2005

Photoexcitation of a Volume Plasmon in C60 Ions

S. W. J. Scully
University of Nevada - Reno

E. D. Emmons
University of Nevada - Reno

M. F. Gharaibeh
University of Nevada - Reno

R. A. Phaneuf
University of Nevada - Reno, phaneuf@unr.edu

A. L. D. Kilcoyne
Lawrence Berkeley National Laboratory, ALKilcoyne@lbl.gov

See next page for additional authors

Photoexcitation of a Volume Plasmon in C_{60} Ions

S. W. J. Scully,* E. D. Emmons, M. F. Gharaibeh, and R. A. Phaneuf
Department of Physics, MS 220, University of Nevada, Reno, Nevada 89557-0058, USA

A. L. D. Kilcoyne and A. S. Schlachter
Advanced Light Source, Lawrence Berkeley National Laboratory, MS 7-100, Berkeley, California 94720, USA

S. Schippers and A. Müller
Institut für Atom- und Molekülphysik, Justus-Liebig-Universität, 35392 Giessen, Germany

H. S. Chakraborty,† M. E. Madjet,‡ and J. M. Rost
Max Planck Institute for the Physics of Complex Systems, 01187 Dresden, Germany
(Received 19 May 2004; published 17 February 2005)

Neutral C_{60} is well known to exhibit a giant resonance in its photon absorption spectrum near 20 eV. This is associated with a surface plasmon, where delocalized electrons oscillate as a whole relative to the ionic cage. Absolute photoionization cross-section measurements for C_{60}^{+}, C_{60}^{2+}, and C_{60}^{3+} ions in the 17–75 eV energy range show an additional resonance near 40 eV. Time-dependent density functional calculations confirm the collective nature of this feature, which is characterized as a dipole-excited volume plasmon made possible by the special fullerene geometry.

DOI: 10.1103/PhysRevLett.94.065503 PACS numbers: 61.48.+c, 33.20.Ni, 36.40.Gk, 79.60.Fr

Buckminsterfullerene (C_{60}) has attracted widespread experimental and theoretical interest since its discovery in 1985 [1]. Its size, structure, and symmetry place its properties and behavior intermediate between those of a free molecule and a solid. The transition from microscopic to macroscopic systems increases the possibility to collectively excite electrons: a well-known example is the excitation of plasmons in metallic clusters due to collective motion of delocalized electrons [2,3]. C_{60} is also known to have a plasmon excitation: the 240 valence electrons contribute to a delocalized electron cloud that can oscillate relative to the carbon ion core forming the C_{60} molecular cage. This oscillation has been described as a dipolar plasmon [4] that produces a giant resonance in the C_{60} photoabsorption and electron-energy-loss spectra at an excitation energy of about 20 eV [5–9].

Experimental results reported in this Letter reveal the existence of an additional giant resonance near 40 eV in photoionization of C_{60} ions. On the basis of calculations using the time-dependent local-density approximation (TDLDA), the giant resonances near 20 and 40 eV are identified as collective phenomena. An analysis using induced surface charges characterizes them as surface and volume plasmons, respectively. The dipolar excitation of a volume plasmon is possible in C_{60} due to its geometry of a charged *shell*. In contrast, the excitation of a volume plasmon in a solid conducting sphere is dipole forbidden, leading to its suppression in photoabsorption by metal clusters.

Measurements of absolute photoionization cross sections for C_{60} ions were performed in the 17–75 eV energy range using the ion-photon-beam end station on undulator beamline 10.0.1 at the Advanced Light Source. A collimated ion beam is merged with a counterpropagating beam of synchrotron radiation, and the yield of charge-state-selected photoions is measured as the photon energy is scanned [10]. The photon energy resolution was 50 meV at 35 eV. The ion beams were produced by evaporating fullerene soot into a 10-GHz electron cyclotron resonance (ECR) ion source [11]. Ions were accelerated by 6 kV and mass/charge selected by a 60° magnetic-dipole mass spectrometer with a resolution of 1%. The photon flux was measured using a calibrated silicon x-ray photodiode (International Radiation Detectors, AXUV-100) [12] and additionally monitored by a gold grid. Three-dimensional beam intensity profiles were measured to quantify their spatial overlap. The present cross-section measurements have a typical relative uncertainty of $\pm 5\%$ and an absolute uncertainty of $\pm 30\%$.

