

Fluorescence of Buckminsterfullerene: UV
Emission of C_{60}^+ and C_{70}^+

S. Trajmar, S. Wang[†], K.F. Man

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

and

M.A. Khakoo

California State University
Fullerton, CA 92633

[†] NRC-NASA Resident Research Associate

Abstract

We report the first observation of UV luminescence from gaseous C_{60} and C_{70} buckminsterfullerenes induced by electron impact excitation. The emission features appear in the 275 to 340 nm wavelength region and originate from radiative decay of the excited ionic species. Emission spectra (at 20, 30 and 103 eV impact energies) and onset values and excitation functions for the five emission features appearing in the emission spectra are presented.

The C_{60} (buckminster fullerene or buckyball) molecule was discovered in 1985⁽¹⁾ but it was only recently⁽²⁾ that substantial amounts of C_{60} and C_{70} molecules could be produced for extensive studies. A large number of investigations aimed at determining the Properties of these molecules has been described in the literature during the past two years. We report here the first observation and study of electron-impact-induced UV fluorescence of vapor phase C_{60} and C_{70} fullerenes and assign these emissions to electronic transitions in the corresponding ions.

Uchida et al.⁽³⁾ reported electroluminescence of solid C_{60} - C_{70} mixture in a diode arrangement. It appeared as a broad emission in the 400 to 900 nm range peaking at around 530 nm. Reber et al.⁽⁴⁾ studied solid C_{60} films deposited on CaI_2 at 20K and observed luminescence in the 700 to 1,100 nm range. The films were excited by light in the 350 to 600 nm wavelength range. Arbogast and Foote⁽⁵⁾ detected weak fluorescence in the 600 to 800 nm region from C_{70} molecules at room temperature in hexane and benzene solutions with UV and visible light excitation, respectively. They also observed fluorescence from glass solution at 77K in the 650 to 725 nm region. No fluorescence from C_{60} could be detected in these studies. Wasielewski et al.⁽⁶⁾ studied phosphorescence spectra of C_{60} and C_{70} in degassed toluene solutions. The optical excitation was achieved by 4 sec flashes at 515 and 450 nm for C_{60} and C_{70} , respectively. They observed phosphorescence at wavelengths ranging from 790 to 890 nm for C_{70} , but not for C_{60} . Based on EPR studies, they concluded that triplet C_{60} was formed but it decayed to the ground state predominantly by non-radiative processes. More recently, Sibley et al.⁽⁷⁾ observed weak fluorescence in glassy toluene solution at 77K for C_{60} and C_{70} in the 625 to 1,000 nm region and in solid

polycrystalline C_{60} and C_{70} in the 650 to 835 and 625 to 770 nm region, respectively. Kim and Lee⁽⁸⁾ found fluorescence from both C_{60} and C_{70} in room temperature toluene and benzene solutions in the 600 to 850 nm region following excitation at 525 nm. The fluorescence peak intensity of C_{60} was about five times weaker than that of C_{70} and appeared at longer wavelengths. All these observed luminescences in the condensed phase were due to slow radiative decay of the low-lying, optically forbidden singlet and triplet levels of the molecules. To our knowledge, no luminescence from gaseous buckminsterfullerene has ever been reported. We describe here the results of our studies concerning electron-impact-induced fluorescence of vapor-phase fullerenes (pure C_{60} and C_{70} and their mixtures).

The buckyball beam for the present studies was formed by heating a crucible containing the sample. The heating was achieved by a double, coaxial wire wound around the crucible. The vapor effused through a 0.75 mm diameter hole and formed the target beam without further collimation. The heater-crucible structure was surrounded by a metal shield and the temperature was monitored by a thermocouple. The molecular beam was crossed by a magnetically collimated electron beam at a distance of about 6 mm from the point of effusion. The electron beam current ranged from few to about 100 micro ampere in various studies, but was nearly constant in each study from 5 eV to 150 eV which was the upper limit of our energy range. The experimental arrangement and procedures were otherwise the same as described by McConkey et al(9).

