

Fullerenes

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Fullerenes have been the subject of many fascinating fundamental dynamical studies within the field of atomic and molecular physics since their discovery in 1985, a discovery that was awarded with the Nobel Prize for Chemistry in 1996. They are an allotrope of pure carbon where the carbon atoms form a closed, hollow cage. The most famous example of the family of fullerenes is Buckminsterfullerene, C_{60} . The molecule has the geometrical form of a truncated dodecahedron with a carbon atom sitting at each corner of the polyhedron. This is the same geometrical structure as a European football and, in fact, the fullerene has roughly the same relationship in size to a football as a football has to the Earth, Fig. 1. A breakthrough in 1990 led to the development of a very simple method for producing bulk quantities of C_{60} . The molecule's high stability, due both to the geometrical form as well as to its closed electronic shell, means that it can be handled very easily. This has made it an attractive subject of study in many areas of physics and it has been shown to have a wealth of interesting properties. One of the most important properties from the point of view of atomic and molecular physicists is that it can be easily sublimed to produce a molecular

beam of isolated molecules in the gas phase. This has opened up a whole new area by providing a convenient and attractive model system for studying the behaviour of complex molecular systems with a large number of degrees of freedom. One very nice example of this is a fullerene beam diffraction experiment, carried out by the group of Anton Zeilinger in Vienna, showing quantum interference behaviour from C_{60} [1].

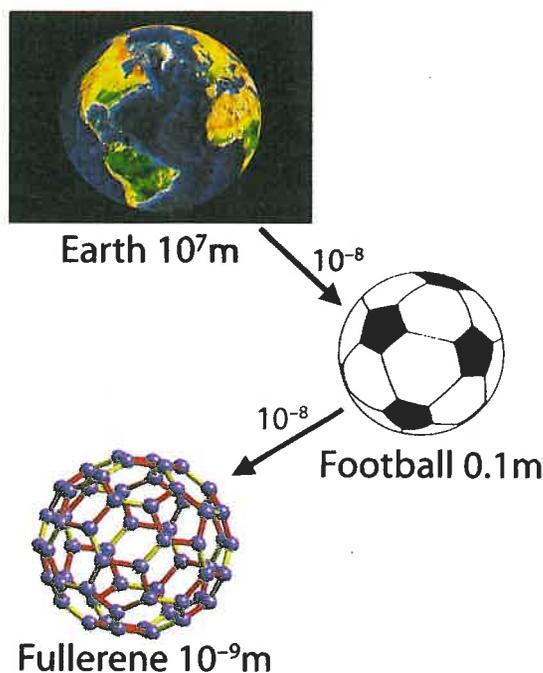
Many of the techniques employed traditionally by atomic physicists have been applied to the study of fullerenes and have greatly increased our insight into the dynamical behaviour of large molecules. In many cases, the experience gained by atomic physicists from experiments with fullerenes is now being applied to obtain insight into the behaviour of even more complex biomolecules. In this article I will try to convey the fascination of studying the fundamental properties of fullerenes in the gas phase and give the reader a flavour of the wide range of activities in this area.

Ionisation Dynamics

The ionisation mechanisms of fullerenes have been the subject of intense investigation since their first discovery. One of the early theoretical predictions was that a collective excitation of the electrons or "giant plasmon resonance" should occur at an excitation energy of approximately 20 eV. This was beautifully confirmed shortly afterwards in single-photon ionisation experiments carried out with synchrotron radiation. Rather different effects are seen when the fullerenes are excited with laser photons with energy less than the ionisation potential of the molecule. If nanosecond pulsed lasers are used for excitation then there is sufficient time available during the laser pulse for energy to be

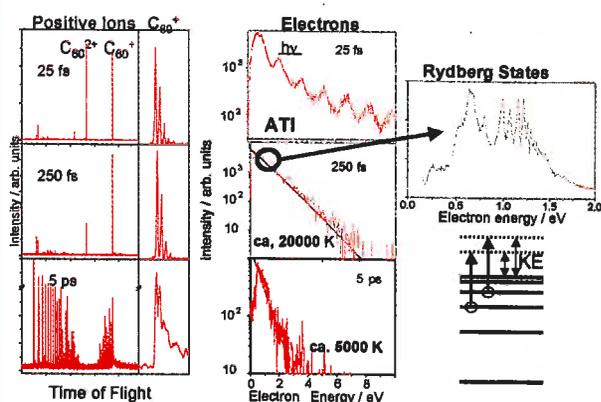
redistributed within the molecule. This leads to a successive absorption of single photons with sufficient time between the absorbed photons for transfer of the electronic energy to vibrational degrees of freedom, thus producing a molecule with a very high vibrational temperature. One outcome of this is that the molecules can ionise thermally in a process akin to thermionic electron emission from hot metals. This is normally observed as a tail on the parent molecular ion peak in time-of-flight mass spectra extending many tens of microseconds to longer arrival times due to the delayed, statistical nature of the electron emission. There are relatively few isolated systems where this phenomenon can be observed so clearly. Normally in large molecules the dissociation energy of the molecule is considerably less than the ionisation potential so the most probable statistical decay channel of a vibrationally excited molecule will be neutral fragmentation. In C_{60} , the relatively low ionisation potential combined with the high dissociation energy means that thermionic electron emission competes with fragmentation. A third, competing decay channel is radiative cooling. Vibrationally excited fullerenes have been shown to emit black-body like radiation corresponding to their vibrational temperature. The understanding of the complex interplay of these different cooling processes and their fundamental mechanisms is presently the focus of experimental and theoretical activities within an EU financed Network ("Delayed Ionisation and Competing Cooling Mechanisms in Atomic Clusters").

