Electronic absorption spectra of the radical anions and cations of fullerenes: C_{60} and C_{70}

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The electronic absorption spectra of the radical ions in the title are observed in γ-irradiated glassy polyatomic matrices at 77 K. The spectral features of all the radical ions are consistent with the available information in the literature which includes photo-electron and resonance Raman spectra of C_{60} and C_{70}. In addition, the observed spectra compare favorably with the results of CNDO/S calculations.

1. Introduction

Since the success of laboratory synthesis of C_{60} and other carbon clusters ("fullerenes"), a spate of papers on the clusters [1] and their chemical derivatives [2] have been reported within a year. As for the ions derived from them, Smalley and co-workers succeeded in producing stable mono- and di-anions of C_{60} by an electrochemical method and forecast that the ionic species may be a potential substance for synthesizing new materials [3]. Recently, the work was extended to detect even the trianion of C_{60} and C_{70}, which brings us closer to our hopes to create new batteries, as suggested [3,4]. Smalley and co-workers also have determined the electron affinity of C_{60} by photodetachment electron spectroscopy of the anion [5]. Ultraviolet photoelectron spectroscopy of C_{60} in a thin film was studied by Lichtenberger et al. [6] which gives insight into the electronic structure of the cationic state. However, to our knowledge, the electronic absorption spectra of the radical ions of fullerenes have not been reported. In this paper, we will present spectral data obtained by the technique developed by the Kyoto group and applied to numerous systems [7].

2. Experimental

Two fullerenes, C_{60} and C_{70}, were prepared by a method similar to that described by Kraetschmer et al. [1,3]. Briefly, 6 mm outer diameter graphite rod was evaporated by arc discharge (typical current of about 60–80 A) under helium gas of 100 Torr. A soot-like material was collected and extracted with benzene. The powder obtained after drying consisted of C_{60} and C_{70} in a ratio of approximately 10:1. Each component was separated by column chromatography on neutral alumina with hexane as the eluent. C_{60} was separated completely from C_{70}, but the latter was contaminated with C_{60} to about 10%.

Both C_{60} and C_{70} were dissolved, separately, in 2-methyltetrahydrofuran (MTHF) and in a freon mixture (FM: an equivolume admixture of $CFCl_3$ and CF_2BrCF_2Br) at room temperature to saturation. Both fullerenes were sparingly soluble in the two solvents, but the saturated solutions at room temperature clearly reproduced the reported spectra of both C_{60} and C_{70} [8]. The solutions were introduced into Suprasil optical cells of path lengths of 1.5 or 5.0 mm. After degassing, we cooled the sample to 77 K to form a transparent glassy solid for both solvents.

The sample was, then, γ-irradiated at 77 K to a dose of, typically, 10^{19} eV g^{-1}. The absorptions were recorded on a Cary 17I spectrophotometer at 77 K.

3. Results and discussion

Saturated solutions of C_{60} in MTHF at 77 K reproduced the authentic spectrum of C_{60} in the literature to every detail [8]. Upon γ-irradiation of the solution, a strong absorption appeared with $\lambda_{max} = 1200$ nm, which is well known to be due to the solvent-trapped electron in the MTHF glass [7]. The absorption was easily photobleached with red light to reveal absorptions in the upper panel of fig. 1, which was plotted as the difference of the optical densities between the photobleached and the unirradiated sample in a 5 mm cell. Concomitantly, the initial absorption due to the solute C_{60} diminished homogeneously.

The above spectral changes can be accounted for by the following reactions:

$$M + \gamma \rightarrow M^+ + e , \tag{1}$$

$$e \rightarrow e_t , \tag{2}$$

$$e_t + h\nu \rightarrow e_m , \tag{3}$$

$$e_m + S \rightarrow S^- , \tag{4}$$

where M and S stand for the matrix MTHF and the solute C_{60}, and e_t and e_m represent the trapped and the mobile electron, respectively. The former is responsible for the strong absorption with $\lambda_{max} = 1200$ nm [7]. If the concentration of S were large enough, the electron produced by reaction (1) would have been "scavenged" by S to give S^- without intervention of the competitive reaction (2) and no absorption due to the trapped electron would have appeared [7]. The mechanism of reactions (1)–(4) has been evidenced by the success in obtaining numerous radical anions [7]. On this basis, the spectrum in fig. 1 (upper part) is assigned to the radical anion of C_{60}.

