Molecules in intense femtosecond laser fields

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Received December 3, 1996; accepted December 6, 1996

Abstract

The interaction of small molecules (Na2, Na3) and larger molecules (C60, C70 and Fe(CO)5) with intense femtosecond laser fields is investigated experimentally. The experiments are performed by combining molecular beam and femtosecond pump-probe techniques with ion- and photoelectron detection. The recently developed femtosecond time resolved photoelectron spectroscopy is used to observe molecular dynamics over a wide range of internuclear distances. A main focus of the paper regarding small molecules is the change of the dynamics of molecular multiphoton ionization from the low laser intensity regime, where perturbation theory still can be applied, to the high laser intensity regime, where the electronic states participating in the multiphoton ionization processes are coupled coherently in Rabi-type processes. In this laser intensity regime, the influence of vibrational wavepacket dynamics on molecular above threshold ionization is also observed. Experiments on larger molecules are performed in a laser intensity regime where the generally accepted description of molecular multiphoton excitation has to be changed and recently proposed mechanisms due to the high field strenghts are discussed to explain the observations.

1. Introduction

Nowadays modern ultrafast laser systems deliver radiation intensities exceeding inneratomic field strengths by orders of magnitude. Moreover, the laser radiation can be concentrated into time scales of nuclear motion in the sub-picosecond range, which has opened up the fascinating research area of femto-chemistry pioneered by A. H. Zewail and coworkers (see for example refs. [1][2] and references therein). The time scale of electronic motion of the order of one femtosecond seems to be within reach by near future laser technologies [3]. Nonlinear, multiphoton, nonperturbative laser induced molecular interactions can now not only be evoked, but can be investigated on the time scale of nuclear motion in great detail.

The study of intense laser field interactions with atomic systems has initiated the new field of intense field molecular physics. Since its first observation in 1979 [4] above threshold ionization (ATI) has been extensively studied in atoms, both experimentally and theoretically, and single electron ATI of atoms is now understood in some detail (see e.g. the reviews [5][6][7][8][9] and references therein). The multiple ionization of atoms in strong laser fields is under detailed investigation [10], and progress has been made to establish the connection between ATI and other intense field effects, such as high harmonic generation [11].

When molecules interact with laser fields, an additional degree of freedom is available by the motion of the nuclei. This may lead to a competition of ionization and fragmentation processes already at moderate laser intensities as has been shown in Na₂ using nanosecond and femtosecond laser pulses [12]. Energy partitioning among fragments and electrons has been investigated for moderate intensities in Na₂

[12] and under strong field conditions in Cl₂ [13]. Multielectron dissociative ionization [14] was recently interpreted in terms of nonadiabatic electron localization [15]. Using H₂ it was demonstrated that the absorption of additional photons is not limited to the ionization process, but can also lead to above threshold dissociation (ATD) [16].

In most of the studies of intense laser interactions with molecules single pulse excitation was used and molecule specific effects were deduced indirectly. For example, an indirect sign of the influence of vibrational motion on the ATI process in molecules has been found in the case of H_2 , where energy transfer to the motion of the nuclei is considered a possible explanation for the observed anomalous energy spacing of the ATI electron peaks [17]. The difficulty of detecting such dynamical effects in the past can be ascribed to the fact, that most experiments have been performed using laser pulses much longer than the typical vibrational periods of the studied molecule. In H_2 , for example, vibrational periods of approximately 15 fs correspond to pulse durations that are still difficult to produce at very high laser intensities.

After a description of our experiment and a short and basic excursion to intense laser field interactions, we shall discuss femtosecond time resolved high laser field interactions with molecules, where the sodium dimer is our prototype system. This molecule, with vibrational periods of the order of 300 fs is an ideal candidate for time resolved measurements. An ultrashort, intrinsically broad laser pulse can coherently couple vibrational levels to form a wavepacket which reflects the classical motion of the nuclei. The internuclear distance in the molecule is again becoming a defined quantity and the nuclear configuration is expected to influence the ionization process. At higher laser intensities, additional effects such as coherent coupling of electronic states are observed. In addition we show, that the molecular ATI electron signal is sensitive to the vibrational motion of the molecule, both in single pulse and pump-probe experiments. In the single laser pulse measurements we exploit the fact, that the propagation of the spatially located nuclear wavefunction is reflected by a change of the electron kinetic energies. Because the vibrational motion occurs on a definite time scale, electrons of different kinetic energies not only correspond to ionization at different internuclear distances, but also to different times of interaction of the molecule with the ionizing laser pulse. We also use transient electron spectroscopy for time resolved measurements of above threshold ionization. Femtosecond pump-probe experiments in combination with kinetic electron detection have only very recently been introduced to the study of molecular dynamics [18] [19] [20] [21] [22]. Here we demonstrate that this technique allows to follow directly in real time the influence of the molecular vibrational motion on threshold ionization and on above threshold ionization as well.

In order to demonstrate that the observation of perturbative and non perturbative coherent effects is not only limited to the one dimensional vibrational motion of a dimer, we present experiments on three dimensional wave-packet motion and coherent coupling of electronic states in the case of the nonlinear sodium trimer. The fullerene C_{60} is an example of a large molecule where we discuss the observation of highly charged fragments after excitation with intense ultrashort laser pulses. Finally we shall report first experimental results on the rapidly decomposing organometallic molecule $Fe(CO)_5$ in an intense laser field.

2. Experiment

In order to study the dynamics of molecules in intense laser fields, three major requirements are to be met. Well defined final states cannot be reached without the preparation of a well defined initial state. Ultrashort, spectrally wide and intense laser pulses at different wavelengths are needed for excitation and ionization of the molecules and a detailed characterization of the final product states must be achieved. In order to meet these requirements a combination of experimental techniques is used. A supersonic (seeded) molecular beam provides the molecules in a collision-free environment and restricts the set of initial states mainly to v'' = 0, J''. Time-of-Flight (TOF) mass spectrometry is used to determine the mass of the ions, the released kinetic energy of the ionic fragments and the energy distribution of the ejected electrons. Because the ion and electron detection angles are fixed, the ion and electron angular distributions can be studied by rotating the laser polarization. We are thus



Fig. 1 Schematic view of the experimental setup. The femtosecond laser beam is crossed with a cold sodium molecular beam. A linear time of flight spectrometer is used for mass and energy resolved ion and electron detection.

able to determine the final continuum states. The collinear femtosecond pump-probe technique is used to induce and to probe molecular transitions, to resolve the interactions and to display the evolution of coherences and populations in real-time.

