Published in final edited form as:

J Phys Chem Lett. 2010 December 16; 1(24): 3510–3513. doi:10.1021/jz1014345.

Photon, Electron and Secondary Ion Emission from Single C₆₀ keV Impacts

F. A. Fernandez-Lima^a, M. J. Eller^a, S. V. Verkhoturov^a, S. Della-Negra^b, and E. A. Schweikert^{a,*}

^aDepartment of Chemistry, Texas A&M University, 3255 TAMU, College Station, Texas 77842-3012

^bInstitut de Physique Nucléaire, B.P. No. 1, F-91406 Orsay Cedex, France

Abstract

This paper presents the first observation of coincidental emission of photons, electrons and secondary ions from individual C₆₀ keV impacts. An increase in photon, electron and secondary ion yields is observed as a function of C₆₀ 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.

Keywords

Photon emission; electron emission; SIMS; surface characterization

CORRESPONDING AUTHOR FOOTNOTE: Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, schweikert@chem.tamu.edu.

SUPPORTING INFORMATION AVAILABLE. Total secondary ion spectra, coincidental single and dual ion spectra with the electron distribution, and emitted electron distributions at different C₆₀ impact energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The use of cluster bombardment (e.g. C₆₀ and Au₄₀₀) 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 emissions from C₆₀ 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 secondary ions (SIs) from single impact sites should be most informative.¹⁴ Studies on electron emission from individual C₆₀ 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 secondary ions from individual C₆₀ keV projectiles impacts. Time-resolved photon spectra, electron and secondary ion distributions were measured as a function of the impact C₆₀ energy.

An experimental setup that comprises a C₆₀ primary cluster beam, an electron emission microscope and a ToF mass spectrometer was used for this study.^{17,18,23} Emitted photons, electrons and secondary ions were collected per projectile impact. Photons were detected using a photo multiplier (PMT, R4220P model from Hamamatsu Photonics), with an active window from 185 to 710 nm, 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 towards an electron emission microscope where the initial signal was amplified ($\times 100$) and later detected using a position sensitive detector (more details in Reference 17). The ToF signals of the SIs were collected using a micro channel plate based detector positioned ~ 100 cm from the target surface, and were stored in a multi-channel 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 C₆₀ impacts on a CsI target. A linear increase in photon emission was observed with C₆₀ 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, and ii) 500 nm with a larger decay time (> 1 μ s) 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 ns, 6–10 ns 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 collision cascade mode of interaction.²³ A single component, fast photon emission has been observed under massive gold projectile impacts ($\text{Au}_{100-400}$) from 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.

A number of secondary ions per impact were observed in coincidence with the emitted photons. The number of secondary ions per impact follows a Poisson distribution, where the mean value increases with the C_{60} impact energy (Figure 2a). The negative secondary ion spectra are characterized by a high abundant cluster ion emission of the form $(\text{CsI})_{n=0-12}\text{I}^-$. 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 are likely a result of water molecules and hydrogen atoms adsorbed to the surface and of $\text{C}_{n=2-4}\text{H}^-$ peaks may be a result of pump oil and carbon contamination on the surface. The $(\text{CsI})_{n=0-12}\text{I}^-$ cluster ion yield Y can be described as $Y \propto \exp(-kn)$, 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 secondary ion formation/fragmentation mechanism.²⁸ For cluster ion bombardment, beside the exponential dependence on the cluster size, a power law yield dependence on the cluster size has also been proposed ($Y \sim n^b$), 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 CsI target in the energy range studied here.

Multi-electron 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 increases 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 have been attributed to the stochastic nature of the particle emission during ion bombardment.¹⁴ Recent experiments using individual C_{60} impacts have shown mainly one 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^- , $\text{C}_{n=2-4}\text{H}^-$, and $(\text{CsI})_n\text{I}^-$) showed that there is no specific electron distribution associated with them (PE1 or PE2), i.e., the electron distribution associated to individual ions showed the same two component electron distribution (PE1 and PE2) as that observed with the total secondary ion signal (see Supporting Information). The same result was observed when the analysis was made with the coincidental emission of two secondary ion signals (e.g., H^- & OH^- , CH^- & C_2H^- , and I^- & $(\text{CsI})_n\text{I}^-$). On the other hand, the inspection of the secondary ion spectra that corresponds to the electron distributions PE1 and PE2 showed differences in the H^- , OH^- and the $(\text{CsI})_n\text{I}^-$ ion yields (see Supporting Information). The larger number of electrons emitted per impact (PE1) is accompanied by a larger emission of secondary ions.

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 C₆₀ keV impacts on a CsI surface has shown the stochastic nature of the co-emission of photons, electrons and secondary ions 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 secondary ion pairs can be used as indicators of the surface content and homogeneity. The Poissonian secondary ion 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 photon, electron and secondary ion yields suggest 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.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by the National Science Foundation (Grant CHE-0750377). F. A. F-L acknowledges the National Institute of Health support (Grant No. 1K99RR030188-01).