The increasing availability of "user-friendly" ultrashort pulsed laser systems in recent years has opened up more opportunities for studying the real-time dynamics of energy flow in molecules. Fullerenes show quite different behaviour depending on the amount of time available to the molecule. This is illustrated in Fig. 2 where positive ion mass spectra and the corresponding electron kinetic energy distributions are shown for fullerenes interacting with laser pulses of different duration from 25 fs to 5 ps. One sees



▲ Fig. 1: A fullerene bears the same relation in size to a European football as the football does to the size of the Earth.

evidence of energy equilibration among the electronic degrees of freedom of the molecule for pulse durations higher than ca. 70 fs. This manifests itself in a clearly thermal electron kinetic energy distribution. On the order of a few hundred femtoseconds the electronic energy starts to couple to vibrational degrees of freedom. This is seen in a dramatic decrease in the electronic temperature (since the same total energy is now divided among electronic and vibrational degrees of freedom), the strong fragmentation observed in the mass spectrum and the delayed ionisation tail on the parent mass peak extending to longer times. The main observations can be explained qualitatively and, partially, quantitatively within the context of relatively simple statistical models. It might appear that C_{60} is behaving more like



▲ Fig. 2: Positive ion mass spectra and corresponding electron kinetic energy distributions obtained from exciting C_{60} with 800 nm wavelength laser pulses with the same energy per pulse (3.5 J/cm^2) but different pulse duration (Campbell et al., Phys. Rev. Lett. 84 (2000) 2128). Three different ionisation mechanisms can be clearly seen in the experiments depending upon the duration of the excitation pulse. For short laser pulses ($< 70 \text{ fs}$) the ionisation is dominated by prompt, direct multi-photon ionisation. Singly and multiply charged parent molecular ion peaks are observed. The electron kinetic energy distribution shows peaks separated by an energy equivalent to the photon energy. This is known as "above threshold ionisation (ATI)" and is well known for atomic ionisation in strong laser fields. The parent ion peaks shows well-resolved structure corresponding to the naturally occurring ^{13}C isotope, indicating prompt ionisation on the time scale of the mass spectrometer ($< 1 \text{ ns}$). For intermediate pulse durations (ca. $70 \text{ fs} - 500 \text{ fs}$) the ATI peaks disappear and the emitted electrons show a thermal distribution but the corresponding positive ions are vibrationally cold, are produced promptly and show no significant fragmentation. For longer pulse durations ($> 1 \text{ ps}$) the electron temperature decreases but the positive ions are obviously highly vibrationally excited with massive fragmentation observed in the mass spectra and a tail to longer arrival times on the parent ion peak showing the presence of delayed, statistical ionisation. This behaviour can be nicely explained by considering the time scales for energy flow among the different degrees of freedom in the highly excited molecule. Superimposed on the thermal electron distribution is a rich structure, clearly seen on the right-hand figure where the low electron energy data is plotted with a linear intensity scale. This has been shown to be due to the single photon ionisation of Rydberg states, produced and ionised within the same laser pulse (Boyle et al., Phys. Rev. Lett. 87 (2001) 273401).