The schematic experimental arrangement of the molecular beam apparatus and the ion and electron TOF-spectrometers is shown in Fig.1. In the following we will describe the experimental set up in detail. To prepare well defined initial states the molecules (Na₂ and Na₃) studied in this contribution are prepared almost completely (>90%) in the lowest vibrational level ($\nu'' = 0$) of their electronic ground states in a supersonic molecular beam. The apparatus consists of two differentially pumped high vacuum chambers with a background pressure of 2·10⁻⁷ torr in the interaction chamber. Vibrationally cold Na₂ is produced by adiabatic expansion



Fig. 2 Overview of our Ti:Sapphire laser system, producing amplified bandwidth limited 40 fs pulses over a wide range of the visible spectrum. For details see text.

through a nozzle of 100 m in diameter with an oven operated at temperatures between 500–600C. The flux of Na₃ molecules is enhanced for higher temperatures and/or by coexpanding the sodium molecular beam with argon at 4 bar (seeded beam technique). The experiments on the fullerenes C_{60} and C_{70} were carried out in the same apparatus at oven temperatures below 530C and a nozzle diameter of 500 m. The metal carbonyl molecule Fe(CO)₅, also discussed in this contribution, was expanded through a nozzle of 50 m diameter at room temperature which corresponds to a vapor pressure of about 40 torr.

The ultrashort intense laser pulses were produced in a laser system (Fig.2) consisting of a Ti:sapphire oscillator, chirped pulse amplification [23] [24] and an optical parametric generator (TOPAS, Light Conversion Ltd.). The home built Ar⁺-ion laser pumped oscillator, which is described in detail in ref. [25] provides 30 fs pulses at a repetition rate of 85 MHz and 2 nJ energy which are subsequently amplified at 1 kHz in a modified commercial regenerative amplifier (Quantronix). This delivers light pulses of 90 fs pulse duration (Gauss) and 1.2 mJ pulse energy at a wavelength of 790 nm and a bandwidth of 22 nm (FWHM). Due to the large bandwidth of this seed pulse, the TOPAS (Travelling Wave Optical Amplification of Superfluorescence) in combination with second harmonic generation and sum frequency mixing can be used to produce laser pulses over a wide range of the visible spectrum. These pulses may be compressed to their bandwidth limit well below the input pulse duration in a prism compressor. For example, at 618 nm 20 J pulses of 40 fs duration are generated. The complete laser system is designed to produce femtosecond laser pulses in a wavelength range from 225 nm up to 2600 nm with J pulse energies at a repetition rate between 10 Hz and the kHz regime. In order to determine the laser pulse duration we use single shot and scanning autocorrelation detection schemes [26] [27]. For the determination of the phase of the light pulses we either use a home built device that takes advantage of the method of frequency domaine phase measurements [28] or we use FROG (frequency resolved optical gating) techniques [29]. An online spectrum analyzer is used to control the spectral distribution and the center wavelength of the laser pulses. In future applications we shall implement a pulse shaping device [30]. In a Michelson interferometer type setup the probe laser pulses are delayed with respect to the pump laser pulses. They are recombined collinearly and weakly focused with a 300 mm achromatic lens into the interaction region. Some of the earlier experiments were carried out using our home-built CPM ring dye laser. Equipped with two excimer laser pumped bow-tie amplification stages this laser system produces 80 fs pulses of 40 J energy at 620 nm with a repetition rate of 100 Hz. Different wavelengths can be produced by selecting and reamplifying different frequency components from the white light continuum generated in a cell containing methanol. This setup is described in detail in [25].

To obtain complete information about the final states produced in our experiments we use ion and electron time of flight (TOF) detection. The same linear TOF spectrometer is used for both mass and energy resolved measurements of ions and ionic fragments and for energy resolved electron detection under very similar conditions. Fragment energies can be determined to an accuracy better than 0.1 eV by well known procedures described for example in [12] [31] [32] [33]. The electron spectrometer is calibrated by producing electrons of different well defined energies via resonance enhanced multiphoton ionization (REMPI) of atomic sodium with a nanosecond dye-laser. Thus an energy resolution of approximately 50 meV is achieved for photoelectrons of 1 eV kinetic energy.

All TOF spectra are recorded with a 2 Gigasamples digital oscilloscope (LeCroy) and averaged over several thousand laser shots. Boxcar averagers (Stanford Research) are used to integrate the signal of individual ion masses or electron energy peaks in some of the pump-probe experiments.

3. A short excursion to intense laser field interactions

Before we discuss our femtosecond time resolved experiments on molecular MPI of Na₂, Na₃, C₆₀ and Fe(CO)₅, we first make some general remarks on intense laser fields and summarize some simple but useful formulas used in high intensity laser physics on atoms and molecules. For a more detailed discussion of this topic see for example the excellent review articles [5] [6] [7] [8] [9].

The electric field amplitude E in a focused laser beam is given by the formula

$$E = \sqrt{\frac{2T}{c \,\varepsilon_0}} \tag{1}$$

where I is the intensity of the focused laser that can be estimated roughly by standard formulas [34] (taking into account the measured pulse energy, pulse duration and spot size), c is the speed of light in vacuum and ε_0 is the vacuum permittivity. If I is expressed in W/cm^2 then E expressed in V/cm is given by $E = 27.4 \sqrt{I}$. The atomic unit of laser intensity is therefore 3.5.10¹⁶ W/cm², corresponding to 5.14.10⁹ V/cm, the atomic unit of the electric field. This is the field experienced by an electron in a hydrogen atom at one Bohr radius from the nucleus. With modern laser systems using chirped pulse amplification pulse intensities of the order of 10²⁰ W/cm² can be obtained [35] [36]. Available commercial laser systems are capable of producing several "atomic units" of light intensity. At these intensities it is obvious that the interaction of light with atoms or molecules cannot be described by perturbation theory anymore. Many important discoveries have recently been made in high intensity laser experiments. As mentioned in the introduction, above threshold ionization (ATI) [4] [9] and its link to high-order harmonic generation (HOHG) [11] [37] [38] [39] as well as above threshold dissociation (ATD) [16] [40] and high field coulomb explosion [14] [15] are prominent examples from atomic and molecular physics. Here in this contribution we are dealing with dynamical aspects of molecular multiphoton ionization (MPI). In general MPI is the ionization with more than one photon, where each photons energy is well below the ionization energy. In the weak field limit of a MPI experiment the rate of ionization R is proportional to the Nth power of the laser intensity I, where N is the number of photons required to reach the ionization limit.

