

## COMMUNICATIONS

High resolution photoelectron spectroscopy of  $C_{60}^-$ Xue-Bin Wang, Chuan-Fan Ding, and Lai-Sheng Wang<sup>a)</sup>*Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99352  
and W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National  
Laboratory, MS K8-88, Richland, Washington 99352*

(Received 30 November 1998; accepted 23 February 1999)

Vibrationally resolved photoelectron spectra of  $C_{60}^-$  are reported at three photon energies: 355, 266, and 193 nm. Complicated vibrational structures were observed for the transition to the  $C_{60}$  ground state with both the  $A_g$  and  $H_g$  modes being active. An extra feature was observed in the energy gap region between the highest occupied and lowest unoccupied orbitals of  $C_{60}$  in the 266 nm spectra only and it was attributed to an autodetachment process. We also report the most accurate measurement of the electron affinity of  $C_{60}$  ( $2.689 \pm 0.008$  eV). © 1999 American Institute of Physics. [S0021-9606(99)02517-9]

One of the remarkable properties of  $C_{60}$  is the fact that among its 174 vibrational degrees of freedom there are only two totally symmetric modes ( $A_g$ ) due to its high symmetry ( $I_h$ ).<sup>1</sup> According to the vibrational selection rules in photo-detachment of molecular anions, only the two  $A_g$  modes were expected to be active in photoelectron spectroscopy (PES) of  $C_{60}^-$ . Indeed, in the early days of fullerene study considerable amount of effort was spent to resolve the presumably simple vibrational structure in PES of  $C_{60}^-$ ,<sup>2-4</sup> which would have provided a powerful piece of evidence for the soccer ball structure of  $C_{60}$ . However, this proved to be a challenging endeavor due to the experimental difficulty to produce sufficiently cold  $C_{60}^-$  and the available instrumental resolution. More importantly, as is now well known, the ground state of  $C_{60}^-$  ( ${}^2T_{1u}$ ) exhibits a Jahn–Teller effect due to vibronic coupling through the  $H_g$  vibrational modes,<sup>5</sup> suggesting that a simple PES spectrum of  $C_{60}^-$  would not have been observed even if the experimental difficulties had been overcome. Indeed, the Jahn–Teller effect in  $C_{60}^-$  has been extensively studied,<sup>5</sup> particularly, because of its relevance to the electron–phonon coupling problem in the superconductivity of alkali doped fullerenes.<sup>6,7</sup> Gunnarsson *et al.* obtained the first vibrationally resolved PES of  $C_{60}^-$  at a resolution of 40 meV and indeed observed that the  $H_g$  modes were active.<sup>8</sup> They studied the Jahn–Teller effect in detail and derived the electron–phonon coupling constants based on a simulation of the PES spectrum. Given the importance of the  $C_{60}$  molecule and its anions, higher resolution PES spectra would be desirable and would allow more accurate electron–phonon coupling constants to be derived. Furthermore, the electron affinity (EA) of  $C_{60}$  is still not accurately known. The most accurate previous measurement has an uncertainty of  $\pm 0.05$  eV.<sup>3</sup>

In this Communication, we report a high resolution PES study of  $C_{60}^-$  at an instrumental resolution of 15 meV

(FWHM) using an electrospray ionization (ESI) technique to generate the  $C_{60}^-$  anions. Indeed, complicated vibrational structures were observed in the PES spectra due to the excitation of both the  $A_g$  and  $H_g$  types of vibrations, even at the higher resolution. We measured the spectra of  $C_{60}^-$  at three photon energies: 355, 266, and 193 nm. Surprisingly, an extra feature was observed in the 266-nm spectra and was attributed to an autodetachment process, consistent with its linear dependence on the ion beam intensity and its photon energy dependence. We also measured accurately the electron affinity of  $C_{60}$  ( $2.689 \pm 0.008$  eV).

Our experiments were performed with a new PES–ESI apparatus, in which a magnetic-bottle time-of-flight (TOF) PES analyzer is coupled to an ESI anion source. The details of this apparatus have been described elsewhere.<sup>9</sup> The preparation of the  $C_{60}$  solution was according to literature procedures used to generate  $C_{60}$  anions in a dimethylformamide solution.<sup>10</sup> This solution was sprayed directly in our experiments. Anions produced from the ESI source were guided into a quadrupole ion trap through a radio-frequency quadrupole ion guide. The anions were accumulated for 0.1 s in the ion trap and pulsed out for TOF mass analyses.<sup>11</sup>  $C_{60}^-$  was the major anion species produced from the ESI source. Although the doubly charged  $C_{60}^{2-}$  existed in the solution and was known to be long-lived in the gas phase,<sup>12</sup> we were not able to observe it, possibly due to the long storage time ( $\sim 0.1$  s) of the anions or collisional loss in the ion trap. The  $C_{60}^-$  anions were mass selected and decelerated before crossing with a laser beam in the detachment zone of the magnetic-bottle PES apparatus. Three photon energies were used in the current experiments: 355 (3.496 eV), 266 (4.661 eV), and 193 nm (6.424 eV). Photoelectron kinetic energies were measured using the magnetic-bottle TOF technique with a 4 m long flight tube. All experiments were done at 10 Hz repetition rate at 355 nm, and 20 Hz at 266 and 193 nm with the ion beam off at alternating laser shots for background subtraction. The kinetic energy scale was carefully

