Ultrafast excitation, ionization and fragmentation of C₆₀

I.V. Hertel ^{*,a,b} T. Laarmann, ^a and C.P. Schulz ^a

^a*Max-Born-Institut, Max-Born-Str. 2a, D-12489 Berlin, Germany*

^b*also at Free University of Berlin, Dept. of Physics*

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Abstract

The C₆₀ fullerenes are fascinating objects and even many years after their discovery the photo-physics of C₆₀ is still full of surprises. With their well defined, highly symmetric structure the fullerenes are challenging model systems and examples of an interface between atoms or small molecules and the solid state. The 60 delocalized π electrons in the C₆₀ fullerene give rise to interesting but complex photo physical processes due to their correlation and interaction with the ionic backbone. This

review discusses the photo dynamics of C_{60} when irradiated with femtosecond laser pulses in an intensity range of 10^{10} to 10^{15} W/cm².

Key words: Fullerenes, high intensity laser fields, ultrafast dynamics, molecules in strong laser fields, fragmentation

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1 Introduction

Ever since their discovery by Kroto, Smalley, Curl, and collaborators (1985) fullerenes in general and the Buckminster fullerene C_{60} in particular have drawn great attention from a broad, interdisciplinary scientific community. C_{60} was first identified as a special molecule by mass spectra obtained from what may be described as a laser driven reactor of hot carbon atoms (giving indeed the initial clue as to the unique structure of the *Bucky ball*). We show in Fig. 1 (left) a sample of these mass spectra adopted from the Nobel lecture of Kroto (2003) because it already shows the key fingerprints of the formation and fragmentation patterns of C_{60} which will be one major subject of the present progress report. It is an interesting historical annotation - as mentioned in the Nobel lecture of Smalley (2003) - that the crucial features were already detected in some earlier work (Rohlfing et al., 1984) as reproduced in Fig. 1 (right), but were apparently not noted or appreciated for their far reaching consequences. These mass spectra show very clearly a bimodal distribution of larger fullerenes C_{2n} separated by C_2 units ranging down to $2n \gtrsim 36$ and a series of small carbon clusters C_n below $n \leq 28$. We will see in the present paper that these patterns are characteristic for the fragmentation of very hot C_{60} after interaction of C_{60} with charged particles or photons provided enough time is available during the interaction process to allow for redistribution of the deposited energy over the many degrees of freedom of C_{60} . As we shall see, these patterns may change dramatically if the interaction time is sufficiently short.

The isolation of pure C_{60} by Krätschmer et al. (1990) provided the basis for a whole new area of material science and technology but also for a host of fundamental experimental and theoretical research studies focussing on an understanding of the energetics and dynamics of C_{60} after energy deposition and charge exchange (or removal). Most of the investigation to date have been performed in the condensed phase and their relevance for new materials and

* Corresponding author

Email address: hertel@mbi-berlin.de (I.V. Hertel).

Fig. 1. Historic mass spectra. *Left*: First mass spectrum with clearly recognized C_{60}^+ ions (Kroto, 2003) which lead to the discovery of the fullerenes by Kroto et al. (1985). The characteristic bimodal structure is again seen very clearly.

Right: Mass spectrum from laser vaporized carbon as observed by the Exxon group (Rohlfing et al., 1984), showing the typical bimodal distribution of carbon cluster ions C_n^+ characteristic for fullerene formation and fragmentation: small carbon clusters with odd and even n up to about $n = 28$ and a long distribution of even numbered clusters starting near 40 and extending up to over 100. The paper does not mention the enhancement of mass 720 due to C_{60} .

processes is obvious. On the other hand, gas phase experiments offer a direct approach to study isolated, well defined finite systems with many degrees of freedom and have concentrated on the mechanisms of energy deposition, redistribution and relaxation, as well as on the subsequently ensuing dynamics of ionization and fragmentation. Note that C_{60} has 174 degrees of freedom for the nuclear motion and 240 valence electrons (60 essentially equivalent, delocalized π - and 180 structure defining, localized σ -electrons), yet its symmetry and the applicability of some simplifying models justify the hope that the observed phenomena may eventually be understood in a quantitative manner. A wide range of processes has been studied which have lead to a detailed understanding of the mechanisms and dynamics involved in the energy deposition, relaxation, ionization, fragmentation and finally cooling of C_{60} and other fullerenes. We mention just a few early and some recent examples out of a wealth of experimental and theoretical studies, ranging from thermal heating (Kolodney et al., 1995), single-photon (Hertel et al., 1992; Yoo et al., 1992; Reinköster et al., 2004) or multi-photon absorption (O'Brien et al., 1988), electron impact (Foltin et al., 1998), collisions with neutral particles (Takayama, 1992), atomic ions, including highly charged ions (Walch et al., 1994; Martin et al., 1998; Schlathölter et al., 1999; Reinköster et al., 2003; Jensen et al., 2004; Brauning et al., 2004) as well as molecular ions (Campbell et al., 1993; Vandenbosch et al., 1998), cluster-ions (Farizon et al., 1997) to surface collisions (Busmann et al., 1993; Yeretizian et al., 1993; Bekkerman et al., 2004). With its large number of degrees of freedom C_{60} is very resilient

and can accommodate a substantial amount of energy before it disintegrates. Hence, different cooling mechanisms following the initial, fast dynamics have also achieved a lot of attention and essentially three types of processes have been identified: the evaporation of electrons (thermionic emission), the release of neutral or charged particles, in particular the evaporation of C_2 and radiative cooling (Campbell et al., 1992; Lépine and Bordas, 2004; Rohmund et al., 2001; Andersen et al., 1996; Hansen and Campbell, 1996). For details the reader is referred to recent reviews e.g. by Campbell and Levine (2000), Campbell and Rohmund (2000) and Lifshitz (2001).

In most of these studies information on the mechanisms and dynamics involved is gleaned from either the mass spectra, showing charge and mass distribution of the products, from electrons emitted or from the changes in energy, direction or charge state of the interaction partners (ions, electrons) - i.e. a long time (ns or μ s) after the primary processes have occurred. However, with the rapid development of ultrafast spectroscopy and the enhanced availability of flexible short pulse laser systems over the past years it has become an obvious challenge to follow these dynamical processes directly while they occur in the system. Moreover, with present day high intensity short pulse laser systems it has become possible to create electromagnetic fields which substantially modify the physics we are used to when describing single or ('weak field') multiphoton experiments. The field strengths available with today's high intensity laser systems may exceed those of the internal atomic and molecular fields ($\approx 10^{16}$ W/cm²) by orders of magnitudes (Ditmire et al., 2004, and references therein). The interaction of intense field laser pulses ($\gtrsim 10^{14}$ W/cm²) with large molecules and clusters leads to highly charged clusters, Coulomb explosion and fast particle emission (see e.g. Köller et al., 1999; Card et al., 2002; Döppner et al., 2003). The latter is discussed and studied even in the context of nuclear fusion, both experimentally (Ditmire et al., 1999) and theoretically (Last and Jortner, 2002; Krainov and Smirnov, 2002, 2003). At somewhat more moderate, but still high intensities the dynamics is still dominated by the field, which may deposit a large number of photons into the system and the atomic or molecular system itself is substantially modified. The ensuing nonadiabatic multielectron dynamics (NMED) and the possibility to control molecular reactions in strong fields is of high current interest (see e.g. Lezius et al., 2002; Levis and Rabitz, 2002; Stolow, 2003; Itakura et al., 2003; Wang et al., 2003; Markevitch et al., 2004, and references therein).

It is this intensity region (10^{15} W/cm² $\gtrsim I \gtrsim 10^{11}$ W/cm²) which we will address in the present progress report. We will concentrate on the dynamics of C_{60} interacting with short laser pulses as a proven, experimentally well accessible and fruitful testing ground for the dynamics of complex and yet well-defined systems. In that sense we view C_{60} as a prototype large finite system and an interesting intermediate between a molecule with an extended electronic π system and a semiconductor surface. In the past years very infor-

mative and challenging experimental and theoretical work has emerged and we aim at a comprehensive progress report on the interaction of short pulse lasers with C_{60} at intermediate intensities. The paper will be structured as follows: In section 2 we will introduce a few notions, facts and findings on C_{60} and the fullerenes. We will, however, in no way attempt to review these wide fields of ongoing research. We then recall or familiarize the reader with some important basic terminology and concepts from the area of atoms and molecules in strong fields. Finally, some experimental aspects of studying molecules in intense, short pulse laser fields will need to be addressed. In section 3 we discuss the ionization process, charge states and fragmentation after short pulse laser interaction with C_{60} as observed by mass spectroscopy. We will address the intensity dependence of these processes in some detail and dwell somewhat on a comparison of saturation intensities for the ionization processes in comparison with what has been established in the past for simple atomic systems. In section 4 we will discuss the so called above threshold ionization (ATI) which has been observed experimentally in photoelectron spectra at various short pulse laser intensities and compare them with recent theoretical results. Comparison with theory will already lead us to a critical discussion of the primary excitation mechanism in an intense laser pulse. The single active electron (SAE) picture which is generally used to describe atoms interacting with low intensity light pulses is, generally speaking, no longer adequate when describing a system with many active electrons interacting with an intense laser pulse. It turns out that many electrons are active (MAE) and may be excited during one laser pulse. This leads us to a description very similar to the band structure model in condensed matter, i.e. for a semiconductor in the case of C_{60} . In section 5.1 will illustrate this with a particularly interesting example: the non-resonant excitation of Rydberg states in C_{60} . As a last topic, in section 5.2, we address fast fragmentation processes of C_{60} beyond the well established statistical fragmentation processes known to occur on the ns to μ s time scale. The report will end (section 6) with a brief conclusion and outlook.

2 Preliminaries

2.1 Introduction to energetics, kinetics and properties of C_{60} in a nutshell

The cleanest methods of studying the electronic properties of C_{60} are certainly based on single photon absorption: a known amount of energy $h\nu$ is deposited and the resulting processes can be directly attributed to transitions between molecular states. Unfortunately the optical vis-uv absorptions spectra of C_{60} are rather blurred as illustrated in Fig. 2 and show only broad bands owing to the many internal degrees of freedom. As can be seen, the absorption bands are somewhat broader in the gas phase than in liquid solution but otherwise

essentially identical. C_{60} has the shape of a truncated icosahedron and is characterized by the point group I_h . The level designations given below refer to elements of that symmetry group - small letters referring to single electron orbitals, capital letters define electronic states. The level diagram displayed in Fig. 2 refers to single electron levels and has been adopted from [Wilk et al. \(1995\)](#) and [Zhang et al. \(2003\)](#). For this system with its 60 π and 180 σ valence electrons this level scheme may be seen as an equivalent to a band structure in the condensed phase and has to be distinguished from the energies of the (multielectron) molecular states to which the designations in the spectra refer (indicated are the final states in transitions from the 1A_g ground state). Owing to the lack of high resolution vis-uv spectroscopic information, the electronically excited states of C_{60} are still only somewhat vaguely known. In addition to the singlet u states indicated in the optical spectra one expects e.g. singlet g states as well as triplet states of the molecule, which are not accessible to optical transitions. The lowest lying triplet states at 1.6 and 1.7 eV ([Haufler et al., 1991](#)) play an important role in the description of statistical decay processes of the molecule, such as thermionic emission ([Héden et al., 2003](#); [Deng et al., 2003](#)).

In contrast to the optical spectra, rich structure is observed in Raman and IR spectra which allows to assign the vibrational modes of C_{60} with high accuracy ([Dresselhaus et al., 1996](#)). For the present subject it suffices to mention the two fully symmetric vibrational modes, the $a_g(1)$ radial breathing mode at 497 cm^{-1} (corresponding to an oscillation period of 67 fs) and the $a_g(2)$ pentagonal pinch mode at 1470 cm^{-1} (22 fs), and the $h_g(1)$ prolate-oblate mode with 273 cm^{-1} (122 fs) - as all other modes with much higher frequencies cannot be observed directly in the time domain with present day fs-laser systems.

One important aspect to bear in mind when studying C_{60} is the high internal energy content $E_{vib} \sim 174 \times k_B T$ due to its 174 degrees of freedom in nuclear motion. To study the isolated C_{60} molecule it has to be brought into the gas phase, i.e. the material must be evaporated and at a typically oven temperature of 770 K we have already $E \sim 4.5\text{ eV}$ in the system ([Rohmund et al., 1996](#)). Even when cooled by liquid nitrogen to 80 K we are still left with about 0.5 eV. It will be a subject to discussion whether, when and how this internal energy can be exploited in an electronic excitation process and will influence the dynamics of the system. For the time being it may suffice to remark that for statistical reasons it is extremely unlikely to channel all this energy into - say - one particular chemical bond, and initiate e.g. C_2 evaporation. It is now well established ([Lifshitz, 2000](#)) that the binding or evaporation energy for C_2 emission from neutral C_{60} is $E_a \geq 9.5\text{ eV}$ and for emission from the C_{60}^+ ion $E_a = 10 \pm 0.2\text{ eV}$ ([Matt et al., 2001](#)). This is an exceptionally large dissociation energy and it is a unique property of C_{60} that its C_2 binding energy is larger than the ionization potential $E_I < E_a$.

Fig. 2. Optical absorption spectrum of C_{60} and single electron energy level diagram. The absorption spectra and designations of transitions from the 1A_g ground state (full multielectron picture) are adopted from Bauernschmitt et al. (1998) (— solution in hexane) and Coheur et al. (1996) (- - - gas phase). The level designations and ordering have been adopted from Wilk et al. (1995) and Zhang et al. (2003), their energetic positions have been adjusted to the absorption spectra. The Rydberg levels from Boyle et al. (2001) are drawn roughly to scale. The ionization potential is adopted from De Vries et al. (1992). Note that in the single electron picture the first optically allowed line arises from the HOMO to LUMO+1 transition and is very weak, while the next strong absorption maximum is from the HOMO-1 to LUMO transition as indicated by dotted arrows. The association of the optically observed transitions between states with certain orbitals is justified by recent calculations from Xie et al. (2004).