$$R \propto I^N \tag{2}$$

This well known formula can be derived by perturbation theory. With the knowledge of the ionization potential, this regime can experimentally roughly be verified by a proper attenuation experiment. However, this dependence is experimentally difficult to test, because a real focused pulsed laser beam has varying intensity in time and across the beam profile. If dynamical aspects of molecular multiphoton ionization in this regime are treated quantum mechanically perturbation theory can be applied. As an example for such a treatment in which theory compares favorably with the experimental data, see refs. [41] [42]. With increased laser intensity, deviations from this simple power law were found. Energy levels can be Stark shifted by large amounts from their unperturbed positions and broadened by the stimulated emission rates to other levels. When population is resonantly excited out of bound states, the onset of depletion in the intense laser field obviously violates basic assumptions of perturbation theory. With the onset of multiphoton Rabi oscillations the concept of perturbation theory fails completely. These topics have been extensively reviewed [43] with respect to model or atomic systems. If dynamical aspects of molecular MPI in this regime have to be calculated, the time dependent Schrödinger equation has to be solved directly by numerical methods. Examples related to our previous work are given in refs. [44] [45]. The more intense the ionizing laser, the more careful one has to look at ionization potentials as is well known from high-laser field atomic physics. Directly after the electron has been liberated from the ionic potential, the electron will oscillate in the electric field of the laser. The average kinetic energy of this rapidly oscillating motion, the so called jitter motion, can be described by Newtons equations, yielding the so called ponderomotive energy U_p of a free electron.

$$U_{\rm P} = \frac{e^2 E^2}{4 m_{\rm e} \,\omega^2} \tag{3}$$

Where e denotes the elementary charge, m_e the electrons rest mass and the ω frequency of the driving laser field. In practical units this becomes $U_p = 9.33 \cdot 10^{-14} I \lambda^2$ where U_p is given in eV, I is given in W/cm² and λ is the wavelength in m. In order to set an electron completely free in an ionization experiment with an intense laser source, it is not enough to reach the zero field ionization limit, the required oscillation energy has to be supplied in addition to that. The ponderomotive energy induces an upshift of the ionization potentials. This behaviour was experimentally veryfied by the observation that low-order peaks in ATI spectra are supressed in intense fields [46]. High lying Rydberg states, where the binding energy of the electron is low, respond to an intense laser field in a very similar way, which is known as the ac-Stark shift.

As mentioned above, the electric field strength in a focused high intensity laser beam may well exceed inneratomic field strengths. If the light field is strong enough and the optical cycle long enough, ionization in that regime tends to a dc-field ionization. The electron is either tunneling through the potential barrier formed by the Coulomb potential and the external field or the over-the-barrier ionization process occurs. Multiphoton ionization, where the electron is set free after absorption of at least N photons, and the just described case of tunnel ionization are the two limiting cases that are distinguished by the so called Keldysh γ parameter. This parameter describes the ratio of the tunneling time through the barrier to the optical cycle time and is given by

$$\gamma = \sqrt{\frac{I_{\rm p}}{2 U_{\rm p}}} \tag{4}$$

4. Na₂ in intense laser fields

In this section we will first describe the dynamics of molecular MPI in weak laser fields, where the sodium dimer has been chosen as a prototype molecule. By recording transient Na_2^+ and Na^+ signals different MPI processes were detected and by recording time resolved photoelectron distributions the molecular dynamics induced by an ultrashort laser pulse is observed over a wide range of internuclear distances simultaneously. A detailed understanding of this molecular dynamics based upon absorption of several photons in the weak field limit is important in order to understand changes in the transients as a function of the laser field strength. The topic of the second part of this section is molecular dynamics in intense laser fields, where again time resolved ion and photoelectron spectroscopy are used.

4.1. Multiphoton ionization of Na_2 in weak laser-fields

Fig.3 shows the relevant potential energy curves for excitation of Na₂ near 620 nm. Ionization is predominantly due to REMPI, while nonresonant multi photon processes play only a minor role. The molecule is excited from the v'' = 0 vibrational level of the neutral ground state to a range of vibrational levels in the 2¹II_g state resonantly enhanced by the A ${}^{1}\Sigma_{u}^{+}$ state [12]. From the 2 ${}^{1}\text{II}_{g}$ state different photoionization and fragmentation processes are possible. Process D is the direct ionization into the ionic ground state ${}^{2}\Sigma_{g}^{+}$ which yields $Na_{2}^{\scriptscriptstyle +}.~(v_{di}{}^{\scriptscriptstyle +})$ Process @ is the excitation of a bound doubly excited neutral Na2** state at large internuclear distances followed by *electronic autoionization* resulting in Na_2^+ (v_{ea}^+) and autoionization induced fragmentation yielding Na(3s) and Na⁺ fragments. When an ultrashort, spectrally broad laser pulse is used for excitation, vibrational wavepackets are formed at the inner turning points of the A ${}^{1}\Sigma_{u}^{+}$ and 2 ${}^{1}II_{g}$ potentials, which oscillate with time constants of about 320 fs and 380 fs respectively. A second time delayed probe laser may then ionize either via process 2 when the 2 'II_g-state wavepacket has propagated to large internuclear distances, or it will transfer population into the bound ionic ground state ${}^{2}\Sigma_{g}^{+}$ (process \mathbb{O}). This is shown in the transient Na⁺ and Na⁺₂ signals in Fig.4, which were obtained using 80 fs pulses at 618 nm from our Ti:Sapphire laser system and which reproduce the data published in reference [47]. The lasers in this experiment were attenuated to such an extent, that neither pump nor probe laser produced a noticeable ion signal. The Na_2^+ transient has maxima each time the probe pulse is fired when the A ${}^{1}\Sigma_{u}^{+}$ state wavepacket has returned to its inner turning point, but shows only a very small contribution from a wavepacket propagating in the 2 1 II_g – state potential. In a classical analysis [48] based on Mulliken's difference potential concept [49] this is because the 2 ${}^{1}\text{II}_{g}$ -A ${}^{1}\Sigma_{u}^{+}$ transition is found to occur at small internuclear distances. The ${}^{2}\Sigma_{g}^{+}$ -2¹II_g transition on the other hand can occur over the whole range of the nuclear coordinate [48], thus Na_2^+ formation by direct photoionization is insensitive to wavepacket motion



Fig. 3 Potential curve diagram for the excitation, multiphoton ionization and fragmentation of Na_2 using 620 nm photons. The different processes are discussed in the text.

in the 2 ${}^{1}\text{II}_{g}$ potential [50]. Quantum mechanical calculations in the perturbative regime nicely reproduce the experimental Na^{$\frac{1}{2}$} transient [41]. Since the doubly excited state Na^{$\frac{1}{2}$} can only be reached, when the 2 ${}^{1}\text{II}_{g}$ state wavepacket is located at large internuclear distances, the Na^{$\frac{1}{2}$} signal is modulated predominantly with the 2 ${}^{1}\text{II}_{g}$ state frequency and is out of phase with the Na^{$\frac{1}{2}$} transient. (The contribution from the A-state to the Na⁺ signal is attributed to fragmentation of Na⁺₂ following direct photoionization (process)). A discussion of this experiment in the context of controlling chemical reactions by femtosecond techniques can be found in [51] [52].