<sup>a)</sup>Author to whom correspondence should be addressed.

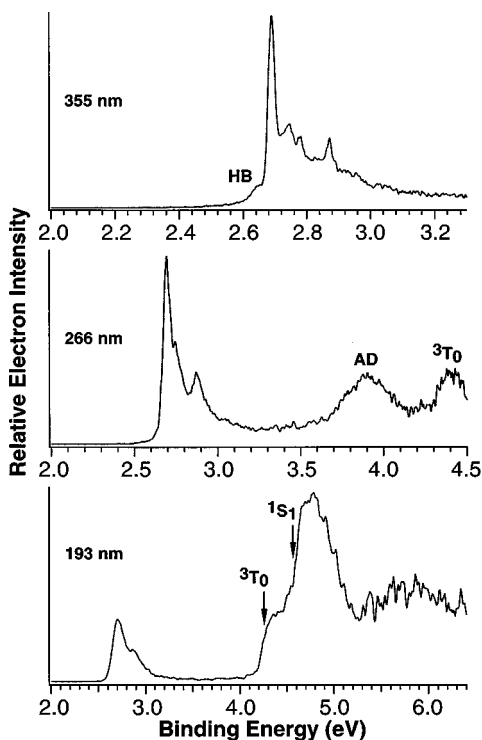


FIG. 1. Photoelectron spectra of  $C_{60}^-$  at 355, 266, and 193 nm with photon fluxes of 5, 1.5, and 0.7  $\text{mJ}/\text{cm}^2$ , respectively. HB refers to hot band transitions. AD stands for "autodetachment". The lowest triplet ( ${}^3T_0$ ) and ( ${}^1S_1$ ) excited states are also indicated. Note that vibrational structures were resolved for the ground electronic state in all three spectra.

calibrated using the known spectra of  $I^-$  and  $O^-$ . Electron binding energy spectra were obtained by subtracting the kinetic energy spectra from the photon energies. The energy resolution of our PES apparatus is  $\Delta E/E \sim 2\%$ , i.e., about 10 meV (FWHM) for 0.5 eV electrons.

The measured PES spectra of  $C_{60}^-$  are shown in Fig. 1 at the three photon energies. The 355 nm spectrum, due to the transition from the ground state of  $C_{60}^-$  ( ${}^2T_{1u}$ ) to that of neutral  $C_{60}$  ( ${}^1A_g$ ), displays well resolved vibrational structures. Hot band transitions at the low binding energy side were also evident.<sup>11</sup> At 266 nm, two additional features at higher binding energies were observed at about 3.9 and 4.4 eV, respectively, besides the vibrationally resolved ground state features. The 4.4 eV feature represents the detachment transition to the lowest excited state of  $C_{60}$  ( ${}^3T_0$ ) as is also evident in the 193 nm spectrum. However, the 3.9 eV feature was puzzling because it happened in the energy gap region and was not present in the 193 nm spectrum, where a dense manifold of higher binding energy features were observed. The spectra shown in Fig. 1 were all taken at fairly low photon fluxes. We found that at higher photon fluxes considerable low energy electrons were present due to thermionic emissions.<sup>3</sup>

The 355 nm spectrum shown in Fig. 1 represents the best resolved PES spectrum of  $C_{60}^-$ . The strongest peak is the 0–0 transition, which defines the EA of  $C_{60}$ . The instrumental resolution at the energy of this peak was about 15 meV. The measured peak width was about 26 meV, suggesting that there were other broadening factors, probably due to rotational and thermal effects. From the position of the 0–0 peak, we measured the EA of  $C_{60}$  to be  $2.689 \pm 0.008$  eV,

