

Fullerene triplet state production and decay: R2PI probes of C_{60} and C_{70} in a supersonic beam

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Lifetimes of the lowest triplet state of the two most stable fullerenes, C_{60} and C_{70} , were measured in a supersonic beam by two-color resonant two-photon ionization. When prepared by intersystem crossing from the singlet manifold, excited at 4.03 eV, these triplet states were found to have lifetimes of 42 and 41 μ s, respectively. The energies of these triplet states (1.7 and 1.6 eV, respectively) were measured by photoelectron spectroscopy of the corresponding negative ions.

1. Introduction

Recently Arbogast et al. [1] have discovered that the lowest triplet state of C_{60} is detectable in benzene solution at room temperature via a triplet-triplet transient absorption, and has a lifetime of roughly 40 μ s. In previous studies with C_{60} and other fullerenes in a supersonic beam [2] it had been established that the ionization potential of such fullerenes was between 6.4 and 7.9 eV^{#1}, and that, in general, there appeared to be no excited electronic states of sufficiently long lifetime in these molecules to provide an efficient pathway for a resonant two-photon ionization, R2PI [4]. These two results are clearly not consistent. While it is true that two-photon ionization of aromatic molecules in supersonic beams typically finds that the gas-phase triplet lifetimes are drastically foreshortened by the excess vibrational energy which follows intersystem crossing [5-7], for cold C_{60} excited in the visible this should only amount to about 1 eV of extra vibrational energy – not much more than what is expected for a typical C_{60} molecule at room temperature in solution. The gas-phase triplet lifetime of laser-excited C_{60} should

therefore be similar to that found in room temperature solutions.

This short Letter provides a resolution of this apparent discrepancy. In fact, R2PI experiments can succeed with such molecules as C_{60} and C_{70} , provided that the much stronger signal due to the two-photon ionization by the probe laser is taken into account. Using an alternative approach to C_{60} supersonic beam generation, direct laser desorption of purified C_{60}/C_{70} solid targets, it is shown to be possible to generate beams of sufficient intensity and stability to observe true two-color R2PI signals even though these are weak. The results provide a measure of the triplet lifetime of these species when excited through the singlet manifold in the gas phase, and point the way to a general means of studying other excited electronic states of these important molecules. Ultraviolet photoelectron spectra (UPS) of intense negative cluster ion beams of these materials are reported as well, providing new data on the singlet-triplet splittings and the process of electronic→vibrational energy decay in these nanometer-sized molecules.

2. Experimental

While it has been clear for over half a decade that

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^{#1} Recent work has narrowed the measured IP range for C_{60} to 7.5–7.7 eV; see ref. [3].

C_{60} and C_{70} can be made in supersonic beams by laser vaporization of graphite [8], the routine production of intense beams of these species cooled to cryogenic temperature has been a substantial challenge. In efforts to produce cold argon van der Waals complexes of C_{60} in a supersonic beam [9], we have discovered a fundamental design flaw in the laser-vaporization supersonic cluster beam source technology originally introduced by this group in 1981 [10,11]. Generally, in such a design all the carrier gas necessary to produce the supersonic cooling is present above the target surface at the moment of vaporization. In order to attain the extreme cooling necessary to remove all internal vibrational excitation in a molecule as large as C_{60} , these nozzles generally require the carrier gas pressure to be over 1 atm. Unfortunately, under these high gas pressure conditions, the laser-produced plasma is effectively confined within an expanding shock wave which cannot move much faster than the speed of sound in the surrounding carrier gas. Particularly with such refractory materials as carbon, wholesale condensation to produce macroscopic aerosol particles often occurs in such circumstances, and very few if any small clusters remain. In order to produce stable intense beams of small and moderately-sized clusters of carbon we have found it to be essential to permit the plume to expand freely for a few microseconds into a low-pressure carrier gas. Extreme cooling can then be obtained later by rapidly increasing the carrier gas density in a "waiting room" of the nozzle prior to the supersonic expansion.