In order to detect molecular dynamics in a pump-probe experiment by measuring the total ion signal or the total laser induced fluorescence signal, excitation and probing have to be localized in space. The detection of the oscillation of the wavepacket motion in the A ${}^{1}\Sigma_{u}^{+}$ state in the total Na⁺₂ signal is only possible due to a probe window located at a specific internuclear distance. In this case the region near the inner turning points (see above) of the molecular potentials is involved. The wavepacket motion in the 2 ¹II_g state is only seen by the excitation and decay of a doubly excited state, which again occurs at a specific internuclear distance, in this case close to the outer turning point of the vibrational motion of the molecule (see above). In order to map molecular dynamics on the whole range of internuclear distances of the neutral intermediate states, we combine molecular beam techniques with femtosecond pump-probe techniques and kinetic energy photoelectron detection [18] [19]. By the Franck-Condon principle the kinetic photoelectron distribution resulting from direct ionisation sensitively depends on the nuclear configuration. Therefore time resolved photoelectron spectroscopy is ideally suited to follow the intermediate state dynamics along all energetically allowed internuclear distances. The advantage of time resolved photoelectron spectroscopy has already been demonstrated in the picosecond time domain [53-56]. However, it exhibits its full potential beautifully in the femtosecond regime, since for example vibrational wavepacket motion, direct dissociation, isomerization and internal conversion occur on this time scale. Reviews on these topics are found in refs. [2,57]. Recently femtosecond time delayed photoelectron spectroscopy has been performed with reports on vibrational energy redistribution in hexatriene [20], on the direct photodissociation of



Fig. 4 Na^{\pm} and Na^{\pm} transient signals obtained from pump-probe measurements using attenuated 80 fs pulses at 618 nm. The power spectra (inserts) obtained from a fast Fourier transformation (FFT) show the different frequency components of the two transients.



Fig. 5 Potential curve diagram for the excitation, multiphoton ionization and above threshold ionization (ATI) of Na₂ using 620 nm photons. The difference potential (Na₂⁺ - 2¹II_g + 2 ω ; ω is the photon energy; dashed line) indicates that upon direct ionisation out of the 2¹II_g state into the Na₂⁺ X²\Sigma_g⁺ state the kinetic energy of the photoelectrons depends on the internuclear distance. The propagation of vibrational wavepacket motion can therefore be monitored along the internuclear distance by detecting energy resolved photoelectrons in pump-probe experiments.

 I_2^{-} [22] and on perturbation of electronic potentials in NO multiphoton ionization [21]. These results clearly demonstrate that this technique is a powerful tool for studying molecular dynamics. Femtosecond time resolved ionization spectroscopy of ultrafast molecular dynamics via detection of kinetic photoelectrons was first proposed by Seel and Domcke in a theoretical publication [58]. Mapping a vibrational wavepacket with the help of femtosecond pump-probe techniques and energy resolved photoelectron spectroscopy was suggested later by C. Meier and V. Engel also in a theoretical publication [59]. We have shown experimentally, that energy resolved photoelectron spectroscopy on a femtosecond timescale allows to monitor the evolution of a vibrational wavepacket along the internuclear distance in real time [18] [19]. In comparison with the ZEKE (zero kinetic energy) photoelectron spectroscopy [60], which has been extended from picosecond [61] to femtosecond time resolution [62,63], this approach has a major advantage. A complete mapping of a vibrational wavepacket motion for example can be achieved with a fixed probe laser wavelength, whereas the mapping of wavepacket motion at different internuclear distances with the ZEKE detection technique requires a wavelength tuning of the probe laser [64].

The excitation scheme of our mapping experiment, basically the same as depicted in Fig.3, is shown in Fig.5. Note again, that direct photoionisation out of the 2 ${}^{1}\text{II}_{g}$ state into the Na₂⁺ (X ${}^{2}\Sigma_{g}^{+}$) state cannot provide the dynamics of the

wavepacket prepared in this state through total Na⁺₂ ion detection [48] [50]. However, by the detection of kinetic energy resolved photoelectrons this dynamical information can be obtained, because electrons of different kinetic energies are formed at different internuclear distances. In such a direct photoionisation process the released kinetic energy of the photoelectrons can be determined by a difference potential analysis [49] [48]. The dashed line in Fig.5 displays the difference potential $^2\Sigma_g^{\scriptscriptstyle +}$ $(Na_2^{\scriptscriptstyle +})$ – 2 1II_g + 2 ω , where ω is the photon energy. The expected photoelectron energy in the photoionisation of the 2 ¹II_g state decreases with increasing internuclear distance. At the inner turning point of the 2 ¹H_g potential curve photoelectrons of about 0.94 eV are formed while at the outer turning point photoelectrons of about 0.78 eV are released. Thus, by recording transient photoelectron spectra we probe molecular wavepacket motion on neutral electronic states along all energetically allowed internuclear distances simultaneously. Note that the autoionisation processes of the doubly excited electronic state (see Fig.3) lead to photoelectrons with less than 0.5 eV kinetic energy [12], which can be separated from the electrons released in the direct photoionisation process. Also included in the figure is the further absorption of photons in the ionic continuum occuring in a more intense laser field, leading to the observation of molecular ATI photoelectrons. This will be discussed in the next section.

In Fig.6 the measured photoelectron TOF distribution is shown as a function of pump- probe delay time. Attenuated 40 fs laser pulses at 618 nm were used in this experiment. The TOF range from 250 ns to 290 ns corresponds to an energy interval of photoelectrons released from 1.2 eV to 0.6 eV. At earlier flight times photoelectrons with higher kinetic energies are released and therefore smaller internuclear distances are probed in our experiment. Longer flight times



Fig. 6 The measured TOF (time of flight) photoelectron distribution as a function of pump-probe delay is shown. Attenuated 40 fs laser pulses at 618 nm were used for excitation and probing. This femtosecond time resolved photoelectron signal shows the vibrational wavepacket motion in the neutral electronic states. Cuts at a constant TOF reveal the wavepacket dynamics at a specific internuclear distance. The inserts display the Fourier transform of transient photoelectron signals obtained at two different cuts (see text).