The cleanest determination of the ionization threshold can be achieved by single photon ionization, but much work has also been done with electron impact. Well established are the values for $C_{60} \rightarrow C_{60}^+$ which is $E_I(C_{60}) = 7.58 \text{ eV}$ (De Vries et al., 1992), for double ionization $C_{60} \rightarrow C_{60}^{++}$ with 19.00 eV , i.e. $E_I(C_{60}^+) = 11.42 \text{ eV}$ (Steger et al., 1992), and triple ionization requires $(35.6 \pm 1) \text{ eV}$, i.e. $E_I(C_{60}^{++}) = 16.6 \text{ eV}$ (Scheier et al., 1994). As an example Fig. 3 shows the photo-ion yield from threshold to 36 eV from early synchrotron work of Hertel et al. (1992) (see also Yoo et al., 1992). Two remarkable observations warrant discussion:

- (1) The broad feature with a maximum from 16 to 24 eV was recognized as a giant plasmon excitation with many electrons contributing. The main

Fig. 3. Photoion yield in single photon ionization of C_{60} as measured at BESSY I by Hertel et al. (1992). Note the steep rise of the signal at threshold and the giant plasmon resonance with a broad maximum at 16-24 eV.

aspects of this feature can be understood by a charged sphere model, as Bertsch et al. (1991) point out. Their tight binding calculations, local density approximation, LDA, (Alasia et al., 1994) and time dependent LDA (Yabana and Bertsch, 1996) show reasonably good agreement with the observed features, considering that in this experiment the ion yield is due to autoionization and can only arise above the ionization threshold. LDA predicts this mode to carry an oscillator strength of ~ 160 (!). Alasia et al. (1994) find that the optical/UV part of the dipole response of C_{60} is dominated by particle hole transitions among π orbitals, however, the agreement with the spectrum shown in Fig. 2 is less favorable than for the Mie resonance at 20 eV (Fig. 3) arising not only from $\sigma-\sigma$ transitions but also, and to a large extent, from particle-hole excitations connecting σ with π and δ orbitals, as well as final states with a higher number of nodes. The width of the Mie resonance is explained due to the decay of the plasmon into single-particle configurations. In the context of these calculation Bertsch et al. (1991) estimated for the polarizability of C_{60} a value of $\alpha \sim 37 \text{ \AA}^3$. Alasia et al. (1994) obtained $\alpha = 88.8 \text{ \AA}^3$, while more recent calculations by Norman et al. (1997) give $\alpha = 85.8 \text{ \AA}^3$. Only very recently a value of $\alpha = 79 \pm 4 \text{ \AA}^3$ was reported from a sophisticated experiment (Ballard et al., 2000). We will refer to the latter in later discussions. Considering C_{60} as a conducting sphere this value would correspond to a radius $R = 4.29 \text{ \AA}$, which roughly corresponds to the outer diameter of the Buckminster fullerene cage.

- (2) The ion signal rises relatively steep directly at the ionization threshold (7.58 eV). No long tail below is observed, no hot bands are seen. We take this as a strong indication that the ionic potential is very similar to that of the neutral ground state and Franck-Condon factors strongly favor transitions with $\Delta v = 0$ for all vibrational modes. Schematically this is illustrated in Fig. 4: each vibrational level which is populated in the

Fig. 4. Schematic of photoionization (left) and a hypothetical resonant excitation of Rydberg states (right) in a one photon process. The Franck-Condon factors in C_{60} are such that a strict propensity rule $\Delta v = 0$ holds in either case.

neutral ground state will also be populated in the ionic ground state. No shift of the ionization potential due to the energy content in the ground state will be observed. We discuss this aspect here in such detail because it will later become relevant, when discussing the excitation of Rydberg states in section 5.1.

Much work has been devoted on the energetics and kinetics of ionization and fragmentation in C_{60} . Pertinent results from these efforts will be discussed later in this report as they are related to the investigations with fs-laser pulses. Here we just communicate some key results which may help us to understand observations seen in the mass spectra with short pulse multiphoton experiments in section 3. A typical example from electron impact ionization and fragmentation is shown in Fig. 5 as derived from [Matt et al. \(1996\)](#) and [Foltin et al. \(1998\)](#).

As clearly seen in Fig. 5, C_{60}^+ is seen for impact energies E_{el} from threshold with an approximately linear rise of the ion yield up to a broad maximum at about 50-100 eV which falls off smoothly for higher impact energies. In contrast fragments C_{60-2m}^+ are only observed above an appearance potential

$$E_A = E_I + mE_a + E_{shift} \quad (1)$$

Fig. 5. Cross sections for electron impact ionization (C_{60}^+) followed by fragmentation (C_{58}^+) over a wide range of electron energies adapted from Foltin et al. (1998) and (C_{58}^+) yield on an expanded scale near threshold from Matt et al. (1996) (lower panel). The insert in the latter shows also a two step process (full line) and was only recorded when increasing the electron current by factor of 10.

far above the energetic threshold, with a so-called *kinetic shift* (E_{shift}). While the energetic threshold for C_{58}^+ would be at about 17 eV, a significant ion yield is only observed for $E_{el} > 47$ eV as shown in Fig. 5, lower panel. The C_{58}^+ signal then rises rather steeply and after reaching a maximum at about 60 eV falls off again much more rapidly than the parent ion (see Fig. 5 top right panel). For larger fragments a similar behavior is observed, the onset of the signals just being shifted by an addition of 10 eV for each ejected C_2 unit. To understand this shift we note that these fragmentation processes do not occur as direct dissociation but rather as a kind of afterthought of the molecule to the initial process of energy deposition by the impact. A large amount of excess energy is distributed in this process over all degrees of freedom of the molecule which acquires thus an effective temperature $T \gtrsim 3000$ K. One finds that even up to 4000 K the system still remains partially intact for a long time. The process observed may schematically be written as

where # stands for internal excitation. (Several # are meant to indicate that for each additional evaporation an additional initial energy of ≥ 10 eV is required). The sequential *evaporation* of C_2 units (Eq. 2b,c) occurs long after the electron impact process is over and time scales of ns, μ s or even ms may be involved, resulting finally in mass spectra very much like those seen in Fig. 1. This unusual stability of C_{60} is again a result of the many internal degrees of freedom. Quite sophisticated RRKM calculation belong today to the work-tools for describing these fragmentation mechanisms as e.g. reviewed by [Scheier et al. \(1996\)](#), [Campbell and Levine \(2000\)](#) and [Lifshitz \(2001\)](#)¹.

Of some special interest in our present context is the feature shown in the insert of the lower panel in Fig. 5. There, following a controversy in the literature, [Matt et al. \(1996\)](#) studied the threshold behavior of the fragments at different currents of the electron gun. At high electron current, 2 step collisions may occur where a second electron hits a molecule which has already been ionized or excited in a first collision. Obviously in that case, the appearance energy is dramatically shifted downwards, a fragment signal is seen just above threshold and the yield peaks at ca. 35 eV. [Matt et al. \(1996\)](#) suggest that the following steps may be responsible:

In this context we draw attention to the more recent studies on electron impact induced fragmentation of ions by [Hathiramani et al. \(2000\)](#) shown in Fig. 6. In contrast to electron impact on neutral C_{60} the fragmentation occurs here without an additional ionization step (essentially following Eq. 3b). Here, the fragment yield rises directly from threshold without an extra kinetic shift. The strong resonance peaking at about 30 eV for all charge states studied resembles very much the giant plasmon resonance observed in the C_{60}^+ photo ion yield from neutral C_{60} as shown in Fig. 3. As [Hathiramani et al. \(2000\)](#) point out, this suggests that the electron impact induced fragmentation process in the ions at low energies is predominantly caused by a plasmon excitation. The fragment ion yield from neutral C_{60} (Fig. 5) shows a similar peak, shifted however to about 60 eV and decreasing more rapidly and to a lower level with electron energy. The peak width in Fig. 6 is also much larger than in the photon ionization experiment (Fig. 3). To understand this, one has to bear in mind that in contrast to the investigations where neutral fullerenes were used as a target, the internal energy of the C_{60}^{q+} ions will contain at least the energy of one plasmon from the ionization in the ECR ion source used in these studies. Hence, they will decay upon excitation of only one additional plasmon. It still

¹ Note added in proof: Probably the most reliable and extended sets of ionisation potentials and dissociation energies for singly and multiply charged fullerenes have been calculated by [Diaz-Tendero et al. \(2003, submitted\)](#).

Fig. 6. Absolute cross sections σ for the electron-impact induced C_2 fragmentation of C_{60}^{q+} from [Hathiramani et al. \(2000\)](#). Circles, $q = 1$; squares, $q = 2$; triangles, $q = 3$. The solid lines are fits through the respective data points at energies higher than 120 eV.

remains surprising that fragmentation of these hot C_{60}^{q+} ions begins without kinetic shift at threshold. For later discussion we just keep in mind that hot C_{60}^{q+} ions readily fragment when some additional energy is deposited.

[Reinköster et al. \(2004\)](#) reported ion yields from a single photon ionization experiment of C_{60} as a function of photon energy $h\nu$ covering a wide energy range from $h\nu = 26$ eV to 130 eV by using synchrotron radiation. A survey of the mass spectra is displayed in Fig. 7 showing C_{60}^{q+} ions with q up to 3 and their respective fragments C_{60-2m}^{q+} . Again, fragments are only observed at photon energies $h\nu \geq E_A$ far above their energetic thresholds, i.e. with high kinetic shifts E_{shift} , which are even systematically 3–7 eV larger than those observed for electron impact ionization and fragmentation by [Scheier et al. \(1994\)](#). This may be due to the fact that in photoionization a larger part of energy is shared by the electron emitted from the C_{60} . For later comparison with fs-laser induced mass spectra (section 3) we draw particular attention to the fact that doubly charged fragments are significantly more abundant than singly charged fragments - and even triply charged fragments are clearly visible. We also note that the singly charged fragments decrease substantially as the photon energy increases while the doubly charged ones remain more or

Fig. 7. Mass spectrum from C_{60} after ionization with a single photon of 26–130 eV energy adopted from Reinköster et al. (2004). The density of points indicates the ion yield at the different parent and fragment masses C_{60-2m}^{q+} . For clarity the appearance energies for C_{58}^+ and C_{56}^+ are indicated by dashed arrows, illustrating a kinetic shift of about 30 eV to their respective energetic thresholds.

less constant. It appear suggestive to connect these findings with the ease of fragments formed from $e + C_{60}^{q+}$ collisions just discussed. It may well be that one of the electrons emitted in the process

contributes by some kind of an internal post-collisional or better *post-ionization* effect to the fragmentation. Now, while in single photon ionization the energy of the ejected electron rises with photon energy and the cross section for fragmentation decreases (see Fig. 6) in double photoionization there is a strong probability that one of the ejected electrons carries only a low energy (Lafon et al., 2001) and hence can efficiently excite the plasmon resonance which in turn leads to fragmentation.

Reinköster et al. (2004) have also discussed the mechanism for the formation of doubly and triply charged ions, invoking *shake processes* - which may or may not be pertinent to the generation of multiply charged ions created by fs-laser pulse interaction (section 3). In this process the electron ‘sees’ the suddenly changed potential of the ionic core due to the ionization and has to adapt to this change via excitation or ionization of another electron, the so-

called shake up or shake off. The probability of this process is proportional to the overlap between the electron orbital in the undisturbed atom and higher lying orbitals including the continuum of the singly charged ion, which are contracted relative to the neutral atom. This describes the situation in the sudden limit and [Reinköster et al. \(2004\)](#) can explain the shape of the multiply charged ion yields as a function of energy sufficiently well in the framework of a simple model developed by [Thomas \(1984\)](#) using essentially one parameter.

2.2 A simple model potential for C_{60}

We have, in the previous subsection, already mentioned a few theoretical approaches to a quantitative understanding of the electronic structure of C_{60} . As already mentioned the spectroscopy and dynamics of the molecule is determined by its 240 valence electrons for which a rigorous theoretical treatment is perhaps just possible with state of the art quantum chemical methods (including TDLDA) and present computers but require a substantial effort. For a number of purposes it is, however, very useful to employ a simple model potential derived from considering the system in a first approximation as charged hollow, polarizable sphere with a radius of $R = 8.11a_0 = 4.29 \text{ \AA}$ (as derived from the polarizability). Based on such a jellium type of approach a number of theoretical studies have been reported in the literature. [Puska and Nieminen \(1993\)](#) e.g., used such a model potential to derive an estimate for the ionization potential and the plasmon resonance and based on this potential with slight modifications [Frank and Rost \(1997\)](#) and [Rüdel et al. \(2002\)](#) were able to describe very precisely a complex oscillatory structure in the photoionization cross section of C_{60} . These oscillations which were first reported by [Xu et al. \(1996\)](#) arise from interferences of electrons originating from different parts of the C_{60}^+ ion cage and may be considered a very rigorous test to any model potential. In its present, improved form also used for calculating energies of C_{60} Rydberg states to be discussed in section 5.1 this one-electron potential reads

$$V_0(r) = \begin{cases} -2e^{-6.69|r-6.69|} - \frac{1}{|r-6.69|} & \text{if } r < 5.13 \\ \frac{-1.5}{1+e^{\frac{|r-6.69|-1.558}{0.006}}} & \text{if } 5.13 \leq r < 5.15 \\ 0.012(6.69-r)^4 - 1.50 & \text{if } 5.15 \leq r \leq 8.23 \\ \frac{-1.5}{1+e^{\frac{|r-6.69|-1.558}{0.006}}} & \text{if } 8.23 < r \leq 8.25 \\ -2e^{-6.69|r-6.69|} - \frac{1}{|r-6.69|} & \text{if } 8.25 < r \end{cases} \quad (5)$$

converging to $1/r$ for large electron distances from the cage and reproduces the ionization potential of C_{60} in a single active electron (SAE) picture. It can also be used as a basis for a multi active electron (MAE) description by using it as a starting point for a jellium model of all active electrons. This approach

Fig. 8. 3 dimensional view of the model potential for C_{60}^+ according to Eq. 5.

has e.g. been used by [Bauer et al. \(2001\)](#) (see also [Bauer, 2002](#)) with a slightly simpler but similar expression. For illustration we show a 3D representation of this potential in Fig. 8.