Figure 1 shows absolute cross-section measurements for single photoionization of C_{60}^{+} together with fits of two Lorentzian curves centered near 22 and 38 eV. The 22 eV feature corresponds to the well-known plasmon phenomenon that has been extensively studied in neutral C_{60} [5–9]. No evidence of fine structure is seen in higher-resolution scans (not shown) of the 22-eV resonance, unlike what has been predicted theoretically [13] and found experimentally for the neutral case [6]. The broader feature at 38 eV is also evident in recent photoionization measurements of neutral C_{60} by Reinköster *et al.* [14] and Kou *et al.* [15]. Its interpretation as a volume plasmon is the main subject of this Letter.

Narrow features near 26 and 34 eV that were observed by Kou *et al.* [15,16] in photoionization of C_{60} also appeared in the present data, but only after normalization of the photoion counts to the photon flux as measured by the Si photodiode. They are attributed to structure in the photo-

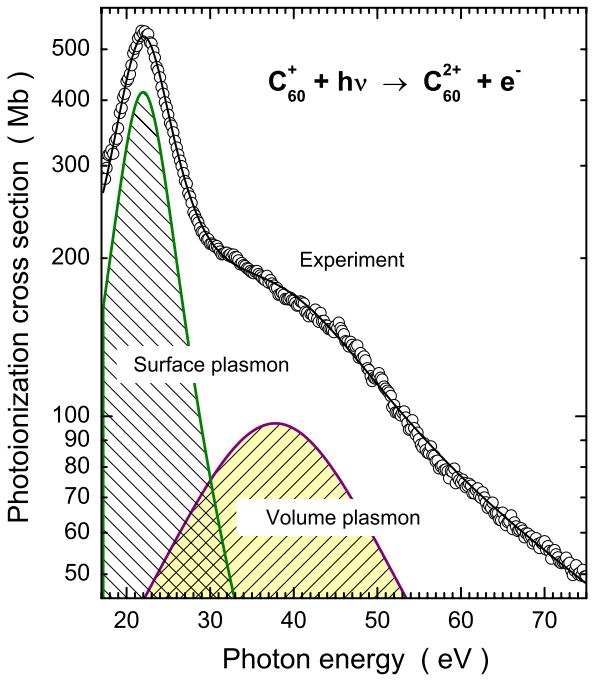

FIG. 1 (color online). Absolute cross-section measurement of single photoionization of C_{60} (open circles). The thin solid line results from the fit to the measured data of a linear background (not shown) plus the two separately displayed Lorentzian curves. These represent the surface and the volume plasmon resonances near 22 and 38 eV, respectively, that correspond to collective excitations of the C_{60}^{+} valence electrons.

diode's response and correspond to third- and fourth-order radiation absorbed at the L $(2p)$ edges of Si (99.8 eV) and SiO_2 (105.4 eV) [12]. These artifacts were avoided by first normalizing the photon flux to relative measurements of secondary electron emission from a high-transmission gold grid inserted into the photon beam, and then using the Si photodiode sensitivity calibration data at discrete energies to place the photoion-yield measurements on an absolute scale. It is noted that a similar Si photodiode was used by Kou *et al.* [15,16].

The integrated area of a Lorentzian line shape fit to the giant resonance at 22 eV gives a value of 45 ± 14 for the effective oscillator strength. This is lower than the theoretical predictions for neutral C_{60} of an oscillator strength between 80 and 180 [2,4] because only the single-ionization channel is measured in the present experiments.