The extinction coefficient of the radical anion of C_{60} can be approximately estimated by referring to the extinction coefficient of the peak of the parent C_{60} at 328 nm, which has been determined to be $(3\pm1)\times10^4$ ℓ mol^{-1} cm^{-1} [10]; the decrease in the optical density of the parent molecule at 328 nm happened to be about the same as the increase of the optical density of the radical anion at 1076 nm. Therefore, by eq. (4), the extinction coefficient of the radical anion at 1076 nm is determined to be $(3\pm1)\times10^4$ ℓ mol^{-1} cm^{-1}.

The vibrationally structured absorptions peaking at 1076 and 952 nm favorably compare with the CNDO/S spectrum in the lower panel of fig. 1. Since the calculation is semiquantitative one can only speculate about the interpretation of the absorption: suppose that the peak at 1076 nm is the 0–0 band of one of the two theoretical peaks predicted at 1190 and 1152 nm. Then, the observed peak at 952 nm, which is separated from the 1076 peak by 1210 cm^{-1}, may be associated with the fundamental of one of the two totally symmetric vibrational modes studied for the parent C_{60} by resonance Raman spectroscopy [11]. The value of 1210 cm^{-1} may correspond to 1469 cm^{-1} assigned to one of the two modes of C_{60} [11]. The other mode of C_{60} was associated with a value of 497 cm^{-1} [11], whose counterpart of the radical anion may be responsible for the apparent progressions of a set of 1076, 1039 and 992 nm and another set of 952, 912 and 884 nm. The above interpretation, however, must be regarded as very
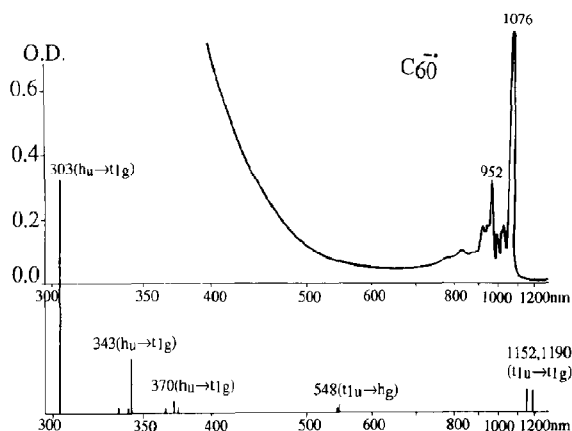

Fig. 1. Absorption spectra of the radical anion of C_{60}. Upper: Observed for a γ-irradiated and photobleached C_{60}/MTHF solution at 77 K in a 5 mm cell. Lower: CNDO/S spectrum for the radical anion. The calculation was made for an icosahedron with a single common length of 1.421 Å for the C–C bond. A test calculation for the parent C_{60} molecule reproduced well the CNDO/S spectrum reported by Larsson et al. [9]. The oscillator strength is relative.

tentative with the assumption that only one of the two transitions predicted at 1190 and 1152 nm was involved. In any case, according to the CNDO/S calculation, the near IR absorptions at around 700 to 1100 nm are to be described mainly by the transitions from the singly occupied to the nearest unoccupied molecular orbital of symmetries of t_{1u} and t_{1g}, respectively, as indicated in the lower panel of fig. 1. In this context, we should like to point out that the (ro)vibronic structure of the transition may be observed for the anion of C_{60} in the gas phase by two-color resonance-enhanced multiphoton ionization (REMPI); the electron affinity of 2.6–2.8 eV for C_{60} [5] is much larger than the transition energy of the radical anion to the first excited state with the 0–0 band at 1076 nm ($= 1.15$ eV). Therefore, the photodetachment via the resonant excitation of the state may be determined sensitively.

The solubility of C_{60} in FM is even smaller than that in MTHF. However, the existence of dissolved C_{60} in FM is evident from the spectrum before irradiation. The spectrum after irradiation exhibited a broad absorption band, which is known to be due to the solvent-trapped positive hole [7]. The band could be photobleached easily with visible light, say, $\lambda > 500$ nm to yield the spectrum in the upper panel of fig. 2.