2.3 Atoms, molecules and clusters in intense laser fields

We will just communicate in a nutshell some concepts and notions to establish the language for the discussion to follow in the next sections. Our first concern is to define what is meant by a ‘strong’ laser field. We will discuss this in a pragmatic manner and see that this notion depends very much on the process and system studied. On an absolute scale an electromagnetic field may be considered strong if its electric field amplitude $\mathcal{E}_0 = \sqrt{2I/(\epsilon_0 c)}$ is comparable to the inner-atomic field. With ϵ_0 the vacuum dielectric constant, and c the velocity of light we find for a ground state H-atom (with its electron in a distance of 1 Bohr radius a_0 from the nucleus) that the field is strong if the intensity is $I \geq 3.5 \times 10^{16} \text{ W/cm}^2$, while above some 10^{17} W/cm^2 relativistic effects as well as the magnetic field component of the field become important. Present state of the art high intensity laser facilities can provide such intensities up to 10^{20} W/cm^2 , using 800 nm Ti:Sapphire lasers with sub 50 fs pulse duration at a comfortable 10 Hz repetition rate (see e.g. [Kalachnikov et al., 2001](#)). However, it turns out that our present object of interest, C_{60} , already completely disintegrates at intensities above 10^{16} W/cm^2 , ejecting essentially fast carbon ions with charge states up to $q = 4$ ([Kou et al., 2000](#)). Since we are concerned here with essentially intact C_{60} our present focus will be on an intensity range from 10^{11} W/cm^2 to 10^{15} W/cm^2 . As we shall see, even at 10^{11} W/cm^2 and below, multiphoton processes dominate the energy deposition and C_{60} is easily ionized by 5 or more photons of 800 nm at this intensity.

Hence, in the present context we consider a field to be strong if the object under study is significantly modified by the field. One relevant quantity is then the

average oscillation energy which a free electron acquires in the radiation field of the laser pulse. This *ponderomotive potential* is given by

$$U_p = \frac{e_0^2}{2m_e \epsilon_0 c \omega_L^2} I \propto \lambda^2 I \quad (6)$$

and numerically by $U_p = 9.34 \times 10^{-20} (\lambda/\text{nm})^2 I/(\text{W cm}^{-2}) \text{ eV}$.

with m_e the mass of the electron, ω_L the angular frequency of the laser radiation. Note that the ponderomotive potential depends quadratically on the laser wave length λ , i.e. is most significant in the infrared wavelength region. To determine whether a field is strong we have thus to compare U_p with the atomic or molecular energy in question. When discussing ionization processes we would consider the *strong field regime* to begin at

$$U_p > E_I \quad (7)$$

where E_I is the ionization potential of the system. For C_{60} with $E_I = 7.58 \text{ eV}$ (De Vries et al., 1992) an 800 nm Ti:Sapphire pulse would in that sense be ‘strong’ when $I > 1.3 \times 10^{14} \text{ W/cm}^2 = I_{crit}$, which conveniently may be achieved by focussing a 50 fs pulse of 400 μJ onto a spot size of 100 μm diameter. Typical multiphoton processes occur for $I \ll I_{crit}$ as illustrated for an atom Fig. 9 (left panel). Indicated are the kinetic electron (e^-) energies expected in above threshold ionization (ATI) as well as the possibility to generate high harmonics of the frequency of the interacting laser pulse. At intensities $I \gtrsim I_{crit}$ the atomic or molecular potentials are significantly deformed by the field as depicted in Fig. 9 (right panel). The electron e^- can escape from the atom in an *above barrier* process and is accelerated in the oscillating laser field. While a completely free electron would not be able to gain energy from the laser pulse (for energy and momentum conservation reasons) with the atom present this is possible. As first pointed out by Corkum (1993), the electron can accumulate energy and - depending on its starting phase with respect to the laser field - may return to the atom with kinetic energies up to about $3.2U_p$. This is schematically illustrated by the trajectory in Fig. 9 (right panel) showing an electron starting at the barrier. This so called *recollision process* has been established to be instrumental in high harmonic generation (HHG) and explains the experimentally observed plateau and cutoff of HHG towards high energies (Schafer et al., 1993; Corkum, 1993). As we shall discuss in section 3 recollision may also contribute to fragmentation of molecules and clusters such as C_{60} in strong laser fields.

Traditionally one also defines a dimensionless quantity, the so called *Keldysh*

Fig. 9. Schematic illustration an atom in a strong field with electron energetics an high harmonic generation. Left: multiphoton ionization (upward arrows indicate photon energies), electron energies (full downward arrows) in above threshold ionization (ATI), and high harmonics generation (dotted downward arrow). Right: above barrier ionization in a strong field, indicating the recolliding electron with a maximum energy of $3.2U_p$.

parameter, introduced by Keldysh (1965),

$$\begin{aligned}\gamma &= \sqrt{\frac{E_I}{2U_p}} = \sqrt{\frac{E_I \epsilon_0 m_e c \omega_L^2}{e_0^2 I}} \propto \frac{t_{ZR}}{t_L} \\ &= 2.31 \times 10^9 \sqrt{\frac{E_I / \text{eV}}{(I / \text{W cm}^{-2}) (\lambda / \text{nm})^2}}\end{aligned}\quad (8)$$

to differentiate between the high and low intensity regime. One can show that γ is also proportional to the ratio of the tunnelling time t_{ZR} of the electron through the barrier in a zero range potential and the period of the laser $t_L = 2\pi/\omega_0$. Hence, in the strong field regime $\gamma \ll 1$ the electron escapes the atom in a time shorter than the field inversion time. In contrast, a weaker field ($\gamma \geq 1$) reverses before the electron can tunnel through the barrier.

Apart from the very dramatic deformations of the atomic (or molecular) potential just discussed we also have to consider the dynamic Stark effect caused by the laser field which may shift atomic and molecular energy levels in a significant manner. For molecules sufficiently strong fields can thus cause potential energy crossings and consequently lead to laser field induced nonadiabatic transitions, a subject of very active current research in many experimental and theoretical studies (DeWitt and Levis, 1998; Kawata et al., 2001; Kono et al., 2002; Lezius et al., 2002; Kono et al., 2003; Sato et al., 2003; Markevitch et al., 2003, 2004; Kono et al., 2004). Such behavior will be most efficient if the laser frequency is close to a resonance of the system studied. Such manifestations of the Autler-Townes effect have long been known in studies of ATI processes (LaGattuta, 1993) and definitively need to be considered also for molecules in intense laser fields. The Autler and Townes (1955) splitting is $\hbar d_{ik} \mathcal{E}_0$ with

d_{ik} being the dipole transition moment between the resonant levels. One easily estimates that such splitting can be in the eV region at rather moderate intensities of 10^{11} W/cm², providing the laser frequency is in resonance with a transition of significant oscillator strength. We will have to keep this in mind when discussing excitation mechanisms in C₆₀.

2.4 Experimental aspects

A few experimental aspects of fs laser pulse interaction studies with C₆₀ deserve to be mentioned. Fig. 10 gives as an example a self explaining schematic of a typical experimental setup used by the group at the Max Born Institute. Time of flight (TOF) instruments are used to study both the electron energy distributions and the mass spectra of the fullerenes. Presently, no simultaneous (coincident) detection of ions and electrons is employed, although in principle possible as shown by [Stern et al. \(1999\)](#). A molecular beam of C₆₀ is usually generated by effusive heating from an oven. In a special study also a liquid nitrogen cooled C₆₀ beam from an aggregation cell was used by [Hansen et al. \(1997\)](#). We mention that the reflectron used here for analyzing the ion masses has a resolution of better than 1000, hence enabling isotope identification in C₆₀ and allowing one to study metastable fragmentation on the μ s time scale. The energy resolution of the electron spectrometer ranges from 5 meV at $E_{el} = 1$ eV to 400 meV at $E_{el} = 20$ eV.

We will not discuss the various laser systems and experimental methods of ultrafast physics. Suffice it to say that typically the basis of all table top short pulsed laser systems used in these studies is the Ti:Sapphire laser at 800 nm which may be converted conveniently to the second harmonics and by using other non-linear conversion schemes orange or near infrared laser wavelength can be employed. Present state of the art techniques are used to manipulate, stretch, shape and characterize the laser pulses. We will discuss, however, a few subtleties concerning the definition of intensities, calibrating them, measuring signal yields as a function of intensity and defining so called ‘saturation intensities’ in the high intensity limit.

Intensity calibration with short pulse lasers is a non trivial problem. What can be measured directly is the pulse energy E_p . But since we never have a constant spatial and temporal distribution of intensity it is important to define clearly to which quantity a given intensity refers. In the most favorable case the spatial and temporal distribution is Gaussian and the intensity I (mostly given in W/cm²) is

$$I(r, t) = I_m \exp(-(r/w)^2) \exp(-(t/\tau)^2) \quad (9)$$

with I_m giving the maximum intensity at $t = r = 0$ with τ and w characterizing

Fig. 10. Typical experimental setup for studying C₆₀ interaction with ultrafast laser pulses used in the present work. Both electrons and ions can be detected by time of flight electron and mass spectrometers, respectively. The laser pulses originate from a Ti:Sapphire fs laser, using various frequency conversion, stretching and shaping methods. A computer facilitates the control of the laser pulses and other experimental parameters as well as data collection.

the temporal and spatial beam profile - quantities which can in principle be measured experimentally by determining the autocorrelation function (for τ) and e.g. the total energy passing a knife edge which is moved into the beam (for w). For a Gaussian one easily works out that

$$\begin{aligned}
 I_m &= \frac{E_p}{\sqrt{\pi}\tau\pi w^2} \simeq \frac{E_p}{t_h(\pi w^2)} \quad \text{or} \\
 &= 0.83 \frac{E_p}{t_h d_h^2}
 \end{aligned}
 \tag{10}$$

with t_h and d_h being FWHM of the temporal and spatial pulse width, respectively. We note that the maximum intensity at the pulse center corresponds to a hypothetical circular beam of constant intensity of radius w . Note, however, that w is the $1/e$ beam waist radius, not the $1/e^2$ radius often given for laser beams! Since the beam parameters are difficult to determine quantitatively, the intensity in typical ion yield experiments is usually not measured absolutely. Rather one calibrates the intensity with a known intensity dependence for a standard ion (typically Xe⁺) or compares photoelectron spectra with known data from the literature (see e.g. Larochelle et al., 1998; Schyja et al., 1998).

One may be worried about the effect the spatial and temporal intensity dis-

tribution has on the experimental intensities, especially so when comparing them with theoretical work which typically assumes a well defined, constant intensity. Indeed, a careful examination of the geometry for each experiment is necessary and the lack of it may explain many discrepancies reported in the literature. The following for consideration shows, however, that well defined Gaussian beams are often best suited to account for this properly. We consider the ion yield expected in a multiphoton ionization process with n photons. For not too high intensities the theoretical prediction (see e.g. [Lambropoulos, 1985](#)) for the ionization probability is $W(I) = \sigma_n(I/h\nu)^n$ with an n photon ‘cross section’ σ_n . We assume a Gaussian laser beam focussed such that the Rayleigh length is significantly larger than the target length ℓ illuminated - a situation which is typical for well collimated molecular beams and not too strong focussing. In this case, the laser intensity a particular target molecule experiences depends only on its radial position and time.² The signal is then derived from

$$S = \beta \ell N_0 \sigma_n \times 2\pi \int_{-\infty}^{\infty} dt \int_0^{\infty} r dr [I(r, t)/h\nu]^n \quad (11)$$

with β an experimental sensitivity parameter and N_0 the target density. Using the laser pulse profile Eq. 9 one obtains after integration

$$S = \beta \pi w^2 \ell N_0 \sigma_n \times \tau (I_m/h\nu)^n / (n\sqrt{n}) \quad (12)$$

with the maximum intensity I_m given by Eq. 10. This is a nice result, showing that the signal still follows a power law and is proportional to the pulse duration τ and beam area at $1/e$ intensity. The only difference compared to hypothetical laser pulse of uniform intensity in space and time is a reduction of the total signal by a factor $1/(n\sqrt{n})$. Hence, it appears a good idea to use Gaussian beams when determining e.g. the slope of a power laws for ionization of C_{60} by a short laser pulse, rather than trying to spatially shape the laser pulse for constant intensity with possibly problematic consequences from diffraction etc.

Slightly more complex is the determination of saturation intensities, i.e. the determination of an intensity at which most of the molecules have undergone the process investigated, i.e. for high intensities and transition probabilities. [Hankin et al. \(2000\)](#) and [Lezius et al. \(2001\)](#) pointed out that the signal for a Gaussian beam may for the general case be written as

$$S = \beta \ell N_0 \pi w^2 \phi \int_0^{I_m} \frac{1 - e^{-W(I)\tau}}{I} dI \quad (13)$$

² Note, however, that in experiments with extremely intense fields one often uses very tight focussing. In that case the evaluation of the signal has to account for a modification of the laser intensity in two dimensions ([Larochelle et al., 1998](#)).

where in addition an ionization branching ratio ϕ has been introduced.³ Note, that once I_m the maximum intensity of the laser pulse is greater than the saturation intensity I_{sat} to ionize an atom with probability $W(I_{sat})\tau = 1$ any further increase of the signal essentially originates from an increase of the beam diameter for which saturation is reached as I_m is further increased. To derive a saturation intensity [Hankin et al. \(2000\)](#) assumed that for $I(r) > I_{sat}$ one may set $e^{-W(I)\tau} = 0$ and that outside the thus defined beam volume V_{sat} no signal is generated. With this assumption the lower limit in Eq. 13 becomes I_{sat} and one derives

$$S = \beta \ell N_0 \pi w^2 \phi [\ln I - \ln I_{sat}] \quad (14)$$

This would imply that in a lin-log plot one may determine the saturation intensity from the intersection of the observed signal (linearly depending on $\ln I$) with the abscissa. In agreement with current literature, we will use this somewhat pragmatic approach in the present report, defining thus an experimental measure for the readiness of a system to achieve a certain charge state in a laser field. We note, however, that we have lost on the way the obvious dependence of a saturation intensity on pulse duration still seen in Eq. 13 and that we have omitted that also for $I < I_{sat}$, i.e. from the wings of the Gaussian beam, a signal is generated. Both effects make the derived saturation intensities slightly dependent on the experimental setup and on the (power) law valid in the intensity regime below saturation.