An important characteristic of a plasmon resonance is the ratio of the oscillation frequency to the width, or, more relevant to this study, the ratio of its resonant energy (E_r) to its full width at half maximum, w [17]. This ratio is a measure of the number of oscillations that the collective motion undergoes before it decays. The fit yields a value of $E_r/w = 2.9$ for the giant resonance at 22 eV (Table I), implying a rapid transfer of the energy of oscillation to the relevant decay channel.

The width $w = 7.6 \pm 0.3$ eV of this resonance is similar to the value of 8 ± 1 eV measured in a recent fast-electron-diffraction experiment [18] but is narrower than that measured for photoionization of neutral C_{60} [6,7] (see Fig. 2). The ECR ion source operates at a much lower partial pressure of C_{60} than is typical in the neutral-C_{60} experiments, corresponding to a lower oven temperature. Since the decrease in width occurs predominantly on the low-energy side of the resonance, it is possible that the ion beam possessed less internal energy than the neutrals. Varying internal energy may also explain differences between the independent measurements of photoionization of neutral C_{60} [6,7,14,15].

Figure 2 compares absolute cross-section measurements for single photoionization of C_{60}^{+} (σ_{12}), C_{60}^{2+} (σ_{23}), and C_{60}^{3+} (σ_{34}) with the results of previous experimental work using neutral C_{60}. Although the absolute cross section decreases as the incident-ion charge state is increased, the giant plasmon resonance near 22 eV still plays a dominant role in the photoionization of ions in the three charge states investigated here. The present results are similar to electron-impact single-ionization measurements [11] in that the σ_{12} and σ_{23} cross sections are almost identical and σ_{34} is smaller. The substantial decrease of σ_{34} is likely the result of decay channels other than single ionization (such as fragmentation) becoming more important, reducing the part of the resonance oscillator strength associated with single photoionization. Studies of electron-induced

TABLE I. Parameters obtained from Lorentzian fits applied to the experimental data for photoionization of C_{60}^{q+} ions. The associated uncertainties are derived from the fitting procedure, except for the oscillator strengths, which reflect the $\pm 30\%$ uncertainty in the absolute cross-section measurements.

Ion charge	Energy E_r (eV)	Width w (eV)	Oscillator strength	E_r/w
Surface plasmon:				
1	22.0 ± 0.1	7.6 ± 0.3	45 ± 14	2.9 ± 0.1
2	21.5 ± 0.1	8.0 ± 0.4	44 ± 13	2.7 ± 0.1
3	23.6 ± 0.1	10.6 ± 0.4	21 ± 6	2.2 ± 0.2
Volume plasmon:				
1	38 ± 2	29 ± 4	40 ± 12	1.3 ± 0.2
2	39 ± 2	40 ± 5	83 ± 25	1.0 ± 0.2
3	40.5 ± 1	30 ± 6	30 ± 9	1.3 ± 0.2

