Effects of Solvent Environment on Vibronic Structures of the C$_{70}$ Fluorescence Spectrum. Reverse Ham Behaviour in Solvent Polarity Dependence

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Strong solvent dependence of vibronic structures in C$_{70}$ fluorescence spectrum, in the opposite direction from the Ham effect observed in benzene and pyrene, is attributed to perturbations in vibronic coupling and/or polarity dependence of excited state potential energy surface.

The properties of fullerenes C$_{60}$ and C$_{70}$ have attracted much attention.[1-3] Electronic absorption and fluorescence spectra of C$_{70}$ in different solvents have been reported.[4-10] It is known that the fluorescence spectra of C$_{70}$ are solvent sensitive. At room temperature in hexane or methylcyclohexane the spectrum is well resolved with fine vibronic structures, but if toluene or benzene is used as the solvent then the spectrum is much broader. Here, we report fluorescence spectra of C$_{70}$ in solvent mixtures composed of hexane and a polar or polarizable solvent. It is found that the vibronic profile depends strongly on solvent polarity and polarizability.

Fluorescence spectra of C$_{70}$ were recorded on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450-W xenon source and a R928 photomultiplier tube using a right-angle geometry (excitation slit 19 nm and emission slit 1.9 nm). As shown in Fig. 1, the spectrum in hexane is well resolved with eight peaks, presumably corresponding to the same number of vibronic bands. As the THF volume fraction in the mixtures increases, the vibronic profile of the fluorescence spectra changes significantly. The most visible is a continuous enhancement in the intensity of the third vibronic peak, which is accompanied by a slight increase in the fourth peak and decreases in the first and second peaks. However, the intensities of the four longer wavelength bands remain essentially unchanged. For a more quantitative description, a plot of the intensity ratio between the first and the third vibronic peaks (I_1/I_3) as a function of THF volume fraction is shown in Fig. 2. Although the polarity of the solvent mixtures is difficult to determine quantitatively because of

microscopic solvation effects, it can be concluded that the polarity of the mixtures increases with increasing THF volume fraction because THF is a polar solvent. Thus, the I_1/I_3 ratio decreases with increasing solvent polarity.

It is well known that solvent environment has profound effects on molecular absorption and emission. While solvatochromic shifts have been studied extensively and understood at least qualitatively, there is only limited information on the effects of solvent on the vibronic profile of electronic absorption and emission spectra. However, a well-established example is the medium-induced spectral changes in the 260 nm region of the benzene absorption spectrum,[11] which was attributed to the effects on the symmetry forbidden 0-0 progression owing to interactions between benzene and solvent molecules.[11] This phenomenon is known as the Ham effect[12] and has also been observed in benzene derivatives and other aromatic molecules; the observation in pyrene (Py) is probably the most dramatic.[13] The 0-0 band intensity in the pyrene fluorescence spectrum is extremely solvent sensitive, varying with solvent polarity and polarizability over a wide range. In fact, the intensity ratio between the first and the third vibronic bands of pyrene fluorescence spectra has been widely used as a solvent polarity scale, known as the Py scale.[14] Thus, for the hexane-THF mixtures, pyrene is employed as a probe. As shown in Fig. 2, the Py values increase monotonically with increasing THF volume fraction in the mixtures. A plot of the I_1/I_3 ratio of C$_{70}$ fluorescence
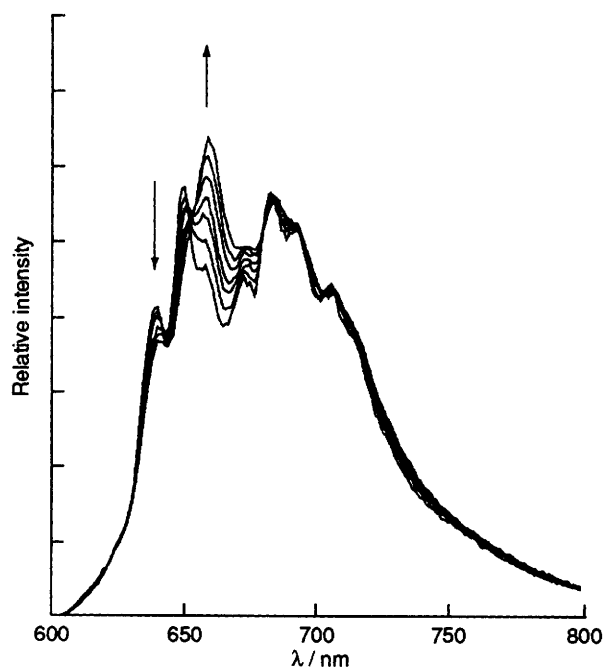

Fig. 1 Fluorescence spectra of C$_{70}$ in hexane-THF mixtures (excitation wavelength 472 nm, uncorrected) with THF volume fractions (in the direction of arrows) of 0, 4, 7, 10, 14, 19 and 25%
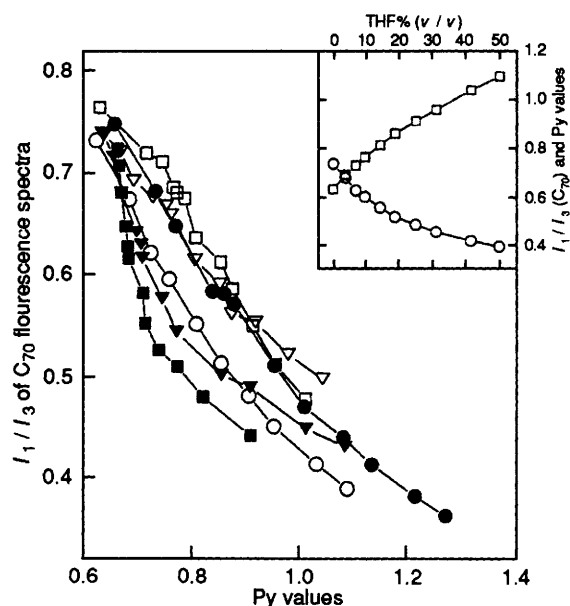