3 Ionization, charge states and fragmentation

3.1 Mass spectra and fragmentation

Already the early photofragmentation experiments by [O'Brien et al. \(1988\)](#) showed that fullerenes have very special ionization and fragmentation properties. A typical example of these mass spectra is shown in Fig. 11. As already recognizable in the first mass spectra as obtained from hot carbon soot (see Fig. 1) two distinct regimes can be distinguished: i.) from the parent ion C_{60}^+ down to C_{32}^+ only fragments with an even number of C atoms are observed while ii.) between C_7^+ and C_{25}^+ mass peaks are separated by one C^+ unit. This bimodal mass distribution has also been observed in various experiments using different excitation mechanisms, e.g. in collisions between C_{60}^+ and neutral rare gas atoms ([Ehlich et al., 1996](#)).

³ Note that this assumes a pulse of constant intensity over a time τ . More precisely, $W(I)\tau$ has to be replaced by an integral over the temporal pulse shape.

y

Fig. 11. Mass spectrum from the first photofragmentation study of mass selected C_{60}^+ obtained with ns laser pulses at 353 nm with a fluence of 59 mJ/cm² from O'Brien et al. (1988).

It is now generally accepted that the dominant mechanism for the formation of the large fragments from C_{60}^+ is by sequential fragmentation,

starting with a highly excited ion. The recent photoionization mass spectra of Reinköster et al. (2004) shown in Fig. 7 appear to support such a view rather nicely. One clearly sees, in particularly so for the doubly charged ions, that each stage of fragmentation needs an additional energy of about the C_2 evaporation energy of 10 eV - in addition to the threshold energy plus the kinetic shift. However, emission of large neutrals has been regularly invoked to explain the observed loss of large-n clusters (see e.g. DeMuro et al. (1992) or Hohmann et al. (1994)) and has even been observed in reionization experiments. For details the reader is referred to a recent, comprehensive study by Rentenier et al. (2004), and references therein. In particular for the fragmentation of multiply charged ions a number of mechanisms have been discussed in the literature, e.g. auto-charge transfer (ACT) and asymmetric fission (AF) such

as:

$$\begin{aligned}
C_{60}^{r+} &\rightarrow C_{m'}^{r+} + C_n^0 \quad \text{or} \\
C_{60}^{r+} &\rightarrow C_{m'}^{(r-1)+} + C_n^+ \quad \text{or} \\
C_{60}^{r+} &\rightarrow C_{m'}^{(r-1)+} + C_n^+ + mC_2
\end{aligned} \tag{16}$$

Obviously, this type process is necessary to explain the small C_n^+ ions observed in the mass spectra with odd and even n .

The particular resilience of C_{60} has lead to the observation of a number of general phenomena which are, however, particularly pronounced in C_{60} photoionization studies. Delayed ionization (or thermionic emission) which occurs microseconds after excitation e.g. with ns laser pulses at photon energies far below the ionization limit (Campbell et al., 1991) has drawn a lot of attention during recent years (see e.g. Campbell and Levine, 2000, and references therein). Delayed ionization in photoabsorption experiments occurs subject to conditions: First, a fast energy redistribution between the electronic excitation energy and the vibrational modes enables the photoexcited species to absorb sequentially many photons and heats up quickly. While this is true for most larger molecules and clusters, usually these systems undergo a fast neutral dissociation since the binding energy between some molecular subunits or cluster constituents is normally much smaller than the ionization potential. For some metallic and metacar clusters and fullerenes in particular the reverse is true as discussed in section (2.1): for C_{60} the binding energy of the C_2 is $E_a \geq 9.5$ eV while the ionization potential is $E_I = 7.58$ eV. Under these conditions the delayed electron emission is one possible decay channel in competition with other decay modes, such as fragmentation or radiative cooling (see e.g. Rohmund et al., 2001).

Mass spectra from multi-photon ionization (MPI) of C_{60} have been studied with various laser parameters (Hohmann et al., 1994; Hunsche et al., 1996; Baumert and Gerber, 1997; Kou et al., 1998), but only relatively recently, systematic studies with short pulse lasers and varying pulse widths have been performed (Tchaplyguine et al., 2000; Campbell et al., 2001a,b). Fig. 12 shows two typical mass spectra obtained for 795 nm excitation with 25 fs and 5 ps pulse duration, respectively. While the 5 ps pulse mass spectrum resembles very much the ‘standard’ bimodal mass spectra, which we have seen before (Figs. 1 and 11) the 25 fs spectrum shows a rather different pattern, most striking perhaps the strong yield of multiple charged species, which have not been observed with laser pulses in the ns time regime even at the highest intensities. We mention, however, that in collision experiments involving fast electronic excitation similar mass spectra are observed, e.g. in high energy electron impact experiments (Völpel et al., 1993; Scheier et al., 1994; Itoh et al., 1999), in collisions with singly and doubly charged high velocity ions (see e.g. Schlathölter et al., 1999; Reinköster et al., 2001, 2003)) in collisions

Fig. 12. Typical mass spectra obtained from C_{60} by ionizing with laser pulses of 795 nm wavelength with 25 fs pulse duration (bottom) and 5 ps (top). The spectra were recorded at roughly equal laser fluence, the corresponding intensities being $\sim 3.2 \times 10^{12} \text{ W/cm}^2$ and $1 \times 10^{15} \text{ W/cm}^2$, respectively, which is equivalent to Keldysh parameters of 4.4 and 0.25 (or to ponderomotive potentials of 0.19 eV and 60 eV). For 5 ps pulses a ‘normal’ bimodal mass spectrum is observed. In contrast, for high intensity 25 fs pulses a series of multiply charged C_{60}^{q+} ions is seen together with their large fragments (C_2 evaporation). However, extremely little fragmentation is detected for singly charged C_{60}^+ - as illustrated by the insert with magnification $\times 200$ - and only few small fragments if any. The peaks marked with asterisks (*) indicate metastable decay processes. The inserts on the right show the characteristic isotope distribution of C_{60}^+ with the isotopomer ratio $[^{12}C_{60}]:[^{12}C_{59}^{13}C]:[^{12}C_{58}^{13}C_2]$ being 1 : 0.65 : 0.21.

with highly charged ions with C_{60} (see e.g. Schlathölter et al., 1999; Jensen et al., 2004), and as illustrated in Figs. 13 and 14.

The common characteristics of these experiments is that the electronic system of C_{60} is excited on a time scale short compared to the electron-phonon coupling which is believed to be on the order of a few 100 fs. We also remark that in the 25 fs laser generated mass spectrum C_{60}^+ shows almost no fragments (only about 0.5% as illustrated by the insert) at these relatively high intensities, the Keldysh parameter (Eq. 8) being $\gamma = 0.25$. In contrast, multiply charged fragments are strongly abundant. We note in passing, that the tail of the C_{60}^+ peak seen in the 5 ps mass spectrum indicates the onset of delayed ionization of C_{60} . The fraction of delayed C_{60} ions increases almost linearly with the pulse duration. No saturation has been found for pulses up to 5 ps, the longest pulse length available in these experiments (Campbell et al., 2001a).

Fig. 13. Mass spectra of the collision products from He^{2+} - C_{60} collisions at different projectile energies given in atomic units from Schlathölter et al. (1999). All spectra are normalized to the C_{60}^+ signal.

Fig. 14. Mass spectra of the collision products from (a) He^+ , (b) O^{5+} , and (c) Xe^{28+} collisions with C_{60} from Schlathölter et al. (1999). The projectile velocity in atomic units is given in each plot. In all three plots the break on the intensity axis is at 33% of the strongest peak.

Further insight into mechanisms and time scales of the various energy transfer processes is gleaned from comparing mass spectra at different pulse duration but *constant* laser intensity (i.e. different pulse energy) (Campbell et al., 2000). Fig. 15 shows three mass spectra at $4 \times 10^{13} \text{ W/cm}^2$ (Keldysh parameter $\gamma = 2.5$) - and for comparison again the 5 ps spectrum already shown in Fig. 12. At short pulse durations (25 fs and 110 fs) one observes mostly intact C_{60}^{q+} ions up triply charged and only little fragmentation. Obviously, with pulse duration between 25 and 500 fs the ratio $\text{C}_{60}^{q+}/\text{C}_{60}^+$ of multiply to singly charged ions increases significantly. In addition, fragmentation becomes also more efficient. When using a 500 fs pulse the abundance of doubly and triply charged ions and fragments C_{60-2n}^{++} and C_{60-2n}^{+++} is already larger than 1. It is difficult to compare the 5 ps laser pulse data directly, since the intensity is much smaller, but the multiply charged ions have completely disappeared and the mass spectrum is dominated by singly charged fragments - one possible reason being asymmetric fission and other processes discussed above (see Eq. 16), which is supported by efficient heating of the system during the long pulse.

Next we compare different laser intensities and wavelengths. The mass spectra in Fig. 16 show a characteristic dependence of charge states and fragment mass distribution on laser pulse intensity. While for both wavelengths, 395 and 790 nm, no fragmentation is seen at low intensities we note that at higher, but similar intensities fragmentation is more prominent at 395 nm. For 790 nm and 25 fs and intensities up to $1 \times 10^{14} \text{ W/cm}^2$ one observes essentially intact C_{60}^{q+} ions only ($q \leq 3$), while at $6 \times 10^{14} \text{ W/cm}^2$ charge states up to $q = 5$ are discernable as well as a significant amount of multiply charged fragments with up to 6 C_2 losses. Nevertheless, with 790 nm the signal from intact C_{60}^{q+} is still larger than each of the respective C_{60-2n}^{+q} fragment signals. In addition, small fragments with odd and even numbers of C atoms appear. In contrast, using 395 nm laser pulses we see massive fragmentation already at $8.9 \times 10^{13} \text{ W/cm}^2$ while at $1.3 \times 10^{14} \text{ W/cm}^2$ fragments dominate. The trends observed here become even more evident when near IR pulses are used for ionization as recently reported by Bhardwaj et al. (2003). They have investigated the ionization of C_{60} at 1800 nm with a pulse duration of 70 fs and intensities up to 10^{15} W/cm^2 - corresponding to a Keldysh parameter $\gamma = 0.11$. In contrast to the 400 or 800 nm experiments, the first optically allowed transitions of C_{60} are very far from 1 or 2 photon resonance with 1800 nm and ionization is supposed to occur either by tunnelling, or “over-the-barrier” ionization - as one certainly expects for a Keldysh parameter $\gamma \ll 1$. Fig. 17 shows a mass spectrum from that work taken with 10^{15} W/cm^2 . Highly charged C_{60}^{q+} ions with $q \leq 12$ are the dominant features of this mass spectrum and almost no fragments are observed. The highly charged intact C_{60}^{q+} ions are explained by ultrafast ionization. Bhardwaj et al. (2003) also discuss the possibility of vibrational excitation due to induced dipole forces - one might call this impulsive Raman excitation - which is obviously only weak and hence the fragmentation rate is small.

Fig. 15. Mass spectra obtained by MPI of C_{60} with 795 nm as a function of laser pulse duration. The laser intensity was $4 \times 10^{13} \text{ W/cm}^2$ (a)-(c) and $4 \times 10^{12} \text{ W/cm}^2$ (d). The inset shows the onset of delayed ionization between 500 fs and 5 ps.

Apparently, in the context of fragmentation, the Keldysh parameter is not a relevant quantity to be discussed, and - as we shall discuss below (section 3.2) - even for clean ionization without fragmentation the classical above barrier concept must be seriously questioned with such a large finite system and its many electronic degrees of freedom. The laser frequency enters obviously in a more specific manner into the process of fragmentation, so to say counterintuitive to what is expected from naively applying the ‘conventional’ wisdom of atomic strong field physics. We believe that electronic resonances may be involved in heating the electronic system prior to ionization. We note that at 395 nm where most fragmentation is observed, the laser radiation is nearly resonant with the first small absorption maximum seen in Fig. 2. Recent theoretical calculations by [Torralva et al. \(2001\)](#) and [Zhang et al. \(2003\)](#) have shown that during a single femtosecond laser pulse even at moderate intensities ($\sim 10^{11} \text{ W/cm}^2$) more than one electron is excited. We emphasize that

these multielectron processes involve sequential absorption of several photons - in contrast to multiphoton absorption of energy by a single electron as well known from atomic physics. It is easily conceivable that several tens of eV can be deposited into the electronic system during a laser pulse at 10^{14} W/cm². This energy can then be redistributed in principle among all degrees of freedom. However, the coupling time between the electronic and vibrational degrees of freedom is on the order of a few 100 fs. Hence, for the shortest pulse durations discussed here, energy redistribution from electronic to nuclear system during the pulse is much less likely. Rather, the ionized electron(s) carry most of the energy and little fragmentation is observed (Shchatsinin et al., to be published). In contrast, for the longer pulses where energy can readily be transferred from the electronic to the nuclear system during the laser pulse, ionization occurs as an afterthought - and patterns as known from fragmentation with ns laser pulses are observed.

Several reasons may be discussed for the particular puzzling lack of C_{60}^+ fragments from MPI with the shortest pulses - even at high intensities. We first note that, again, similar trends are seen in the fast collision spectra, where in the experiments with highly charged Xe^{28+} (Fig. 14) almost no fragments are detected at all for any charge state of C_{60}^{q+} . Referring again to the single photoionization experiments (Fig. 7) we recall that the singly charged C_{60-2m}^+ signals decrease significantly as the photon energy is increased while C_{60-2m}^{2+} and C_{60-2m}^{3+} are prominent and do not decrease at higher photon energy. Obviously, this somewhat mysterious higher abundance of multiply charged fragments cannot simply be attributed to the amount of energy deposited into the system. We recall in this context our earlier discussion (section 2.1) where we were lead to relate multiply charged fragments to some kind of post-ionization effect with not too fast electrons emerging in a multiple ionization process. This is consistent with the missing fragmentation in collisions with very highly charged ions (c.f. Fig. 14): in this case electrons are just extracted from C_{60}^+ very rapidly by the strong Coulomb field so that no time for post-ionization interaction with C_{60}^{q+} remains. A similar situation appears to dominate the 1800 nm results shown in Fig. 17 where only very little fragmentation, if any, is seen: the above barrier process occurs at these wavelengths and intensities extremely fast.

