# Single photon thermal ionization of large molecules

We have demonstrated that gas phase $C_{60}$ can ionize in a quasi-thermal process where the absorption of a single photon at energies of several tens of eVs leads to the formation of a transient hot electron gas, while the vibrational degrees of freedom remain cold. The existence of the hot electron gas is signalled by the emission of thermal electrons with Boltzmann-like kinetic energy distributions with temperatures of 10000−20000 K. The ionization mechanism is expected to be general for large molecules and will have, *e.g.,* astrophysical consequences.

The kinetic energy of photo-electrons emitted upon irradiation of the matter, as postulated by Einstein, is given as the difference between the photon energy and electron binding energy, *i.e.*, the higher the photon energy, the higher kinetic energy of photoelectrons. We have observed that $C_{60}$ when ionized with 13.5−65 eV photons surprisingly emits low velocity photoelectrons with kinetic energies that do not shift with photon energies. The spectra of the low velocity electrons were observed to have an exponential form.

This remarkable observation was made in an Elettra experimental campaign undertaken at the GasPhase beamline aiming at measuring XUV photoelectron spectra of $C_{60}$ with a velocity map imaging (VMI) detector. The $C_{60}$ molecules were sublimated at the temperature of ≈480 °C into an interaction region where they were irradiated with a nearly monochromatic XUV beam. The VMI detector was equipped with an ion mass spectrometer that enabled us to measure photoelectrons and corresponding photoions in coincidence. The latter was essential in order to obtain $C_{60}$ photoelectron spectra

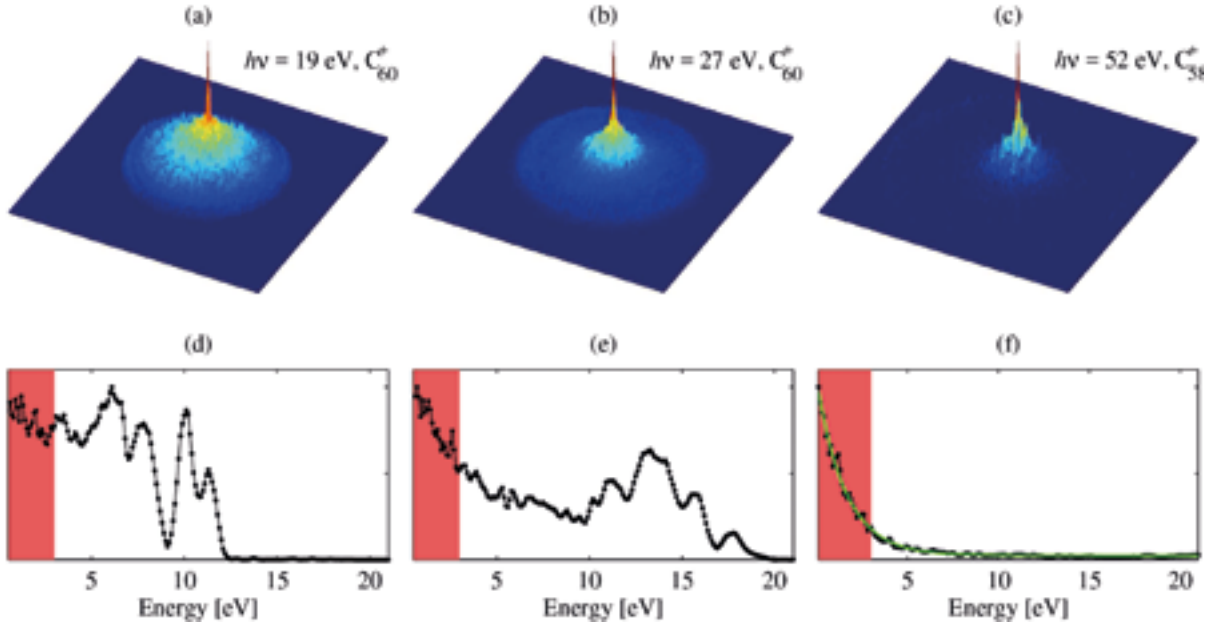


**Figure 1:** Raw VMI images of photoelectrons measured at different photon energies in coincidences with $C_{60}^+$ (a, b) and $C_{58}^+$ (c) and the deconvoluted photoelectrons spectra are respectively shown in (d, e, f). The red areas in (d, e, f) highlight low kinetic energies electrons with energies below 3 eV. The green curve in (f) is $10^{-3}$ + 0.04 exp ($-E_k/kT$) with $kT$ = 1.58 eV. Adapted with permission from K. Hansen et al., *Phys. Rev. Lett.* **118**, 103001 (2017). ©The American Physical Society.

