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On the triplet lifetime in free, photo-excited C_{60}

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It has recently been suggested that the lifetime of the lowest triplet state in multiphoton-excited C_{60} is much longer than anticipated. If true, this would invalidate the assumption of internal thermal equilibrium in the description of statistical decay processes of the molecule, such as thermionic emission. We present pump–probe measurements which show that the lifetime is below 1 μs at vibrational excitation energies of 6.5 eV, and that it decreases further to 40 ns at 10 eV. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1574801]

The lowest triplet state of C_{60} plays an important role in the multiphoton ionization of the molecule.[1,2] Recently it was suggested that also the delayed ionization is affected by it.[3,4] In these experiments, neutral C_{60} was photo-excited to high internal energies, causing delayed ionization of the molecule. The temporal dependence of the ion yield was interpreted in terms of a long lifetime of the lowest triplet state of C_{60}. In Ref. 4 it was held responsible for the observed quasi-exponential cutoff in the delayed ion yield on the timescale of several tens of microseconds. A lifetime on that scale is consistent with pump–probe measurements on cold C_{60} produced in a laser vaporization source,[1] but not with later measurements at higher temperatures.[5]

A long-lived triplet state will have ramifications not only for the understanding of delayed ionization but also for the value of the much disputed C_{58}–C_2 binding energy of C_{60}. The quantitative description of delayed ionization is connected to the value derived for this binding energy because that energy determines the temporal behavior of the yield of C_{60}^+ in delayed ionization. The latter has been found experimentally to be a power law with an exponent -0.64 ± 0.10 which can be interpreted as the ratio of the ionization potential (IP) to the C_{60} binding energy.[6] If delayed emission occurred out of a long-lived triplet state, it would reduce the IP by 1.7 eV, or some 20% and hence the deduced value of the dimer binding energy by the same fraction.

The question of the lifetime of the triplet state can be resolved by a pump–probe experiment where one, or a countable number of, photon(s) is absorbed from a pulsed pump laser, and the surviving population of molecules in the triplet state is monitored versus time by a probe laser pulse that can ionize with a single photon.

In the experiments reported here, the C_{60} was vaporized from a copper cell kept at 450 °C. The beam was collimated to a diameter of 2 mm and intersected at 90° by two spatially overlapping pulsed laser beams in the static extraction field of a time-of-flight mass spectrometer. The 3rd harmonic of a Nd:YAG (355 nm, 3.49 eV, pulse duration 9 ns FWHM, collimated and mildly focused to a beam diameter of 3 mm) was used as pump laser. An ArF excimer laser (193 nm, 6.4 eV, pulse duration 17 ns FWHM, collimated to a diameter of 2 mm) served as probe laser.

The spatial overlap of the two laser beams was optimized by moving the probe beam collimator while monitoring the C_{60} ion yield. The temporal overlap and the duration of the laser pulses quoted above (which present averages over many shots) were determined with a fast photodiode of 1 ns resolution. We also employed this photodiode, together with a pulse-height analyzer and a fast–slow coincidence circuit, to limit shot-to-shot energy fluctuations of the probe laser beam to $\pm5\%$ (worst case). Details will be presented elsewhere.[7]

Figure 1 summarizes our data recorded as a function of pump–probe delay, for pump laser fluences of 2.7, 6.4, and 28.4 mJ/cm^2 (open dots, solid dots, and solid squares, respectively). Even though this represents a tenfold variation in pump fluence, the increase of the ion yield, for a fixed delay, is surprisingly small. By contrast, a very dramatic dependence of the yield of delayed C_{60}^+ ions (or electrons) on laser fluence is obtained in a one-color experiment, for photon energies $h\nu=3.49$ eV.[8]

For lowest laser fluence, the semilogarithmic plot of the data in Fig. 1 shows essentially one lifetime, of order 1 μs, but closer inspection reveals a negative curvature. The negative curvature indicates the presence of several different lifetimes in the ensemble. As discussed in more detail below, this reflects the distribution of vibrational energies in the canonical ensemble of C_{60} that effuse from the oven at 450 °C. The experimental data in Fig. 1 (open dots) are successfully fitted (dotted line) with a log-normal distribution of lifetimes, i.e., a distribution that is Gaussian on a log(τ) scale. The average lifetime is obtained as $\tau_1=0.74\pm0.01$ μs, and the rms width of the distribution is $\sigma_{\log\tau}=0.25$, which is equivalent to a factor 1.8 in τ.