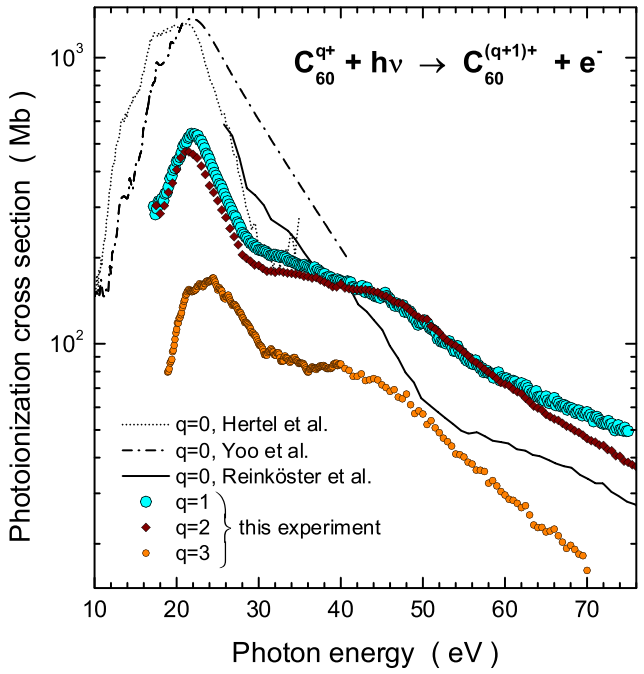

FIG. 2 (color online). Absolute cross sections for single photoionization of C_{60}^{+}, C_{60}^{2+}, and C_{60}^{3+}. The single-photoionization cross sections of neutral C_{60} measured by Hertel *et al.* [6], Yoo *et al.* [7], and Reinköster *et al.* [14] are also shown for comparison. The present cross sections for C_{60} ions are on an independently absolute scale. The only previous absolute photoabsorption cross-section measurements for fullerenes were performed by Smith [26] and Yasumatsu *et al.* [27] for neutral C_{60} at photon energies below 11 eV. Berkowitz [28] normalized the photoionization data of Hertel *et al.* and Yoo *et al.* to these measurements. Reinköster *et al.* used the total C_{60} photoionization cross section reported by Berkowitz for 40.8 eV photons to scale their relative data.

fragmentation of fullerene ions suggest that ions in initially higher charge states fragment more readily [19].

The second resonance near 38 eV is also evident in photoionization of C_{60}^{2+} and C_{60}^{3+}. Table I presents parameters obtained from Lorentzian fits of the single-ionization cross sections of the ions in Fig. 2. The E_r/w ratio is smaller for the second resonance in each case, suggesting that these oscillations are not as stable against decay as the first giant resonance. Table I also shows that the E_r/w ratio is the same for each plasmon, independent of the initial charge state. This is to be expected if the plasmon oscillations depend solely on the electron density.

Density functional theory is a powerful tool to handle the electronic collective dynamics in large finite systems [3] and is applied here to C_{60}^{+} in a manner similar to that reported in Ref. [20]. The ground-state structure of C_{60}^{+} is described by treating the 239 valence electrons as delocalized. The Kohn-Sham equations for this system are then solved by representing the residual C^{4+} ions by a classical spherical jellium shell with a radius $R = 0.354$ nm and a thickness $\Delta = 0.15$ nm, as recently derived from a photoemission experiment with C_{60} [20]. The solution forms single-particle $\sigma(n = 1)$ and $\pi(n = 2)$ states. The TDLDA [21,22], which includes important many-body correlations, is then applied to calculate collective effects in the ionization response of the system to the external electromagnetic field. The exclusion of tightly bound atomic $1s$ electrons (binding energy $\sim$290 eV) is not considered critical in the present context, since collective plasmon resonances are largely created by the valence $2s2p$ electron cloud.

Figure 3 compares the results of the effective single-particle local-density approximation (LDA) and the TDLDA with the experimental data for photoionization of C_{60}^{+}. The TDLDA calculation reproduces the main features of the experimental cross section. To match the position and height of the 22 eV giant resonance with experiment, the TDLDA cross sections were blueshifted (as customary, see [20] and references therein) by 5.5 eV and scaled by a factor of 1/4 to account for fragmentation channels that were not measured.

The results in Fig. 3 confirm that both giant resonances in the photoionization spectrum are indeed of collective character, since they are clearly present in TDLDA while they are absent in the effective single-particle LDA approximation. Moreover, as shown in the inset, the TDLDA calculation also reveals that σ electrons contribute dominantly to the plasmon near 38 eV. Both σ and π electrons contribute to the giant resonance near 22 eV.