However, in a very recent MPI study of C_{60} at 1500 nm (70 fs) Bhardwaj et al. (2004) found a measurable, albeit small abundance of C_{60-2m}^{3+} and C_{60-2m}^{4+} . They observed the ratio of $C_{60-2m}^{3+}/C_{60}^{4+}$ and $C_{60-2m}^{4+}/C_{60}^{5+}$ to depend strongly on the ellipticity of the laser pulse. This clearly indicates that electrons which recollide during one laser oscillation cycle with the C_{60}^{q+} ion contribute significantly to the fragmentation process (c.f. the discussion in section 2.3). Bhardwaj et al. (2004) calculated the distribution of return energies in the classical recollision model (Corkum, 1993) and found that the maximum energy in C_{60}^{q+} recollision is significantly larger than the well known $3.2U_p$ value for atoms.

From this they were able to explain why in their experiment only fragments with $q \geq 3$ were observed. Hence, we conclude that such recollision processes may in part also be responsible for the high abundance of fragments in the mass spectra observed with shorter wavelength. A corresponding experiment has still to be done.

We summarize the observations and interpretations on the short pulse laser MPI of C_{60} as follows: For very short laser pulses (< 70 fs), ionization occurs predominantly via direct multiphoton ionization with negligible vibrational heating. At intermediate pulse durations (a few hundred fs) we still observe essentially unfragmented, singly charged ions with only some indication of C_{60-2m}^+ fragments and an increasing yield of higher charge states which also fragment, i.e. vibrational heating occurs during the laser pulse but does not lead to direct formation of singly charged fragments. Finally, for pulse durations beyond several hundred femtoseconds strong fragmentation is observed, multiply charged ions are no longer detected and the ionization process is followed by “thermionic” electron emission on a microsecond time scale. As one hypothesis to explain - at least partially - the fragmentation behavior observed we propose efficient post-ionization interaction of low energy photo-electrons with $C_{60}^{+ \#}$ vibrationally preheated during the excitation process. Additional evidence for this explanation is found in the observation that the fragmentation is strongly wave length dependent, being nearly suppressed for 1800 nm. In these comparatively slowly oscillating laser fields electrons are extracted most rapidly from ions and charge states up to $q \leq 12$ are detected. Furthermore, recollision processes may play a role in the fragmentation dynamics as documented for the weak fragmentation at 1500 nm.

A careful analysis of the mass spectra taken with a RETOF mass spectrometer (illustrated in Fig. 12) revealed that fragments are always accompanied by metastable fragmentation on a time scale of 10 to 100 μ s (Tchaplyguine et al., 2000; Campbell et al., 2001b). This is somewhat unexpected - at least at first thought - and tells us that all these large fragments with several C_2 units missing from C_{60}^{q+} are generated in an essentially statistical process: Once created they are still hot and can loose energy by C_2 evaporation (and by thermal emission of electron or by radiation). The key question to which we have given some tentative answers is, how the energy $\gtrsim 40$ eV needed for fragmentation and ionization on the given time scale is initially deposited into the system. We feel that this cannot be explained in the familiar single active electron (SAE) picture. Rather, many active electrons (MAE) will be involved in the processes. Mass spectra give fingerprints of the final outcome of these energy deposition processes. We note, that the picture evoked here is somewhat similar to that for describing femtosecond pulse excitation and electron relaxation on metal- or semiconductor-surfaces (see e.g. Knoesel et al., 1996): C_{60} may be seen as an intermediate on the way to condensed matter and we can visualize its excitation as filling of the conduction band with electrons.

We will come back to this notion in section 4 and 5.

3.2 Intensity dependence and power laws

At this point it is appropriate to look more quantitatively at the dependence of the ion yields on the laser intensity. Fig. 18 (lower panels) summarizes the results of Tchapyguine et al. (2000) at 795 and 400 nm. By measuring the total ion yield as a function of incident laser intensity and assuming a power law ($S \propto I^n$) Tchapyguine et al. (2000) found the C_{60}^+ ion signal to rise with a power $n = 5 \pm 1$ at 795 nm. This corresponds to a direct multiphoton ionization process with five 795 nm photons of 1.56 eV, as required to overcome the ionization potential of 7.6 eV.⁴ The yield of C_{60}^{2+} ion formation follows a power law with $n = 8 \pm 1$. The energy of eight red photons ($8h\nu = 12.5$ eV) gives clear evidence for a stepwise ionization mechanism with the order of the process being that required to remove an extra electron from C_{60}^+ (11.4 eV). At 400 nm ($h\nu = 3.12$ eV) the slope is - according to Fig. 18 (lower right panel) - $n = 3 \pm 1$ and 6 ± 1 for the yield of singly and doubly charged ions, respectively. While to ionize $C_{60} \rightarrow C_{60}^+$ one needs indeed at least three blue photons ($2h\nu = 6.24$ eV $< E_I = 7.58$ eV $< 3h\nu = 9.36$ eV), for ionization of $C_{60}^+ \rightarrow C_{60}^{2+}$ four blue photons ($4h\nu = 12.48$ eV) would suffice, rather than 6 as indicated by the slope. This probably illustrates the limitations of a strictly sequential ionization model for such a complex system.

As seen in the lower panels of Fig. 18 the signals saturate for higher intensities, indicating that all available target molecules have reached a certain ionization stage as discussed in section 2.4. Determining and interpreting saturation intensities is an interesting, but yet not completely solved puzzle in the strong field, ultrafast photoionization of large molecules. The Ottawa group has analyzed the ionization rate in intense laser fields for many polyatomic, organic molecules (Hankin et al., 2000, 2001; Lezius et al., 2001, 2002) (see also DeWitt and Levis, 1998; Markevitch et al., 2003, 2004) with the result that saturation intensities for molecules studied were generally much higher than predicted by the so called ADK tunnelling theory (Ammosov et al., 1986), a well established model for strong field ionization of atoms. Also our own measurements for C_{60} show a large deviation of the calculated ADK ionization rates as reported by Campbell et al. (2001b). Shown in Fig. 18 (upper panels), we have replotted the data in a lin-log plot as suggested by Hankin et al. (2001) for better comparison. As discussed in section 2.4 the linear rise of the signal at

⁴ Earlier reports of a slope $n = 13$ by Hunsche et al. (1996) seemed to indicate the excitation of the plasmon resonance at 20-30 eV. This observation has never been reproduced and the discrepancy remains unresolved, possible explanations being connected with broad, low intensity pre-pulses or with the special manner in which the geometry was defined in these experiments.

Fig. 18. C_{60}^+ (left) and C_{60}^{2+} (right) ion yield S as a function of the laser intensity I for 400 nm (circles) and 800 nm (squares). The lower panels give the standard log-log plot illustrating the power law $S \propto I^n$, where n corresponds to the order of the processes (the number of photons involved in one step). The top panel shows the same measurements in a lin-log plot as suggested by [Hankin et al. \(2001\)](#). The intercept of the fitted straight line with intensity axis defines the saturation intensity I_{sat} .

the high intensity limit essentially reflects the increase of the ion yield due to an increase of the volume in which saturation is reached. The intersection of the linear slope with the abscissa gives a pragmatic, experimental measure for the saturation intensity. The results of our own measurements as well as those from [Bhardwaj et al. \(2003\)](#) are shown in Fig. 19 as a function of final charge state along with two slightly different approaches to compare these results with the classical ‘over the barrier’ model in an SAE picture. [Bhardwaj et al. \(2003\)](#) have described the ionization process $C_{60}^{q+} \rightarrow C_{60}^{(q+1)+}$ in the laser field by using a q fold charged, conducting and polarizable sphere for the interaction of the active electron with C_{60}^{q+} . Saturation is assumed to occur when the thus derived barrier falls below the ionization energy for C_{60}^{q+} . We compare this conducting sphere model with the very well tested potential $V_0(r)$ for an electron in the field of C_{60}^+ Eq. (5)⁵. We need to add the laser field (c.f. see section 2.1), the field induced dipole and the centrifugal barrier of the C_{60} ground state electron in a spherical approximation ([Boyle et al., 2001](#)), i.e. we

⁵ Lacking any better approximation we replace the terms $1/(r - R)$ in Eq. (5) by $(q + 1)/(r - R)$ for the higher charge states.

Fig. 19. Saturation intensities I_{sat} for $C_{60} \rightarrow C_{60}^{q+}$ ionization with short laser pulses as a function of the final charge state q of the ion. Experimental results for 1800 nm, 70 fs (triangles) and estimates for over that barrier ionization using the conducting sphere model (dashed line) are taken from [Bhardwaj et al. \(2003\)](#). The data for 395 nm, 45 fs (circles) and 790 nm, 25 fs (squares) pulses are derived from [Campbell et al. \(2001b\)](#). We compare this also with an estimate from the model potential Eq. (5 and 17) with polarization screening in the field and centrifugal barrier for $\ell = 5$ (full line). For comparison the latter is also used without centrifugal barrier (dotted line).

use the overall interaction potential (in atomic units)

$$V(r) = V_0(r) + \mathcal{E}_0(r \cos \vartheta - \frac{\alpha}{r^2}) + \frac{\ell(\ell+1)}{2r^2} \quad (17)$$

with $\mathcal{E}_0$ the laser field amplitude, α the polarizability of C_{60} , and $\ell = 5$.

The comparison shown in Fig. 19 between the conducting sphere model of [Bhardwaj et al. \(2003\)](#), our present model potential, and the experimental points is not entirely satisfactory. While the model potential fits the 1800 nm data for $q = 1$ nicely, it fails completely for higher charge states. The opposite is true for the conducting sphere model, with a general tendency that the experimental data are higher than both theoretical predictions - except for the 395 nm data which may be influenced by the 1^1T_{1u} resonance (Fig. 2). We note that the model potential Eq. (5) was designed for singly charged C_{60}^+ ions only and the scaling used for higher charge states is probably not adequate. On the other hand, the charged sphere model of [Bhardwaj et al. \(2003\)](#) is missing the centrifugal potential. Clearly, as indicated by the dotted line in Fig. 19 for low charge states the centrifugal potential is essential. As documented by the experimental points in Fig. 19 the saturation intensities also depend on the wavelength - a notion which is not directly compatible with

Fig. 20. 2D plot of potential energy of a hypothetical atom with $E_I = 7.6 \text{ eV}$ (left) and the screened model potential for C_{60} at different field intensities: $1.3 \times 10^{13} \text{ W/cm}^2$, $5.5 \times 10^{12} \text{ W/cm}^2$, and $1.8 \times 10^{14} \text{ W/cm}^2$ in the left, middle and right graph, respectively. The white planes indicate the energetic position of the ground state energy and the possibilities for electrons to undergo above barrier ionization.

the classical ‘over the barrier’ or ADK models. In a more rigorous approach one would have to consider dynamical polarization screening which might be particularly important for the 790 nm data.

In general it is probably fair to give a warning not to take these classical models too literal. Fig. 20 illustrates the $e^- - C_{60}^+$ potentials in a laser field at two different intensities in comparison with an fictitious atom with a $1/r$ potential and 7.6 eV ionization potential.⁶ It is evident from these graphs that with a complex structure as C_{60} one cannot expect that maximum ionization probability and saturation really coincide with the intensity at which the barrier equals to the binding energy of the electron.

Recently, more realistic theoretical approaches for the interaction of C_{60} with intense, short laser pulses have been reported in the literature (Torralva and Allen, 1999; Torralva et al., 2001; Bauer et al., 2001; Bauer, 2002; Zhang et al., 2003; Zhang and George, 2004). Directly comparable with the experimental results is at present only the elaborate TDDFT calculation of Bauer et al. (2001) which is extended in Bauer (2002). Starting point is a jellium like potential, very similar to the one described in Eq. (5), which is then used to calculate Kohn-Sham orbitals for all relevant π and σ electrons. The specific route of nonlinear TDDFT used allows one to distinguish between ionization, single particle transitions, or plasmons, and also accounts for higher order processes beyond single particle hole excitations. In Fig. 21 results from this theory are shown, nicely illustrating the validity of the experimentally observed $n = 5$

⁶ For these plots, it was assumed that the external field cannot penetrate inside the C_{60} . While this assumption is true for a conducting sphere calculations of Delaney and Greer (2004) show that such screening indeed exists but is by no means complete as assumed here.

Fig. 21. TDDFT calculation for the probability of removing the first electron as a function of the peak intensity of a ten cycle 800 nm $\sin^2$ - pulse (solid line) from [Bauer et al. \(2001\)](#). A multiphotonlike behavior $\propto I^n$ with $n = 5$ is evident. Instead, $n = 13$ photons would be necessary to excite a 20 eV Mie resonance. Fragmentation threshold and C_{60}^+ saturation intensity from [Tchaplyguine et al. \(2000\)](#) are also indicated (vertical dashed lines).

power law for C_{60}^+ ionization [Tchaplyguine et al. \(2000\)](#). ⁷

4 Above threshold ionization

Kinetic energy spectra of photoelectrons give valuable complementary information for a deeper understanding of the excitation and ionization mechanisms of C_{60} in strong laser fields. We have studied photoelectron spectra under many different excitation conditions. The spectra given in this section originate from all electrons collected by the detector regardless of the ion from which they are ejected (singly and multiply charged C_{60}^{q+} as well as all fragments).

Fig. 22 shows photoelectron spectra taken at 790 nm with 25 fs pulse duration ([Campbell et al., 2001b](#)). The intensity increases from top to bottom. At the lowest intensity of 3.7×10^{13} W/cm² one clearly observes an above threshold ionization (ATI) peak structure with an energy difference of 1.57 eV corre-

⁷ Note added in proof: Very recently [Uiterwaal et al. \(2004\)](#) reported a new, rather simple and surprising approach to intense field photoionization, assuming that m photons of energy E_{ph} arriving within a typical electronic response time are effectively equivalent to a single photon of energy mE_{ph} by which they were able to estimate saturation intensities for a whole variety of molecules, including C_{60} .

