

Figure 3. Time-dependent rate constant k(t) (-), eq 10, compared to the one-coordinate approximations, $k_q(t)$ (---) and $k_{\Delta E}(t)$ (---), eq 12. The two latter are indistinguishable (there is a slight difference when t $\rightarrow 0^+$), which expresses the fact that the two variables $\bar{q}(t)$ and $\Delta E(t)$ change their signs almost always simultaneously.

We have applied the preceding treatment to two choices of X:X= $\Delta E = (2n_R - 1)(E_1 - E_0)$, where E_0 and E_1 are the ground and first-excited energy levels (ΔE can be viewed as the instantaneous energy splitting between the protonic diabatic states associated with the product and reactant configurations; this choice is a natural one for charge-transfer reactions¹⁶); and $X = \bar{q} = \langle \psi_0 | q | \psi_0 \rangle$, the ground-state expectation value of the proton position operator.

Free energy curves are displayed for the three systems I, II, III in Figure 2. For weak solvent-complex coupling (case I), the potential in ΔE is confined, with no energy barrier; this corresponds to a situation in which the system oscillates (cf. upper curve in Figure 1). For stronger couplings (case II and III), the potentials broaden and a small barrier builds up (see the two lowest curves in Figure 1). The same trend is observed for the potential in \bar{q} but is not displayed here. For the largest coupling, the activation energy is about $2.3k_BT$ for $X = \Delta E$ and $5.3k_BT$ for X $= \bar{q}$. In this case, one can try to apply the formalism derived above for first-order reactions. The calculated values of k_X^{TST} are respectively 0.23 ps⁻¹ for $X = \Delta E$ and 0.22 ps⁻¹ for $X = \bar{q}$. In the case of system II, there is only a very low barrier (especially along ΔE) and the existence of a well-defined rate constant may be questionable: it is hard indeed to define a plateau time, as required in eqs 8, 9, and 11.

We plot in Figure 3 the time variation of k(t), $k_q(t)$, and $k_{\Delta E}(t)$ for system III. The curves have been obtained by averaging over a cumulated run of 1 ns, accounting for about 200 spontaneous crossings of the transition state, $n_{\rm R} = 1/2$. After a rapid decay in about a picosecond, all functions seem to reach a plateau value for times superior to 2 ps. The accuracy is limited (a better estimate would require an analysis of an ensemble of trajectories starting from the top of the barrier, $\bar{q} = 0$ or $\Delta E = 0^{20}$) and the range of times over which a plateau can be defined is rather short; since the barrier is small, the chemical and transient molecular times differ only by a factor of 20 (see below). However, from the plateau values for $2 < t_p < 5$ ps, it is possible to define a rate constant that can be estimated as $k \simeq k_q \simeq k_{\Delta E} \simeq 0.05 \text{ ps}^{-1}$. This rate is reduced by a factor of 4-5 compared to the calculated TST values, k_q^{TST} and $k_{\Delta E}^{\text{TST}}$, which indicates multiple recrossings of the transition state before the system gets trapped in a reactant or product configuration.

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Direct Detection of Neutral Products from Photodissociated C₆₀

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Neutral products from photodissociated C₆₀ detected with one-photon ionization are reported for the first time. The distribution of neutral fragments is very similar to the distribution of ion fragments. This suggests that multiphoton ionization/fragmentation of C₆₀ does not require a ladder-switching mechanism.

The understanding of the photophysical processes that occur in C₆₀ and other fullerenes promises to strengthen our understanding of processes that occur in very large molecular systems, such as biological species and nanomaterials.^{1,2} Additionally, C_{60} or ionic forms of C_{60} have been conjectured to exist in the interstellar medium.^{3,4} The stability and the resilient nature of C_{60} have been attributed to the closed-cage structure of fullerenes and the large activation barrier for dissociation.^{5,6} There have been numerous studies on the photodissociation of $C_{60}^{+,7-9}$ but only preliminary studies have been carried out on *neutral* C_{60} .¹⁰ In an effort to further elucidate the photophysical properties of C_{60} , we have measured neutral products of photodissociated C_{60} . This is the first report of experimental observations of neutral fragments after photofragmentation of C₆₀ molecules, and proves that C_{60} dissociates through a neutral channel.

