0^2\right) = 3E_{\mathrm{trans}}.$$

This corresponds to a partitioning between translational to quadrupole vibration energy of 1:2.

This model predicts a linear decrease in rebound energy when the collision energy is reduced below 15 eV. Unfortunately the energetic resolution of our apparatus does not allow us to investigate this domain with sufficient precision. [At very low collision energies (a few eV), the attraction between the surface and the molecule could change this prediction of a linear behavior.]

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