Fig. 22. Photoelectron spectra from C_{60} as a function of laser intensity (25,fs pulses at 790 nm wavelength). The oscillatory structure is due to above threshold ionization with the maxima separated by 1.57 eV. The structure disappears at an intensity of $\approx 1 \times 10^{14} \text{ W/cm}^2$. Also given is the Keldysh parameter γ for each intensity.

sponding to the laser wavelength. This ATI structure is a convincing proof of the multiphoton character of the ionization under these conditions. At increasing intensities up to $7.5 \times 10^{13} \text{ W/cm}^2$ the ATI structure is still visible but the peaks become broader and the relative amplitudes decrease. At the highest intensity a smooth unstructured electron spectrum is detected. Also given in Fig. 22 is the Keldysh parameter according to Eq. (8). It is inter-

Fig. 23. Photo electron ATI spectra calculated by [Bauer \(2002\)](#) from the most ionizing Kohn-Sham (KS) orbital after a 10 cycles 800 nm laser pulse for three different peak intensities (5.5×10^{12} , 1.8×10^{13} and 2.0×10^{13} W/cm² from top to bottom). The vertical, dotted lines indicate the expected peak positions including the ponderomotive shift. *Left panels:* All KS orbitals were propagated in time (MAE picture). At lowest laser intensity (top) a clear ATI structure is visible. At an intermediate intensity (middle) the ATI peaks appear splitted and are completely washed out at even higher intensity (bottom). *Right panels:* Only the outermost KS orbital was propagated in time (SAE picture) while all others were kept “frozen”. Peak splittings are visible for the two higher intensities. The lines remain narrow. Ionization is higher than in the MAE case where energy may be distributed among the electrons.

esting to note that the disappearance of the ATI structure roughly coincides indeed with $\gamma \approx 1$ - separating the multiphoton regime ($\gamma \gtrsim 1$) from the above barrier/tunneling region ($\gamma \ll 1$). As discussed in the previous section, the underlying classical models should be taken with a grain of salt when describing such a complex system as C₆₀. These approximation work reasonably well for atoms, but appear to substantially overestimate γ for polyatomic, aromatic molecules, as it has e.g. been shown by [DeWitt and Levis \(1998\)](#) and [Lezius et al. \(2002\)](#). It is hence very instructive to compare the TDDFT results of [Bauer \(2002\)](#) who has calculated ATI spectra by the TDDFT method as shown in Fig. 23.

The experimentally observed ATI structure of C₆₀ on a broad background is born out very clearly. To a first approximation one expects the ATI peaks to

occur at

$$E_{el} = nh\nu - E_I - U_P \quad (18)$$

as indicated by the dashed vertical lines in the figure, the ponderomotive potential being $U_P = 0.33, 1.1$ and 1.2 eV for the intensities employed in the theory (top to bottom panel in Fig. 23, respectively). The ponderomotive shifts derived in the simulation are smaller which is attributed to the fact that also the initial state has a Stark shift. Indeed, in the experiment too only a small shift of the ATI peaks if any due to changing U_P was observed. Generally speaking, the full MAE treatment shown in the left panels in Fig. 23 reproduce the trends observed experimentally very well, although several differences warrant discussion. Following [Bauer \(2002\)](#) we note firstly, that the peaks in the calculated ATI spectra are narrower. [Bauer \(2002\)](#) attributes this to the facts that in the theoretical simulation there is no “blurring” due to laser focus effects (where different electrons “see” different laser intensities) and that the trapezoidal model pulses have a well defined peak intensity over cycles, minimizing ponderomotive sweeping which also leads to a broadening of ATI peaks. Secondly, the jellium model is slightly easier to ionize than real C_{60} . This together with the Gaussian profile is the reason why the disappearance of ATI peaks occurs in the model already around 2×10^{13} W/cm² whereas in the experiment this occurs at about 10^{14} W/cm². Thirdly, the electron temperatures derived by [Campbell et al. \(2000, 2001b\)](#) are lower than those obtained from the model (~ 40000 K). As a fourth point, we note that the theoretical ATI peaks are split while such a splitting cannot be observed experimentally due to the peak broadening. [Bauer \(2002\)](#) attributes this to Autler-Townes splitting caused by intermediate resonances already discussed in section 2.3. When a resonant coupling of two bound states leads to almost complete Rabi flops the ATI peaks not only show a substructure but split in two equally strong peaks, separated by the Rabi frequency (see e.g. [LaGattuta, 1993](#)). One nice possibility of theoretical simulations is that one can switch on and off certain interactions. The photoelectron spectra shown in the right panels of Fig. 23 have been calculated by freezing all KS orbitals except for the outermost one, i.e. by suppressing all MAE effects and following the SAE dynamics exclusively. We see that the lines are much narrower in the SAE picture. Moreover, in the SAE model the ionization degree is higher because energy cannot be transferred to the other electrons. Moreover, the population of σ levels is suppressed. And clearly the damping at higher intensities is not reproduced. Hence, the disappearance of ATI peaks in laser C_{60} interaction appears to originate from multiple peak splittings (a SAE effect) in combination with line broadening due to electron-electron interaction. For a realistic description of the dynamics we need the full MAE picture.

In section 3 (Fig. 15) we have presented mass spectra taken at different laser pulse durations and gave a rough classification of the time scales of the different energy relaxation processes. We can refine this picture now by looking at photoelectron spectra taken with the same laser parameters as Fig. 15. Fig. 24

Fig. 24. Photoelectron spectra as a function of laser pulse duration. The laser intensity was kept constant at $4 \times 10^{13} \text{ W/cm}^2$ (a)-(d), and $4 \times 10^{12} \text{ W/cm}^2$ (e). The loss of the ATI structure with increasing pulse duration is indicative for recoupling of the electronic energy. Reproduced from [Campbell et al. \(2000\)](#)

shows this series. The laser intensities for Fig. 24 (a) to (d) was kept almost constant at about $4 \times 10^{13} \text{ W/cm}^2$ while Fig. 24 (e) was obtained with an intensity of $4 \times 10^{12} \text{ W/cm}^2$. The shortest pulse width of 25 fs gives the reference for a clear ATI structure as just discussed. As the laser pulse gets longer, this ATI structure becomes less pronounced already for 70 fs while at 110 fs a broad structureless background signal begins to dominate, which becomes dominant at 500 fs pulse duration. What has already been indicated in the mass spectra is now born out very clearly in the photoelectron spectra. The results have been interpreted by [Campbell et al. \(2000, 2001b\)](#) in terms of a two step relaxation process: Electron-electron coupling occurs on a time scale of 100 fs or even less and electrons thermalize if the interaction with the laser field persists that long, hence the ATI peaks are lost. From the TDDFT point of view ([Bauer, 2002](#)) the wobbling electrons give rise to a quasi stochastic time-dependent effective potential with not precisely defined energy levels. However, well defined energy levels are a prerequisite to predict the position of the ATI peaks. Therefore, the rapidly time-dependent effective potential “washes out” the ATI structure.

On a time scale of several 100 fs the hot electron gas in turn interacts with the nuclear core (electron-phonon interaction), electrons cool even more while the nuclear vibrational modes are heated so that fragmentation may eventually occur on a long (many ps, ns, μs) time scale. These hot $\text{C}_{60}^{q+\#}$ are then, as already discussed, particular susceptible to secondary processes, such as multiple ionization by not too fast ejected electrons.

5 Multielectron excitation, energy redistribution and coupling to nuclear motion

As we have discussed in section 3 and 4, one of the fascinating but also difficult to analyze facets of intense laser field interaction with Buckminster fullerenes is the broad scope of potential responses of C_{60} , ranging from atomic to solid-like behavior such as above-threshold ionization on the one side and thermionic electron emission on the other end, or from single photon absorption to plasmon excitation - depending on how we interrogate this large finite molecular system. This raises a quite general question of laser matter interaction: If many electrons are present in a laser field, how do they interact with each other to generate the finally observed outcome? Which of them are most strongly affected and how do they contribute to the overall response of the systems? Or more specifically, when does the single active electron (SAE) dynamics which dominate the strong field response of atoms, give way to a richer multielectron response expected in large finite systems? Using theoretical modelling this aspect can be worked out as we have already seen in the analysis of the ATI peaks (see Fig. 23). A particular illustrative view from the time dependent

Fig. 25. Spectrum of Kohn-Sham (KS) orbital resolved dipole response from TDDFT calculation of [Bauer et al. \(2001\)](#) for C_{60} . Shown is the response of 70 KS orbitals as a function of frequency after a delta kick to the system. Also shown is the total dipole response.

calculation of Kohn-Sham (KS) orbitals by [Bauer et al. \(2001\)](#) is shown in Fig. 25. The 2D intensity plot of dipole responses of individual KS orbitals after a delta kick to the system shows that all orbitals contribute in a broad spectral range while the individual action cannot be extracted from the overall response of the system shown on top of Fig. 25.

While such detailed information can never be extracted from experiment we may possibly try to identify specific aspects of the response of C_{60} to strong field interaction as being attributable to the one or the other of these “two faces”. One example is the observation of Rydberg states: while the population mechanism of these states is clearly driven by multielectron excitation processes (MAE) the binding energies of the Rydberg states themselves can be derived in a very simple SAE approach describing the almost atom like single Rydberg electron on its orbital far away from the C_{60} core. Consequently, this is an ideal observable to address these questions. From a detailed understanding of the underlying excitation processes one may, in principle, glean deep insight into the photodynamics of large molecular systems with delocalized π electrons in strong laser fields. This will be discussed in the following subsection 5.1 with the focus on multielectron excitation by absorption of many photons, followed by energy redistribution within the “hot” electron cloud and

accompanied coupling to nuclear motion.

As we have already seen, the efficient excitation of the electronic and the subsequent heating of the nuclear system lead to extensive fragmentation depending on the laser parameters. Many aspects of this process such as the high excitation threshold for fragmentation (kinetic shift) and the bimodal fragment distribution at high excitation energies can be explained very well in terms of statistical theory, essentially on the basis of knowing the energetics of the system as described e.g. by [Campbell and Levine \(2000\)](#). However, recent experiments give also evidence to direct, non-statistical processes driven by bond-softening and/or repulsive state crossings induced by the strong laser field. This leads back to a more molecular description of dissociation, where the system “surfs” on potential energy surfaces rather than being exclusively controlled by statistics. This coexistence will be discussed in the second subsection 5.2 underlying the complexity of fullerenes, which are full of surprises.

5.1 *Population of C_{60} Rydberg states - Beyond the single active electron picture*

One fascinating recent experimental finding in short laser pulse interaction with C_{60} was the observation of very pronounced sharp structures in the photoelectron spectra on top of the ATI-peaks or a broad thermal electron background distribution by [Boyle et al. \(2001\)](#) as shown in Fig. 26 for several laser intensities. The structure is most clearly observed with a laser pulse duration of 1.5 ps at 800 nm wavelength with intensities on the order of 10^{12} W/cm².

The left panels in Fig. 26 give the photoelectron signal on a log-lin scale over a wide range of energies as essentially already seen in Fig. 22, illustrating the thermal nature of the background electron distribution. At the lowest intensity the ATI peaks are just barely visible. The right panels show a rich structure of the photoelectron yield on a linear scale, blown up for the energy of the first ATI peak. With increasing laser intensity the structure becomes blurred as documented in Fig. 26, obviously not only due to the dramatically enhanced background signal but also due to an effective broadening of the peaks. This might be expected from the respective ponderomotive shift - if it were fully active on the observed energy levels and the ionization potential would not change correspondingly. However, as the discussion of the ATI peaks has shown (see Fig. 23), this broadening in the more intense field may also be due to electron-electron interactions. The series of peaks is seen most clearly in the lower right panel of Fig. 26 and has been studied extensively since its discovery. The observed kinetic electron energies E_{el} were found to converge towards the photon energy $\hbar\omega$. A numerical analysis based on fitting the spectra with

Fig. 26. Photoelectron spectra of C_{60} for 800 nm, 1.5 ps laser excitation at different laser intensities. The left panels on a log-lin scale show the signal over a wide range of electron energies. For the lowest intensity, the ATI structure is just barely visible. On the right a blow up with linear yield scale show pronounced structures on top of the ATI peaks.

Lorentzian line profiles gives

$$E_{el} = h\nu - E_B(n_i) = \hbar\omega - \frac{R_y}{(n_i - \delta_i)^2} \quad (19)$$

with R_y being the Rydberg constant, n_i a quantum number of the states with binding energy $E_B(n_i)$, and δ_i an almost constant quantum defect for at least two series. This allows the conclusion that the observed structures arise from single-photon ionization of high lying Rydberg states of the neutral C_{60} fullerene, defined by one active electron. The same series was found when using 400 and 660 nm laser radiation for excitation and detection, again converging towards the respective photon energies (Boyle et al., 2004).

By solving the Schrödinger equation for one active electron in the jellium-like model potential Eq. (5) adapted from Puska and Nieminen (1993), the

Fig. 27. *Left*: Model potential for C_{60} according to Eq. (5) with ground state energy (heavy line) and some Rydberg levels (light lines). *Right*: Comparison of peak positions from experimental fits (open symbols) and calculated binding energies (filled symbols and lines) for $\ell = 3$ (triangles), 5 (circles), and 7 (squares).

peaks could be assigned quantitatively to the several Rydberg series (Boyle et al., 2001). These Rydberg states are assumed to be excited by a multiphoton process, whose nature warrants further discussion, and to be subsequently ionized by one additional photon from the same laser pulse (an assumption confirmed by independent experimental tests). As a result, one obtains binding energies of the Rydberg states involved, which are in excellent agreement with the measured kinetic energy distribution of photoelectrons as shown in Fig. 27 (right). It is quite surprising that this highly simplified model works so well, keeping in mind that the large number of delocalized valence electrons responds “simultaneously” to the external laser field. However, as illustrated by the model potential reproduced in Fig. 27 (left), together with energies of some of the observed Rydberg states, one easily verifies that once a Rydberg state is populated, its characteristic radius is significantly larger than the fullerene radius of approximately $5 \text{ \AA}$. Hence, the effective one particle treatment (SAE) of the energetic problem is a very valid approximation, the active electron interaction with the C_{60}^+ ion core being sufficiently well described by a phase shift which in turn determines the quantum defect.