Fig. 1 shows schematic cross sections of two fast-pulsed supersonic nozzles we have developed with this waiting room idea in mind. The design is similar to that published by others in this group for the production and direct injection of clusters into a Fourier transform ion cyclotron resonance apparatus [12]. However, in the nozzle designs shown in fig. 1 we have arranged twin fast-pulsed nozzles to feed gas into opposite sides of the (waiting room) channel into which the laser-vaporized carbon plume is injected. This doubles the peak gas pressure, and maintains a symmetrical, swirling gas flow as the carbon vapor plume expands off the surface of the graphite target. The pulsed nozzles were custom-mounted versions of a commercial implementa-

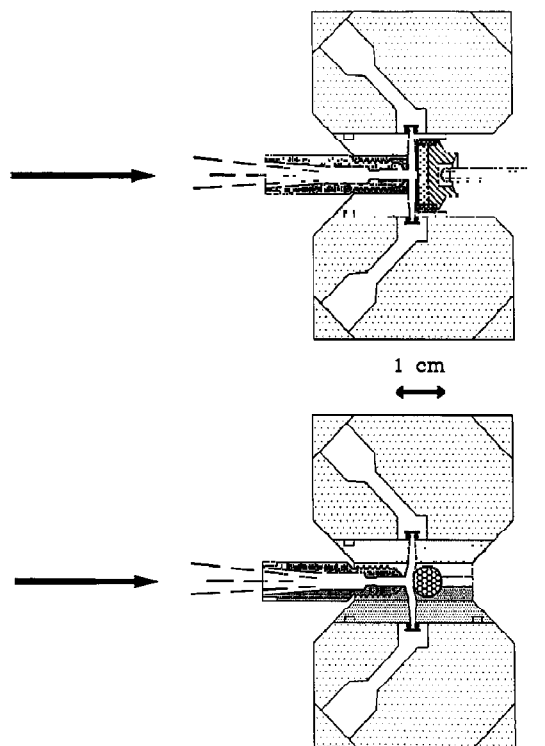


Fig. 1. Schematic cross-sectional view of the rotating/translating disc (top panel) and rod (bottom) versions of the pulsed supersonic fullerene beam source. In both cases the vaporization laser is directed down the axis of the nozzle.

tion #2 of the magnetic current loop design first proposed by Dimov [13], and developed for supersonic beam work in our laboratory [14], and that of Gantry and Gieze [15]. These nozzles use a fast (30 μ s) current impulse to excite the fundamental harmonic vibration of a copper-beryllium leaf spring (4 kHz resonant frequency), providing a very fast (10–20 μ s) risetime gas pulse with very little pulse-to-pulse timing jitter (<3 μ s). When operated with helium at a backing pressure of 10 atm, the twin nozzles delivered gas pulses of 0.2 to 0.3 cm³ atm in a pulse of 100–130 μ s duration. The 1 cm long, 0.3 cm diameter cylindrical "waiting room" channel shown in fig. 1, was terminated by a 0.2 cm diameter orifice prior to the supersonic expansion cone in order for this waiting room to act as a surge region with a 25 μ s pump out time.

#2 PSV Pulsed Supersonic Valve, R.M. Jordon Company, Grass Valley, CA.

The top panel of fig. 1 shows a rotating/translating disc variant of this design, while the bottom panel shows one using a rotating rod. Both versions were used for this study with the fullerenes; the rod version for the R2PI supersonic beam study of the triplet states, the disc version for the UPS study of the negative ions. Details of these R2PI [5,6,9] and UPS [16,17] beam machines have been published elsewhere.

Samples of a C_{60}/C_{70} mixture were prepared by operation of a carbon arc in a helium atmosphere at 150 Torr by soxhlet extraction of the resulting graphitic soot which toluene [18,19]. Concentrated solutions of these fullerenes in toluene were then used to coat the laser vaporization target by evaporation of the solvent. In the case of the rod source this target was 6 mm OD graphite rod; for the disc source it was a 12.5 mm OD copper disc. In both cases the target was moved under computer control such that the Nd:YAG second harmonic vaporization laser (focused to a 1 mm diameter spot) hit a fresh region of the coated target each shot. As is evident in fig. 1, this vaporization laser was directed down the main expansion axis of the supersonic beam.

