

Relative Energies and Entropies of Fullerene Triplet States in Solution

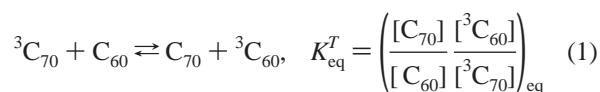
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Electronically excited states are, of course, fundamentally important in molecular photochemistry and photophysics. Although the energies of excited species may be deduced using spectroscopy or photoacoustic or photothermal calorimetry, their entropies are much more elusive. We present here results from a novel method that measures relative entropies as well as energies of triplet-state molecules in mixed solutions. This method is suitable for samples in which energy transfer between species is more rapid than deactivation. The resulting preequilibrated balance of triplet excitation is deduced by analyzing transient absorption spectra. Measuring the triplet equilibrium constant as a function of sample temperature lets one extract both ΔH° and ΔS° for the transfer of triplet energy between species. We have applied this approach to the fullerenes C_{60} , $(CH_3)_2C_{60}$, and C_{70} in toluene solution, and we find that the triplet energies of C_{60} and C_{70} are equal within 0.2 kJ mol^{-1} , whereas that of $(CH_3)_2C_{60}$ lies ca. 3.4 kJ mol^{-1} lower. From ΔS° values we find evidence for a 3-fold orbital degeneracy in triplet C_{60} , implying only limited Jahn–Teller splitting. Our entropy result for C_{70} indicates a nondegenerate lowest triplet state lying ca. 600 cm^{-1} below a doubly degenerate triplet.

In many fullerenes, including those studied here, optical excitation is followed by nanosecond-scale radiationless decay that generates the lowest triplet state with near-unit efficiency.¹ It was shown several years ago that in samples containing two different fullerene solutes, triplet-state molecules produced in this way can readily transfer their excitation to unexcited fullerenes of the other type.² The rate constants for such triplet energy exchange are high enough (ca. $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) to allow exchange to kinetically dominate deactivation even at micromolar concentrations. As a result, a mixed sample's triplet population quickly partitions between species, reaching a preequilibrated balance reflecting the difference in standard Gibbs free energies between triplet excitation of the two compounds. For a mixture of C_{60} and C_{70} we have



To determine the value of K_{eq}^T one needs the ratios of ground and triplet state concentrations at preequilibrium. Triplet state concentrations can be found by analyzing the sample's transient spectrum as a superposition of transient spectra from the two individual fullerenes. This analysis requires reliable molar absorptivity calibration of the single-component transient spectra, as is achieved with an accuracy of a few percent using a recently developed photometric method.³ Ground-state concentrations can be easily deduced from the prepared sample composition, corrected if necessary by subtracting triplet concentrations. Once K_{eq}^T has been found as a function of temperature, conventional analysis gives ΔH° and ΔS° . These values describe the enthalpy

and entropy differences between exciting a dissolved C_{60} molecule from its ground state to its relaxed triplet state and performing the same excitation in a C_{70} molecule. Because changes in enthalpy and internal energy are nearly identical in solution, we will interpret the ΔH° results as energies.

To perform this study we first measured induced spectra of pure fullerene solutions as a function of temperature. The purities of our commercial C_{60} and C_{70} samples were greater than 99.8%, as verified by HPLC analysis. We used a Cosmosil Buckyprep HPLC column to isolate the 1,2-isomer of $(CH_3)_2C_{60}$ from an electrochemically synthesized sample that also contained the 1,4-isomer.⁴ All samples were dissolved in Optima grade toluene (Fisher Scientific) that had been purified by distillation from $LiAlH_4$ and then from P_2O_5 . Our transient absorption spectrometer, described previously,⁵ used 532-nm pulses from a Q-switched Nd:YAG laser to excite the samples and a tungsten–halogen lamp and monochromator to probe for induced changes in sample absorbance. Carefully degassed sample solutions were held in a 5-cm path length cell thermostated by a water jacket.

