

Photofragmentation of C_{60} Molecules following Resonance Excitation and Ionization near the C 1s Edge

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Fragmentation spectra of C_{60} molecules after selective resonant excitation and ionization of C 1s electrons have been found to differ remarkably. At the π^* preedge resonances the multiply charged ions show strong fragmentation. Above the 1s threshold the C_{60}^+ ion yield indicates that the slow photoelectrons can get recaptured. Relative fragmentation of the parent C_{60}^+ ions has been found to increase strongly above the threshold towards a maximum of about 20 eV kinetic energy of the photoelectron; this may be due to the excitation of the giant plasmon resonance.

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Since the first observations and the general availability of the highly symmetric C_{60} molecule [1,2], there have been many studies of the electronic properties of this very special molecule in both the solid and vapor phase (see, e.g., Refs. [3–14]). Many questions related to the dissociation pathways, and to the electronic dynamics of the system as it gains energy in excitation or ionization processes, were raised by these studies. In most earlier studies of fragmentation, such as multiphoton ionization [15] and heavy-ion excitation [10,11], the molecule was ionized by stripping the outermost electrons. Single photon excitation has been employed only in a few cases, and mostly at energies only affecting the valence electrons of the molecule. Tunable synchrotron radiation in the energy range close to the C 1s ionization threshold provides a unique method for studying the decay channels of different core-excited resonances.

We have excited gas-phase C_{60} molecules with photons of energies 280 to 313 eV from the MAX-I storage ring, and have recorded time-of-flight (TOF) spectra of the resulting ions. The goal of the experiment was to selectively excite 1s electrons to different bound, unoccupied valence levels and to the continuum, and to compare the dissociation pathways as the excited state was changed. The ionic states created in core-hole decay processes are essentially different for resonant excitation below and ionization above the 1s ionization threshold. Because of the very low fluorescence yield, resonant excitation is practically always accompanied by the resonant Auger process leaving the molecule singly ionized, whereas photoionization of the 1s electron gives rise to the normal Auger process leading to a doubly ionized molecule. In both cases a fast Auger electron is emitted (in the case of photoionization also a slow photoelectron). These electrons carry the released transition energy but can lose part of it in multielectron processes (shakeup, plasmon excitations) to the remaining ionic system, which then further relaxes towards its energy-minimized final state. In these secondary

processes, subsequent electrons and/or C_n fragments are emitted, giving rise to multiply charged C_{60}^{q+} ions or to different C_{60-n}^{q+} fragment ions. The interaction between the fast electrons emitted in resonant or normal Auger processes and the rest of the C_{60} molecule may be assumed to be very similar, because differences in the kinetic energies are only a few eV at 260–270 eV. Instead, slow photoelectrons with varying kinetic energies can cause, as we will show later, enhanced fragmentation, following possible excitation of a giant plasmon resonance.

The measurements took place on the Finnish beam line (BL51) [16] at MAX-Laboratory in Lund, Sweden. The modified SX-700 monochromator [17] coupled with a unique short-period undulator [18] provides an intense source of photons in the 60–600 eV range. The photon bandwidth for the PEPICO (photoelectron-photoion coincidence) and the pulse mode measurements was about 1 eV, and the total ion yield spectra were measured with a resolution of 250 meV. C_{60} molecules were produced in a resistively heated oven from a high-purity powder sample (MER Corp., Tucson, AZ) heated to about 500 °C. A time-of-flight mass spectrometer analyzed the ions produced by the interaction of the photons with the C_{60} vapor target.

Our linear TOF mass spectrometer applying space-focusing conditions [19] is briefly described in Ref. [20]. TOF spectra were obtained both in the PEPICO and pulse modes. In the pulse mode a repulsive voltage step of +990 V and of the duration of 2.0 μ s was applied with 20 kHz frequency to the ion repeller. Pulses from the microchannel plates were collected in a logic analyzer, which provided the timing information. The specially developed computer software selected the coincidence counts from the raw data and constructed the TOF spectrum. A detailed presentation of the experimental apparatus and the applied electronics will be published elsewhere [21].

The total ion yield spectrum near the carbon 1s edge is shown after slight smoothing in the inset of Fig. 1.

It is quite similar to the published solid and vapor phase absorption spectra [7–9]. Our spectrum shows broader structures than the matrix-isolated or solid state spectra of C_{60} because the C_{60} molecules may be in initially excited vibrational states at the high temperature of the oven ($\sim 500^\circ C$). The sharpest features *A*, *B*, and *C* in the spectrum are due to the excitation of the $1s$ electron to the $5t_{1u}$, $2t_{2g}$, $5t_{2u}$, and $4a_g$ orbitals of the π^* character. In the presence of a core hole the I_h ground-state symmetry is broken resulting in C_s symmetry [8] producing a splitting of the ground-state orbital energies. The ionization threshold (~ 290 eV) is followed by intense σ^* resonance structures up to around 310 eV as shown in detail by Terminello *et al.* [7].