The laser desorption/laser ionization mass spectrometer has been discussed in detail before, necessitating only a brief discussion here. The mass spectrometer is a linear time-of-flight (TOF) instrument of 120 cm length (see Figure 1). Particles are removed from the sample by a pulsed desorption laser, postionized with a second laser, and brought to drift potential (8 keV) by a twostage acceleration field. Ion detection is accomplished with a dual channel-plate assembly at a moderate postacceleration potential. Data are recorded in a transient recorder with a maximum time

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Figure 1. Detailed view of the ion beam optics and placement of the three laser beams for the present experiment. The sample is at 8 kV, the first acceleration grid is at 7.6 kV, and the second acceleration grid is at ground potential. The potentials are optimized for maximum resolution for ions formed by the ionization laser. The spacing between the sample and the first grid and between the first and second grid is 4 mm each. The desorption laser impinges the sample at $\approx 77^{\circ}$ with respect to the surface normal. The 308-nm fragmentation laser beam and the 118-nm ionization laser beam counterpropagate parallel to and 2 mm above the neutral C₆₀ sample. The relative delays between the three lasers are independently adjusted for maximum signal.

resolution of 5 ns. Further processing of the data is accomplished in a PC-based software system. The typical operating vacuum is 2×10^{-9} Torr. The maximum mass resolution $(m/\Delta m)$ of the instrument is approximately 1500 (fwhm) using a 5-ns laser pulse.

The 532-nm focused output of a Q-switched, mode-locked Nd³⁺:YAG laser (the macropulse of 532-nm pulses of \sim 100-ps pulse duration each) is used for desorption from a solid C_{60} sample evaporated onto a stainless steel substrate. A XeCl excimer laser (308 nm, 4 eV) photodissociates the neutral, gas-phase C_{60} molecules. Ionization of the neutral fragments is accomplished by 118-nm laser radiation. The 118-nm light (vacuum-UV radiation) is produced by frequency tripling the third harmonic of a Nd:YAG laser in a Xe/Ar mixture.¹¹⁻¹³ The 118-nm beam is spatially separated from the 355-nm laser beam using the dispersion of a MgF₂ lens, and the 355-nm laser beam is blocked with a translatable beam stop in vacuum. The lasers are triggered independently, allowing their relative timing to be adjusted. An iris is used to pick out the central portion of the desorption laser beam. A series of neutral-density filters is used to keep the beam intensity below the desorption threshold for positive ion desorption. The desorption laser is obliquely incident on the sample, and the energy is typically less than 0.01 mJ/pulse with an irradiated area of $<10^{-3}$ cm². The position of the desorption laser spot is monitored in real time with a video camera.

Figure 2 displays three different low-resolution mass spectra. The 532-nm desorption pulse is present for all spectra to provide neutral C₆₀. The top spectrum displays photodissociation/photoionization with 308-nm photons only ($\sim 100 \text{ mJ/cm}^2$). This spectrum exhibits the characteristic fragmentation pattern for C_{60} (loss of C_2 units) and also the peculiar tails on the C_{60} parent ion signal. These tails arise from delayed ionization of the excited C_{60} molecule after multiphoton absorption and have been attributed to thermionic emission.^{14,15} The middle spectrum displays photoionization via 118-nm radiation only. As discussed in our earlier publications, this 10.5-eV radiation yields direct ionization of C_{60} without fragmentation.^{14,16} Yoo et al.¹⁷ have studied the



Figure 2. Three distinct spectra displaying the evidence for neutral fragmentation of C₆₀. The 532-nm desorption pulse is present for all data shown. The top panel is photodissociation/ionization with 308-nm radiation. The middle panel is 118-nm photoionization only (the small peak at 28 μ s is indicative of prompt ions from surface ionization by the desorption laser pulse). The bottom panel displays spectra observed when all three lasers are present. Notice the features between 30 and 32 μ s from neutral fragment ionization.



Figure 3. Higher time resolution spectrum of the three-laser experiment. The fragment species are clearly evident. The time delay between the 308-nm dissociation laser and the 118-nm ionization laser has been adjusted to display the fragment neutral species between the time peaks due to ions formed from the 308-nm dissociation laser.

process of direct ionization over a wide energy range and have observed little or no fragmentation up to 40 eV for one-photon excitation/ionization. The bottom spectrum displays the case when the 308-nm photodissociation laser precedes the 118-nm photoionization by 3 μ s. Since the ionization potentials for the large fragments (C_n, 48 < n < 58) are less than the ionization potential for C_{60} (7.6 eV),¹⁸ the neutral fragment species are one-photon ionized by the 118-nm light and are observed as the small peaks between 30 and 32 μ s arrival time. The widths of these small peaks are limited by the time resolution of the digitizer.