Emission spectra of C_{60} , C_{70} and their mixture were obtained in the 180 to 500 nm region at electron impact energies ranging from 20 to 103 eV, but strong emission features were observed only in the 275 to 340 nm wavelength region. Some spectra were taken with

2.5 nm resolution but these showed no more detail than the spectra taken with 5 nm resolution. Therefore, to optimize the experimental conditions, we performed most of the measurements at the lower resolution. The initial investigation was carried out with a buckyball mixture containing about 66% C₆₀, 25% C₇₀ and 3% each of C₇₆, C₇₈ and C₈₄. For the final measurements the substantially more expensive pure C₆₀ and C₇₀ samples were used. The mixture and pure C₆₀ (better than 99.5% purity) samples were procured from Materials and Electrochemical Research Corporation. The C₇₀ sample was prepared by Srivastava and Jong^{10a} by heating the mixture at around 350°C for several days to eliminate the C₆₀ which has a vapor pressure about 10 times higher than C₇₀ at this temperature.¹¹ The composition of the vapor was monitored by time of flight mass spectrometry (using electron impact ionization) and indicated the elimination of C₆₀. Electron-impact ionization studies carried out by Srivastava et al.^{10b} indicated that no fragmentation of buckyballs could take place at the electron impact energies used in the present study.

Wavelength calibration of the emission spectra was achieved by obtaining spectra of buckyball and He (and buckyball and N₂) simultaneously and utilizing the triplet transition lines of He and the second positive bands [(C³P_u(v') - > B³P_g(v'')] in N₂. The permanent gases were introduced through an auxiliary capillary. The wavelength scale is accurate to about ± 5 Å. The relative response function of the system is expected to be constant over the 275 to 340 nm region (based on the photomultiplier response, window transmission and grating efficiency). This was also checked against the relative excitation function values of He lines and N₂ bands. Therefore, the spectra recorded in the present experiment represent the true relative excitation functions for the emission features.

Typical emission spectra are shown in Fig. 1 for C_{60} and C_{70} at 20, 30 and 103 eV impact energies. The emission features are broad (~13 nm) compared to the wavelength resolution (~4 nm) of the apparatus and no shift in the position or width of the features is apparent for the two cases. The relative intensities of the emission features differ little for C_{60} and C_{70} , but show significant changes with impact energy. Emission spectra obtained at 20, 30 and 103 eV impact energies demonstrate the change with impact energy. There are five distinguishable features in these spectra indicated as 1 to 5. Features 1 and 2 and features 3 and 4 heavily overlap, but are distinguishable at 103 eV impact energy where features 2 and 4 become stronger. Feature 5 is recognizable only at higher impact energies. There is a clear indication for a different impact energy dependence of the emission features 2, 4 and 5 compared to 1 and 3. The mean wavelengths corresponding to these features are listed in Table 1.

Onset values at wavelengths corresponding to the peak of the five features were obtained in a two-step procedure. First, relative onset values were measured for pure C_{60} and C_{70} samples. In the second step onset values were obtained for He and for feature 3 of C_{60} (C_{70}) under identical experimental conditions. In these measurements He and buckyball species were simultaneously present in the interaction region. Emission intensity as a function of impact energy were measured at fixed wavelengths corresponding to the five peak values of buckyballs and the various He lines in the onset region with 0.05 eV steps. For the calibration of onset values, He rather than N_2 was used since the onset for the He triplet emission features were sharper and better defined than those of N_2 . The contact potential was determined from the difference between the measured and well known onset

values for the He ($n 3_p \rightarrow 2^3S$), $n = 3, 4$ and 5 (lines 388.9 , 318.8 and 294.5 nm, respectively). It was found to be consistent for these three lines to within 0.10 eV and typically of the order of 3.0 eV. The contact potential was found to be sensitive to electron beam current and He input pressure. This was due to space charge and surface effects. The correct contact potential was obtained from the low-current, low-pressure measurements. The relative onset values measured in pure C_{60} and C_{70} samples were then corrected for the contact potential to get the absolute onset values. Feature 4 overlaps with the 318.8 nm He line and at this wavelength the onsets for He and C_{60} (C_{70}) can be directly compared. For this case the contact potential was also consistent with those measured as described above to within ± 0.10 eV.

Relative excitation functions ("band" emission cross sections) were obtained by measuring the emission intensities as a function of electron impact energy from below threshold to 150 eV (with 0.25 eV steps). Figure 2 shows these functions for the five emission features in C_{60} and C_{70} . The curves fall into two main categories. For features 1 and 3 the onset is sharp and a well defined peak appears at just a few eV above threshold. For features 2 and 5 the onset is much more gradual and only a very broad, not clearly defined peak appears at about 50 eV above threshold. Feature 4 shows an intermediate character with its peak at about 25 eV. The excitation function curves for C_{60} and C_{70} were found to be similar. The electron impact energy values corresponding to the emission onsets and peaks for the various features are also given in Table I.