We first determined that the induced absorption spectra of pure solutions of C_{60} , C_{70} , and $(CH_3)_2C_{60}$ remained essentially unchanged from 2 to 76 °C. Then we prepared sample solutions containing binary mixtures: $19.2 \mu\text{M } C_{60}$ with $51.5 \mu\text{M } C_{70}$, $3.97 \mu\text{M } C_{60}$ with $53.6 \mu\text{M } C_{70}$, $4.2 \mu\text{M } (CH_3)_2C_{60}$ with $50.1 \mu\text{M } C_{70}$, and $10.0 \mu\text{M } (CH_3)_2C_{60}$ with $50.0 \mu\text{M } C_{70}$. Induced spectra covering 600 to 1050 nm were recorded as a function of delay after excitation as samples were held at temperatures between 2 and 76 °C. Figure 1 shows the time evolution of the induced spectrum for a solution of C_{60} and C_{70} . For clarity, all of these traces have been normalized to the 970-nm peak arising from $T_n \leftarrow T_1$ absorption in C_{70} . The changing spectrum reflects net transfer of triplet energy to C_{60} from C_{70} , which is preferentially excited because of its larger ground-state absorptivity at 532 nm. The ratio of induced absorbances at 750 and 970 nm smoothly increases with time and remains constant beyond ca. 40 μs . This marks the preequilibration of triplet energy between the two species. Induced spectra beyond the preequilibration onset were averaged and then analyzed as a superposition of the two individual induced spectra. Our analysis method should be more reliable than that reported by Yamaji et al.⁶ because we fit the entire spectrum rather than just two wavelengths. Figure 2 shows the single-component spectra as broken lines, the preequilibrated data points as circles, and the best linear-combination fit as a solid curve. This fit matches the data very closely and provides secure values for the concentrations of triplet C_{60} and C_{70} . The deduced values were then used in eq 1 to find K_{eq}^T .

We repeated this process for each fullerene mixture over the full range of temperatures using samples of two different composition ratios. Surprisingly, at the highest temperatures the spectral simulations were less successful both for C_{60}/C_{70} and $(CH_3)_2C_{60}/C_{70}$ mixtures. Systematic deviations became apparent between the measured data and the best fits from combining the two single-component spectra. Investigation of this anomaly revealed the presence of a third transient species with an absorption maximum near 850 nm. This third species persists far longer than the preequilibrated triplet pool, implying that it is a transient side-product and does not alter the value of K_{eq}^T . We therefore accounted for it through a third component in the spectral fitting to obtain proper values for fullerene triplet concentrations. The identity of the third transient species remains to be clarified.

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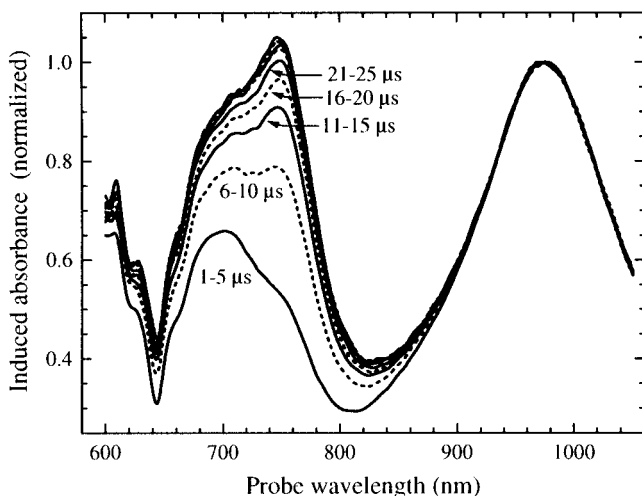


Figure 1. Induced absorbance in a toluene solution of 4.0 μM C_{60} plus 53.8 μM C_{70} at 23.8 $^{\circ}\text{C}$. Spectra at different delays after excitation have been scaled to match at 970 nm.

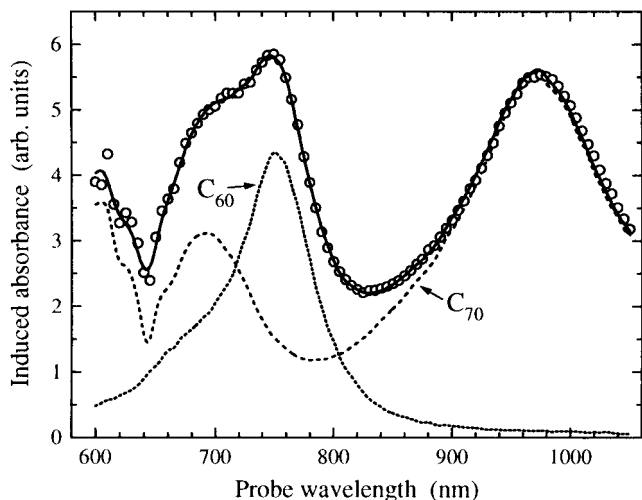


Figure 2. Preequilibrated induced spectral data for the mixed sample of Figure 1 (circles), induced spectra of pure C_{60} and C_{70} solutions (broken lines), and a simulation of the mixed data as a superposition of the C_{60} and C_{70} spectra (solid line).