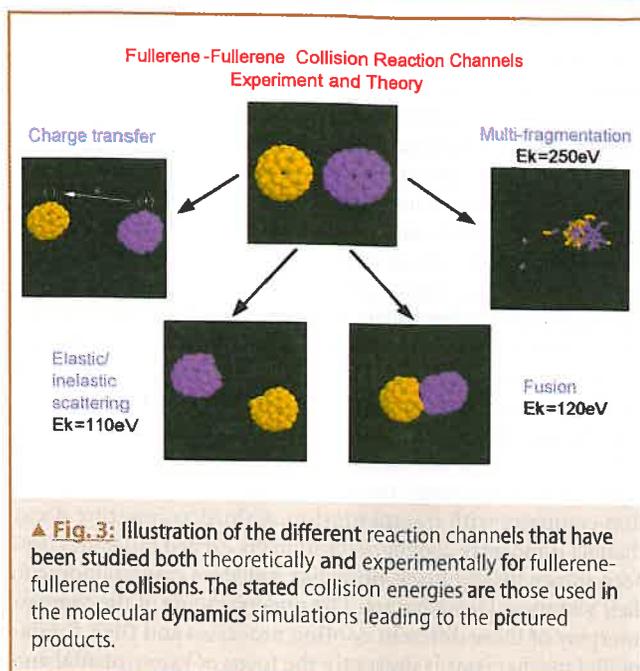
a little nano-sized piece of bulk matter rather than like a molecule, however, if one looks carefully at the electron kinetic energy distributions one sees a very nice indication of the molecular nature. Superimposed on the dominant thermal electron emission is a rich structure that turns out to be due to the multi-photon excitation and subsequent single-photon ionisation of Rydberg states. This is perhaps one of the most interesting aspects of working with fullerenes: the dynamical behaviour is truly intermediate between that of individual molecules and bulk matter with characteristics from both molecular physics and solid state physics.

Another interesting aspect of C_{60} ionisation is the ease with which electrons can be removed from the molecule. Very recently a group at the Steacie Institute in Canada has shown that it is possible to remove up to 12 electrons from C_{60} without inducing significant fragmentation by using an intense ultrashort IR laser pulse. This has just exceeded, by one electron, the record set by the community studying highly-charged ion collisions with C_{60} and it will be interesting to see how far this limit can be pushed in the future. Highly-charged ion collisions with C_{60} is one of the most active research areas involving fullerenes within atomic and molecular physics. The projectile ion captures the transferred electrons initially into highly excited states, forming a so-called hollow ion with many vacancies in the inner shells. Similar processes are studied by colliding highly-charged ions with surfaces, however, the disadvantage in these collisions is that the hollow ion crashes into the surface soon after its formation. By studying collisions with gas phase fullerenes it is possible to follow the development of the hollow ion on a considerably longer time scale.

Collisions

Many different collisional processes have been and are continuing to be studied using fullerenes: from thermal reactions to MeV fullerene ion implantation. Charge transfer and collision induced fragmentation are the most studied reaction channels. The unique hollow structure with its relatively large diameter, the highly delocalised electronic system and the large number of vibrational degrees of freedom can all significantly affect the charge transfer dynamics and provide a challenging problem for theoretical treatment. In collision induced fragmentation studies, depending on the time scale of the collision and the transient potentials produced, one can induce predominantly vibrational excitation in the fullerene or, for very high energy ion collisions, can induce predominantly electronic excitation. The fragmentation behaviour in the former case is very similar to what is observed for nanosecond laser excitations whereas the products from very high energy collisions have a strong resemblance to the fragmentation spectra seen in electron collisions or for femtosecond laser excitation.

Apart from the more "traditional" reaction channels, some collision processes are so far unique to fullerenes. It is e.g. possible to shoot atoms or ions inside the fullerene cage in gas phase collisions. This occurs for collision energies of a few tens of eV and provides a remarkably efficient way to produce endohedral fullerenes (fullerenes doped internally by having foreign atoms inside the cage). However, almost the entire centre-of-mass collision energy is transferred to the cage, in these collisions, which is then unstable and fragments on the microsecond time scale. A method has been developed to produce macroscopic amounts of such endohedral fullerenes by ion implantation into C_{60} , based on the gas phase collision experiments. The fullerenes are first deposited on a metal substrate before ion implantation that serves to conduct away the excess internal energy before the fullerene



can undergo statistical unimolecular decay. It is then possible to dissolve the endohedral fullerenes and purify them by liquid chromatography. These molecules are interesting building blocks for nanoelectronics or even as q-bits for quantum computers and two EU-supported collaborative projects are presently exploring these possibilities.

Finally, I would like to mention the various reaction channels that occur in fullerene-fullerene collisions, Fig. 3. The availability of macroscopic amounts of purified fullerenes has made it possible to experimentally study single collisions between clusters and bridge the gap between studies of colliding atomic nuclei and macroscopic liquid droplets. The most interesting channel, from my point of view, is molecular fusion between the two colliding fullerenes to produce a metastable larger fullerene. We have been able to study this in detail over the years and could show that although there are some initial similarities with the dynamics of colliding atomic nuclei, there are also some significant differences that can be rationalised in terms of phase space arguments and competing reaction channels[‡].

Fullerenes have proved to be very fruitful and fascinating model systems for studying the dynamics of molecular systems with a large number of degrees of freedom. I am convinced that fullerenes will continue to surprise and delight us for many years to come and in the process teach us a great deal more about the behaviour of complex molecular systems.

Further Reading

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References

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[2] E.E.B. Campbell et al., *C.R. Physique* 3 (2002) 341