TOF ion spectra were collected for incident photon energies of the resonance peaks *A*, *B*, and *C* (Fig. 1) and above the C $1s$ ionization threshold at photon energies of 292, 295, 297, 300, 305, and 313 eV. Here we concentrate on the pulse-mode spectra, because they provide more reliable intensity ratios between different ions, which are essential for this study. Our relative ion yields measured in the pulse mode for rare gases agree with the results of Holland *et al.* [22]. The set of spectra measured in pulse mode is shown in Fig. 1.

Our spectra show rich structure revealing peaks due to multiply charged C_{60}^{q+} ($q = 1-4$) ions and associated mass-loss peaks. Some general features of the spectra are obvious. At the π^* resonances the C_{60}^{2+} lines dominate but the relative intensities of the C_{60}^{2+} peaks are rather high even for these resonant excitations, where the resonant Auger decay process leaves the molecule initially in a singly ionized state. The high intensity of the $2+$ ions

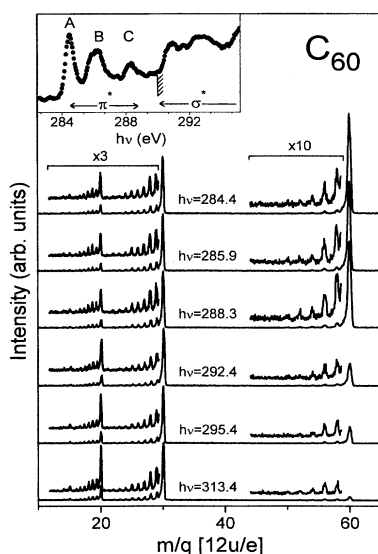


FIG. 1. A set of time-of-flight ion spectra measured at the indicated photon energies. The total ion yield spectrum is shown in the inset.

clearly indicates that second-step Auger transitions are energetically possible for a large fraction of the final states ($\sim 40\%$) populated in the course of the resonant Auger process. Multiply charged ions could also be produced by shakeoff processes during the resonant Auger transition, but this is not believed to be a significant channel.

Different populations of the same energy levels of a singly charged molecule via resonant photoexcitation and subsequent deexcitation or via direct photoionization are related to the fact that the former process can be described by two-electron matrix elements, while the latter is described by dipole matrix elements. Experimentally this appears as different intensity distributions in the resonant Auger and valence photoelectron spectra. Increased production of multiply charged ions as compared to the valence photoemission can thus be related to the increase in population of singly ionized states above the double/triple ionization limit.

The relative intensity of singly charged C_{60} and its fragment ions decreases strongly (Fig. 2) when the photon energy crosses the ionization threshold. At these energies, the normal Auger process is taking place instead of resonant Auger processes, and the primary mechanism for producing C_{60}^{2+} ions should be direct photoionization of valence electrons. However, the relative intensity of C_{60}^{2+} lines does not drop suddenly but decreases gradually above the threshold (~ 290 eV) from 25% at 292.4 eV to 6% at 313.4 eV. This could be explained with an analogous process to the recapture of the slow photoelectron in atoms [23].

Singly ionized C_{60} molecules created by resonant excitations appear as a very weak pattern of lighter fragments ($\sim 10\%$ from the parent line intensity), whereas doubly and triply ionized parent molecules are accompanied by a rather intense “loss series” in which the peaks are separated by a mass difference of C_2 . The relative intensity of the loss pattern strongly increases (Fig. 3) in going from the $2+$ to $3+$ ions. For resonant excitation the sum intensity of C_{60-n}^{2+} pair-loss peaks is about 50% of the parent C_{60}^{2+} line intensity, but 140%–170% for C_{60-n}^{3+} peaks from the corresponding parent line. The relative fragmentation has clearly the highest values for $3+$ and $2+$ ions at the π^* resonances. The corresponding fragmentation intensities in the case of above-threshold ionization are 25%–40% and 80%–95% of the C_{60}^{2+} and C_{60}^{3+} parent lines, respectively. Thus the fragmentation probability is roughly a factor of 2 lower above the threshold than at the π^* preedge resonances. We deduce that the singly ionized C_{60} molecule is still rather stable at the π^* resonances, but the C_2 ejection rapidly increases when the molecule becomes doubly or triply ionized. The fact that we can see mass-loss peaks separated by C_2 does not exclude the possibility that larger neutral fragments are also emitted.

