

ABSORPTION AND EMISSION SPECTRA FOR C₆₀ ANIONS

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Absorption spectra are detected for C₆₀⁻ and C₆₀²⁻ produced electrolytically in solution at room temperature. Theoretical analysis of the spectrum of C₆₀⁻ by CNDO/S calculations gives an interpretation of the characteristic near-IR bands, the weak visible bands, and the strong bands in the UV region. The emission spectrum of C₆₀⁻ is a mirror image of the near-IR absorption band, and the detection of the emission reconfirms our original assignment of the absorption spectrum. The nature of the spectrum of C₆₀²⁻ is characterized by a similar orbital picture to that of C₆₀⁻. Further laser experiments of significance are proposed.

KEY WORDS: C₆₀ negative ion, near IR absorption, CNDO calculation, Jahn-Teller distortion

INTRODUCTION

Since our report of the electronic absorption spectra of the radical cation (C₆₀⁺) and anion (C₆₀⁻) in γ -irradiated glassy polyatomic matrices at 77K¹, many investigations of these radical ions have been performed. Similar spectra have been obtained not only in Ar matrix² but also in the electrolyzed solutions^{3,4,5,6}, but some contradictory interpretations were reported as to the nature of the near-IR absorption band of C₆₀⁻. In order to settle this contradiction, a consistent interpretation for the electronic absorption and newly detected emission spectra of C₆₀⁻⁷ are proposed here in connection with the assignment of the absorption band of C₆₀²⁻.

EXPERIMENTAL

C₆₀ was prepared by a method similar to that described by Krätschmer et al.⁸ C₆₀⁻ and C₆₀²⁻ were produced by controlled-potential electrolysis using a flow cell equipped with a reference electrode. The solvent and the electrolyte used for electrolysis are methylenechloride and tetra-n-butyl ammonium perchlorate purified by standard procedures. The solution of methylenechloride containing about 2.5×10^{-4} mol/l of C₆₀ and about 0.1 mol/l of the electrolyte was deoxygenated by argon gas bubbling. The

quantitative-electrolysis method used here can achieve 100% efficiency for the electrochemical reduction; the concentration of mono- and di- anions can be controlled quantitatively by adjusting the electrode potential and the flow rate of the solution. Potentials of -0.8V and -1.6V vs. I_2/I^- (acetonitrile) were used to reduce C_{60} to the mono- and di- anion. In this way the extinction coefficient of C_{60}^- at $1,073\text{ nm}$ was determined as $1.55 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and that of C_{60}^{2-} at 950 nm as $2.09 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. The absorptions were recorded on a Hitachi U-3400 spectrometer and the emission spectrum by a Bomem DA 3.36 FT spectrometer in combination with a Nd:YAG laser.

RESULTS AND DISCUSSION

The spectra for C_{60}^- and C_{60}^{2-} are shown in Figure 1. Both spectra reveal specific near-IR bands starting at 1073 nm for C_{60}^- and 950 nm for C_{60}^{2-} , weak visible bands around 600 nm , and very intense UV bands. Although the detailed band shape in the UV region was not obtained because of overlapping absorption due to the neutral C_{60} and the electrolyte, an increasing absorbance was measured.

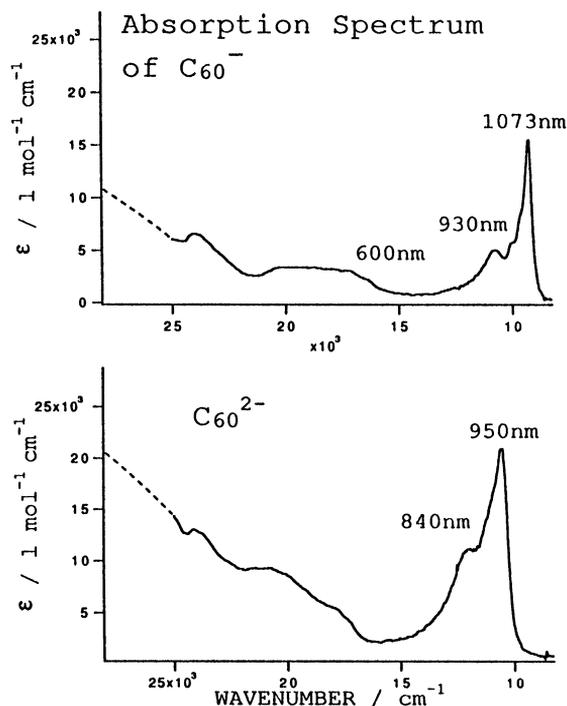


Figure 1 Absorption spectra for C_{60}^- and C_{60}^{2-} produced electrolytically in solution at room temperature.