The ionization potentials for C_{60} and C_{70} have been found to be identical within experimental error limits. Zimmerman et al.¹², using charge transfer bracketing techniques, obtained 7.61 ± 0.11 eV (adiabatic value) for both species. The vertical ionization potential was measured by Lichtenberger et al.¹³ as 7.61 ± 0.02 for C_{60} (based on photo electron studies) and by Hertel et al.¹⁴ as 7.54 ± 0.04 and 7.3 ± 0.2 eV for C_{60} and C_{70} , respectively (using photoionization). Baba et al.¹⁵ obtained a value of 8.5 ± 0.5 eV from the electron impact ionization onset curve. For the present discussion we use the value of 7.54 eV. It is evident from the onset values that the observed radiation is due to decay of the excited cations generated by electron impact. This mechanism is consistent with the onset value of about 11.5 eV, photon energy of about 4.0 eV and ionization potential of about 7.5 eV. It is interesting to note that in the photoionization studies of Hertel et al.¹³ the ion yield versus photon energy curve for C_{60} clearly shows a sudden increase at about 11.5 eV. We interpret this as an opening of a new channel for ionization which is identical with the one responsible for the radiation observed in the present study. Autoionization, as a possible contribution to this rise, can be eliminated since we found no discrete feature in the electron-impact energy-loss spectra of C_{60} ¹⁶. The analogous ionization curve obtained by Hertel et al.¹⁴ for C_{70} looks somewhat different than the C_{60} curve. Opening of a new ionization channel at around 11.5 eV is not as clear in this case but there is a definite hint for it. The lack of prominence may be due to lower signal to noise ratio for the C_{70} curve, or to a diminished relative importance of this channel in the case of C_{70} . The latter assumption is consistent with our observations concerning the emission intensities of C_{60} and C_{70} . Lichtenberger et al.¹³, based on their photoelectron spectroscopic studies of thin solid

(3-layers) C_{60} , assigned values of 8.95 and 10.82 to 11.59 eV to the second and third vertical ionization potentials, respectively. The ionization channel that we find in connection with the near 4 eV fluorescence, most likely corresponds to the third ionization channel and the onset value indicated by the work of Lichtenberger et al. is in good agreement with our measurement. Some change going from the condensed to the gas phase may occur but no significant shift is expected. *3

There has been a great deal of speculation concerning the possible presence of fullerenes, their ions or hydrogenated forms of fullerenes in the interstellar and circumstellar clouds. It has been suggested that these species may be responsible for some of the unidentified diffuse interstellar absorption and emission bands, the strong UV absorption at 217 nm and/or the unidentified infrared emission features. Recent discussions and summaries concerning these matters can be found in Refs 17 to 23. It has been concluded, however, that there is no clear-cut evidence for C_{60} or C_{70} and their ions to be the carriers of the unidentified interstellar features. The present study confirms this conclusion. We found no emission from neutral fullerenes in the 180 to 500 nm spectral region. The emission observed and attributed to C_{60}^+ and C_{70}^+ do not correspond to any of the unidentified interstellar features. On the other hand, the present study establishes the presence of emission by buckminsterfullerenes under electron impact and the wavelengths associated with these emissions, thus clearly defining the signature of emission which can be used for the identification of C_{60}^+ and C_{70}^+ in the interstellar environments. The present observation also has an important implication concerning the performance of ion engines contemplated to utilize buckyballs as propellant.²⁴

Acknowledgements

This work was carried out at the Jet Propulsion Laboratory, California Institute of Technology and was supported by the National Aeronautics and Space Administration and by Air Force Office of Scientific Research, Grant No. F49620-92-J-0453. We wish to express our gratitude to S. K. Srivastava for supplying the C_{70} sample and for valuable discussion.