free of spurious contributions. The surface of the detector was oriented parallel to the light polarization axis enabling reconstruction of electron kinetic energy spectra from the two-dimensional VMI images.
The low kinetic energy electrons observed by us have the following distinct features: 1) their kinetic energies do not correlate with the photon energy (Fig. 1a-c), as already mentioned above; 2) their spatial distribution is isotropic; 3) the relative amount of these electrons to those originating from direct ionization grows with the photon energy (Fig. 1d-e); 4) their energy distribution can adequately be described with a Boltzmann distribution (Fig. 1f). These features imply that the energy deposited into the $C_{60}$ molecules upon a XUV photon absorption is distributed over some or all of the valence electrons in a statistical manner, causing a valence electron to be boiled off from the extremely warm electron subsystem. Comparisons with previous infrared femtosecond (fs) pulses measurements suggest that the electron boiling off occurs on a few hundred fs timescale before the excess energy possessed by the valence electrons is thermalized with nuclear degrees of freedom. During this time the system is best described as a very hot electron gas with the nuclei being spectators. Indeed, this assertion is supported by the observation that the signals of the more conventional thermionic emission is absent from both the mass and the electron spectra. Instead, when the photon energy is sufficiently high to activate the delayed $C_{58}^+ + C_2$ dissociation channel (≈50 eV), the boiled off electrons no longer appear in coincidence with $C_{60}^+$ but with the $C_{58}^+$ fragment product ions (Fig. 2). It also seems that the emission of the low kinetic energy electrons does not correlate with excitation of the surface plasmon, which overlaps partly with the studied photon energy range.
In contrast to the thermal ionization of large molecules that has been observed previously upon multiple photon absorption, the process we have observed involves absorption of a single photon, which makes it distinct among other known thermal ionization mechanisms. Apart from the fundamental interest, this process is of immediate importance for astrophysics, in the description of the generation of charged particles close to new-born stars. In the future we plan more experimental studies to gain deeper insight into the phenomenon we have discovered. For example, we aim to answer the question of how the importance of this process relates to molecular size and to study the details of the time scales involved.

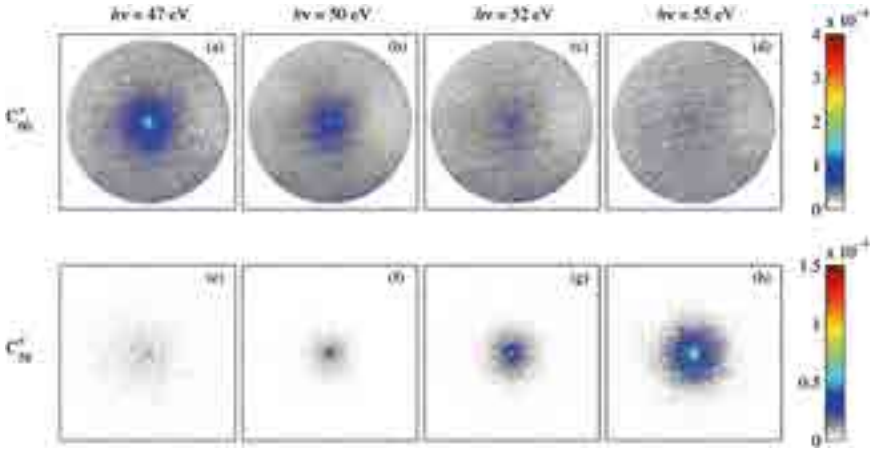


**Figure 2:** Raw VMI images of photoelectrons measured in coincidence with $C_{60}^+$ (a-d) and $C_{58}^+$ (e-h) at the photon energies of 47 eV (a, e), 50 eV (b, f), 52 eV (c, g), and 55 eV (d, h). Adapted with permission from K. Hansen et al., *Phys. Rev. Lett.* **118**, 103001 (2017). ©The American Physical Society.

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## Original Paper

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