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Photon, Electron, and Secondary Ion Emission from Single C_{60} keV Impacts

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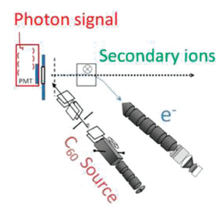
ABSTRACT This Letter presents the first observation of coincidental emission of photons, electrons, and secondary ions from individual C_{60} keV impacts. An increase in photon, electron, and secondary ion yields is observed as a function of C_{60} projectile energy. The effect of target structure/composition on photon and electron emissions at the nanometer level is shown for a CsI target. The time-resolved photon emission may be characterized by a fast component emission in the UV−Vis range with a short decay time, while the electron and secondary ion emission follow a Poisson distribution.



SECTION Dynamics, Clusters, Excited States

The use of cluster bombardment (e.g., C_{60} and Au_{400}) for surface analysis and characterization has shown significant advantages due to enhanced emission of molecular ions, low damage cross section, and reduced molecular fragmentation.[1−3] Although a large number of practical applications have been envisioned,[4−6] the underlying physical processes that govern the cluster−target interaction remain to be elucidated. A few reports on secondary ion (SI) emissions from C_{60} keV impacts for a variety of targets and experimental conditions (e.g., projectile energy and incidence angle) can be found in the literature.[7−11] We have previously shown the benefits of studying the projectile−target interaction of temporally and spatially discrete ion impacts.[12,13] In particular, the inspection of co-emitted photons, electrons, and SIs from single impact sites should be most informative.[14] Studies on electron emission from individual C_{60} keV impacts are sparse;[15,16] recently, we reported the effect of surface composition and topography on the number of emitted electrons.[17,18] Although several explanations have been proposed to describe the unexpected electron emission under massive cluster impacts,[19,20] the electron emission mechanism remains a subject of investigation. While photon emission from surfaces exposed to ion bombardment is well-documented,[21,22] little is known about the photon emission from individual cluster impacts. We have recently reported the first evidence of photon emission from individual impacts of massive gold projectiles for several projectile−target combinations.[23] In this Letter, we report the first experimental observation of co-emitted photons, electrons, and SIs from individual C_{60} keV projectile impacts. Time-resolved photon spectra, electron, and SI distributions were measured as a function of the impact C_{60} energy.

An experimental setup that comprises a C_{60} primary cluster beam, an electron emission microscope, and a ToF mass spectrometer was used for this study.[17,18,23] Emitted photons, electrons, and SIs were collected per projectile impact. Photons were detected using a photomultiplier (PMT, R4220P model from Hamamatsu Photonics), with an active window from 185 to 710 nm and a maximum 22% detection efficiency at 410 nm and positioned behind the target (solid angle of 0.6 π sr). Electrons emitted from the impact site were accelerated and then deflected using a weak magnetic field toward an electron emission microscope where the initial signal was amplified (×100) and later detected using a position-sensitive detector (more details in ref 17). The ToF signals of the SIs were collected using a microchannel-plate based detector positioned ∼100 cm from the target surface and were stored in a multichannel time-to-digital converter (TDC). The photon signal from individual impacts was time-delayed and stored on one of the TDC channels. Cesium iodide powder was obtained from Sigma Aldrich (St. Louis, MO) and used as received. Surface target homogeneity was achieved by using a vapor deposition technique. All samples were deposited onto a 70−100 Ω/sq indium tin oxide coated glass (ITO/glass) substrate from Sigma Aldrich (St. Louis, MO).

Photon emission was detected from single C_{60} impacts on a CsI target. A linear increase in photon emission was observed with C_{60} projectile energy (Figure 1 inset). The time-resolved photon spectrum can be characterized by a narrow peak distribution (∼2 ns at fwhm) with a short decay time (Figure 1). Photon emissions from CsI targets under mono- and polyatomic projectile impacts have been previously reported.[12,13] In general, light emission from CsI crystals after electronic excitation comprises a photon electron emission at (i) 310−320 nm with a short decay time (∼16 ns) due to interatomic transitions, which represents 70% of the observed light,

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and (ii) 500 nm with a larger decay time (> 1 μs) associated with defects on the crystal.[24] During cluster impacts, a different mechanism of energy transfer/deposition into the solid occurs, mainly because of a different ionization density and path length. In the energy range studied here, we can associate the two-component peak distribution of the fast photon emission to the structure/composition of the CsI polycrystalline surface. Previous investigations have shown fast photon emission with a strong dependence on the CsI target preparation methods (e.g., the observation of multiple fast components with 0.7−2, 6−10, and 28−36 ns decay times).[24−27] Photon emissions from atomic and polyatomic projectiles have shown a long tail distribution with a 7−8 ns lifetime from CsI targets related to the collision cascade mode of interaction.[23] A single-component, fast photon emission has been observed under massive gold projectile impacts ($Au_{100-400}$) from the same target associated to projectile coherent motion.[23] In the case of C_{60}, we attribute the two fast components to the hollow nature of the projectile, which dissociates after penetrating a few layers and induces collision cascades involving projectile constituents and surface target atoms.