References:

1. H.W. Kroto, U.R. Heath, S.C. O'Brien, R.F. Curl and R.F. Smalley, *Nature* 318, 162 (1985).
2. V. Krätschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman, *Nature*, 347, 354 (1990).
3. M. Uchida, Y. Ohmori and K. Yoshino, *Japanese J. of Appl. Phys.* 30,1.2104 (1991).
4. C. Reber, L. Yet, J. McKiernan, J.I. Zink, R.S. Williams, W.M. Tong, D.A.A. Ohlberg, R.L. Whetten and F. Diederich, *J. Chem. Phys.* 95, 2127 (1991).
5. J.W. Arbogast and C.S. Foote, *J. Am. Chem. Soc.* 113, 8886 (1991), *J. Am. Chem. Soc.* 113, 2774 (1991).
6. M. R. Wasielewski, M.P. O'Neil, K.R. Lykke, M.J. Pellin and D.M. Green, *J. Am. Chem. Soc.* 113, 2774 (1991).
7. S. P. Sibley, S. M. Argentine, and A. H. Francis, *Chem. Phys. Lett.* 188, 187 (1992).
8. D. Kim and M. Lee, *J. Am. Chem. Soc.* 144, 4423 (1992).
9. J.W. McConkey, S. Trajmar, K.F. Man and J.M. Ratliff, *J. Phys. B.* ZS219'7 (1992).
- 10 a. S. K. Srivastava and G. Jong, Jet Propulsion Laboratory, Pasadena, CA 91109.
b. S. K. Srivastava, G. Jong, S. Lieffer and W. Saunders (to be published, private communication, 1993).
11. J. Abrefah, D.R. Olander, M. Balooch and W.J. Sickhaus, *Appl. Phys. Lett.*, 60, 1313 (1992).
12. J. A. Zimmerman, J. R. Eyler, S. B. H. Buch and S. W. McElvany, *J. Chem. Phys.* 94, 3556 (1991).
13. D. L. Lichtenberger, K. W. Nebesny, C. D. Ray, D.F. Huffman and D. L. Lamb, *Chem. Phys. Lett.* 176, 203 (1991).
14. I. V. Hertel, H. Steger, J. DeVries, B. Weiner, C. Menzel, B. Kamke and W. Kamke, *Phys. Rev. L* 68, 784 (1992).
15. M. S. Baba, T. S. L. Narasimhan, R. Balasubramanian and C. K. Mathews, *Int. J. of Mass Spectrometry and Ion Processes*, 114, R 1 (1992).

16. S. Trajmar, S. Wang and M. A. Khakoo (Submitted to J. Phys.B.)
17. M. Braga, S. Larsson, A. Rosen and A. Volosov, Astron. Astrophys. 245, 232 (1 991).
18. J.P. Hare and H.W. Kroto, Ace. Chem. Res. 25 106 (1992).
19. A. Webster, Mon. Not. Astr. Sot. 255, 41p (1992).
20. W.B. Somerville and I.A. Crawford, J. Chem. Sot. Faraday Trans. 89, (1993).
21. J. R. Miller and P. J. Surre, J. Chem. Soc. Faraday Trans. 89, ----(1993).
22. F. Salame and L. J. Allamandola, J. Chem. Soc. Faraday Trans. 89, ----(1 993).
23. W. Krätschmer, J. Chem. Sot. Faraday Trans 89. ----(1993).
24. S.D. Leifer, D. Rapp, and W.A. Saunders, J. of Propulsion and Power, 8, 1297 (1992).

Table 1. Summary of emission peak wavelengths and onset and peak energy values for the excitation functions of C_{60} and C_{70}

Feature No.	Emission Peak		Excitation Function		
	λ (Å)	ΔE (eV)	Onset (eV)		Peak (eV)
			C_{60}	C_{70}	
1	2840 ± 10	4.36	11.8 ± 0.2	11.7 ± 0.2	12 ± 2
2	2885 ± 10	4.30	11.7 ± 0.2	11.7 ± 0.2	60 ± 20
3	3100 ± 10	4.00	11.7 ± 0.2	11.6 ± 0.2	13 ± 12
4	3145 ± 10	3.94	11.7 ± 0.2	11.6 ± 0.2	15 ± 5
5	3265 ± 10	3.80	11.9 ± 0.2	11.6 ± 0.2	50 ± 10

FIGURE CAPTIONS

1. Electron-impact **photoemission** spectra of gaseous C_{60} and C_{70} buckminsterfullerenes. The emission features are **numbered** 1 to 5 and indicated by arrows. The two digit numbers next to the spectra refer to the electron impact energy in eV.
2. Relative electron-impact excitation functions for emission features 1 to 5 in C_{60} and C_{70} molecules. See text for discussion.