correspond to photoelectrons having lower kinetic energies, which are generated at larger internuclear distances. The dynamics of vibrational wavepacket motion in the two neutral electronic states A ${}^{1}\Sigma_{u}^{+}$ and 2 ${}^{1}H_{g}$ is beautifully resolved along all energetically allowed internuclear distances. By taking cuts along a constant time of flight the dynamics at a specific internuclear distance can be analysed. The inserts give two examples. The power spectrum density (PSD) of a Fast Fourier Transformation (FFT) is displayed for a "fast" photoelectron transient, corresponding to a cut at 263 ns (small internuclear distances) and for a "slow" photoelectron transient corresponding to a cut at 274 ns (large internuclear distances). Two frequency contributions seen in the inserts are centred at 90 cm⁻¹ and at 107 cm⁻¹. These are the frequencies of oscillating wavepackets in the 2 ${}^{1}\text{II}_{g}$ and A ${}^{1}\Sigma_{u}^{+}$ states, respectively. According to the excitation scheme, at the inner turning point both the A ${}^{1}\Sigma_{u}^{+}$ state wavepacket and the 2 ¹II_g state wavepacket contribute to the "fast" photoelectron transient. This is why the frequencies of both wavepackets are seen in the "fast" FFT with almost equal PSD, whereas in the "slow" FFT-resembling the dynamics at large internuclear distances-the frequencies of the 2 ¹II_g state wavepacket dominate the spectrum. The small contribution of the A ${}^{1}\Sigma_{u}^{+}$ state frequencies in that FFT is attributed to the limited energy resolution of our spectrometer. This experiment clearly demonstrates, that by means of transient kinetic photoelectron spectroscopy a vibrational wavepacket motion can be mapped simultaneously over a wide range of internuclear distances.



Fig. 7 Transient Na $_2^+$ spectra as a function of delay between identical 80 fs, 620 nm pump and probe pulses for three different laser intensities (top) and corresponding Fourier transforms (bottom).

4.2. Multiphoton Ionization of Na₂ in intense laser-fields

As mentioned in section three, the onset of Rabi cycles between different electronic states determines the breakdown of perturbative descriptions in MPI of atomic or molecular systems. In the following we will discuss the change of molecular MPI of Na_2 with increasing laser intensities. From transient ion and -electron data we will first deduce the Rabi cycling between the neutral electronic states participating in the MPI before we discuss our results on molecular ATI. That is the absorption of photons in excess of the minimum number required for ionization where the additional energy is observed as kinetic energy of the photoelectrons formed.

For a discussion of molecular MPI at the onset of Rabi-type cycles we look again at the Na₂ system at 620 nm. Using 80 fs laser pulses (CPM laser) of three different intensities $(I_0,$ $0.5I_0$ and $0.1I_0$) the Na⁺₂ transients displayed in Fig.7 are obtained [44]. The modulation frequency of the transient ion signal changes as a function of laser intensity, which can best be seen from the corresponding Fourier transforms. While at more moderate intensities mainly the A-state frequency (110 cm^{-1}) contributes to the transient ion signal, the 2 $^{1}\text{H}_{g}$ state frequency (90 cm⁻¹) starts to dominate at higher intensities. For the highest laser intensity shown, a vibrational wavepacket motion is detected even in the electronic ground state X ${}^{1}\Sigma_{u}^{+}$ (157 cm⁻¹). It is created through stimulated emission pumping during the time the ultrashort pump pulse interacts with the molecule and is detected via direct three photon ionization by the time delayed probe pulse [44]. The formation of vibrational wavepackets in the electronic ground state was predicted by Hartke et al. [65]. Other experimental verifications were recently reported by Banin and Ruhman [66] and from the Wöste group [67]. Although the terminology "impulsive stimulated Raman scattering" of the preparation of the ground state wavepacket in these experiments is different, the physics is the same.



Fig. 8 Variation of the population in the three electronic states involved in the multiphoton ionization of Na₂ during the interaction with ultrashort laser pulses of different intensities. The calculations were performed for 60 fs pulses at 618 nm and $I_0 = 3 \cdot 10^{10}$ W/cm².



Fig. 9 Transient signal of the electrons formed upon direct ionization of Na₂ (process in Fig.3) as a function of time delay between identical 40fs, 618nm pump and probe pulses for three different laser intensities (top) and corresponding Fourier transforms (bottom).

Similar transient signals were obtained from time dependent quantum mechanical calculations performed by Meier and Engel, which well reproduce our experimental results [44]. The calculations show that for different laser field strengths the electronic states involved in the MPI are differently populated in Rabi-type processes. In Fig.8 the population in the neutral electronic states during interaction of the molecule with 60 fs pulses at 618 nm is calculated by solving the Schrödinger equation directly, where we have used the methods described in [45]. We find that for lower intensities the A ${}^{1}\Sigma_{u}^{+}$ state is preferentially populated by the pump pulse, and the A ${}^{1}\Sigma_{u}^{+}$ state wavepacket dominates the transient Na2 signal. However, for the higher intensities used in the experiment the calculations indicate, that the situation may well be reversed and consequently the contribution from the 2 'II_g state is dominant in the measured transient signal of Fig.7. This demonstrates that by varying the intensity of an ultrashort laser pulse, the population transferred to the various neutral electronic states of Na2 can be modified.

The drop in the Na_2^+ signal for zero pump-probe time delay at the highest laser intensity used (Fig.7) is attributed to fragmentation of Na_2^+ by absorption of another photon after ionization. At higher laser intensities it is therefore



Fig. 10 Variation of the population in the three electronic states involved in the multiphoton ionization of Na₂ during the interaction with ultrashort laser pulses of different intensities. In comparison to Fig. 8 the calculations were now performed for shorter (30 fs) laser pulses at 618 nm and $I_0 = 2 \cdot 10^{11} \text{W/cm}^2$

advantageous to record the transient electron spectrum rather than the Na⁺₂ signal when the interest is in the bound state population. Fig.9 shows the transients of electrons formed upon direct ionization of Na₂ (process \oplus in Fig.3)



Fig. 11 Diabatic (top) and adiabatic (bottom) dressed states relevant for the multiphoton ionization of Na_2 with 618 nm photons. The adiabatic dressed states were calculated for a laser intensity of $5 \cdot 10^{11}$ W/cm².

recorded for three different laser intensities using intense 40 fs transform limited pulses. The observation of the vibrational frequencies of the 2 ¹II_g state wavepacket can be attributed either to stimulated emission processes to the lower lying electronic states due to the probe laser interaction when the 2 ¹II_g wavepacket reaches the inner turning point, where excitation takes place or to an R dependent transition dipol moment. This time the contribution of a 2 III_g state wavepacket is disappearing at the highest intensities and the ground state eventually dominates the transient signal. Again, the result is in agreement with calculations of the actual population in the bound electronic states after pump pulse excitation (Fig.10). Despite the high laser intensities applied the 2 ¹II_g state population has dropped again to zero after interaction with the pump pulse. The calculations also show, that for extremely short pulses (Fig.10) Rabi-oscillations take place predominantly between the X ${}^{1}\Sigma_{g}^{+}$ and the A ${}^{1}\Sigma_{u}^{+}$ electronic states while for longer pulses (Fig.8) the oscillations are observed between the A ${}^{1}\Sigma_{u}^{+}$ and the 2 ${}^{1}II_{g}$ state. This pulse length effect could be due to the fact that the A-X transition is enhanced only at small internuclear distances. On the other hand the A ${}^{1}\Sigma_{u}^{+}$ -hv and 2 ${}^{1}\Pi_{g}$ -2hv dressed state potentials (see for example [40] [68]) calculated for a laser intensity of 5.10¹¹W/cm² (Fig.11) are almost parallel which indicates that 2 ${}^{1}\text{II}_{g}$ -A ${}^{1}\Sigma_{u}^{+}$ transitions are no longer *R*-dependent over a wide range of internuclear distances in intense laser fields. The fact that 2 ${}^{1}\text{II}_{g}$ -A ${}^{1}\Sigma_{u}^{+}$ transitions occur over a wide range of internuclear distances due to potential curve deformation may actually lead to a loss of selectivity in pump-probe schemes detecting total ion or total electron signals.