REFERENCES

1. Tempez A, Schultz JA, 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. [PubMed: 14966842]
2. Winograd N, Postawa Z, Cheng J, Skazal C, Kozole J, Garrison BJ. Improvements in SIMS continue: Is the end in sight? *Appl. Surf. Sci* 2006;252:6836–6843.
3. Verkhoturov SV, Rickman RD, Guillermier C, Hager GJ, Locklear JE, Schweikert EA. 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. [PubMed: 16623517]
6. Pacholski ML, Winograd N. Imaging with Mass Spectrometry. *Chem. Rev* 1999;99:2977–3005. [PubMed: 11749508]
7. Russo MF, Szakal C, Kozole J, Winograd N, Garrison BJ. Sputtering Yields for C₆₀ and Au₃ Bombardment of Water Ice as a Function of Incident Kinetic Energy. *Anal. Chem* 2007;79:4493–4498. [PubMed: 17503768]
8. Kozole J, Willingham D, Winograd N. The effect of incident angle on the C₆₀⁺ bombardment of molecular solids. *Appl. Surf. Sci* 2008;255:1068–1070. [PubMed: 19554201]
9. Van Stipdonk MJ, Harris RD, Schweikert EA. 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 RD, Baker WS, Van Stipdonk MJ, Crooks RM, Schweikert EA. 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. [PubMed: 10407327]
11. Harris RD, van Stipdonk NJ, Schweikert EA. keV Cluster Impacts: Prospects for Cluster-SIMS. *Int. J. Mass Spectrom. Ion Proc* 1998;174:167–177.
12. Baudin K, Parilis ES, Blankenship JF, Van Stipdonk MJ, Schweikert EA. Sublinear effect in light emission from cesium iodide bombarded by keV polyatomic projectiles. *Nucl. Instrum. Methods Phys. Res. B* 1998;134:352–359.
13. Kaercher RG, da Silveira EF, Blankenship JF, Schweikert EA. Solid-state luminescence: Probe for ion-solid interactions. *Phys. Rev. B* 1995;51:7373–7376.
14. da Silveira EF, Duarte SB, Schweikert EA. Multiplicity analysis: a study of secondary particle distribution and correlation. *Surf. Sci* 1998;408:28–42.
15. Aumayr F, Betz G, Mark TD, Scheier P, Winter HP. 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 YL, Parilis E. Secondary Electron Emission Yields from a CsI Surface Under Impacts of Large Molecules at Low Velocities (5×10^3 – 7×10^4 ms⁻¹). *Rapid Commun. Mass Spectrom* 1997;11:353–362.
17. Verkhoturov SV, Eller MJ, Rickman RD, Della-Negra S, Schweikert EA. Single Impacts of C₆₀ on Solids: Emission of Electrons, Ions and Prospects for Surface Mapping. *J. Phys. Chem. C* 2009;114:5637–5644.
18. Eller MJ, Verkhoturov SV, Della-Negra S, Schweikert EA. Electron Emission from Hypervelocity C₆₀ Impacts. *J. Phys. Chem. C* 2010;114:17191–17196.
19. Toghiofer K, Aumayr F, Kurz H, Winter H, Scheier P, Mark TD. Near-Threshold Electron Emission from Slow Cluster Impact on Clean Gold. *Europhysics Lett* 1993;22:597–602.
20. Winter HP, Vana M, Betz G, Aumayr F, Drexel H, Scheier P, Mark TD. Suppression of potential electron emission for impact of slow multicharged fullerenes on clean gold. *Phys. Rev. A* 1997;56:3007–3010.
21. Colligon JS. Surface compositional analysis using low energy ion bombardment induced emission processes. *Vacuum* 1974;24:373–388.
22. Tolk NH, Tsong IST, White CW. In situ spectrochemical analysis of solid surfaces by ion beam sputtering. *Anal. Chem* 1977;49:16A–30A.
23. Fernandez-Lima FA, Pinnick VT, Della-Negra S, Schweikert EA. Photon emission from massive projectile impacts on solids. *Surf. Interf. 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. 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. A* 2002;480:494–500.
26. Belsky AN, Vasil'ev AN, Mikhailin VV, Gektin AV, Shiran NV, Rogalev AL, Zinin EI. *AIP* 1992;Vol. 63:806–809.
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. A* 1991;303:374–380.
28. Benguerba M, Brunelle A, Della-Negra S, Depauw J, Joret H, Le Beyec Y, Blain MG, Schweikert EA, Assayag GB, Sudraud P. Impact of slow gold clusters on various solids: nonlinear effects in secondary ion emission. *Nucl. Instrum. Methods Phys. Res. B* 1991;62:8–22.
29. Brunelle A, Della-Negra S, Depauw J, Jacquet D, Le Beyec Y, Pautrat M, Baudin K, Andersen HH. Enhanced secondary-ion emission under gold-cluster bombardment with energies from keV to MeV per atom. *Phys. Rev. A* 2001;63:022902.
30. Krebs KH. Secondary electron release at metal surfaces due to positive molecular ions. *Ann. Phys* 1964;13:97–100.
31. Winter HP, 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. B* 1996;115:224–232.

32. Moshhammer R, Matthaus R. J. de Physique 1989;50:C2–C111.
33. Rickman RD, Verkhoturov SV, Hager GJ, Schweikert EA. Multi-ion Emission from Large and Massive keV Cluster Impacts. Int. J. Mass Spectrom 2005;245:48–52.

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.

Figure 2.

a) Secondary ion 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.

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 distribution (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.