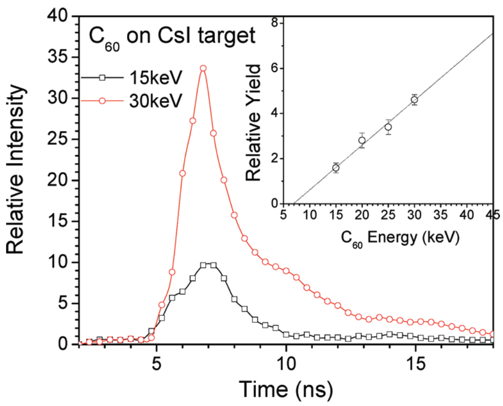

Figure 1. Time-resolved photon emission spectra from individual C_{60} impacts on a CsI target. In the inset, photon yield dependence on the C_{60} impact energy.

A number of SIs per impact were observed in coincidence with the emitted photons. The number of SIs per impact follows a Poisson distribution, where the mean value increases with the C_{60} impact energy (Figure 2a). The negative SI spectra are characterized by a high abundant cluster ion emission of the form $(CsI)_{n=0-12}I^-$. In the low mass region (m/z < 100), some other peaks were observed (full spectra in Supporting Information). For example, the presence of H^- and OH^- peaks is likely a result of water molecules and hydrogen atoms adsorbed to the surface, and the presence of $C_{n=2-4}H^-$ peaks may be a result of pump oil and carbon contamination on the surface. The $(CsI)_{n=0-12}I^-$ cluster ion yield Y can be described as $Y \propto a\exp(-kn)$, where k = 1.1 and 0.7 for n < 5 and n > 6, respectively (Figure 2b and spectra in the Supporting Information). Parameters a and k are directly related to target material and projectile characteristics (particularly on its charge state, velocity, incidence angle, mass, and molecular structure). In the case of atomic ion bombardment, an exponential coefficient k dependence on the cluster size has also been observed and has been attributed to the SI formation/fragmentation mechanism.[28] For cluster ion bombardment, besides the exponential dependence on the cluster size, a power law yield dependence on the cluster size has also been proposed ($Y \approx n^b$), where the power coefficient b is determined by the SI emission volume.[29] A similar trend is observed in the case of single C_{60} projectile impacts on the CsI target in the energy range studied here.

Multielectron emission was observed under single C_{60} projectile impacts on CsI targets, below the kinetic emission threshold for electron emission observed for atomic ions.[19] In particular, two main electron distributions (PE1 and PE2) following a Poisson distribution were observed (Figure 3). Mean values of the electron distributions (γ_e) are related as 1:2, where the PE1 and PE2 distributions account for 70−80 and 20−30% of the total number of electrons emitted per impact, respectively. The mean values of the electron distribution increase linearly with C_{60} impact energy (see inset of Figure 3). Electron distributions from atomic ion bombardment have also shown a Poisson-like distribution,[30,31] which