In intense laser fields atoms or molecules may absorb photons in excess of the minimum number required for ionization and the additional energy is observed as kinetic energy of the electrons formed. This so called above threshold ionization (ATI) has been extensively studied in atoms both experimentally and theoretically and single electron ATI of atoms is now understood in some detail (see reviews [5] [6] [7] [8] [9]). When molecules interact with intense laser fields an additional degree of freedom is given by the motion of the nuclei. In the study of molecular ATI, molecule specific effects have so far only played a minor role. This is mainly due to the fact, that the laser pulses used in former experiments were much longer than a typical vibrational period of the molecule studied. In the Na₂ molecule vibrational wavepackets can be excited with intense ultrashort, intrinsically broad laser pulses and the influence of vibrational motion on molecular ATI can be studied. In the following we present time-resolved observations of molecular above threshold ionization and we show both in single pulse and pump-probe experiments, that threshold and above threshold ionization signals are sensitive to the vibrational wavepacket dynamics. Fig.12 shows ATI spectra of Na₂ at three different laser intensities recorded with 80 fs CPM-laser pulses at 618 nm. Io is approximately 10¹² W/cm², corresponding to a ponderomotive potential of about 35 meV (eq. (3)), which is within the resolution of our spectrometer. Keldysh γ parameter (eq. (4)) yields a value of 8 at these intensities, indicating that we are still in the MPI regime, which is confirmed by the three peaks separated by the photon energy and observed at 0.9 eV, 2.9 eV and 4.9 eV. These energies correspond to ionization of Na_2 with 3, 4 and 5 photons out of the v'' = 0 level of the electronic ground state (see Fig.5), and are due to threshold and above threshold ionization, respectively. In addition electrons of slightly lower energy are formed with increasing laser intensity and eventually dominate the spectrum. The observed energy distribution can be understood from the semiclassical argument given above and only shortly repeated here. In terms of the Franck-Condon principle, the nuclear kinetic energy is con-



Fig. 12 Threshold and above threshold ionization (ATI) electron spectra of Na₂ for three different laser intensities (I_0 approx. 10¹² W/cm²).



Fig. 13 Transient electron signal of electrons having energies between 2.7 and 3.1 eV (first order ATI) obtained with 40 fs pulses of approximately 10^{11} W/cm² (top) and of electrons having energies between 0.6 and 1.1 eV (threshold ionization) at a five times lower intensity (bottom).

served during electronic transitions. Applying a difference potential analysis to the ionization step, the kinetic energy of the released photoelectrons is seen to decrease with increasing nuclear separation (see Fig.5). It can therefore serve as a measure of the internuclear distance at which ionization occurs. This leads to the following interpretation of the electron spectra. Excitation with an ultrashort laser pulse of only moderate intensity leaves the nuclei in the molecule essentially fixed. They have no time to move apart before the laser is turned off and threshold and above threshold ionization take place with the nuclear wavefunction peaked at small internuclear distances. In a much more intense laser field, however, population is transfered to the resonantly excited states already during the leading edge of the laser pulse. The vibrational wavepackets in these states spread earlier and propagate to larger internuclear distances during the molecule-laser interaction, leading to the appearance of less energetic threshold and above threshold photoelectrons in Fig.12. In a further, time resolved experiment we have applied femtosecond pump-probe techniques to the detection of threshold and ATI electrons using 40 fs pulses at 618 nm from the Ti: Sapphire laser system. The transient threshold electron signal, shown in the lower part of Fig.13, is composed of vibrational frequencies of wavepackets propagating in the $A^{1}\Sigma_{u}^{+}$, $2^{1}II_{g}$ and $X^{1}\Sigma_{g}^{+}$ states of Na₂. At a five times higher pump and probe laser intensity (approx. 10^{11} W/cm₂) an oscillating transient is also observed for electrons from above threshold ionization which directly shows that above threshold ionization is still sensitive to the wavepacket motion in the $A^{1}\Sigma_{u}^{+}$ and $2^{1}II_{g}$ states (upper part of Fig. 13.). A more detailed discussion of this experiment can be found in [69].

5. Na₃ in intense laser fields

Coherent coupling of electronic states in an intense laser field is a phenomenon not only restricted to atoms or simple



Fig. 14 Schematic potential curve diagram of the relevant electronic states for the interaction of Na_3 with 620 nm laser pulses.

diatomics, but can also be observed in nonlinear molecules as we now demonstrate for the case of Na₃. This molecule is produced in our molecular beam apparatus at high oven temperatures and/or by using Argon at 4 bar as a seedgas. The excitation scheme for Na₃ using laser pulses near 620 nm can be seen in Fig.14. The B-state extends from 600 nm to 625 nm [70] and can be reached by one photon excitation. A second photon can ionize Na₃ yielding Na₃⁺ in its electronic ground state. Three photon absorption leads to fragmentation of Na₃⁺. In the ionic ground state Na₃⁺ has an equilateral triangle configuration, while the neutral ground state and the B-state of Na₃ are slightly deformed due to the Jahn-Teller effect. Due to these different geometric structures one expects configuration dependent transition probabilities from the Franck-Condon principle. It should therefore be possible to generate and probe vibrational wavepacket motion. Fig.15 shows the Na⁺₃ transient with the corresponding Fourier transform obtained with strongly attenuated 80 fs pulses at 618 nm. The dominant frequency component around 105 cm⁻¹ maps the symmetric stretch oscillation (B_{ss}) of the molecule excited by the pump pulse in the B-state. A smaller contribution near 72 cm⁻¹ can be tentatively assigned to the asymmetric stretch (B_a) and bending (B_{as}) normal modes in the same electronic state. The frequencies observed below 40 cm⁻¹ (Δj) agree well with those obtained by Broyer et al. [70] [71]



Fig. 15 Transient Na_3^+ signal for strongly attenuated 80 fs pump and probe laser pulses of 618 nm. The frequencies observed in the Fourier transform are due to vibrational wavepacket motion and pseudorotational wavepacket motion on the B-state potential.