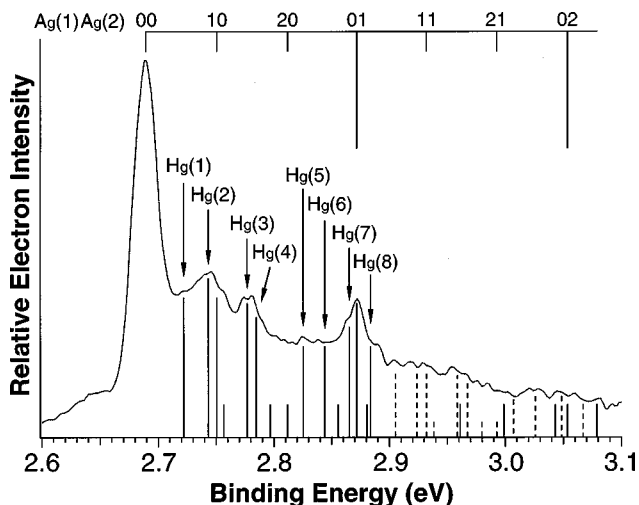


FIG. 2. Details of the vibrational structures of  $C_{60}^-$  at 355 nm. The positions for the excitation of the two  $A_g$  modes are indicated at the top of the figure. The vertical lines in the figure depict the positions for the excitation of the two  $A_g$  and eight  $H_g$  modes.<sup>13</sup> Short lines represent the overtone of each mode. The dashed lines show the combination bands of the  $H_g$  modes and one quantum of the  $A_g(2)$  mode.

compared to  $2.65 \pm 0.05$  eV previously measured using a threshold photodetachment technique.<sup>3</sup> Our calibration error was about  $\pm 0.003$  eV within a 14 h experimental run (calibration spectra were taken both at the beginning and the end of the run). The  $\pm 0.008$  eV uncertainty was derived by taking into account 10 meV thermal broadening to the peak of the 0–0 transition.

To examine the vibrational structures, we show an expanded portion of the 355 nm spectrum in Fig. 2. Several vibrational features were well resolved. The peak at 2.871 eV gives a vibrational excitation of  $1470 \pm 30$   $\text{cm}^{-1}$ , in excellent agreement with the vibrational frequency of the  $A_g(2)$  mode of  $C_{60}$ .<sup>13</sup> The features between the 0–0 peak and the 2.871 eV peak cannot be assigned to a single progression of the  $A_g(1)$  mode. Peak positions corresponding to the  $A_g(1)$  mode, as well as those of its overtone and combination bands with the  $A_g(2)$  mode, are shown at the top of the figure. Clearly other vibrational modes due to the  $H_g$  symmetry were active because of the Jahn–Teller effect in the ground state of the anion. There are eight  $H_g$  vibrational modes,<sup>1</sup> whose positions are depicted in Fig. 2 by the vertical lines at the bottom of the figure.<sup>13</sup> The  $v=2$  vibrational levels for each mode are indicated with the short vertical lines. The dotted lines represent combination bands of the  $A_g(2)$  mode and the  $H_g$  modes with one vibrational quantum of the  $A_g(2)$  mode. It appears that all the  $H_g$  modes were active. The vibrational features were simulated previously by Gunnarsson *et al.*,<sup>8</sup> including all the  $H_g$  modes. From the simulation, they obtained the electron–phonon coupling constants, which were used to evaluate the superconducting transition temperatures in the alkali doped fullerenes. However, we believe that the higher resolution spectrum presented here should allow more accurate coupling constants to be obtained. Particularly, we feel that the coupling of the  $A_g$  modes were underestimated previously, given the fact that

the present spectrum shows more clearly the excitation of the  $A_g$  modes.

The ground state vibrational structures were also resolved in the 266 nm spectrum, where excitations in the  $H_g(2)$  and  $A_g(2)$  modes were evident. Vibrational features due to the  $A_g(2)$  mode in the ground state were even resolved in the 193 nm spectrum. The highest occupied molecular orbital (HOMO) of  $C_{60}$  is the fivefold degenerate  $h_u$  orbital.<sup>14</sup> In  $C_{60}^-$ , the extra electron enters the lowest unoccupied molecular orbital (LUMO) of  $C_{60}$ ,  $t_{1u}$ , which also has a closely spaced LUMO+1 level with  $t_{1g}$  symmetry. Besides the detachment feature due to removal of the  $t_{1u}$  electron, the 266 and 193 nm photons can also access higher energy detachment channels. The next higher energy detachment feature should be due to the removal of an  $h_u$  electron, leading to the lowest excited state of  $C_{60}$ , a triplet state. The 193 nm spectrum indicates that this excited state feature is at 4.26 eV, giving a triplet-singlet excitation of  $1.57 \pm 0.03$  eV for  $C_{60}$ . Although the singlet excited states of  $C_{60}$  have been extensively studied,<sup>15</sup> the triplet excited states of  $C_{60}$  are not well known because they are optically forbidden transitions. The lowest singlet excited state of  $C_{60}$ , also derived from removal of an  $h_u$  electron in  $C_{60}^-$ , is known to be at  $15\,200\text{ cm}^{-1}$  above the ground state,<sup>15</sup> corresponding to the onset of the strong peak around 4.6 eV (Fig. 1). However, we could not resolve the excited state manifold due to the extremely high density of electronic states and the Jahn–Teller effects associated with these highly degenerate excited states.