The dashed line in Fig. 1 represents a fit to the medium-

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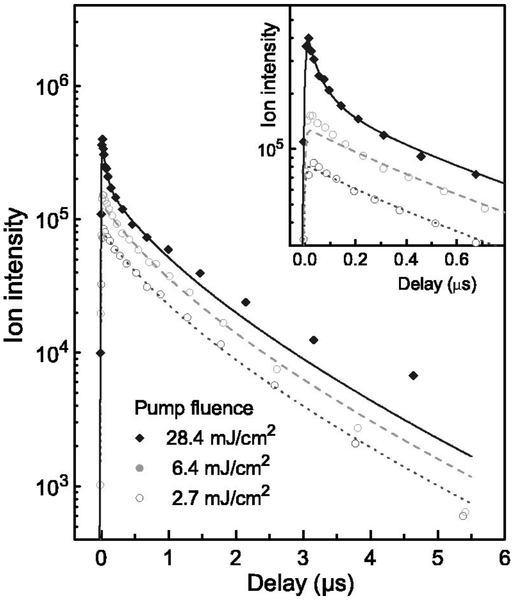

FIG. 1. Open and solid dots: Yield of C_{60}^{+} as a function of the delay between pump and probe laser for three different pump fluences, as indicated in the figure. The inset provides a more detailed view of the same data for short delays. The dotted and dashed lines represent fits of a log-normal distribution of lifetimes; the solid line is a superposition of two distributions with distinct average lifetimes.

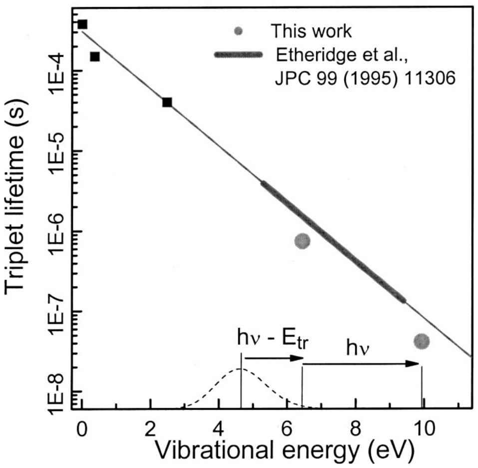

FIG. 2. Solid dots: Lifetimes of the triplet state extracted from the data in Fig. 1, plotted versus the computed vibrational energy for C_{60} that, initially at 450 °C, has been pumped into the triplet state upon absorption of either one or two photons at 355 nm. The line running diagonally across the figure is from Ref. 5. The solid squares represent previously published experimental data as presented in Ref. 5.

fluence data using the same average lifetime, and distribution of lifetimes, as for the low fluence data. The fit is reasonable,[9] but the inset in Fig. 1 reveals that this set of parameters does not properly describe the data for very short delays.

This appearance of another, much shorter lifetime is most clearly seen for data recorded at highest fluence (solid diamonds). The solid line represents a fit of two lifetimes, each with the same (fixed) distribution as described above. The value of τ_1 is kept at 0.74 μs; the value of the short lifetime is obtained as $\tau_2 = 0.041$ μs. A fit of two lifetimes to the medium-fluence data does, in fact, produce about the same value for τ_2, although with larger uncertainty.

We first note that the observed lifetimes are much shorter than the tens of microseconds suggested in the analysis in Ref. 4. They are also much shorter than the 42 microseconds found in Ref. 1 where the experimental goal was to probe very cold C_{60}.

For a more detailed analysis, we interpret the data in terms of the temperature or, equivalently, the vibrational energy dependence of the triplet lifetime. We need to consider the vibrational energy in the fullerenes that contribute to the ion yield, i.e., fullerenes that can be one-photon ionized with the probe laser because they are in an electronically excited state. After absorption of *n* photons from the pump laser, the total excitation energy is the sum of the thermal energy acquired in the source, and the absorbed photon energy. For low pump fluence, one-photon absorption dominates. A fraction of these one-photon excited C_{60} may relax into the lowest triplet state (energy $E_{\mathrm{triplet}} = 1.7$ eV) rather than into the electronic ground state; their vibrational energy is

$$E_{\mathrm{vib}} = E_{\mathrm{vib}}(450\,^{\circ}\mathrm{C}) + n\mathrm{h}\nu - E_{\mathrm{triplet}} = 6.45 \ \ \mathrm{eV}, \qquad (1)$$

where $n = 1$. Similarly, absorption of two photons $(n = 2)$ produces C_{60} in the lowest triplet state with $E_{\mathrm{vib}} = 9.94$ eV. These energies are assigned to the values of $\tau_1 = 0.74$ and $\tau_2 = 0.041$ μs, respectively.