The spectral changes observed can be accounted for by the following reactions:

$$F + \gamma \rightarrow F^+ + e \,, \tag{5}$$

$$e + F \rightarrow F^{\cdot} + X^- \,, \tag{6}$$

$$F^+ \rightarrow (F^+)_t \,, \tag{7}$$

$$(F^+)_t + h\nu \rightarrow (F^+)_m \,, \tag{8}$$

$$(F^+)_m + S \rightarrow F + S^+ \,, \tag{9}$$

where F, $(F^+)_t$, and $(F^+)_m$ stand for freon molecules and the positive hole in the trapped and the mobile states, respectively. Reaction (6) implies that the electron is disposed of by the dissociative attachment of the electron to a freon molecule to yield an immobile halide anion X^- and a fragment radical derived from the freon molecule [7].

Compared with the spectrum of the radical anion of C_{60} in fig. 1, the spectrum in fig. 2 to be associated with the radical cation of C_{60} by reactions (5)–(9) is less structured, but the peak at 980 nm ($= 1.27$
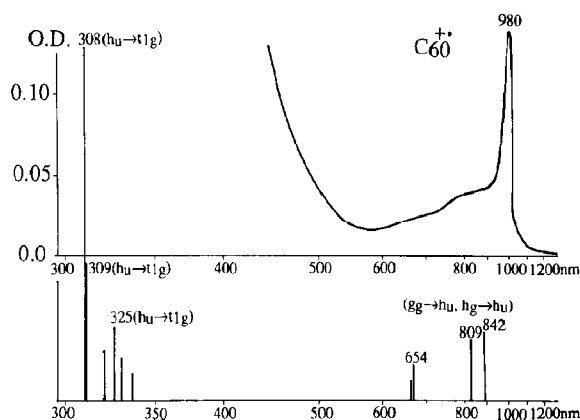

Fig. 2. Absorption spectra of the radical cation of C_{60}. Upper: Observed for a γ-irradiated and photobleached C_{60}/FM solution at 77 K in a 5 mm cell. Lower: CNDO/S spectrum for the radical cation (see the caption to fig. 1).

eV) is fairly close to the separation of 1.35 eV between the first and the second photoelectron peaks at 7.6 and 8.95 eV, respectively [6]. The correlation between the difference of ionization potentials of a parent molecule and the electronic transition of its radical cation has been shown in a previous paper [12]. The peak at 980 nm seems to correspond to the 0–0 band of the transitions at 842 and 809 nm predicted by the CNDO/S calculation for the radical cation (see the lower part of fig. 2). The very broad and feeble bumps at about 850 nm are reproducible so that they are considered to be related with the peaks at 654 and 652 nm of the CNDO/S spectrum. The reason for the broadening is not known at the moment. Since the first three highest occupied molecular orbitals of the parent C_{60} are of the symmetries of h_u, h_g and g_g, there should be many low-lying electronic transitions for the radical cation of C_{60} which are both allowed and forbidden. The broad absorption at $\lambda < 900$ nm is considered to comprise these transitions.