Laser desorption has been used recently to sample films of C_{60} and other fullerenes by mass spectrometry [20,21]. However, to our knowledge the following experiments constitute the first extension of this technique to an integral supersonic beam source of sufficient gas density and intensity to provide the extensive cooling necessary for detailed spectral study.

3. Results

Fig. 2 shows typical time-of-flight mass spectra (TOFMS) of the cold supersonic fullerene beams generated by these techniques. The bottom panel shows TOFMS of neutral C_{60} and C_{70} as generated by laser vaporization in the rotating rod source using a fluence of only 1 mJ in a 1 mm diameter spot, which is roughly 10 times less than would have been required to produce significant direct vaporization of the graphite target. The time of arrival of these neutral clusters as the supersonic beam passed through the ionization region of the TOF mass spectrometer was as expected for a supersonic helium source at near room temperature, and the arrival time profile

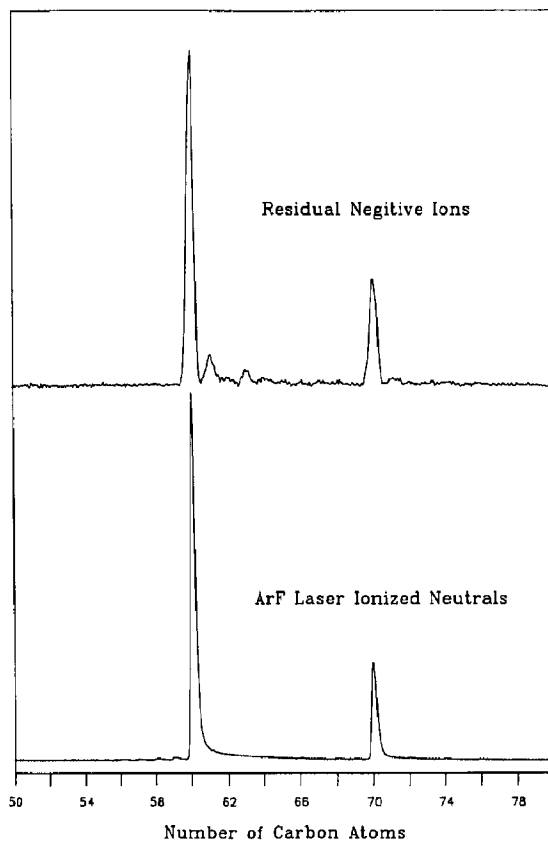


Fig. 2. Time-of-flight mass spectrum of (top) negative fullerene cluster ions produced by the rotating disc source with 6 mJ vaporization laser pulse energy in a 1 mm spot, and (bottom) the neutral fullerene clusters detected by ArF excimer laser photoionization (at 1 mJ cm^{-2}) produced by the rotating rod source using 1 mJ vaporization laser energy.

displayed a roughly exponential tail, as expected from the calculated "pumpout time" of the supersonic nozzle. We therefore expect these C_{60} molecules to have received the full cooling of the supersonic expansion. The C_{60}^+ signal intensity obtained by ArF excimer ionization was found to be several orders of magnitude higher than we have ever obtained by direct laser vaporization of graphite targets in such a beam apparatus.

In order to produce the negative fullerene cluster ion beam whose TOFMS is shown in the top panel of fig. 2, it was necessary to increase the vaporization laser fluence above 5 mJ in a 1 mm spot so that a small amount of ionization was produced in the source. Even so, the arrival time profile of the re-

sidual negative cluster ions from this rotating disc source (top panel of fig. 1) indicated the cluster received the full cooling expected from a supersonic helium source at near room temperature. Again, the intensity of these negative fullerene clusters was found to be several orders of magnitude greater than previously obtained [22] by this source using direct laser vaporization of graphite targets.