Fig. 16 Transient Na₃⁺ signal for intense 80 fs pump and probe laser pulses of 623 nm. In addition to the B-state frequencies that are due to vibrational wavepacket motion (B_{ss}) and pseudorotational wavepacket motion ($\Delta j, \omega$) also observed for low intensities, the Fourier transform now also shows contributions assigned to wavepacket motion on the ground state potential (X_b, X_{as} and X_{ss}).

Delacrétaz et al. [72] and Rakowsky et al. [73] from nanosecond laser experiments and an analysis of pseudorotation in the B-state. A discussion of this pseudorotational wavepacket motion can already be found in [62]. Recently performed perturbative calculations on the three dimensional wavepacket motion on the B-state of Na₃ [74] [75] [76] give the symmetric stretch motion as the dominant dynamical feature of a femtosecond pump-probe experiment in a weak laser field. This result has also been found in recent femtosecond experiments performed by the Wöste group [77] [76].

Using higher laser intensities, however, the ionization transient changes dramatically as shown in Fig. 16 [62]. The higher laser intensity is immediately apparent from the drop in the Na₃⁺ signal for zero pump-probe delay time, which is due to three photon ionization and fragmentation. Much more frequencies now contribute to the signal in this case. Besides the wavepacket propagation on the B-state potential surface already observed at low laser intensities now there are also contributions at 50 cm⁻¹, 90 cm⁻¹ and 140 cm⁻¹. These frequencies can be assigned (see again the work performed by Broyer et al. [71]) to the bending mode X_b, the asymmetric stretch mode X_{as} and the symmetric stretch mode X_{ss} in the ground state of Na₃. This shows that the intense pump laser pulse has coherently transferred population back into the neutral ground state thus creating wavepacket motion on this potential surface, which is subsequently probed by two photon ionization. As in the case of Na₂, population transfer between electronic states in Rabi-type processes can therefore be controlled by varying the laser intensity and can be monitored in a pump-probe experiment.

6. C₆₀ in intense laser fields

A challenging task in the investigation of the behavior of the fullerenes following multiphoton excitation is the uncovering of processes leading to ionization and fragmentation of these molecules. It is well known that multiphoton ionization of C_{60} and C_{70} with visible and UV ns-laser pulses leads to delayed ionization. This can be explained in the model of thermionic emission [78][79]. At laser wavelengths shorter than 215 nm delayed ionization starts to vanish [80][81]. In experiments using coherent two-photon ionization with subpicosecond laser pulses at 248 nm only direct ionization is observed [82]. The other important question concerns the fragmentation of the fullerenes leading to the observed bimodal fragmentation pattern [83]. This fragmentation is often explained in terms of successive statistical evaporation of the vibrational excited parent molecule [84]. Another possible process is the ejection of larger fragments C4, C6, . . . in a single event. A hint which of these two processes is more favorable could be drawn from the kinetic energy release of the ionic fragments. But with ns-laser experiments it is difficult to distinguish between directly formed ionic fragments and ions that are produced by photoionization of the ejected neutral fragments. In experiments applying ultrashort laser pulses whose duration is short compared to the fragmentation time scale of the molecule this problem is overcome [12].

In this experiment we have employed femtosecond laser pulses centered at 620 nm generated in our colliding pulse modelocked (CPM) dye laser, amplified in a multipass dye amplifier and in addition in a subsequent Bethune cell. An effusive molecular beam of C_{60} and C_{70} is generated as de-



Fig. 17 Ion TOF spectrum for two photon ionization of C_{60} and C_{70} . a) Excimer laser excitation at 308 nm and 15 ns pulse duration; the spectrum shows tails at longer flight times for the mass peaks of C_{60}^+ and C_{70}^+ because of delayed ionization. b) Excitation at 310 nm with pulses of 120 fs duration and a pulse energy of about 1 J; delayed ionization is totally absent. c) Same as b) but increased laser intensity; note the onset of multiphoton induced fragmentation.

scribed in the experimental section. Again, the ionization region of the time of flight mass spectrometer, the molecular beam and the laser beam intersect at right angles in a plane perpendicular to the ion drift direction in the TOF spectrometer as indicated in Fig. 1. The ion TOF spectrum obtained for two photon ionization with a 15 ns long excimer laser pulse at 308 nm is displayed in Fig. 17a. The spectrum shows typical tails at longer flight times for the mass peaks of C_{60}^+ and C_{70}^+ because of delayed ionization. Broad fragment peaks down to C_{50}^+ are observed, whereas Fig. 17b shows that for two photon ionization with a 120-fs laser pulse at 310 nm delayed ionization is totally absent. For the applied pulse energy of 1 µJ no fragmentation is observed. With increasing laser pulse energy broad fragment peaks at shorter flight times occur which belong to the ionic fragments C_{58}^+ , C_{56}^+ and so on (Fig. 17c).

Ion TOF spectra have also been measured at 620 nm and a laser pulse duration of 60 fs. The TOF-spectrum obtained with high laser pulse intensity (pulse energy 100 μ J, leading to a pulse intensity of approximately 10¹⁴W/cm² and therefore to a Keldysh γ well below one) is shown in Fig. 18. Extensive fragmentation of C₆₀ is observed down to C⁺₄₂. At shorter



Fig. 18 Ion TOF spectrum obtained from C_{60} and C_{70} after excitation with pulses at 620 nm at a pulse duration of 60 fs and a pulse energy of 100J. Note extensive fragmentation due to high laser intensities and the observation of multiply charged fragments.

flight times doubly and triply charged parent ions and fragments of C_{60} and C_{70} can be seen. Note that the peak height of the doubly charged fragments exceeds that of the singly charged (this is the case for the fragments of C_{60} as well as for C_{70}). Despite the higher detection efficiency of multiply charged particles of the same mass in the MCPs it is still striking that the number of doubly charged fragments is at least of the order of magnitude of the singly charged fragments. Fig. 19 shows that for short flight times small ionic fragments in the mass range from C_{15}^+ down to C^+ are observed. A possible detection of C_{60}^{4+} is hampered by the fact that C_{15}^+ has the same flight time and coincides with a C_{60}^{4+} mass peak. Stronger evidence for the existence of quadruply charged C₆₀ and its fragments in the mass spectrum comes from the fact, that the mass peak right next to C_{15}^{+} at shorter flight time can only be assigned to C_{58}^{4+} . It is known that the singly charged C_{29}^+ only appears in very small amounts after photoinduced fragmentation of C_{60} [80], hence the existence of C_{29}^{2+} is very unlikely. The fact that doubly, triply and probably quadruply charged ions and ionic fragments of C₆₀ are produced by the fs-laser pulse is astonishing. Values that



Fig. 19 Shorter flight times of the ion TOF spectrum of Fig. 18 are displayed. Doubly, triply and probably quadruply charged ions and ionic fragments of C_{60} are produced by the intense fs-laser pulse.