Fig. 2 Plots of the I_1/I_3 ratio of C$_{60}$ fluorescence spectra vs. Py values in hexane-THF (O), hexane-acetone (●), hexane-chloroform (∇), hexane-dichloromethane (▼), hexane-ethanol (□) and hexane-toluene (■) mixtures with the second component volume fraction from 0 to 50%. Insert: plots of the I_1/I_3 in C$_{70}$ (O) and Py values (□) as a function of THF volume fraction in hexane-THF mixtures. The uncertainties for the data are estimated in the range of ±10%.

spectra *vs.* the Py values of the same hexane–THF mixture compositions is shown in the insert in Fig. 2. The relationship is close to linear, but with a negative slope.

The solvent dependence of C_{70} fluorescence spectra is not limited to hexane–THF mixtures. Fluorescence spectra of C_{70} obtained in solvent mixtures of hexane–acetone, hexane–dichloromethane, hexane–chloroform, hexane–ethanol and hexane–toluene show the same pattern. Among the solvents in these mixtures, acetone is a polar solvent similar to THF, dichloromethane and chloroform are also polar but with heavy chlorine atoms, ethanol is a protic solvent, and toluene is a nonpolar solvent with high polarizability. As the same behaviour is observed in these very different solvent mixtures, it is concluded that the variations in vibronic profile are dictated by changes in solvent polarity and polarizability. Similarly, pyrene is used as a probe for the characterization of these solvent mixtures. As shown in Fig. 2, the fluorescence intensity ratios (I_1/I_3) of C_{70} always decrease monotonically with increasing Py values obtained under the identical solvent conditions, though the quantitative relationships in different solvent mixtures are somewhat different.

The dramatic solvent dependence of the Py values is a result of perturbations in vibronic coupling due to solute–solvent interactions (Ham effect).[14] For C_{70}, it appears that there is a reverse Ham effect in the solvent dependence of the fluorescence vibronic profile. The I_1/I_3 ratios in C_{70} vary with solvent polarity and polarizability in an opposite direction from that of the Py values (Fig. 2). The behaviour is a reflection of characteristic properties of C_{70} electronic-vibrational structures. However, the analysis for planar aromatic systems such as benzene and pyrene is not readily applicable because the electronic transitions of C_{70} are not well understood. Two possible explanations for the observation are perturbations in vibronic coupling and a polarity dependence of excited state potential energy surface.

It is known from both semiempirical and *ab initio* calculations that the occupied frontier orbitals of C_{70} (belonging to the D_{5h} symmetry group) have e_1'' and a_2'' symmetries for HOMO – 1 and HOMO, respectively.[15,16] The energy levels of the unoccupied frontier orbitals (LUMO and LUMO + 1) remain a question. In a Hückel calculation, the LUMO is a_1'' and non-bonding.[15] However, in an *ab initio* calculation with the minimum basis set and at the optimized geometry,[16] the inclusion of electron repulsion causes the a_1'' orbital to be above the e_1'' orbital, which is the LUMO + 1 in the Hückel calculation. Therefore, two possible low-lying electronic transitions should be considered, $A_2' \leftarrow A_1'$ and $E_1' \leftarrow A_1'$. As the two excited states $(A_2'$ and $E_1')$ are very close, it is not possible to make a reliable prediction about the lowest excited state based on these calculations. If the lowest emitting singlet state is A_2', the transition is not symmetry allowed. As a result, vibronic coupling may play a role in the fluorescence of C_{70}. Thus, the solvent dependence of the vibronic profile could be due to the same mechanism as the one for pyrene, namely that the behaviour is dictated by perturbations in vibronic coupling due to solute–solvent interactions. However, a difficult question is why the solvent dependence in C_{70} follows an opposite trend from that in planar aromatic molecules such as benzene and pyrene. Although the vibrational fundamentals of ground state C_{70} have been calculated[17] and some of them have been determined experimentally,[18–20] an assignment of the fluorescence vibronic structures is difficult because of too many degrees of freedom.

Alternatively, the redistributon of vibronic band intensities could be due to a dependence of the excited state potential energy surface on solvent polarity and polarizability. A change in the shape of the multidimensional energy surface could affect the vibronic overlaps between electronic excited and ground states, resulting in variations in the fluorescence vibronic profile.

The behaviour could also be a combined result of both mechanisms. Nevertheless, an interesting feature in the solvent dependence is that the four longer wavelength bands are essentially unchanged. The explanation for such behaviour may be related to the significant discrepancy between the calculated and experimental transition probabilities of C_{70}.[8]

Finally, it is likely that the broadness of the C_{70} fluorescence spectrum in solvents such as benzene and toluene is due to solvent polarizability effects, not specific interactions such as formation of C_{70}–benzene complexes, because similar broad spectra are observed at high polar component fractions in all of the solvent mixtures used in this study.

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