Figure 2 shows the emission spectrum of C₆₀⁻ obtained with a Nd:YAG laser excitation at 1,064 nm together with the absorption spectrum. The emission spectrum is a mirror image of the near-IR absorption band, and the emission and absorption spectra both show vibrational progressions with fundamentals of 1,310 and 390 cm⁻¹, and 1,410 and 370 cm⁻¹ respectively. The mirror image pattern of emission and absorption spectra supports our assignment¹ of the near-IR bands at 1,073 nm and 930 nm to vibronic structure, not to two different electronic states as suggested by Negri et al.⁹ or Lawson et al.⁶ The near-IR absorption band can be characterized as the first optically allowed transition on the basis of results obtained by our CNDO/S¹ calculation and a SCF-X α -SW calculation by Heath et al.⁵ Negri et al.,⁹ however, proposed a different assignment of the band, namely to a second optically allowed transition, from the results of PPP calculation. The detection of the emission band favors our interpretation. The near-IR band indeed corresponds to the first optically allowed transition unless C₆₀⁻ belongs to the exceptional case of a breakdown in Kasha's law.

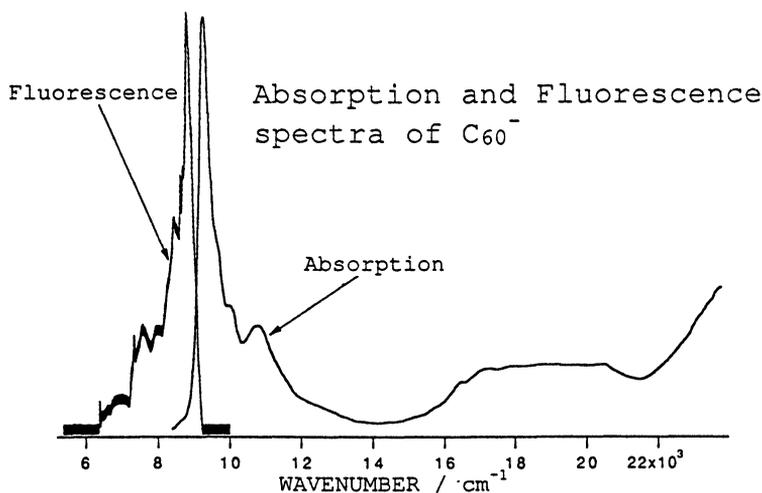


Figure 2 Absorption and emission spectra of C₆₀⁻ produced by electrolysis and measured at room temperature.

This experimental support for our assignment encourages us to interpret the absorption bands of C₆₀⁻ and C₆₀²⁻ consistently in terms of the results of a revised CNDO/S calculation. Figure 3 shows the absorption spectrum of C₆₀⁻ together with a stick diagram which exhibits the oscillator strength at each transition energy obtained by the CNDO/S calculation. The CNDO/S calculation was done by using the Jahn-Teller distorted molecular geometry which Koga et al.¹⁰ optimized at ab-initio level of theory. They showed that small Jahn-Teller distortions took place to give the D_{2h}, D_{3d}, and D_{5d} symmetry structures. The results of the CNDO/S calculation for the D_{2h} symmetry are shown in Figure 3. The near-IR band is well associated