As depicted in Fig. 3 the relative fragmentation of C_{60}^{2+} ions behaves remarkably above the $1s$ threshold

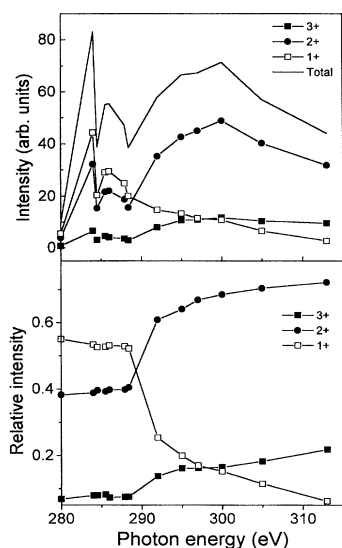


FIG. 2. Upper part: yield of different ions (area of main C_{60}^{q+} lines and their fragments) as a function of photon energy. Topmost curve (total) is the sum over charge states $q = 1-3$. Lower part: intensities of differently charged ions relative to the sum of states $q = 1-3$ as a function of photon energy.

increasing dramatically towards the 80% level at our highest photon energy of 313.4 eV. Unfortunately, our data points do not cover enough higher energies to show an unambiguous decline of this trend. This behavior is most probably connected to the excitation of the broad resonance observed by Hertel *et al.* [6] and Yoo, Ruscic, and Berkowitz [4] in photofragmentation of C_{60} molecules by UV radiation. They observed a strong resonance around the photon energy of 20 eV, interpreted in Ref. [6] as the giant plasmon resonance of Bertsch *et al.* [24]. In our case the kinetic energy of the C $1s$ photoelectrons is also around 20 eV. It is likely that the photoelectrons lose their kinetic energy to the creation of plasmon excitation with high probability, and the photoelectron stays or

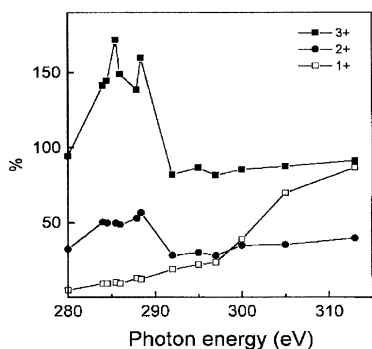


FIG. 3. Total fragmentation intensities (as peak areas) relative to the main C_{60}^{q+} ($q = 1-3$) lines as a function of photon energy.

returns to the ion. The created plasma oscillation then breaks the molecule into lighter fragments.

Our PEPICO spectra (not shown here) reveal that, in striking contrast to the 2+ and 3+ loss patterns, the C_{60}^{4+} peak (coinciding with C_{15}^{+} and C_{30}^{2+}) is followed by weak peaks in the spectra which are separated by C_4 indicating that the C_2 losses abruptly vanish and C_4 emission starts to dominate. The very low intensity of the lightest fragments (C^+ , C_2^{2+} , C_2^+ , and C_4^{2+}) indicates clearly that the main fragmentation mechanism is neutral C_2 and C_4 emission from multiply charged C_{60} ions.

The dissociation seems to be strongly connected to the preceding multiple ionization of the C_{60} molecule and also to the specific character of the ionization stage. This is seen in the significant difference between the relative fragmentation of the similarly charged ions generated via resonant Auger or normal Auger primary processes. Because of the strong intra-atomic character of the Auger process, the final-state holes are localized on the same carbon atom where the $1s$ excitation took place. When several valence holes are created on one site the resulting cluster of broken bonds can more easily lead to reorganization of the molecule, observable as fragmentation. In the multiple ionization by UV photons the holes are not expected to be spatially localized.

The relative yields of multicharged C_{60} ions do not vary significantly for excitation to different orbitals of π^* character, but a substantially lower degree of fragmentation is observed in the case of above-threshold ionization. This can be related to the population of valence-hole states (e.g., valence double hole states of C_{60}^{2+} , valence triple hole states of C_{60}^{3+}), which differs distinctly depending upon the transition pathways, e.g., normal Auger or resonant Auger followed by second-step Auger process. The difference in population is a direct consequence of the different transition matrix elements. The population ratio of final states, provided that all of them are characterized by slightly different dissociation dynamics, thus results in differences in the fragmentation—as observed here. In conclusion, the present results indicate the importance of the specific character of electronic transitions in the production of fragments. A further important finding is that the slow (~ 20 eV) $1s$ photoelectrons can create strongly enhanced fragmentation of singly ionized molecules. High-resolution resonant Auger electron spectra of C_{60} molecules near the C $1s$ edge could provide more useful and complementary information about these processes. A more precise comparison with calculations would also become feasible.

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