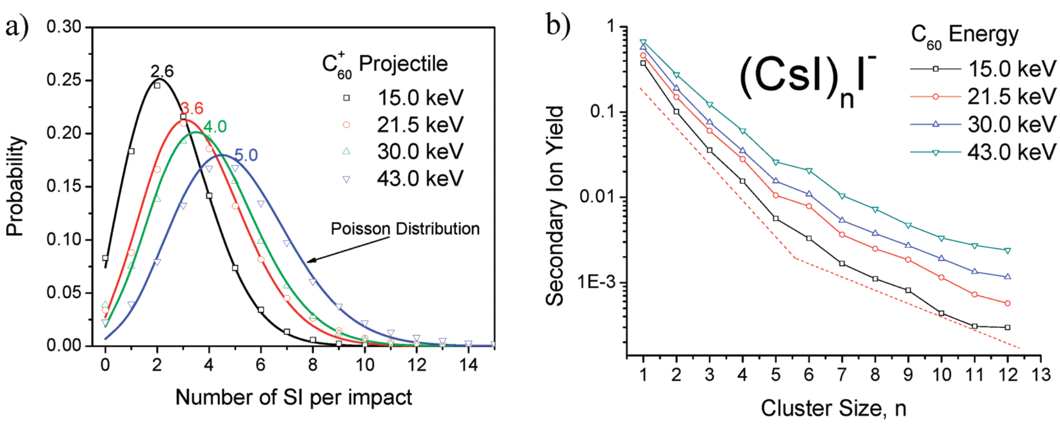

Figure 2. (a) SI distributions from individual C_{60} impacts on CsI at different C_{60} impact energies. Notice that the experimental data follow a Poisson distribution where the mean value increases as a function of the C_{60} impact energy. (b) $(CsI)_nI^-$ cluster ion yield as a function of the cluster size at different C_{60} impact energies.

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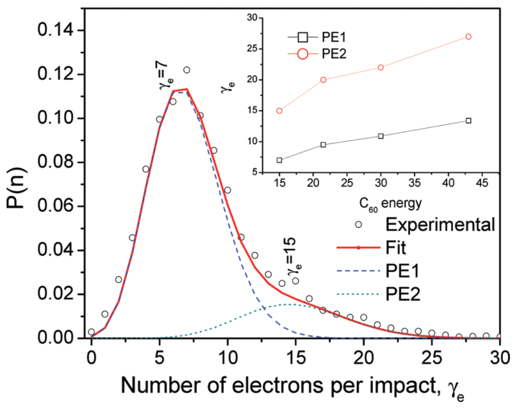

Figure 3. Electron probability distributions from individual 15.0 keV C_{60} impacts on a CsI target. The experimental data follow the sum of two Poisson distributions (PE1 and PE2). In the inset, notice the increment of the mean values γ_e as a function of the C_{60} impact energy. Experimental values are not corrected for detection efficiency.

has been attributed to the stochastic nature of the particle emission during ion bombardment.[14] Recent experiments using individual C_{60} impacts have shown mainly a single electron distribution, where the mean value of the distribution varies as a function of target composition and morphology.[17,18]

The analysis of the number of electrons emitted with a specific ion (e.g., H^-, OH^-, $C_{n=2-4}H^-$, and $(CsI)_nI^-$) showed that there is no specific electron distribution associated with them (PE1 or PE2), that is, the electron distribution associated with individual ions showed the same two-component electron distribution (PE1 and PE2) as that observed with the total SI signal (see Supporting Information). The same result was observed when the analysis was made with the coincidental emission of two SI signals (e.g., H^- and OH^-, CH^- and C_2H^-, and I^- and $(CsI)I^-$). On the other hand, the inspection of the SI spectra that correspond to the electron distributions PE1 and PE2 showed differences in the H^-, OH^-, and $(CsI)_nI^-$ ion yields (see Supporting Information). The larger number of electrons emitted per impact (PE1) is accompanied by a larger emission of SIs. Thus, we infer the two Poisson distributions as a consequence of the structure/composition of the CsI surface. The dependence of the number of emitted electrons with the CsI surface characteristics is in good agreement with previously reported measurements.[16,32]

The analysis of individual C_{60} keV impacts on a CsI surface has shown the stochastic nature of the co-emission of photons, electrons, and SIs from a nanometric size emission volume. Inspection of the photon and electron emissions shows that the emission profiles are correlated with the target structure/composition at the nanometer level, with the particularity that co-emitted photons, electrons, and SI pairs can be used as indicators of the surface content and homogeneity. The Poissonian SI distribution suggests that the measured ions represent a small percent of the total number of desorbed particles, in good agreement with previous experiments with massive gold cluster bombardment.[33] We interpret the Poisson form of the electron distribution as a consequence of a small number of electrons emitted from the excited impact site, which can be related to the electron escape and detection probability. Projectile energy dependence on photons, electrons, and SIs yields suggests that higher-energy cluster projectiles are promising candidates as nanometric probes of the target structure, composition, and homogeneity. Further experiments with higher-energy cluster projectiles should permit a better description of photon wavelengths and their relationship with target characteristics. Moreover, characteristics of the projectile−target interaction can be extracted from the photon emission.

