Fluorescence of Buckminsterfullerenes: UV Emission of \( C_{60} \) and \( C_{70} \)

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Abstract

We report the first observation of UV luminescence from gas phase C\textsubscript{60} and C\textsubscript{70} buckminster fullerenes induced by electron impact excitation. The emission features appear in the 2.75 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 $C_{60}$ - 1 $C_{70}$ mixture in a diode arrangement. It appeared as a broad emission in the 400 to 900 nm range peaking at around 530 nm. Becker et al.\(^4\) studied solid $C_{60}$ films deposited on CaF$_2$ at 20K and observed luminescence in the 700 to 1,100 nm range. The films were excited by light in the 350 to 630 nm range. Albogast and Poole\(^5\) 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 1:3 PR studies, they concluded that triplet $C_{60}$ was formed but it decayed to the ground state predominantly by nonradiative processes.

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 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 microampere 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 MeConkey 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
S nm resolution but these showed no more detail than the spectra taken with 5 nm resolution. In order 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% C$_{60}$, 25% C$_{70}$ and 3% each of C$_{76}$, C$_{78}$ and C$_{84}$. For the final measurements the substantially more expensive pure C$_{60}$ and C$_{70}$ samples were used. The mixture and pure C$_{60}$ (better than 99.5% purity) samples were procured from Materials and Electrochemical Research Corporation. The C$_{70}$ sample was prepared by Srivastava and Jong$^{10a}$ by heating the mixture at around 350°C for several days to eliminate the C$_{60}$ which has a vapor pressure about 10 times higher than C$_{70}$ 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 C$_{60}$. 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 N$_2$) simultaneously and utilizing the triplet transition lines of He and the second positive bands $[(C^3Π_u(v') \rightarrow B^3Π_g(v''))]$ in N$_2$. 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 2.75 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 N$_2$ 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 \( (n \, 3_{\text{p}} \rightarrow 2 \, \text{S}) \), \( n = 3, 4 \) and 5 (lines 388.9, 318.8 and 294.8 mm, 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 \( Ie \) 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 \( \pm 0.10 \) 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 1.
The ionization potentials for $C_{60}$ and $C_{70}$ have been found to be identical within experimental error limits. Zimmerman et al.\textsuperscript{12}, using charge transfer bracketing techniques, obtained $7.61 \pm 0.11$ eV (adiabatic value) for both species. The vertical ionization potential was measured by Lichtenberger et al.\textsuperscript{13} as $7.61 \pm 0.02$ for $C_{60}$ (based on photo electron studies) and by Hertel et al.\textsuperscript{14} as $7.54 \pm 0.04$ and $7.3 \pm 0.2$ eV for $C_{60}$ and $C_{70}$, respectively (using photoionization). Baba et al.\textsuperscript{15} obtained a value of $8.5 \pm 0.5$ CV 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.\textsuperscript{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 $C_{60}$\textsuperscript{16}. The analogous ionization curve obtained by Hertel et al.\textsuperscript{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.\textsuperscript{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 mission bands, the strong UV absorption at 217 nm and/or the unidentified in frared 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

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References:


10 a. S. K. Srivastava and G. Jong, Jet Propulsion Laboratory, Pasadena, CA 91109.


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

<table>
<thead>
<tr>
<th>Feature No.</th>
<th>λ (Å)</th>
<th>ΔE: (eV)</th>
<th>Excitation Function</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Onset (eV)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C$_{60}$</td>
</tr>
<tr>
<td>1</td>
<td>2840 ± 10</td>
<td>4.36</td>
<td>11.8 ± 0.2</td>
</tr>
<tr>
<td>2</td>
<td>2885 ± 10</td>
<td>4.30</td>
<td>11.7 ± 0.2</td>
</tr>
<tr>
<td>3</td>
<td>3100 ± 10</td>
<td>4.00</td>
<td>11.7 ± 0.2</td>
</tr>
<tr>
<td>4</td>
<td>3145 ± 10</td>
<td>3.94</td>
<td>11.7 ± 0.2</td>
</tr>
<tr>
<td>5</td>
<td>3265 ± 10</td>
<td>3.80</td>
<td>11.9 ± 0.2</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

1. Electron-impact photoemission spectra of gaseous \( \text{C}_{60} \) and \( \text{C}_{70} \) 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 \( \text{C}_{60} \) and \( \text{C}_{70} \) molecules. See text for discussion.
The diagrams show the intensity (arb. units) versus wavelength (nm) for \( C_{60} \) and \( C_{70} \) materials. The arrows indicate specific wavelengths 275, 290, 305, 329, and 335 nm. The intensity peaks at these wavelengths, with notable peaks at 305 and 329 nm for both materials.