The calculation shows that the observed electronically excited states correspond mainly to the Rydberg series with angular momentum quantum numbers $\ell = 3$ (*f*), 5 (*h*), and 7 (*j*). Since in the spherical model used here the highest occupied molecular orbital of C_{60} (HOMO) has an angular momentum of $\ell = 5$ (*h*), the observed spectra result from the absorption of an effective even number of photons. At first glance, this may seem to indicate a direct excitation process of the Rydberg states. However, some important aspects warrant further discussion, mostly the observed energy mismatch $E_B(n_i) - E_I - n\hbar\omega$ between the excitation energy of the Rydberg states $E_B(n_i) - E_I$ and the n number of exciting photons. Simply speaking, it is not possible to be in resonance with all the Rydberg states at once with n photons of a given energy at these low intensities. The bandwidth of the laser (Fourier limited) is much

too narrow to allow for the excitation of Rydberg states covering an energetic range of 1–2 eV depending on the photon energy. And since the spectra can be observed at very weak intensities too, broadening and energy sweeping by the ponderomotive potential (< 100 meV) as first identified as a key mechanism for atomic systems in strong fields (Freeman et al., 1987) cannot explain the Rydberg excitation process in the present case.

To explain this energy mismatch and to understand the excitation mechanism, several scenarios have to be discussed and to date no finally conclusive scheme has been ascertained. One at first sight plausible explanation might be that energy is drawn from the nuclear motion of the system. As we have already discussed in section 2.1 several eV of energy are stored in the $3n - 6 = 174$ vibrational modes of C_{60} after preparation in an effusive beam at a temperature of ≈ 770 K. However, such concerted energy transfer from many nuclear degrees of freedom into the electronic system is very unlikely to happen in a direct multiphoton process. As already discussed in section 2.1 and illustrated in Fig. 4 Franck-Condon factors are expected to be prohibitive for such a mechanism, the geometry of neutral C_{60} being very similar to the singly charged C_{60}^+ to which the Rydberg states converge. Thus, we expect a strong propensity for ionization without change of any vibrational quantum numbers ($\Delta v = 0$) as illustrated in Fig. 4 (right). Consequently, the probability to excite the Rydberg state manifold directly from the molecular ground state is low even when including nuclear vibrations into the picture - as typically done in the so called inverse Born-Oppenheimer approximation as described by Remacle and Levine (2001): in this approximation each vibrational degree of freedom (considered slow in comparison with the Rydberg orbiting time) carries its series of Rydberg levels. While this picture explains why we observe sharp Rydberg series at all, it does not give us a genuine clue as to how they may be excited in the first place.

However, the situation can be rather different if we invoke excitation of intermediate electronic states during the laser pulse by single- or multi-photon processes, possibly with subsequent internal conversion (IC) or even transitions induced by the strong laser field itself through a ‘doorway state’. Such processes have recently received great attention in the literature and a number of theoretical models have been discussed, including excitation from the ground state to an excited doorway state (Lezius et al., 2002; Markevitch et al., 2004), nonadiabatic multielectron dynamics (NMED) (Lezius et al., 2001, 2002) and field induced, time dependent potential energy crossings (Kono et al., 2003, 2004). NMED has been used successfully to describe the dissociative ionization dynamics of different aromatic molecules as a function of their characteristic length and the extension of the π -electron delocalization (Markevitch et al., 2003, 2004). From time-of-flight mass spectroscopy supported by results of numerical simulation, the authors developed a model of the fs-laser interaction consisting of three key elements: (i) nonadiabatic excitation from the

ground state to the excited-state quasi-continuum via a “doorway” state, (ii) dynamic polarization of the entire electronic system which leads to an exponential enhancement of this transition, and (iii) sequential energy deposition in the neutral molecule and the molecular ion before undergoing fragmentation. The concept of doorway electronic states originates from the fact that the initial rate-limiting step in the nonadiabatic excitation can be regarded as a kind of bottleneck for the energy coupling into the electronic system. Recent theoretical calculations on laser-induced ultrafast dynamics in isolated C_{60} using time-dependent density-functional (Torralva et al., 2001) and matrix formalisms (Zhang et al., 2003; Zhang and George, 2004) reveal that even at relatively low laser intensities of 10^{10} – 10^{11} W/cm² many electrons are excited during a typical fs-laser pulse. Note, that such processes where many electrons (MAE) are sequentially excited (possibly into the same set of unoccupied levels) involve absorption of a corresponding number of photons. However, in contrast to genuine multiphoton processes, in this case we cannot glean information on the number of photons involved from the intensity dependence. Rapid thermalization of the excited electrons may then follow, first by electron interaction and on a slower time scale by electron-phonon coupling. In a classical molecular picture one would typically invoke doubly excited states and internal conversion to describe such processes. We note here in passing that similar Rydberg structures have been reported for several organic molecules (see e.g. Schick and Weber, 2001; Kuthirummal and Weber, 2003). The excitation mechanism is explained there by ‘superexcited’ states. In the context of the finite system C_{60} MAE/NMED processes may be seen as the multielectron equivalent to such superexcited states.

In the model calculations by Zhang et al. (2003) multi-electron excitation of the LUMO+1 level of C_{60} is accompanied by strong vibrational excitation and massive energy exchange with the $a_g(1)$ breathing mode. Excitation of this mode has been reported from ultrafast excitation of undoped (Dexheimer et al., 1993) and doped (Fleischer et al., 1997) C_{60} -thinfilms. However, intuitively, in a strong oscillating electric field one would expect the $h_u(1)$ prolate-oblate mode to be excited (Bhardwaj et al., 2003) rather than the total symmetric a_g modes. Nevertheless, one may envisage this mode to become active if several electrons are excited into an anti-bonding electronic state in which electron repulsion would tend to inflate the Buckyball. More recently, the model calculations of Zhang and George (2004) have shown that such excitation depends strongly on pulse duration and intensity. Although an experimental proof of such oscillating energy exchange of several eV between electronic and vibrational motion is still missing, the picture appears attractive to explain the observed non-resonant Rydberg excitation. In the left panel of Fig. 28 reproduces essentially the orbital energy diagram introduced in Fig. 2 - adding the Rydberg levels at their respective binding energies as observed experimentally. Two possible scenarios, a and b, for Rydberg excitation with 800 nm photons are indicated (scenario c refers to the pump probe experiment

Fig. 28. Left: Schematic orbital energy level diagram of C_{60} (see also Fig. 2) including here the Rydberg states observed by Boyle et al. (2001) and some intermediate states (Dresselhaus et al., 1996) following the terminology applied in Zhang et al. (2003), in order to illustrate the excitation cascade. Occupied HOMO and HOMO-1 states (black boxes), unoccupied LUMO and LUMO+1 states (shaded boxes), fast thermalization within the excited electrons and coupling to the nuclear vibrations (double arrow) visualize non-adiabatic multielectron effects. Three scenarios (a-c) indicate potential excitation steps. Right: Excitation by an 800 nm 26 fs pulse calculated in the TDDFT approximation by Bauer et al. (2001) at two different intensities. The dark lines give the dipole strength during, the gray lines after the pulse. For details see text.

discussed below). As seen, the $(LUMO+1)t_g$ level is 2-photon resonant and we assume it to be the ‘doorway state’. In the strong field its excitation is possible as documented in the right panel of Fig. 28 which reproduces the dipole response calculated in TDDFT approximation with a strong second harmonic component (Bauer et al., 2001). In addition to the already broad response which originates from electron-electron coupling the interaction with the nuclear motion (not included in the TDDFT model) may lead to a significant broadening of the excited level and to non-adiabatic, field induced coupling with other excited levels (e.g. with the $LUMOt_u$) as indicated by thick double arrows. This may eventually also lead to internal conversion with irreversible exchange of energy between electronic and vibrational motion. Scenario (a) illustrates how we can thus picture the excitation of a lower Rydberg state from the thus populated doorway state(s) by two or three red photons. Scenario (b) indicates how high lying Rydberg states are excited. In both cases a further red photon is used for finally ionizing the system as detected by emission of an electron (downward arrows labelled e^-). We mention here, that these population mechanisms appear to be rather fast, since even when using pulses as short as 30 fs some traces of Rydberg excitation can still be observed - albeit unresolved due to a spectral broadening which corresponds to the Fourier limited bandwidth.

Fig. 29. (a) Contour plot of the photoelectron signal as a function of the time-delay between 400 nm pump 1×10^{11} W/cm² and 800 nm probe pulse 2×10^{12} W/cm². (b) Kinetic energy distribution of photoelectrons for zero delay time, which corresponds to a vertical cut in (a) along the dotted line. Reproduced from Boyle et al. (2004).

A recent pump probe study gives additional experimental evidence that NMED may indeed be the key mechanism to understand the energetics and ultrafast dynamics of C₆₀ in optical fs-laser fields (Boyle et al., 2004). In these experiments a blue pump pulse of comparatively low intensity which is quasi resonant to the dipole-allowed HOMO $h_u \rightarrow$ (LUMO + 1) t_g transition deposits energy very efficiently into the electronic system. The dynamics of the energy redistribution within the excited electron cloud and accompanied coupling to the nuclear motion is then probed by a time-delayed red probe pulse. The polarization of the two pulses is perpendicular, pointing into the detector direction for the red pulse. The photoelectron spectra recorded as a function of the time-delay between 400 nm pump (1×10^{11} W/cm²) and 800 nm probe-pulse (2×10^{12} W/cm²) are shown by the contour plot in Fig. 29(a). A cut through this contour plot for zero time-delay along the vertical dotted line is given in Fig. 29(b). It corresponds to a photoelectron spectrum which essentially reproduces the features obtained in the one color (800 nm) experiments (Fig. 26) - except for the poorer spectral widths of the peaks due to the enhanced temporal resolution. One can immediately see that in order to observe a signature of populated Rydberg states, the resonant pre-excitation of the (LUMO+1) t_g state by the weak blue laser pulse is essential. In con-

Fig. 30. *Left*: Photoelectron signal for a kinetic energy corresponding to the $4g$ Rydberg state as a function of short delay times between blue and red laser pulse. Zero intensity has been set at the (low) level for negative delay times and $\Delta t = 0$ to the turning point of the error function. *Right*: same on a longer time scale for 3 Rydberg levels with blue at $1 \times 10^{11} \text{ W/cm}^2$. Red (probe pulse) is always at $2 \times 10^{12} \text{ W/cm}^2$. Fits indicate a range of decay times for accessible excitation in the doorway state. Reproduced from Boyle et al. (2004).

trast, if the red pulse leads the blue pulse (negative time delay) almost no photoemission signal from excited Rydberg states is observed. The photoelectron yield changes dramatically once pump and probe pulse overlap, with a maximum population of the Rydberg series 50–100 fs above zero time delay. The population of the LUMO+1 state is clearly identified as the bottleneck in the excitation cascade. It acts as a doorway to the Rydberg state population followed by single-photon ionization from the excited states. At time delays > 400 fs the signal remains nearly constant for several picoseconds. In Fig. 30 this is shown more quantitatively as recorded by the photoelectron yield from the $4g$ Rydberg state. The spectrum results from a cut through the contour plot along the Δt axis at an electron binding energy corresponding to the $4g$ Rydberg state. Two different blue pump intensities are compared in the left panels of Fig. 30.

The interpretation of these experimental data has benefited from recent theoretical work by Zhang et al. (2003) already mentioned. In these simulations the laser frequency is tuned to the first dipole allowed transition $\text{HOMO } h_u \rightarrow (\text{LUMO} + 1) t_g$ state. Hence, although their pulse duration of 10 fs and the

laser intensity of $3 \times 10^{10} \text{ W/cm}^2$ used do not exactly match the experimental conditions of the time-resolved two-color experiment, some interesting general trends described in the theoretical work are highly pertinent for the present discussion. The simulations predict, that the initial configuration of the C_{60} lattice and all the 60π electrons occupying the 30 lowest energy levels change significantly upon laser irradiation. At the beginning of the excitation, the energy is exclusively absorbed by the electronic subsystem. The time evolution of the electron density in the excited state increases approximately linearly with increasing pump intensity. At the end of the 10 fs short laser pulse even at these low intensities about 2 electrons are excited to the $(\text{LUMO} + 1)$ orbital. The total energy absorbed energy indicates that the excited electron cloud has become slightly overheated with respect to the $\text{HOMO/LUMO}+1$ band gap energy. As already discussed above, this is followed by a very efficient coupling of electronic excitation to nuclear vibrations. Scenario (c) indicated in Fig. 28 illustrates the excitation of a low lying Rydberg state. The main difference to the single color experiments with 795 nm is the very efficient pre-excitation with the blue pulse. Guided by these theoretical predictions it is assumed that the time-dependent electron signal in the two-color experiments shown in Fig. 30 results from the combined effect of the doorway state population due to multielectron excitation, plus an additional fast relaxing channel indicated by the hump in the photoelectron yield. The fast relaxation is attributed tentatively to a thermalization of the multiple excited electrons in the $\text{LUMO}+1$ state. A relaxation time within the electronic degrees of freedom of about 95 fs is derived from a detailed analysis of the data by Boyle et al. (2004). This value is comparable to the characteristic time for thermalization due to electron-electron scattering below ca. 100 fs, previously concluded from single pulse experiments (Campbell et al., 2000; Hansen et al., 2003). At lower blue intensity the hump disappears, indicating possibly that less electrons are injected into the excited state bands. Note that the life time of the doorway state after the pulse is over is surprisingly long as derived from the decay of the pump probe signal monitored in different exit channels. We have to bear in mind that the population of the doorway state is probed here via the population of the Rydberg states which are excited resonantly from the doorway states by two or three red photons - as indicated by scenario (c) in Fig. 28. The extended time scale shown in the right panel of Fig. 30 show that this life time may be several ps up to ns, increasing with the energy stored in the doorway state.