In order to probe the triplet lifetime of the neutral fullerenes, a XeCl excimer laser beam, at a fluence of 5 mJ cm^{-2} , was directed down the axis of the supersonic beam, and a probing ArF excimer laser beam at a fluence of 0.1 mJ cm^{-2} was directed coaxially and adjusted in diameter to be entirely within the profile of the XeCl pump beam. True two-color resonant two-photon ionization, R2PI, signals were readily observed as long as the ArF probe laser fluence was kept low. The timing of the lasers was adjusted under computer control to repetitively scan the pump to probe interval. Fig. 3 shows the observed results for the buildup and decay of the transient two-color R2PI signal. TOF mass spectra of the two-color R2PI signal revealed only increases in the channels corresponding to C_{60}^+ and C_{70}^+ , with no evidence of fragmentation. Least-squares fits to these data sets using a single-exponential decay model are shown in fig. 3 as a solid line superimposed on the data points. The measured lifetime of the excited state produced by the XeCl laser was found to be $42 \pm 4 \text{ } \mu\text{s}$ for C_{60} , and $41 \pm 7 \text{ } \mu\text{s}$ for C_{70} . In the case of C_{60} this is remarkably close to the measured triplet lifetime in solution at room temperature [1].

Fig. 4 displays the UPS spectrum of the mass-selected cold negative ions of C_{60} (top panel) and C_{70} (bottom panel) taken in our supersonic cluster UPS apparatus [16,17] using an ArF excimer laser (6.4 eV) as the photodetachment light source. When compared with the previously published UPS data for these molecules on this apparatus [22,23], these new spectra are markedly better resolved. This is not due to any improvement in the intrinsic resolution of the UPS apparatus. Instead, it is a consequence of the much better vibrational cooling achieved by the new supersonic fullerene negative ion source.

We note in passing that the recent availability of gram quantities of C_{60} have permitted UPS experiments to be performed by conventional techniques on neutral C_{60} molecules both in the gas phase [24]

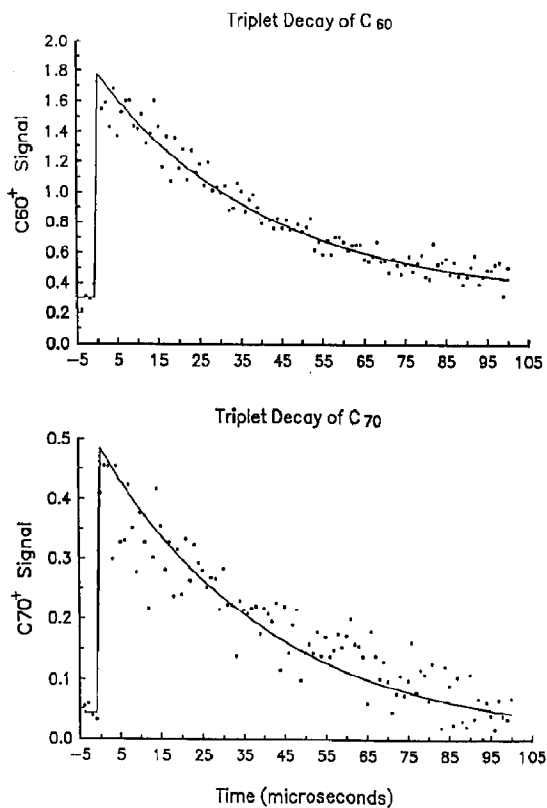


Fig. 3. Triplet formation and decay curves for C_{60} (top) and C_{70} (bottom). The horizontal axis is the computer-controlled delay time between the firing of a XeCl laser to excite the clusters and form the triplet state, and the firing of an ArF excimer laser to ionize the clusters at the right time to be monitored by time-of-flight mass spectrometry.

and deposited on surfaces [25,26]. These spectra are in excellent agreement with the photoelectron spectra recorded earlier for the mass-selected negative ion [22]. Prior to the availability of bulk C_{60} , these highly structured UPS spectra of C_{60}^- provided one of the most stringent tests of the predictions of the truncated icosahedron structural hypothesis [23,27].