SUPPORTING INFORMATION AVAILABLE Total secondary ion spectra, coincidental single and dual ion spectra with the electron distribution, and emitted electron distributions at different C_{60} impact energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Tempez, A.; Schultz, J. A.; Della-Negra, S.; Depauw, J.; Jacquet, D.; Novikov, A.; Lebeyec, Y.; Pautrat, M.; Caroff, M.; Ugarov, M.; et al. Orthogonal Time-of-Flight Secondary Ion Mass Spectrometric Analysis of Peptides Using Large Gold Clusters As Primary Ions. *Rapid Commun. Mass Spectrom.* **2004,** *18*, 371–376.
(2) Winograd, N.; Postawa, Z.; Cheng, J.; Skazal, C.; Kozole, J.; Garrison, B. J. Improvements in SIMS Continue: Is the End in Sight? *Appl. Surf. Sci.* **2006,** *252*, 6836–6843.
(3) Verkhoturov, S. V.; Rickman, R. D.; Guillermier, C.; Hager, G. J.; Locklear, J. E.; Schweikert, E. A. Molecular Ion Emission from Single Large Cluster Impacts. *Appl. Surf. Sc.* **2006,** *252*, 6490–6493.
(4) Winograd, N. The Magic of Cluster SIMS. *Anal. Chem.* **2005,** *77*, 142A–149A.
(5) Cheng, J.; Wucher, A.; Winograd, N. Molecular Depth Profiling with Cluster Beams. *J. Phys. Chem. B* **2006,** *110*, 8329–8336.
(6) Pacholski, M. L.; Winograd, N. Imaging with Mass Spectrometry. *Chem. Rev.* **1999,** *99*, 2977–3005.
(7) Russo, M. F.; Szakal, C.; Kozole, J.; Winograd, N.; Garrison, B. J. Sputtering Yields for C_{60} and Au_3 Bombardment of Water Ice as a Function of Incident Kinetic Energy. *Anal. Chem.* **2007,** *79*, 4493–4498.
(8) Kozole, J.; Willingham, D.; Winograd, N. The Effect of Incident Angle on the $C_{60}{}^+$ Bombardment of Molecular Solids. *Appl. Surf. Sci.* **2008,** *255*, 1068–1070.
(9) Van Stipdonk, M. J.; Harris, R. D.; Schweikert, E. A. A Comparison of Desorption Yields from $C_{60}{}^+$ to Atomic and Polyatomic Projectiles at keV Energies. *Rapid Commun. Mass Spectrom.* **1996,** *10*, 1987–1991.
(10) Harris, R. D.; Baker, W. S.; Van Stipdonk, M. J.; Crooks, R. M.; Schweikert, E. A. Secondary Ion Yields Produced by keV Atomic and Polyatomic Ion Impacts on a Self-Assembled Monolayer Surface. *Rapid Commun. Mass Spectrom.* **1999,** *13*, 1374–1380.

