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Experimental Evidence for the Photoisomerization of Higher Fullerenes

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The emerging challenge posed by the bandwidth limitations of electronics has paved the way for the development of optical materials which can be used for faster optical switching. Over the past years, there has been an increasing interest in the study of organic and inorganic materials that exhibit optical switching behavior for optical gating.[1] Such materials find use in the development of optical computing and optical communication systems. Ideal compounds for optical gating should exhibit a strong excited-state absorption and a weak absorption in the ground state. Several systems such as phthalocyanines,[2] metal[3] or semiconductor[4] nanoparticles, and the fullerenes[5] are interesting candidates for fast optical gating on the femtosecond time scale. Fullerenes, which are colored due to weak absorption throughout the visible spectrum, are very promising candidates for this application. Over the past years, a considerable amount of research has been devoted to understanding the dynamics of C_{60}.[6,7] Previous measurements reveal the presence of the excited singlet state at <100 ps and the lowest triplet state at ≥1 ns delay time,[6] which clearly distinguishes faster relaxation processes from triplet state formation. Transient absorption measurements show that the time constant for the intersystem crossing (ISC) of C_{60} is 1100 ± 26 ps, which agrees well with previously reported values.[7] The broad transient absorption band of C_{60} suggests the usefulness of fullerenes as optical limiters. On the other hand, for larger fullerenes with >70 carbon atoms, only very little is known about their excited-state dynamics. In this communication, we focus the experiments toward the higher fullerenes in the size range of C_{70}−C_{96} using femtosecond time-resolved spectroscopy in the time domain of <100 ps to reveal the initial formation of the lowest excited singlet state. The larger fullerenes are indeed an interesting challenge for the spectroscopic investigator because the number of possible isomers and electronic states increases rapidly with increasing size.[8] Accordingly, more complex relaxation dynamics are anticipated for the larger fullerenes. As a reference compound, the highly symmetric C_{60} is used.

The fullerenes C_{60}, C_{70}, C_{76}, C_{84}, C_{86}, and C_{90}, investigated in this study, are thermodynamically also the most stable ones.[8] The samples used were produced by a standard arc discharge method, followed by Soxhlet extraction using *N*,*N*-dimethylformamide (DMF, 99.9%, BDH) and HPLC separation.[9] Mass spectroscopic studies on the fullerenes showed their purity to be greater than 99%. The femtosecond time-resolved experiments were carried out with a pump−probe setup in which all reflective optics are used to minimize group velocity dispersion of the probe light, such that the rise and decay of the broad transient absorption can be monitored free of distortion. The samples were excited at 388 nm, the second harmonic of an amplified fiber laser producing 130 fs pulses at 775 nm (Clark-MXR CPA 2001). Pump energies of 100 nJ per pulse were used. All fullerene solutions were excited with identical laser flux. To exclude nonlinear effects and prevent the destruction of the material, the power dependence of the transient absorptions was investigated. We found that for excitation densities below 5 μJ/pulse, there is a linear intensity dependence, and no bleaching of the sample occurs during long-term exposure to the femtosecond laser pulses.

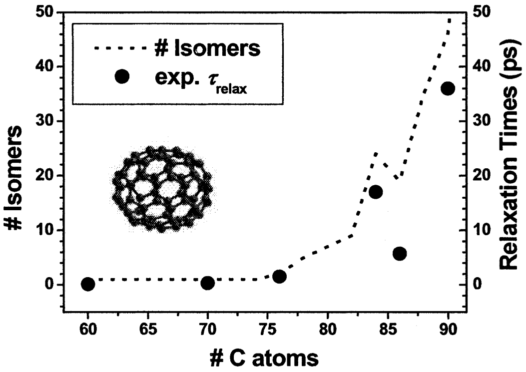

Figure 1. Correlation between the number of isomers (dotted line as a visual guide) for each fullerene and the time constant for the formation of the lowest excited singlet state monitored at 550 nm (dots).

For the larger fullerenes, the understanding of the electronic structure is more complicated because the different isomers show different symmetries and therefore different transitions. The number of isomers based on the isolated-pentagon rule[8] for the investigated fullerenes increases as shown in the following brackets: C_{60} [1], C_{70} [1], C_{76} [2], C_{84} [24], C_{86} [19], and C_{90} [46]. The increase of isomers versus number of carbon atoms is illustrated in Figure 1. The increase is not monotonic; C_{86} (19 isomers) has less isomers than C_{84} [24]. This correlates well with the measured relaxation time of the initially excited state. Illustrated in Figure 2 are the unusually broad transient singlet state absorption spectra of C_{84}, which are similarly observed for the other fullerenes. For all fullerenes, a fast rise time with $\tau_{rise} \leq 100$ fs is observed. This rise occurs over the whole visible range simultaneously, providing an optical gate on the femtosecond time scale. The kinetic traces measured at 550 nm and shown in Figure 3 illustrate that the time needed to populate the lowest singlet state S_1 depends on the number of existing isomers. This correlation was also observed in the NIR range up to 1200 nm.