We now turn to the extra broad feature observed in the 266 nm spectrum at  $\sim 3.9$  eV. This feature appeared in the HOMO–LUMO gap region and existed regardless of the laser fluxes used. There were three possibilities for this feature: (1) a shakeup process, (2) an inelastic energy loss, and (3) an autodetachment process. The shakeup process, due to electron correlation effects, involves detachment of an electron and excitation of another electron into a higher orbital with the same photon.<sup>16</sup> There is no such channel available in the current case at 266 nm. Thus, the 3.9 eV feature had to be due to either an inelastic energy loss or an autodetachment process. We noticed that this feature is about 1.2 eV above the ground state feature. A 1.2 eV electron energy loss feature was observed in doped fullerides due to the excitation of a  $t_{1u}$  electron to the next higher LUMO level ( $t_{1g}$ ) of  $C_{60}$ .<sup>17</sup> We also noted that in the solution phase  $C_{60}^-$  has a strong absorption near 1.15 eV due to the same excitation.<sup>18</sup> Thus, the 3.9 eV feature could be due to a similar excitation of the undetached  $C_{60}^-$  anions by the primary electrons corresponding to the ground state features. Such an inelastic energy loss was expected to depend on the parent  $C_{60}^-$  anion beam intensity and scale as the square of the ion beam intensity. However, ion-beam-intensity-dependent studies revealed no such scaling of the intensity of the 3.9 eV feature. We found that at constant photon fluxes the relative intensity of the 3.9 eV feature (to the ground state features) did not change at different parent  $C_{60}^-$  ion beam intensity. Furthermore, if the inelastic energy loss mechanism were true, one would expect a similar feature in the 193 nm spectrum. However, the 193 nm spectrum (Fig. 1) showed no indication of this feature at 3.9 eV binding energy.

Therefore, we attributed the 3.9 eV feature in the 266 nm spectrum to autodetachment to the highly excited vibrational levels of the  $C_{60}$  ground state. Autodetachment involves resonant excitation of the parent anion to an electronic excited state that is above the detachment threshold. The highly excited anion can then autodetach and produce non-Franck–Condon features. For example, such non-Franck–Condon autodetachment was previously observed in PES spectra of  $Cr_2^-$  at 476–514 nm.<sup>19</sup> Although a 4.6 eV excited state is not known for  $C_{60}^-$ , low-lying excited states for small carbon cluster anions have been observed in low temperature matrices.<sup>20</sup> A 4.6 eV excited state is certainly conceivable for  $C_{60}^-$  given its high density of unoccupied levels. The photon energy dependence of the 3.9 eV feature is also consistent with the autodetachment mechanism.

In conclusion, we reported high resolution photoelectron spectra of  $C_{60}^-$  in the gas phase and a more accurate measurement of the electron affinity of  $C_{60}$  ( $2.689 \pm 0.008$  eV). Complicated vibrational structures were observed in the ground state detachment transition due to the Jahn–Teller effect in  $C_{60}^-$ . The higher resolution spectra should allow better electron–phonon coupling constants to be determined. A surprising feature was observed at 266 nm in the HOMO–LUMO gap region of  $C_{60}$ . This feature was assigned to be due to an autodetachment process, consistent with its photon energy dependence.

Support of this research by the National Science Foundation CAREER Program (DMR-9622733) is gratefully acknowledged. The PES–ESI apparatus was built through support by the Office of Basic Energy Sciences, Chemical Science Division, U.S. Department of Energy. The research was performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by DOE’s Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated for DOE by Battelle under Contract DE-AC06-76RLO 1830. L. S. W. is an Alfred P. Sloan Foundation Research Fellow.

<sup>1</sup>D. E. Weeks and W. G. Harter, *J. Chem. Phys.* **90**, 4744 (1989).

<sup>2</sup>S. H. Yang, C. L. Pettiette, J. Conceicao, O. Cheshnovsky, and R. E. Smalley, *Chem. Phys. Lett.* **139**, 233 (1987); R. F. Curl and R. E. Smalley, *Science* **242**, 1017 (1988); R. E. Haufler, L. S. Wang, L. P. F. Chibante, C. Jin, J. Conceicao, Y. Chai, and R. E. Smalley, *Chem. Phys. Lett.* **179**, 449 (1991).