The top panel of fig. 3 shows the absorption spectrum of C_{70} dissolved in MTHF and measured at 77 K in a 1.5 mm cell. The spectrum is very similar to that reported in the literature [8], except that the absorbance of the 331 nm peak is larger than that reported, on account of the contaminating C_{60} which happens to absorb strongly at 328 nm [8]. The hatching indicates the contribution of the absorption
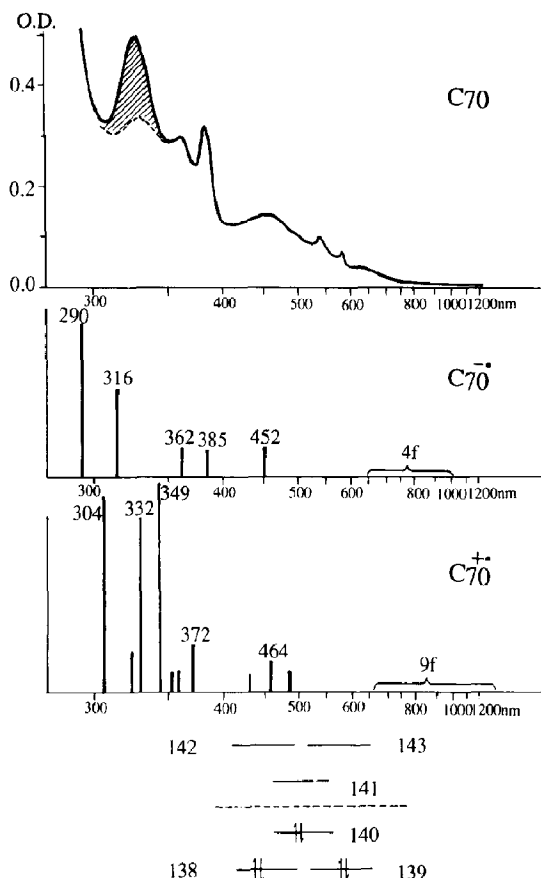
Fig. 3. Spectra of C_{70}, C_{70}^-, and C_{70}^+. Top: Observed for an unirradiated C_{70}/MTHF solution at 77 K in a 5 mm cell. The spectrum is favorably compared with the authentic spectrum for C_{70} in the literature [8] except for the hatched part which is due to the absorption of the coexisting C_{60} (see section 2). Second: CNDO/S spectrum for C_{70}^-. The calculation was carried out assuming a C–C bond length of 1.421 Å. Only the relatively significant transitions are shown. The notation 4f indicates that there are four symmetry-forbidden transitions in the region of the curly bracket. Third: CNDO/S spectrum for C_{70}^+. Bottom: Schematic representation of the active molecular orbitals calculated for the parent C_{70} molecules. The numbers denote the order of orbital.

due to C_{60}. After γ-irradiation and the subsequent photobleach with red light, the sample exhibited only a slight signal of the radical anion of C_{60} which coexists with C_{70} to about 10% (see section 2) and broad absorptions at $\lambda < 400$ nm which increased monotonously towards shorter wavelengths. In other words, we failed to detect any structured absorption attributable to the radical anion of C_{70}. However, this apparently negative result is compatible with CNDO/

S calculations, the result of which is shown in the second panel of fig. 3. The first two predicted transitions at 2840 nm are allowed which involve the configurations ($141 \rightarrow 142$) and ($141 \rightarrow 143$) where the numbers denote the molecular orbitals for the parent molecule of C_{70} (see the scheme at the bottom of fig. 3). However, the mid-IR transition with a very small oscillator strength is far from the experimentally surveyed spectral region so that the transition may have eluded the detection in our experiment. The next four transitions predicted at 1023 to 693 nm are symmetry-forbidden. Therefore, the failure to detect any structured absorption is reasonable.

Finally, the C_{70}/FM system was also examined to find that no significant absorption attributable to the radical cation of C_{70} appears in the visible and the near-IR regions. The result is consistent with the CNDO/S calculation for the cation as shown in the middle of fig. 3; the first two transitions, consisting mainly of ($138 \rightarrow 140$) and ($139 \rightarrow 140$) configurations, are predicted at 5560 nm with a fractional oscillator strength and the next nine transitions at 1271 to 653 nm are symmetry-forbidden as in the case of the anion. Although the CNDO/S calculations for both the anion and the cation of C_{70} predict absorptions at 400–500 nm and in the shorter wavelength region, these must be overlapped by the absorptions due to solvent radicals [7], and will not be analyzed in detail.

4. Conclusion

The present work provides spectral information on the radical ions of C_{60} and C_{70} which are not obtained by conventional techniques such as the alkalimetal reduction. The major results may be recapitulated as follows: Both the radical anion and the cation of the two fullerenes can be produced in γ-irradiated frozen polyatomic matrices and the electronic spectra of the ions measured in the visible and the near-IR regions. As for the peak at 1076 nm for the anion of C_{60}, a semiquantitative extinction coefficient is obtained. All the spectral data are consistent with related experimental data such as photoelectron and resonance Raman spectra and with the results of CNDO/S calculations.

Acknowledgement

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