In Fig. 2 we compare the lifetimes $\tau_1(E_{\mathrm{vib}})$ and $\tau_2(E_{\mathrm{vib}})$ extracted from our present data (solid dots) with various results from the literature. In particular, the heavy line represents a deconvolution of pump–probe absorption measurements in a vapor cell around 1000 K, with $E_{\mathrm{vib}}(T)$ derived from the caloric curve of C_{60}; the thin line is an extrapolation.[5] The three solid diamonds for low energy are experimental results, again with E_{vib} derived from the known, or estimated,[1] temperature of C_{60}.

Next we consider the *distribution* of vibrational energies in C_{60}. At a given temperature *T*, this distribution can be derived from the calculated vibrational frequencies.[10] The dashed line in Fig. 2 represents this vibrational energy distribution at 450 °C. It is very nearly Gaussian, with an average energy of 4.66 eV (thin vertical line in Fig. 2), and a rms width of 0.73 eV.

Each of the subensembles which result from absorption of either one or two photons will be characterized by an energy distribution with this source rms width of 0.73 eV. Reflecting this distribution off the $\tau_1(E_{\mathrm{vib}})$ curve suggested by Etheridge *et al.*,[5] one expects that each subensemble of C_{60}, having been pumped into the triplet state after absorption of *n* photons, will be characterized by a log-normal distribution of lifetimes with a width 0.259. This is indeed found to be the case, with an excellent agreement between this value and the width of 0.25 that resulted from the fit to our low-fluence data in Fig. 1. We therefore conclude that both the mean and the width of the lifetime distribution are consistent with the expected vibrational energy dependence of the lifetime of the lowest triplet state of C_{60}.

Note that the subensembles of one-photon and two-photon excited C_{60} do not contribute to delayed (thermally activated) ionization because their vibrational energy is way

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too low. This is also evident from the fact that the pump-only ion yield is vanishingly small for low fluence, 2.7 mJ/cm^2. It would require absorption of several more photons to cause thermally activated electron emission, whether out of the ground state, or the lowest triplet state. Unfortunately, subensembles with lifetimes being much less than the convoluted duration of the laser pulses (19 ns) remain invisible in our experiment. Figure 2 suggests that this rules out the direct detection of any component that has absorbed more than two photons. We also note that whereas recent pump–probe experiments by Campbell and co-workers[11] did not reveal any lifetimes significantly shorter than 1 μs, this may be because their experiment did not cover sufficiently short pump–probe delays.

However, highly excited fullerenes would affect the pump–probe spectra in a different way, namely, for *large* delays. In fact, the fit to the high fluence data shown in Fig. 1 clearly underestimates the amount of probe signal beyond 2 μs, and the signal does not go parallel with the low fluence points. One could argue that this signal is due to a higher number of photons absorbed and that it therefore indicates a *long* lifetime at high excitation energy ($E_{\text{vib}} \geqslant 13.5$ eV), thus a reversal of the trend shown in Fig. 2. This conclusion would be premature. When lifetimes are sufficiently short, on the order of the probe laser pulse or shorter, the photoionization dynamics in a pump–probe experiment is not determined by the lifetime but rather by the thermal population of the triplet state. This gives rise to a nonexponential time dependence which will be the subject of a future publication.[7]

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[1] R. E. Haufler, L. S. Wang, L. P. F. Chibante, C. Jin, J. Conceicao, Y. Chai, and R. E. Smalley, Chem. Phys. Lett. **179**, 449 (1991).

[2] Y. Zhang and M. Stuke, Phys. Rev. Lett. **70**, 3231 (1993).

[3] G. von Helden, I. Holleman, A. J. A. Vanroij, G. M. H. Knippels, A. F. G. Vandermeer, and G. Meijer, Phys. Rev. Lett. **81**, 1825 (1998).

[4] F. Rohmund, M. Heden, A. V. Bulgakov, and E. E. B. Campbell, J. Chem. Phys. **115**, 3068 (2001).

[5] H. T. Etheridge, R. D. Averitt, N. J. Halas, and R. B. Weisman, J. Phys. Chem. **99**, 11306 (1995).

[6] K. Hansen and O. Echt, Phys. Rev. Lett. **78**, 2337 (1997).

[7] R. Deng, M. Treat, O. Echt, and K. Hansen, unpublished results.

[8] R. P. Deng and O. Echt, J. Phys. Chem. A **102**, 2533 (1998).

[9] A discrepancy between the fit and the medium-fluence data for long delays is most likely due to problems with background subtraction. The pump-only signal is on the order of 1% of the pump–probe signal obtained for short delays.

[10] R. E. Stanton and M. D. Newton, J. Phys. Chem. **92**, 2141 (1988).

[11] M. Heden, A. V. Bulgakov, K. Mehlig, and E. E. B. Campbell, contribution to ISSPIC11, Strasbourg, September 9–13, 2002.

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