At this point one is tempted to question again the role of initial vibrational excitation of the C_{60} . Although that energy cannot be accessed in a direct multiphoton excitation or ionization process, energy exchange between electronic and vibrational system in the doorway state(s) as just described may significantly profit from the thermal energy stored in the system. Also, a change of the excited state geometry will change the Franck-Condon region for subsequent excitation of the Rydberg states, thus giving access to at least some

Fig. 31. Comparison of photoelectron signal as a function of kinetic energy from hot (770 K) and cold (80 K) C_{60} . Red photons of 100 fs (2.5×10^{12} W/cm²) were used for Rydberg excitation and detection. The two curves are normalized to each other at an electron energy of 2 eV where only a thermal electron distribution is detected. Reproduced from Boyle et al. (2004).

of the vibrational energy content. Hence, experiments have been performed comparing ‘hot’ (770 K) and ‘cold’ (80 K) C_{60} target molecules (Boyle et al., 2004). This may allow one to control the strength of vibrational coupling in the excitation cascade. Note, that in the ‘hot’ C_{60} about 23% and 8% of the molecules are in the vibrationally excited $v = 1$ and $v = 2$ states of the $h_g(1)$ mode, respectively, while at 80 K the molecule is predominantly in its vibrational ground state with the population of the lowest vibrationally excited state being as low as 0.6%. The data have been taken in a one color experiment with a single pulse of 800 nm photons and 100 fs duration. The result is shown in Fig. 31. The photoelectron spectra recorded for hot fullerenes exhibit the rich structure of Rydberg states discussed above. In contrast, the structure has completely disappeared in the photoelectron spectrum from cold C_{60} . Following the above discussion this may be understood in terms of the much higher population of vibrationally excited states for the hot molecule which increases the effective phonon density and consequently enhances electron-phonon coupling. Similar effects have been observed, for instance, in 2-photon photoelectron spectroscopy on silver surfaces (Knoesel et al., 1996). The coupling of electronic excitation to vibrational modes of the molecule may be viewed as giving rise to a relatively broad energy band. As seen in case of hot C_{60} , this broadening is essential for accessing the manifold of excited Rydberg

states. Without coupling, electron emission is mainly statistical.

Summarizing our discussion on the population dynamics of Rydberg states in fullerenes we refer again to the energy level diagram of C_{60} in Fig. 28. It illustrates the main excitation steps for the one color as well as for the two-color pump probe experiment. We must be aware of the limitations of the commonly used single-active electron picture when dealing with at least the 60 most weakly bound π electrons and their response to the laser field. Multielectron excitation, electron-electron and electron-phonon coupling and thermalization have to be considered when describing any excitation process. As shown by TDDFT calculations, the SAE picture - although it may describe some observations for low intensity and particularly short pulses rather nicely - is not sufficient to describe the details of just the electronic response. If the nuclear degrees of freedom enter also into the picture - which is obviously the case for Rydberg excitation as shown by comparing hot and cold target molecules - one needs to study the full picture, involving all couplings and degrees of freedom. Such a rigorous theoretical treatment would be highly desirable and one may look forward to some serious approaches which are presently undertaken by several theory groups. In the end it may turn out that a lot of the notions used presently - such as NMED, time dependent potential surfaces, field induced crossings and Autler-Townes splitting can be combined into one uniform, rigorous approach.

5.2 *Ultrafast fragmentation of C_{60} - Beyond a purely statistical description*

Photofragmentation of C_{60} has been studied soon after the discovery of fullerenes using nanosecond laser excitation in combination with mass spectroscopy (O'Brien et al., 1988). The characteristic bimodal distribution of heavy and light fragments was observed as mentioned in section 2.1 and 3. The large fragments C_{2m}^+ observed are formed mostly by sequential evaporation of C_2 units on a time scale of nano- to microseconds. With laser pulse durations below 100 femtosecond laser pulses one observes significantly less fragments but a large amount of multiply charged ions instead, as discussed in detail in section 3. Here too, the large fragments observed are believed to arise from evaporative cooling of the hot C_{60}^{q+} ions which are formed and excited during the C_{60} interaction with the laser pulse. The observed metastable fragmentation on a time scale of several microseconds gives evidence for further evaporative cooling of still hot parent fragment ions with a temperatures of a few thousand Kelvin. Since this is similar to the value derived after ns-irradiation of C_{60} one assumes that the fragmentation patterns of C_{60} after short pulse laser interaction are also to a large extend of statistical origin (Campbell et al., 2001b), the major difference being a strong contribution of multiply charged species.

On the other hand, small carbon cluster ions C_n^+ with odd and even numbers of carbon atoms must be formed in a different manner, possibly by asymmetric fission as discussed by [Rentenier et al. \(2004\)](#) for fast collisional processes or by post ionization of fast neutral fragments during the laser pulse. We note, however, that the abundance of such small fragment ions after short pulse interaction with C_{60} is much smaller than in the case of longer pulses (see e.g. Fig. 12). In this context, we would like to recall that using single pulse excitation in combination with ‘standard’ time-of-flight techniques allow to detect only charged interaction products and information on neutral fragmentation can only be derived indirectly. Little is known therefore about neutral fragments which may nevertheless be byproducts of the formation of (multiply) charged large fragments C_{2m}^{q+} . Since the majority of fragmentation channels results in at least one neutral fragment (typically the smaller fragment), the pump-probe post-ionization method is a useful technique to study directly their formation dynamics. And from detecting initial kinetic energies one may even glean some information on the distances from the parent ion in which these fragments are ionized. In such a pump probe experiment the first pulse initiates a (multielectron) dynamics which is then probed by a delayed pulse. The latter further excites and ionizes the C_{60} parent by a multiphoton process. Alternatively it ionizes already formed neutral fragments. The respective ion yield as a function of the time delay between pump and probe can give information on the characteristic time scales for the formation of neutrals. This technique has been previously employed by [Lykke and Wurz \(1992\)](#); [Lykke \(1995\)](#) using ns laser pulses. They detected the interaction products C^+ , C_2^+ , C_3^+ , and C_4^+ . The appearance of C^+ and C_3^+ was unexpected, since the fragmentation pattern of larger fullerenes results only peaks of C_{60-2n}^+ . However, C^+ and C_3^+ could not be necessarily assigned to the fragmentation of fullerenes, or successive fragmentation of already dissociated fragments. Furthermore, the ns time scale is quite long compared to typical times for energy redistribution.

Recently, the observation of fast fragmentation of C_{60} using the pump-probe post-ionization technique has been reported applying bandwidth limited 800 nm pulses of 120 fs duration ([Boyle et al., 2005b](#)). The shorter pulse duration compared to the pioneering work by Lykke and Wurz allows for enhanced time resolution beyond the characteristic time scales for a fully-statistically driven fragmentation processes. In the following, these experimental results are discussed. Time-of-flight mass spectrometry has been used to detect the post-ionized neutral fragments. In these experiments a pump pulse at an intensity of $5 \times 10^{13} \text{ W/cm}^2$ deposits energy into the electronic system by exciting one or more electrons into higher lying states (see section 5.1). The multielectron dynamics initiated is probed by a weaker probe pulse of $1.8 \times 10^{13} \text{ W/cm}^2$, which further excites and ionizes by a multiphoton process. Fig. 32 shows the formation of C^+ , C_2^+ , C_3^+ , and C_4^+ . For negative time delays, the weak pulse leads the strong pulse and a constant signal for each fragment is observed. When

Fig. 32. Time dependent C^+ , C_2^+ , C_3^+ , and C_4^+ ion signals formed by short pulse laser (800 nm, 100 fs) interaction of C_{60} at $5 \times 10^{13} \text{ W/cm}^2$ (pump) and ionization at $1.8 \times 10^{12} \text{ W/cm}^2$ (probe). For positive delay times, the stronger pulse leads the weaker pulse.

the strong pulse initiates the multielectron dynamics, a dramatic increase in the C^+ – C_3^+ ion yields is observed as the separation of the pulses is changed, whereas C_4^+ exhibit nearly no dynamic behavior. At time delays > 50 ps the signal remains almost constant up to the longest time scales studied in these experiments (~ 100 ps). It is possible to fit the dynamics using single exponential curves with time constants of 11 ps (C^+), 12 ps (C_2^+) and 18 ps (C_3^+). The time constants are found to be almost independent of the weak probe pulse energy, which indicates that the weak probe pulse is not active in the formation process of small neutral fragments (Boyle et al., 2005b). Furthermore, the absence of small fragments in single pulse experiments indicates that the small fragments are initially uncharged. The addition of the second pulse excites and ionizes these neutral fragments by multiphoton absorption.

It is important to note that although a rapid formation of small neutral fragments is observed, it cannot be distinguished whether they come directly from a fullerene-like fragment or from another fragment that has dissociated before, for example, C_8 . Future fs-laser experiments, using the post-ionization method in combination with the photoion-photoion coincidence technique with a position sensitive detector will clarify this aspect. Pioneering coincidence experiments have been performed by Vandenbosch et al. (1998), in order to study

fragmentation partners using collisional dissociation of 75-keV C_{60}^- with H_2 gas. They have shown that odd- n as well as even- n light fragments are fragmentation partners to even- n heavy fragments, indicating a sequential decay. The combination of the coincidence information with the time resolution of the pump-probe technique will allow one to obtain an almost complete picture of the ultrafast fragmentation dynamics.

Unfortunately, the time resolution in the above discussed one-color experiments was limited by interference fringes once pump and probe pulses overlap in time. Consequently, it was not possible to reach the limit given by the laser pulse duration of 120 fs. Nevertheless, even with the present resolution of 2–3 ps we can conclude that fast fragmentation processes of C_{60} happen at a time when its internal energy is not completely equilibrated among all degrees of freedom and thus fragmentation is not purely statistically driven. However, the measured time scale for the formation of small neutral fragments in the ps-range suggests that electronic energy has already been transferred to some extent into nuclear vibrations via electron phonon coupling. For isolated fullerenes, Hansen et al. (2003) have recently determined this coupling time to be ~ 240 fs by modelling experimental Penning ionization data. The Penning ionization yield depends on electron emission and coupling to the nuclear degrees of freedom. The electronic density of states of C_{60} and the Penning ionization yields was used by Hansen et al. (2003) in order to determine a single fitting parameter, the electron-vibration coupling time constant. This model, however, is again purely statistical and does not provide insight to systems not in equilibrium.

On the theoretical side, ultrafast fragmentation of C_{60} after fs-laser pulse excitation has been simulated by Torralva et al. (2001) and Jeschke et al. (2002). It was found that the laser field efficiently excites the $a_g(1)$ breathing mode accompanied by fragmentation on a sub-picosecond time scale. Torralva et al. (2001) used a combination of tight-binding electron dynamics and density-functional theory to simulate the ultrafast response of C_{60} exposed to fs-laser fields. With a 10-fs laser pulse of 2.0 eV photon energy, they predict the excitation of the $a_g(1)$ and the $a_g(2)$ vibrational modes for low fluences (0.006 J/cm^2). As the fluence increases, fragmentation occurs. The lowest fluence producing fragmentation within 1 ps derived from these calculations is 0.117 J/cm^2 , which corresponds to an intensity of $\sim 10^{13} \text{ W/cm}^2$. A different theoretical model was used by Jeschke et al. (2002). They considered tight binding energy levels with a time-dependent fractional occupation number. For a laser pulse of 80 fs duration, which deposits 3.5 eV per atom into the system, they found that the cage is torn open 90 fs after the pulse maximum and begins to fragment at 140 fs. These calculations indicate that non-adiabatic multielectron effects discussed in section 5.1 in the context of the Rydberg population mechanism are also active in the fragmentation processes of the molecule.

The pump-probe post-ionization experiments on small neutral fragments seem to be able to access this new regime of ultrafast fragmentation dynamics predicted by theory. To investigate the formation in more detail, analogue time-resolved *two-color* pump-probe measurements are currently on the way. These will allow one to look into the sub-ps time regime and resolve the influence of electron phonon coupling.

6 Conclusion and outlook

It is hoped that the present report gives a useful introduction to the present status of ultra fast laser interaction with C_{60} as a model case for a large finite system with many active electrons and vibrational degrees of freedom. Since we have summarized the results of the different aspects touched in this review at the end of each individual chapter we may refrain here from repeating this effort. We simply remind the reader that most of observations and insights discussed here have emerged during the last few years. A variety of new phenomena has emerged from these studies and much has been learned about this ever fascinating object C_{60} exposed to hitherto unused conditions in strong, but not too strong laser fields. We are, nevertheless, still far from fully understanding the intricacies of intense field interaction with such a relatively complex system. The directions to continue this research have been indicated as far as obvious. On the one hand, rigorous theoretical efforts are needed to quantitatively explain the key aspects of the experimental observations presented here and those to emerge in the near future: the nature of the ionization processes beyond the simple above barrier ionization model, the fragmentation mechanisms which produce predominantly multiply charged fragments, the excitation dynamics for the population of Rydberg states, mechanisms for ultrafast fragmentation, the long life times observed in the doorway state. On the other hand, further experimental work is desirable (Boyle et al. (2005a)) - preferentially with even shorter pulses(and better tunability of the fs light sources to perform sophisticated and direct multi color pump probe experiments. Experimental detection schemes need to become more sophisticated, e.g. the full exploitation of state of the art techniques for dynamical imaging promises a whole new multi dimensional view into the dynamics discussed here. One other fascinating aspect of this type of pertinent subject might be quantum or optimal control - presently an extremely active and fascinating field of research applicable to a broad range topics (see e.g. Levis and Rabitz, 2002; Rabitz, 2003). Assume we would like to do more than just study the fragmentation patterns of C_{60} after interaction with an intense laser pulse as documented by the mass spectra we have discussed. Could we try to modify these fingerprints of the interaction at will? We just show one of the first examples of such studies presently emerging from our laboratory (Schulz et al.,

Fig. 33. First results from a fragmentation experiment with temporally shaped pulses. The lower left panel shows a ‘standard’ C_{60} mass spectrum after interaction with a 50 fs 800 nm laser pulse. Its temporal and spectral profile is shown in the lower right panel as obtained from an X-FROG analysis. The mass spectrum in the top left panel documents a mass spectrum after 100 generations of iterative trial to maximize the C_3^+ fragment. The temporal and spectral characteristics of the pulse responsible for this mass spectrum is given in the top right panel.

to be published). Using temporally shaped laser pulses one may try to amplify specific fragmentation reactions rather than just compare short and long laser pulses as shown in Fig. 12.

Fig. 33 shows how one may with such shaping techniques optimize the fragment C_3^+ ion. A signal enhancement of about 10 is found when C_{60} is exposed to the structured multiple pulse characterized by the pattern in the upper right panel as opposed to a short 50 fs pulse of equal total fluence. Presently there is not even a clue of how to understand this observation in terms of the fullerene dynamics in strong fields discussed in this report. We are, however, confident that with detailed analysis and strong theoretical support such patterns will help us to reveal a much more detailed insight into these processes in the near future.

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