Photoionisation Dynamics of C_{60}

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The fragmentation and ionization pattern of neutral C_{60} has shown a strong dependency on the duration of the exciting laser pulse [1]. Three distinct ionization regimes were identified by mass and photoelectron spectroscopy. Mass spectra resulting from ultrashort pulses (25fs) are characterized by multiply charged C_{60} resulting from direct multi-photon ionization (MPI) and show only little fragmentation or C_2 evaporation. A pulse duration of hundreds of fs (intermediate region) allows for statistical redistribution of energy among electronic degrees of freedom during the energy deposition process and leads to a combination of multiply charged heavy fragments and small singly charged fragments. Mass spectra for yet longer pulse durations (ps) are characterized by a "typical" bimodal distribution, with singly charged C_{60} and its large fullerene fragments and the smaller carbon clusters resulting from additional absorption of photons after the redistribution of energy from electronic to vibrational degrees of freedom. The statistical ionization from the electronically hot molecule and the energy coupling to vibrational degrees of freedom is modelled with a simple statistical model. Very good agreement is obtained with measured photoelectron spectra recorded as a function of laser pulse duration and fluence.

Superimposed on the statistical electron energy distributions for pulse durations greater than ca. 70 fs is a rich, reproducible structure related to the formation and subsequent single-photon ionization (within the same laser pulse) of excited Rydberg states [2]. This is the first time that resolved Rydberg states of fullerenes have been measured. The Rydberg states are only observed from molecular beams of fullerenes with high internal energy (ca. 400-500 ^{o}C). If a beam of cold (vibrational ground state) fullerenes is used for the photoelectron spectroscopy experiments no Rydberg states are observed. This confirms the previously suggested formation mechanism in which the level of the Rydberg state excitation is such as to be outwith the Born-Oppenheimer approximation but not yet sufficiently high to correspond to the inverse Born-Oppenheimer approximation. This implies that states of the same total energy are mixed. The observed Rydberg states therefore correspond to excitation energies given by the absorption of four laser photons plus the relevant amount of vibrational energy.

Finally, pump-probe experiments will be discussed in which the dynamics of the energy flow can be observed in "real time". These results largely confirm the earlier single pulse measurements but provide some interesting further details of the energy coupling. In particular, some evidence is found for a bottleneck in the vibrational energy redistribution within the fullerene on the ps timescale [3] which helps to explain the time dependence of the development of microsecond delayed ionization [4] as well as some earlier pump-probe measurements on solid C_{60} samples.

References

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