The origin and nature of the two dominant collective resonances predicted by TDLDA theory may be most easily understood in classical terms [23]. A classical di-

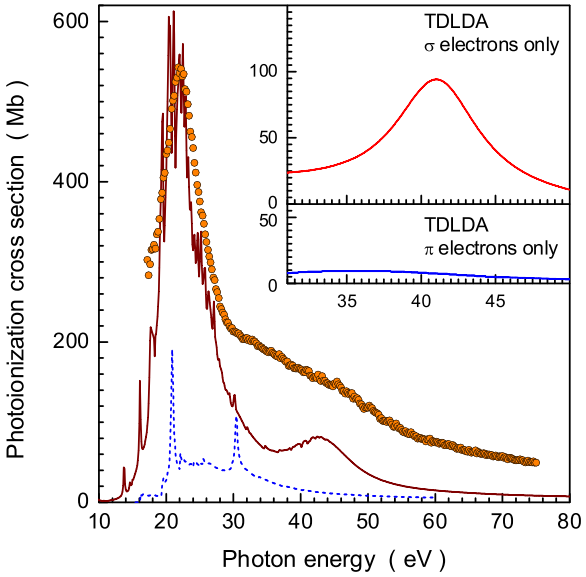

FIG. 3 (color online). Single-photoionization cross section of C_{60}^{+} from experiment (circles) and from TDLDA (solid line) and LDA (dashed line) calculations. The theoretical data are convoluted with a Gaussian of width 0.1 eV, and the TDLDA result is scaled to match the giant resonance near 22 eV (see text). The inset shows the contributions of σ and π electrons to the second giant resonance

electric sphere exhibits two types of excitation modes, namely, surface plasmons and volume plasmons. The volume plasmon mode, with a frequency ω_p determined by the electron density only, corresponds to a local radial compression of the electron density. The (dipole) surface plasmon with frequency $\omega_s = \omega_p/\sqrt{3}$ represents a collective oscillation of an incompressible electron density relative to the ionic background. Classical theory forbids the dipole excitation of the volume plasmon. Quantum mechanically, however, the photon-induced electron-density fluctuations of the delocalized electron cloud are of nonlocal character and break this symmetry rule, so that surface and volume plasmon excitations are coupled and shifted with respect to their classical frequencies [24].

The volume plasmon carries only a small fraction of the oscillator strength of the dominant surface plasmon in metal clusters, since its excitation is classically forbidden. In contrast, in C_{60} ions the surface and the volume plasmon carry oscillator strengths of the same order of magnitude, indicating that both should originate in a classically allowed process. This process can be understood if C_{60} is envisaged as a classical charged spherical shell [21,23,25].

The induced charge densities at the inner and outer edges are coupled and oscillate with two frequencies $\omega_{\mp}$ corresponding to in-phase (ω_+) and out-of-phase (ω_-) motion. This means that the in-phase oscillation $\omega_+ < \omega_p$ of the two surface charges takes the role of the dipolar surface plasmon, and, as in metal clusters, the delocalized electron cloud oscillates as a whole relative to the ionic background. On the other hand, in the antisymmetric mode $\omega_- > \omega_p$, the charge density oscillates only over the width of the electron shell. A compression of the electron density is created that is local with respect to the C_{60} sphere, and corresponds in effect to a volume plasmon excitation that is dipole allowed.

In summary, the present absolute cross-section measurements for photoionization of C_{60}^{q+} ions ($q = 1, 2, 3$) show evidence for a second broad resonance. The collective character of this resonance is revealed by a time-dependent density functional calculation. It is interpreted as a volume plasmon that can be excited because of the cage geometry of C_{60}.

This research was funded by the U.S. Department of Energy and by the Deutsche Forschungsgemeinschaft. R. A. P. gratefully acknowledges support from the Alexander von Humboldt Foundation.

*Present address: Department of Pure and Applied Physics, Queen's University, Belfast BT7 1NN, United Kingdom.
†Present address: James R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, KS 66506-2604, USA.
‡Present address: Freie Universität Berlin, Institut für Chemie (Kristallographie), Takustrasse 6, D-14195 Berlin, Germany.

