

Relative partial cross sections for formation of singly-, doubly-, and triply-charged ions from C₆₀, C₇₀ and C₈₄

C. Huang,¹ H. Yagi,¹ B. P. Kafle,² Md. S. I. Prodhan,² H. Katayanagi,^{1,2} Y. Kubozono,³ and K. Mitsuke^{1,2}

¹*Department of Photo-Molecular Science III, The Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*

²*Graduate University for Advanced Studies, Myodaiji, Okazaki 444-8585, Japan*

³*Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan*

Fullerenes, C₆₀ and C₇₀ have attracted much scientific interest because they are exceptionally stable and symmetric cluster with low sublimation temperatures that allow us to study large clusters in gas phase. The thermodynamic data obtained from gas-phase experiments, such as bond and dissociation energies, ionization energies have been studied by means of photoionization¹ and electron impact ionization mass spectrometric methods.² The dynamics of excitation and ionization of fullerenes have been observed due to the high symmetry of fullerenes, such as collective plasmon oscillation of valence electrons³ and interference in the standing waves of the ionized electron inside a fullerene cage.⁴ However, difficulties in acquiring a sufficient quantity of the sample have hindered many investigators in acquiring even fundamental spectroscopic information in the extreme UV region. This situation is now being altered, for the techniques of synthesis, isolation, and purification have advanced so rapidly that appreciable amounts of fullerenes can be readily gained. For instance, the C₈₄ molecules are the third most abundant species in the fullerene synthesized by arc-discharge method,⁵ and hence they can be fully isolated from C₆₀, C₇₀, and other higher fullerenes.⁶ Determining relative partial cross sections for photoions from these fullerenes is beneficial in elucidating the universal mechanism of energy relaxation in excited fullerene ions.

In the present study, we investigated the three fullerenes, C₆₀, C₇₀ and C₈₄, using a linear time-of-flight mass spectrometer (TOFMS) combined with tunable synchrotron radiation at $h\nu = 25 - 120$ eV.⁷ The photoionization yield curves of singly-, doubly- and triply-charged ions produced from the three samples were measured, with particular attention being paid to the ratios between the partial cross sections for the multiply- and singly-charged ions. The dependence of the detection efficiencies on the mass-to-charge ratio was evaluated by using the formula proposed by Twerenbold et al.⁸ Corrections of the detection efficiency were found to be critical to obtaining accurate partial cross sections for photoionization of fullerenes. The Partial cross sections were calculated using the formula.

$$\sigma_{abs}(m, z+) \propto R(m, z+)/\Phi n L \eta(C_m^{z+}) f \tau \quad (1)$$

Here, $R(m, z+)$ is the signal count rate of all the ions in a charge state z produced from the fullerene C_m ; Φ is the photon flux of synchrotron radiation; n is the number density of C_m in the ionization region; L is the length of the ionization volume along the light path; $\eta(C_m^{z+})$ is the relative detection efficiency of the apparatus for C_m^{z+} ; f is the repetition rate of the pulsed electric field applied to the ionization region; and τ is the average residence time of the ions in the ionization volume without the pulsed electric field. It should be emphasized that the contribution of the second order light of synchrotron radiation was subtracted when we deduced the partial cross-section curves of all the ionic species involved in the experiment. To our best knowledge, the partial cross section curves

for multiply-charged ions from C_{70} and C_{84} over a wide $h\nu$ range are reported for the first time. The ratios between the cross sections for double and single photoionization increase with $h\nu$ and reach saturated values of 0.78 at 85 eV for C_{60} , ~ 1.3 at 100 eV for C_{70} and ~ 0.9 at 80 eV for C_{84} . In contrast, the ratios at 120 eV between the cross sections for triple and single photoionization of C_{60} , C_{70} and C_{84} amount to be 0.14, ~ 0.38 and ~ 0.18 , respectively. We can arrange the ratios in descending order as $\sigma(70, 2+)/\sigma(70, +) > \sigma(84, 2+)/\sigma(84, +) > \sigma(60, 2+)/\sigma(60, +)$ and $\sigma(70, 3+)/\sigma(70, +) > \sigma(84, 3+)/\sigma(84, +) > \sigma(60, 3+)/\sigma(60, +)$.

Formation mechanism of multiply-charged fullerene ions will be discussed in terms of valence-electron excitation to antibonding unoccupied orbitals and/or spherical standing waves inside the cavity of a fullerene. This excitation could be followed by Spectator Auger processes and transmission of the excess electronic energy among numerous vibrational degrees of freedom. Fig 1 shows that the cavity-resonance state is formed by promotion of the $3g_g$ or $5h_g$ electron when C_{60} absorbs a 50 eV photon.

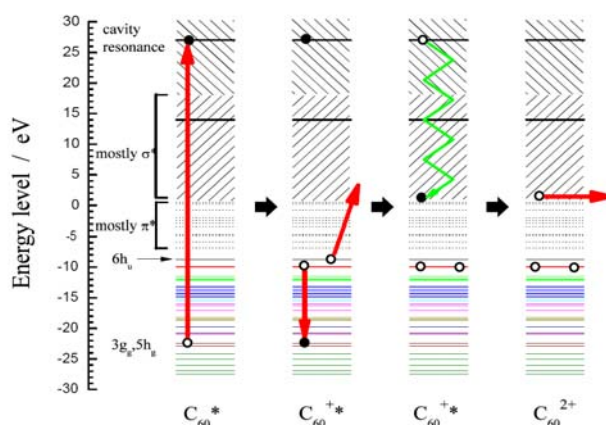


Fig.1 Schematic picture illustrating the decay mechanism of the cavity-resonance state formed by excitation of the $3g_g$ electron of C_{60} .

References

- (1) Yoo, R. K.; Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1991**, *96*, 911-918.
- (2) Wörgötter, R.; Dünser, B.; Scheier, P.; Märk, T. D. *J. Chem. Phys.* **1994**, *101*, 8674-8679.
- (3) Hertel, I. V.; Steger, H.; Devries, J.; Weisser, B.; Menzel, C.; Kamke, B.; Kamke, W. *Phys. Rev. Lett.* **1992**, *68*, 784-787.
- (4) Xu, Y. B.; Tan, M. Q.; Becker, U. *Phys. Rev. Lett.* **1996**, *76*, 3538-3541.
- (5) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; L., W. R. *J. Phys. Chem.* **1990**, *94*, 8630-8633.
- (6) Kikuchi, K.; Nakahara, N.; Wakabayashi, T.; Suzuki, S.; Shiromaru, H.; Miyake, Y.; Saito, K.; Ikemoto, I.; Kainosho, M.; Achiba, Y. *Nature* **1992**, *357*, 142-145.
- (7) Mitsuke, K.; Katayanagi, H.; Kafle, B. P.; Huang, C. Q.; Yagi, H.; Prodhan, S. I.; Kubozono, Y. *J Phys. Chem. A* **2007**, *in press*.
- (8) Twerenbold, D.; Gerber, D.; Gritti, D.; Gonin, Y.; Netuschill, A.; Rossel, F.; Schenker, D.; Vuilleumier, J. L. *Proteomics* **2001**, *1*, 66-69.