A portion of these spectra was acquired with higher time resolution and with a $2-\mu s$ delay between the dissociation laser and the ionization laser and is presented in Figure 3. The peaks originating from either photodissociation/photoionization with 308-nm light or photoionization with 118-nm light are labeled for clarity. The time delay between pulses is selected to interleave

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TABLE I: List of the Most Important Processes Occurring after Multiphoton Excitation of C₆₀

$\rightarrow C_{58} + C_2$ Iragmentation (neu	trals)
\rightarrow (C ₆₀)* \rightarrow C ₆₀ + $h\nu'$ photon emission	
$\rightarrow C_{ss}^{+} + C_{s} + e^{-}$ fragmentation (ions	5)
$\rightarrow C_{60}^{+} + e^{-}$ delayed ionization	<i>.</i>
$C_{58}^+ + C_2$ delayed fragmentat	ion
↓	
$C_{56}^+ + C_2$ sequential fragment	tation
↓	
$C_{54}^+ + C_2$ sequential fragment	tation
$\rightarrow C_{60-2n}^{+} + C_{2n}^{-} + e^{-}$ fragmentation via C _n loss	
$C_{58} + n(h\nu) \rightarrow C_{56}^{+} + C_2 + e^-$ photofragmentation	of
neutral fragment	. S
$C_{58}^+ + n(h\nu) \rightarrow C_{56}^+ + C_2$ photofragmentation ionic fragments	of

the mass peaks from 308-nm ion production and from 118-nm ion production. The distribution of neutral fragments is very similar to the distribution of ion fragments. The relative intensities between the 118- and 308-nm ionization signals are not meaningful. The 118-nm signal is simply a measure of the fraction of photodissociated species remaining in each neutral fragment channel.

Table I lists most of the possible decay channels for C_{60} (unimolecular decay) following multiphoton absorption. In this work, neutral products from dissociation of C₆₀ have been measured for the first time. This indicates that a ladder-switching mode¹⁹ of ionization does not need to be invoked to explain the multiphoton ionization occurring in C_{60} . In fact, there is no proof that ladder-switching even occurs for these large polyatomic species.^{20,21} It is assumed that the neutral products from C_{60} dissociation include the detected species (C58, C56, etc.) and small C_n units that have not been detected in this study. The large ionization potentials of C and C₂ (\sim 11.3 and 12.1 eV, respectively) preclude their detection with the 10.5-eV photons utilized in this work.

A coherent picture is beginning to emerge involving the multiphoton processes at work in fullerenes. Basically, these species contain so many degrees of freedom that conversion of electronic excitation to vibrational excitation is extremely rapid. Thus, the molecule can store large amounts of excitation for extended periods of time before degradation of the molecule (ionization or frag-mentation) is observed.^{20,22,23} A recent RRKM calculation,¹⁷ using 4.6-eV dissociation energy and calculated vibrational frequencies, predicts that C_{60} will have a 10⁵ s⁻¹ dissociation rate for 30-eV internal energy in the molecule. The pathways for energy loss from this photoexcited species include direct photoionization, fragmentation (atom evaporation), photon emission, delayed ionization (thermionic emission), and fragmentation followed by photoionization during the 10-ns laser pulse. These types of energy-loss phenomena also exist in macroscopic species, such as thin films and systems where heat transport is negligible.

In conclusion, we have presented the first experimental observation of the neutral channels in multiphoton dissociation of C_{60} . We think that these phenomena not only occur for photo excitation of \mathbf{C}_{60} but are ubiquitous in nature and also have to be considered for other large molecules, especially the fullerenes. Further work is in progress to quantify the various processes occurring in this fascinating system.

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Study of Thermally Activated Radical Pair Separation in the Anthraguinone/Triethylamine Photoredox System by Fourier Transform EPR

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The generation of free radicals in the photoreduction of anthraquinone (AQ) by triethylamine in alcoholic solutions is monitored with FT-EPR with a time resolution of 10 ns. Spin-polarized AQ⁻⁻ radicals, emissively polarized by the triplet mechanism, are generated with typical time constants of 100 ns, whereas the primary photoreduction step proceeds with a time constant of approximately 1 ns, only. This delay can be attributed to the generation of a Coulomb-stabilized intermediate radical pair, from which FT-EPR observable free radicals are escaping by thermal activation. The strong solvent dependence of the escape rate can be accounted for mainly by considering the solvent's dielectric constant, shielding the attractive potential. A quantitative analysis results in a fictitious binding potential of 2.6 eV.

Introduction

Photochemical reactions in liquids quite generally proceed via an intermediate radical pair (RP), as a result of the primary electron-transfer step. In contrast to well-studied photosynthetic reaction centers for which the lifetime of the primary radical pair

is only of a few picoseconds, in recent publications¹⁻³ it was proven that in the absence of subsequent electron-transfer reactions, the

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