We believe the markedly better resolution in the current apparatus is due not only to the reduction of vibrational "hot bands" from the spectrum, but also to the minimization of a low-energy electron-energy loss process as the soon-to-be-detached electron begins to leave the molecule. For a bulk surface this would be an electron-phonon scattering process, the rate of which depends on the phonon density of states. For a fullerene of the size of C_{60} at room tem-

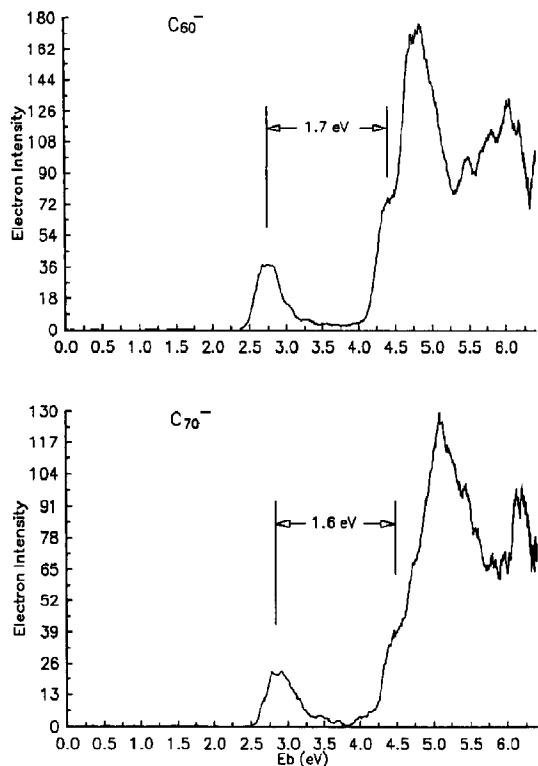


Fig. 4. Ultraviolet photoelectron spectrum of C_{60}^- (top) and C_{70}^- (bottom) generated by vaporization of the purified solid film of these materials in a supersonic nozzle. An ArF excimer laser (6.4 eV) was used for the photodetachment.

perature, the average molecule will contain roughly 0.5 eV of vibrational energy and the density of vibrational states is already over 10^{10} per cm^{-1} . Cooling the molecule to a vibrational temperature below roughly 70 K will effectively freeze out all vibrational motion beyond the zero-point motion, and drastically reduce the rate of such a molecular electron-“phonon” loss process.

We have observed this sort of behavior before with metal clusters [16], where the UPS patterns appear to sharpen as the energy of the detachment laser is increased, even though the resolution of the time-of-flight photoelectron spectrometer decreases. Photoelectron spectra of C_{60}^- reported from this group several years ago with an F_2 excimer laser at 7.9 eV also showed this marked sharpening of the spectral features with higher photon energy [23].

Given the much improved effective resolution in these UPS data it is now possible to estimate with

confidence the lowest electrical excitation energy in neutral C_{60} and C_{70} as the interval between the first major feature, corresponding to formation of the ground state of the neutral, and the next major detachment feature, corresponding to the lowest excited triplet state. As shown in fig. 4, we estimate these excitation energies as 1.7 and 1.6 eV for C_{60} and C_{70} , respectively. In the case of C_{60} this is in excellent agreement with the range deduced from triplet quenching experiments for the molecule in solution by Abrogast et al. [1]. With this new supersonic beam data it is clear that the lowest triplet states of C_{60} and C_{70} are therefore remarkably similar to each other.

As with other aromatic molecules, we expect that production of these triplet states by intersystem crossing from lower excited levels of the singlet manifold will result in substantially longer lifetimes [5–7]. The triplet lifetime of these molecules in isolated matrices at liquid helium temperatures may be in the millisecond to second range.

We expect the negative cluster ion beams of these molecules can be cooled even further by using more gentle means of producing the ionization in the nozzle, thereby permitting a much better estimate of the energies of the excited states of the molecules, and an indication of the extent of Jahn–Teller distortion in the degenerate electronic states of the negative and neutral forms. Threshold photodetachment spectra of the cold negative ions of the sort recently done for metal clusters [28,29] may be extremely interesting. For both the negative and neutral supersonic beams it is clear that gentle laser vaporization of C_{60}/C_{70} films will provide an excellent route to detailed spectral probes using R2PI for the neutrals, and resonant two-photon detachment, R2PD, for the cold negative ions.

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