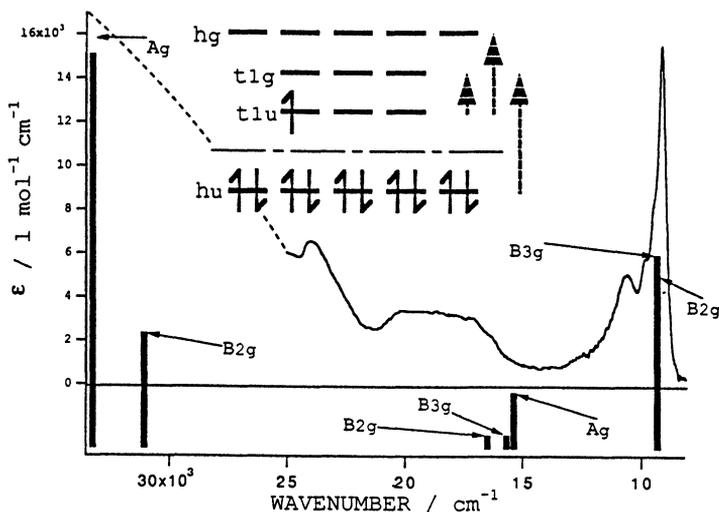


Figure 3 Absorption spectrum for C_{60}^- with a stick diagram exhibiting the relative oscillator strengths obtained by CNDO/S calculation for an optimized geometry of C_{60}^- in the D_{2h} symmetry. The inset shows the schematic representation of the three patterns of allowed transitions of C_{60}^- in terms of molecular orbitals.

with the $B_{1u} \rightarrow B_{2g}$ and $B_{1u} \rightarrow B_{3g}$ transitions, the weak visible band with the $B_{1u} \rightarrow A_g$, $B_{1u} \rightarrow B_{3g}$, and $B_{1u} \rightarrow B_{2g}$ transitions, and the intense UV band with the $B_{1u} \rightarrow B_{2g}$ and $B_{1u} \rightarrow A_g$ transitions. Considering the small amplitude of the Jahn–Teller distortion as shown in the theoretical calculation by Koga et al., and the correlation of the state between the D_{2h} and hypothetical I_h symmetries, the specific features of the absorption bands of C_{60}^- are classified into three transitions as shown in the inset of Figure 3. The near-IR band is approximately interpreted in the orbital picture as an electron jumping from a t_{1u} to a t_{1g} orbital ($t_{1u} \rightarrow t_{1g}$ jump), the visible band as a $t_{1u} \rightarrow h_g$ jump, and the intense band in UV region as a $h_u \rightarrow t_{1g}$ jump. Furthermore, the absorption bands of C_{60}^{2-} would be also characterized by the same orbital picture. An ESR measurement¹¹ has indicated that the ground state of C_{60}^{2-} is a triplet state, thus two electrons having parallel spin are assigned to two of the three t_{1u} orbitals, and the near-IR, visible, and UV bands for C_{60}^{2-} correspond to the optically allowed first, second, and third transitions similar in nature to those of C_{60}^- as shown in the inset of Figure 3.

The electronic absorption spectra of C_{60}^- and C_{60}^{2-} measured at room temperature in solution are well interpreted by the approximate orbital picture without considering any Jahn–Teller distortion. On the other hand we reported that the effect of the Jahn–Teller distortion was reflected in the value of the g factor⁴ and the spectral line shape⁷ of the ESR measurement for C_{60}^- . But neither the magnitude nor the direction of the Jahn–Teller distortion could be obtained from the ESR spectra of C_{60}^- . In this regard, it is worth pointing out that two further experiments using a laser are possible and significant for investigating the detailed electronic and

molecular structure of Jahn–Teller distorted C₆₀⁻. One is an electronic resonance Raman measurement for C₆₀⁻ in solution. Excited states which are lifted from the T_{1u} ground state in I_h symmetry by the Jahn–Teller distortion lie close in energy with the ground state. For example for the geometry in D_{2h} symmetry, B_{1u}, B_{2u}, and B_{3u} states are lifted from the T_{1u} state and the amount of the splitting energy was calculated as about 2,100 cm⁻¹ by Koga et al. The small energy difference between B_{2u}, B_{3u} and B_{1u} would be measured as the value of the Raman shift. A further experiment of interest is the resonantly enhanced multiphoton ionization of C₆₀⁻ in the gas phase. The electron affinity of 2.6–2.8 eV for C₆₀¹² is much larger than the transition energy of C₆₀⁻ to the first excited state at 1,073 nm. Therefore, the photodetachment via the resonant excitation of the state could be detected, and the energy levels for the (ro)vibronic structure in the excited state of C₆₀⁻ could be obtained.

CONCLUSION

The detection of the emission spectrum of C₆₀⁻ gives strong support to our original assignment of the first electronic absorption band. The features of the absorption bands for both C₆₀⁻ and C₆₀²⁻ are consistently interpreted by this assignment.

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