(11) Harris, R. D.; Van Stipdonk, N. J.; Schweikert, E. A. keV Cluster Impacts: Prospects for Cluster-SIMS. *Int. J. Mass Spectrom. Ion Processes* **1998,** *174*, 167–177.
(12) Baudin, K.; Parilis, E. S.; Blankenship, J. F.; Van Stipdonk, M. J.; Schweikert, E. A. Sublinear Effect in Light Emission from Cesium Iodide Bombarded by keV Polyatomic Projectiles. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1998,** *134*, 352–359.
(13) Kaercher, R. G.; da Silveira, E. F.; Blankenship, J. F.; Schweikert, E. A. Solid-State Luminescence: Probe for Ion—Solid Interactions. *Phys. Rev. B* **1995,** *51*, 7373–7376.
(14) da Silveira, E. F.; Duarte, S. B.; Schweikert, E. A. Multiplicity Analysis: A Study of Secondary Particle Distribution and Correlation. *Surf. Sci.* **1998,** *408*, 28–42.
(15) Aumayr, F.; Betz, G.; Mark, T. D.; Scheier, P.; Winter, H. P. Electron Emission from a Clean Gold Surface Bombarded by Slow Multiply Charged Fullerenes. *Int. J. Mass Spectrom.* **1998,** *174*, 317–328.
(16) Brunelle, A.; Chaurand, P.; Della-Negra, S.; Beyec, Y. L.; Parilis, E. Secondary Electron Emission Yields from a CsI Surface Under Impacts of Large Molecules at Low Velocities ($5 \times 10^3 - 7 \times 10^4$ ms^{-1}). *Rapid Commun. Mass Spectrom.* **1997,** *11*, 353–362.
(17) Verkhoturov, S. V.; Eller, M. J.; Rickman, R. D.; Della-Negra, S.; Schweikert, E. A. Single Impacts of C_{60} on Solids: Emission of Electrons, Ions and Prospects for Surface Mapping. *J. Phys. Chem. C* **2009,** *114*, 5637–5644.
(18) Eller, M. J.; Verkhoturov, S. V.; Della-Negra, S.; Schweikert, E. A. Electron Emission from Hypervelocity C_{60} Impacts. *J. Phys. Chem. C* **2010,** *114*, 17191–17196.
(19) Toglhofer, K.; Aumayr, F.; Kurz, H.; Winter, H.; Scheier, P.; Mark, T. D. Near-Threshold Electron Emission from Slow Cluster Impact on Clean Gold. *Europhys. Lett.* **1993,** *22*, 597–602.
(20) Winter, H. P.; Vana, M.; Betz, G.; Aumayr, F.; Drexel, H.; Scheier, P.; Mark, T. D. Suppression of Potential Electron Emission for Impact of Slow Multicharged Fullerenes on Clean Gold. *Phys. Rev. A* **1997,** *56*, 3007–3010.
(21) Colligon, J. S. Surface Compositional Analysis Using Low Energy Ion Bombardment Induced Emission Processes. *Vacuum* **1974,** *24*, 373–388.
(22) Tolk, N. H.; Tsong, I. S. T.; White, C. W. In Situ Spectrochemical Analysis of Solid Surfaces by Ion Beam Sputtering. *Anal. Chem.* **1977,** *49*, 16A–30A.
(23) Fernandez-Lima, F. A.; Pinnick, V. T.; Della-Negra, S.; Schweikert, E. A. Photon Emission from Massive Projectile Impacts on Solids. *Surf. Interface Anal.* **2010**, doi: 10.1002/sia.3592.
(24) Kubota, S.; Sakuragi, S.; Hashimoto, S.; Ruan, J.-z. A New Scintillation Material: Pure CsI with 10 ns Decay Time. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1988,** *268*, 275–277.
(25) Amsler, C.; Grögler, D.; Joffrain, W.; Lindelöf, D.; Marchesotti, M.; Niederberger, P.; Pruys, H.; Regenfus, C.; Riedler, P.; Rotondi, A. Temperature Dependence of Pure CsI: Scintillation Light Yield and Decay Time. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2002,** *480*, 494–500.
(26) Belsky, A. N.; Vasil'ev, A. N.; Mikhailin, V. V.; Gektin, A. V.; Shiran, N. V.; Rogalev, A. L.; Zinin, E. I. American Institute of Physics: Woodbury, NY, 1992; Vol. 63, pp 806—809.
(27) Keszthelyi-Lándori, S.; Földvári, I.; Voszka, R.; Fodor, Z.; Seres, Z. Decay Time Measurements on "Pure" CsI Scintillators Prepared by Different Methods. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1991,** *303*, 374–380.
(28) Benguerba, M.; Brunelle, A.; Della-Negra, S.; Depauw, J.; Joret, H.; Le Beyec, Y.; Blain, M. G.; Schweikert, E. A.; Assayag, G. B.; Sudraud, P. Impact of Slow Gold Clusters on Various Solids: Nonlinear Effects in Secondary Ion Emission. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1991,** *62*, 8–22.
(29) Brunelle, A.; Della-Negra, S.; Depauw, J.; Jacquet, D.; Le Beyec, Y.; Pautrat, M.; Baudin, K.; Andersen, H. H. Enhanced Secondary-Ion Emission under Gold-Cluster Bombardment with Energies from keV to MeV per Atom. *Phys. Rev. A* **2001,** *63*, 022902.
(30) Krebs, K. H. Secondary Electron Release at Metal Surfaces Due to Positive Molecular Ions. *Ann. Phys.* **1964,** *13*, 97–100.
(31) Winter, H. P.; Vana, M.; Lemell, C.; Aumayr, F. Interaction of Slow Multicharged Ions with Solid Surfaces: Current Concepts and New Information on Slow Electron Emission. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1996,** *115*, 224–232.
(32) Moshammer, R.; Matthaus, R. *J. Phys.* (*Paris*) **1989,** *50*, C2–111.
(33) Rickman, R. D.; Verkhoturov, S. V.; Hager, G. J.; Schweikert, E. A. Multi-Ion Emission from Large and Massive keV Cluster Impacts. *Int. J. Mass Spectrom.* **2005,** *245*, 48–52.