The observed dynamics could be rate-limited by the nonradiative internal conversion (IC), $S_n \rightarrow S_1$. However, according to Fermi's Golden rule, if IC would be rate limiting for the monitored relaxation process, a higher density of states should lead to an

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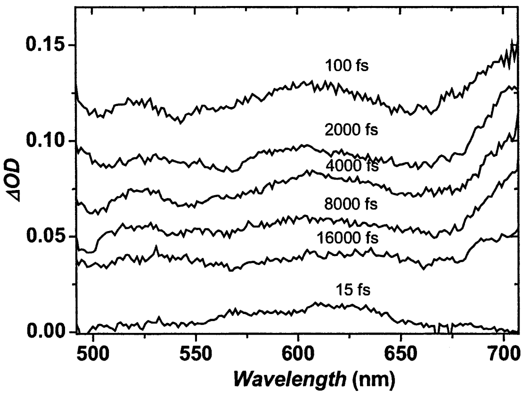

Figure 2. Dispersion-free measurement of the femtosecond transient absorption spectra of C_{84} at different delay times revealing ultrafast optical gating over the whole visible range.

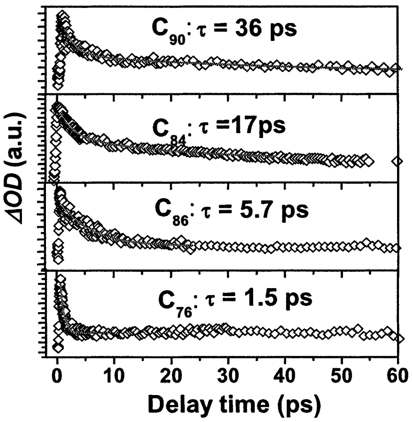

Figure 3. Femtosecond transient absorption of the investigated fullerenes monitored at 550 nm.

acceleration of the IC, and therefore the largest fullerenes should have the quickest relaxation. The later case was not observed, and the larger fullerenes in fact have the longest measured relaxation times. Moreover, the measured relaxation times did not increase monotonically with the number of carbon atoms in the fullerenes; instead they followed the number of possible isomers for each carbon cluster. One explanation for the slowing in relaxation rate of the higher fullerenes could be the formation of photoisomers from the initial excited state. The density of accessible isomers states increases with cluster size, and the energy differences for isomers of the same symmetry are in the meV range.[8] Additional relaxation channels accelerate the depopulation of the initial state.[10] However, it can also lead to long-lived transients because the relaxation of each isomer could have a different rate.[11] Here, after excitation of the higher fullerenes $C_{>70}$, excited-state intermediates are formed which delay the population to the lowest S_1 state. For example, C_{84}, which has 24 isomers, has a longer S_1 formation time (17 ps) than the larger C_{86} fullerene (5.7 ps), which only has 19 isomers. A mechanism to form isomers was suggested by Stone and Wales.[12] The Stone−Wales (SW) isomerization involves the rotation of a carbon bond that enables a pair of hexagons and a pair of pentagons to interchange positions within the fullerene. Thermally, this isomerization is Woodward−Hoffmann forbidden with a high activation energy of >5 eV.[13] Therefore, it is not likely to occur on a fast time scale. However, using semiempirical methods with an extensive configuration interaction, we calculated the excited-state SW isomerization on the four-ring patch. The calculation showed that the SW photoisomerization is barrierless, which confirms the Woodward−Hofmann rules for photoinduced reactions. The excited-state pathway might lead into a conical intersection and repopulate, at least partially, the ground state.[10] Clearly, an in-depth computational study of this femtosecond relaxation dynamics is desirable.

The energy difference of the excited-state isomers is in the low meV range,[8] and back-isomerization to form the lowest excited state is expected to occur in the picosecond time regime. This is in agreement with the relaxation times shown in Figures 1 and 3.

In summary, the observed transient spectra of higher fullerenes are spectrally broad, which is also anticipated for fullerene isomers. The ultrafast formation of the broad optical gate was monitored, practically free of dispersion. The small differences in optical transition energies for the involved species might be resolved at low temperatures. Femtosecond time-resolved spectroscopy enabled us to monitor the formation dynamics of the lowest excited singlet state and thereby provides experimental evidence of the predicted photoisomerization of the higher fullerenes.

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