In Figure 3 we show van't Hoff plots of the deduced triplet equilibrium constants. Linear least-squares fitting gives the results in Table 1. We find the lowest triplet states of C_{60} and C_{70} in toluene solution to be isoenergetic within our error limit of approximately 0.2 kJ mol^{-1} . However, the relaxed triplet state of $(\text{CH}_3)_2\text{C}_{60}$ lies 3.4 kJ mol^{-1} below that of C_{70} or C_{60} . Lowering of the triplet state energy by derivatization has previously been observed in C_{60} through phosphorescence spectroscopy.⁷

Although the ΔS° values associated with triplet energy transfer may (in principle) have small contributions from changes in vibrational or solvation entropies, we expect electronic entropy effects to dominate strongly. The I_h and D_{5h} symmetries of C_{60} and C_{70} allow orbital degeneracies of up to five or two, respectively, in addition to the 3-fold spin degeneracies of all triplet states. No such orbital degeneracies are possible in $(\text{CH}_3)_2\text{C}_{60}$ because of its C_{2v} symmetry. Our experimental $\Delta S^{\circ}/R$ value for triplet energy transfer from $(\text{CH}_3)_2\text{C}_{60}$ to C_{60} is found from the Table 1 data by subtracting -0.48 from 0.70 to obtain 1.18 ± 0.13 . Using the expression $\Omega = \exp(S^{\circ}/R)$, this value gives an electronic degeneracy ratio, $\Omega^T(\text{C}_{60})/\Omega^T((\text{CH}_3)_2\text{C}_{60})$, of 3.25 ± 0.4 , indicating 3-fold orbital degeneracy of the lowest C_{60} triplet. This result agrees with spectroscopic and theoretical assignments of ${}^3\text{T}_{2g}$ symmetry for this state.⁸⁻¹⁰ It also indicates

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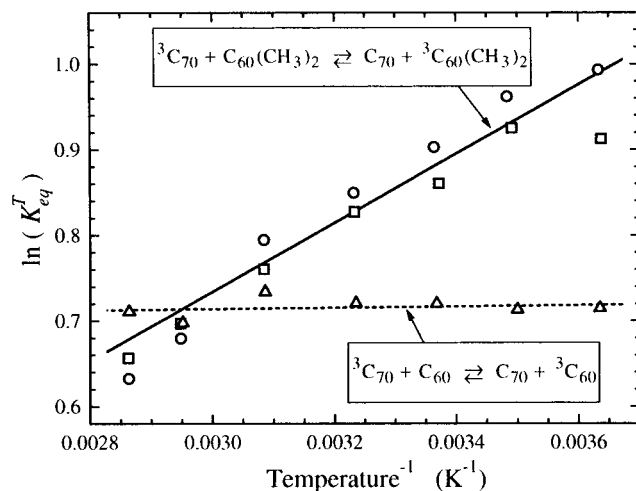


Figure 3. Van't Hoff plot of equilibrium constant data for exchange of triplet energy between C_{70} and C_{60} (Δ), and between C_{70} and $(\text{CH}_3)_2\text{C}_{60}$ with initial $[\text{C}_{70}]/[(\text{CH}_3)_2\text{C}_{60}]$ ratios of 5:1 (\circ) and 12:1 (\square). Straight lines are linear best fits to the data.

Table 1. Thermodynamic Quantities Found for Triplet Energy Transfer between Fullerenes in Fluid Toluene Solution

triplet energy transfer		ΔH°		ΔS°	
from	to	(kJ mol^{-1})	(cm^{-1})	($\text{J mol}^{-1} \text{K}^{-1}$)	/ R
C_{70}	C_{60}	-0.1 ± 0.2	-8 ± 16	5.8 ± 0.5	0.70 ± 0.06
C_{70}	$(\text{CH}_3)_2\text{C}_{60}$	-3.4 ± 0.3	-285 ± 25	-4.0 ± 1.0	-0.48 ± 0.12

that its three components remain thermally populated, despite theoretical predictions of large Jahn–Teller splittings.^{11,12}

On the basis of the triplet-state degeneracies of 1 for $(\text{CH}_3)_2\text{C}_{60}$ and 3 for C_{60} , our measured ΔS° values imply that the entropy of triplet state C_{70} is $0.42 \pm 0.05 R$. This entropy is too low for a doubly degenerate T_1 state but too high for a singly degenerate T_1 unless there is also a nearby, thermally populated T_2 state. Although theory predicts that the lowest triplets of C_{70} are ${}^3\text{A}_2'$ and ${}^3\text{E}_1'$,¹³⁻¹⁵ spectroscopic studies have disagreed as to the ordering.¹⁶⁻¹⁹ Our result implies that ${}^3\text{A}_2'$ is the lowest triplet state in C_{70} and that ${}^3\text{E}_1'$ lies $600 \pm 50 \text{ cm}^{-1}$ higher in room-temperature toluene solution. The most recent spectroscopic study deduced the same ordering with a state spacing near 165 cm^{-1} in a cryogenic matrix.¹⁹ We believe that further relative entropy measurements will help to characterize the triplet manifolds of many other interesting molecules.

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