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).
[2] M. Y. Amusia and J.-P. Connerade, Rep. Prog. Phys. **63**, 41 (2000).
[3] M. Brack, Rev. Mod. Phys. **65**, 677 (1993).
[4] G. F. Bertsch, A. Bulgac, D. Tománek, and Y. Wang, Phys. Rev. Lett. **67**, 2690 (1991).
[5] G. Gensterblum, J. J. Pireaux, P. A. Thiry, R. Caudano, J. P. Vigneron, P. Lambin, A. A. Lucas, and W. Krätschmer, Phys. Rev. Lett. **67**, 2171 (1991).
[6] I. V. Hertel, H. Steger, J. de Vries, B. Weisser, C. Menzel, B. Kamke, and W. Kamke, Phys. Rev. Lett. **68**, 784 (1992).
[7] R. K. Yoo, B. Ruscic, and J. Berkowitz, J. Chem. Phys. **96**, 911 (1992).
[8] N. Ju, A. Bulgac, and J. W. Keller, Phys. Rev. B **48**, 9071 (1993).
[9] T. Pichler, M. Knupfer, M. S. Golden, J. Fink, and T. Cabioc'h, Phys. Rev. B **63**, 155415 (2001).
[10] A. M. Covington *et al.*, Phys. Rev. A **66**, 062710 (2002).
[11] R. Völpel, G. Hofmann, M. Steidl, M. Stenke, M. Schlapp, R. Trassl, and E. Salzborn, Phys. Rev. Lett. **71**, 3439 (1993).
[12] E. M. Gullikson, R. Korde, L. R. Canfield, and R. E. Vest, J. Electron Spectrosc. Relat. Phenom. **80**, 313 (1996).
[13] P. Colavita, G. D. Alti, G. Fronzoni, M. Stener, and P. Decleva, Phys. Chem. Chem. Phys. **3**, 4481 (2001).
[14] A. Reinköster, S. Korica, G. Prümper, J. Viefhaus, K. Godehusen, O. Schwarzkopf, M. Mast, and U. Becker, J. Phys. B **37**, 2135 (2004).
[15] J. Kou, T. Mori, M. Ono, Y. Haruyama, Y. Kubozono, and K. Mitsuke, Chem. Phys. Lett. **374**, 1 (2003).
[16] J. Kou, T. Mori, S. V. K. Kumar, Y. Haruyama, Y. Kubozono, and K. Mitsuke, J. Chem. Phys. **120**, 6005 (2004).
[17] J. P. Connerade, J. Phys. B **17**, L165 (1983).
[18] L. G. Gerchikov, P. V. Efimov, V. M. Mikoushkin, and A. V. Solov'yov, Phys. Rev. Lett. **81**, 2707 (1998).
[19] D. Hathiramani, K. Aichele, W. Arnold, K. Huber, E. Salzborn, and P. Scheier, Phys. Rev. Lett. **85**, 3604 (2000).
[20] A. Rüdel, R. Hentges, U. Becker, H. S. Chakraborty, M. E. Madjet, and J. M. Rost, Phys. Rev. Lett. **89**, 125503 (2002).
[21] M. J. Puska and R. M. Nieminen, Phys. Rev. A **47**, 1181 (1993).
[22] M. E. Madjet and P. A. Hervieux, Eur. Phys. J. D **9**, 217 (1999).
[23] P. Lambin, A. A. Lucas, and J.-P. Vigneron, Phys. Rev. B **46**, 1794 (1992).
[24] W. Ekardt, Phys. Rev. B **31**, 6360 (1985).
[25] D. Östling, S. P. Apell, and A. Rosen, Europhys. Lett. **21**, 539 (1993).
[26] A. L. Smith, J. Phys. B **29**, 4975 (1996).
[27] H. Yasumatsu, T. Kondow, H. Kitagawa, K. Tabayashi, and K. Shobatake, J. Chem. Phys. **104**, 899 (1996).
[28] J. Berkowitz, J. Chem. Phys. **111**, 1446 (1999).