<sup>3</sup>L. S. Wang, J. Conceicao, C. Jin, and R. E. Smalley, *Chem. Phys. Lett.* **182**, 5 (1991).

<sup>4</sup>L. S. Wang, O. Cheshnovsky, R. E. Smalley, J. D. Carpenter, and S.-J. Hwu, *J. Chem. Phys.* **96**, 4028 (1992); L. S. Wang, J. M. Alford, Y. Chai, M. Diener, G. E. Scuseria, and R. E. Smalley, *Chem. Phys. Lett.* **207**, 354 (1993).

<sup>5</sup>W. H. Green, Jr., S. M. Gorun, G. Fitzgerald, P. W. Fowler, A. Ceulemans, and Bruno C. Titeca, *J. Phys. Chem.* **100**, 14892 (1996) and references therein.

<sup>6</sup>R. C. Haddon, *Acc. Chem. Res.* **25**, 127 (1992); C. M. Varma, J. Zaanen, and K. Raghavachari, *Science* **254**, 989 (1991).

<sup>7</sup>S. Chakravarty, M. P. Gelfand, and S. Kivelson, *Science* **254**, 970 (1991); O. Gunnarsson and G. Zwicknagl, *Phys. Rev. Lett.* **69**, 957 (1992).

<sup>8</sup>O. Gunnarsson, H. Handschuh, P. S. Bechthold, B. Kressler, G. Gantefor, and W. Eberhardt, *Phys. Rev. Lett.* **74**, 1875 (1995).

<sup>9</sup>L. S. Wang, C. F. Ding, X. B. Wang, and S. E. Barlow, *Rev. Sci. Instrum.* **70**, 1957 (1999); X. B. Wang, C. F. Ding, and L. S. Wang, *Phys. Rev. Lett.* **81**, 3351 (1998).

- <sup>10</sup>R. Subramanian, P. Boulas, M. N. Vijayashree, F. D'Souza, M. T. Jones, and K. M. Kadish, *J. Chem. Soc. Chem. Commun.* **1994**, 1847.
- <sup>11</sup>The temperatures of the anions from the trap were expected to be at or slightly above room temperature. See, for example, *Practical Aspects of Ion Trap Mass Spectrometry*, edited by R. E. March and J. F. J. Todd (CRC, New York, 1995), Vol. I–III.
- <sup>12</sup>R. L. Hettich, R. N. Compton, and R. H. Rotchie, *Phys. Rev. Lett.* **67**, 1242 (1991); P. A. Limbach, L. Scheinhard, K. A. Cowan, M. T. McDermott, A. G. Marshall, and J. V. Coe, *J. Am. Chem. Soc.* **113**, 6795 (1991).
- <sup>13</sup>The vibrational frequencies used for the  $A_g$  and  $H_g$  modes are all taken from Ref. 8.
- <sup>14</sup>R. C. Hadon, L. E. Brus, and K. Raghavachari, *Chem. Phys. Lett.* **125**, 459 (1986).
- <sup>15</sup>X. L. R. Dauw, M. V. Bronsveld, A. Kruger, J. B. M. Warntjes, M. R. Witjes, and E. J. J. Groenen, *J. Chem. Phys.* **109**, 9332 (1998); D. J. Heuvel, G. J. B. Berg, E. J. J. Groenen, J. Schmidt, I. Holleman, and G. Meijer, *J. Phys. Chem.* **99**, 11644 (1995); F. Negri, G. Orlandi, and E. Zerbetto, *J. Chem. Phys.* **97**, 6496 (1992).
- <sup>16</sup>S. Suzer, S. T. Lee, and D. A. Shirley, *Phys. Rev. A* **13**, 1842 (1976).
- <sup>17</sup>A. I. Liechtenstein, O. Gunnarsson, M. Knupfer, J. Fink, and J. F. Armbuster, *J. Phys. E. Condens. Matter* **8**, 4001 (1996).
- <sup>18</sup>M. A. Greaney and S. M. Gorun, *J. Phys. Chem.* **95**, 7142 (1991); T. Kato *et al.*, *Chem. Phys. Lett.* **186**, 35 (1991).
- <sup>19</sup>S. M. Casey and D. G. Leopold, *J. Phys. Chem.* **97**, 816 (1993).
- <sup>20</sup>P. Feivogel, J. Fulara, M. Jakobi, D. Forney, and J. P. Maier, *J. Chem. Phys.* **103**, 54 (1995).