have been measured for the third ionization potential of C_{60} are higher than 33 eV [85]. Thus for the formation of $C_{60}^{\scriptscriptstyle 44}$ more than 17 photons of 620 nm (2 eV) have to be absorbed! For the formation of triply charged fragments and C_{60}^{4+} even more photons are required. Additionally the formation of small odd numbered singly charged ionic fragments can no longer be understood in the model of a fragmentation process only involving two fragments. A possible explanation for the observed intense ionization and fragmentation of C₆₀ might be given based on a model used by Wülker et al. in a recent publication [86]. Because of the large extent and the homogeneous structure of the C_{60} cluster it is conceivable that multiple ionization and instantaneous ejection of several electrons in intense laser fields occurs simultaneously at different locations. Because the ionized electrons do not leave the molecule instantaneously further ionization through electronelectron impact can take place. When the molecule reaches a critical total charge it is no longer stable because of the repulsive force of the Coulomb interaction. Thus the molecule can undergo fragmentation in several ionic fragments by Coulomb explosion. Another explanation was recently given by Hunsche et al. [87] based on the intensity dependence of ionization and fragmentation of C₆₀ in MPI excitation experiments at 1.56 eV photon energy. They propose that multiple multiphoton excitation of the plasmon resonance around 20 eV of C_{60} [88] [89] [90] takes place prior to fragmentation or multiple ionization and Coulomb explosion.

Another experiment to study the dynamical processes after multiphoton excitation in real time has been performed. In this pump-probe experiment the laser pulses at 620 nm are split into two identical pulses using a Michelson arrangement. The transient C_{60}^+ and C_{70}^+ signal is measured as a function



of delay time between pump and probe pulses as depicted in Fig. 20a,b. Pump and probe pulses are identical, hence the signal is symmetric around zero delay. The signal level at the maximum delay time of 600 fs lies 20 % above the sum of the signal levels produced by either the pump or probe pulse alone. The comparison of the transient C_{60}^+ -signal with the measured background-free autocorrelation function (Fig. 20c) indicates a clear pump-probe effect. In contradiction to a recently performed experiment [91] our results show that the resonant intermediate is not only involved in a passive way. The time dependence of the measured ionization signal of C for delay times longer than 100 fs can be fitted by a double exponential function with time constants of 100 20 fs and 3.0 0.5 ps. Moreover in addition to the double exponential decay the transient C_{60}^+ -signal exhibits an oscillatory structure. We observe a modulation of the pump-probe signal with a time period of 30 fs.

7. Fe(CO)₅ in intense laser fields

The photochemistry of metal carbonyls has received a wealth of interest in the last decades [92]. Metal carbonyls are important photocatalysts of many organic reactions [93] and, in addition, the complete photodissociation of these compounds has been applied in microelectronics as a means of growing thin ultrapure metal films onto surfaces [94]. Therefore, it has become important in recent years to understand the mechanism by which these complex molecules photodissociate loosing one or several CO groups. In the case of polynuclear metal carbonyls, the topic is to distinguish between the metal-metal and metal-ligand cleavage dynamics. $Fe(CO)_5$ has been considered, among others, as a prototype molecule whose study could provide a good understanding of the mechanism of photodissociation. For this molecule, much theoretical information is available about its molecular and electronic structure (see for example [95] [96] and references therein) and many ab initio calculations have been performed in order to provide accurate values of the first



Fig. 21 Energetics of the $Fe(CO)_5$. The information contained in the figure is a compilation of the experimental and theoretical data concerning the neutral and ionic molecules. The absorption spectrum measured in the gas phase [98] is shown schematically and the assignments to LF and MLCT transitions are indicated with horizontal arrows.

and subsequent (up to 5) dissociation energies of the Fe-CO bonds, not only for the neutral $Fe(CO)_5$ [96], but also for the ion molecule $Fe(CO)_5^+$ [97]. The energetics of this molecule is presented in Fig.21. The gas phase absorption spectrum measured experimentally [98] is also shown schematically. This spectrum is rather structureless and exhibits a strong band centered at about 50,000 cm⁻¹ with a shoulder at 41,600 cm⁻¹ (indicated by arrows in the figure). These two bands have been assigned to metal to ligand charge-transfer (MLCT) $d \rightarrow \pi^*$ transitions. The absorption starts at about $25,000 \text{ cm}^{-1}$ and shows two weak shoulders at $30,300 \text{ cm}^{-1}$ and $35,700 \text{ cm}^{-1}$ that have been assigned to ligand field (LF) $d \rightarrow d$ transitions. The most recent experimental value for the first ionization potential of Fe(CO)5 was reported by Norwood *et al.* [99] $(7.897 + / -0.025 \text{ eV}; 63.689 \text{ cm}^{-1})$. Many studies have been published on the photodissociation of Fe(CO)₅ in the gas phase using nanosecond lasers in combination with other techniques (for a recent experiment see for example [100] and references therein). Experiments on organometallic compounds in the gas phase using ultrafast laser technology have only recently been reported by Zewail and coworkers [101]. In a cornerstone experiment on $Mn_2(CO)_{10}$, the metalmetal and metal-ligand bond cleavage dynamics, occurring on a time scale of hundreds of femtoseconds, were distinguished.

In [102], we present experiments where the photodissociation dynamics of $Fe(CO)_5$ in a molecular beam has been studied with femtosecond time resolution. Ionization transients for the parent molecule and every fragment have been measured. The analysis of these transients gives the dynamics of the photodissociation of $Fe(CO)_5$ in the neutral system at a total excitation energy of 50000 cm⁻¹. $Fe(CO)_5$ dissociates up to $Fe(CO)_2$ on a femtosecond time scale (about 100 fs). $Fe(CO)_2$ further dissociates and looses the two remaining CO-ligands on a longer time scale. The analysis of the transients indicates that the dissociation of $Fe(CO)_2$ and Fe(CO) occurs due to a sequential mechanism whereas the fragmentation of the parent molecule and the largest fragments seems to be dominated by a loss of CO ligands within about 100 fs.

In this section we will concentrate on the TOF spectra obtained at 400 nm and 800 nm for different intensities. The results are displayed in Fig.22. As can be seen from the spectra, the parent molecule, all the fragments, and even doubly charged species (if the intensity of the lasers is high enough) are observed at both wavelengths. In general, it is well known that the ion fragment distribution will depend on the wavelength, pulse duration and the intensity of the laser. For both wavelengths at the lowest laser intensities, the only mass peak observed corresponds to the parent molecule. Note that the parent molecule was not observed in previous MPI experiments using ns-laser pulses due to the ultrafast photodissociation in the excited neutral intermediate electronic states. It is interesting to note that at least six photons of 800 nm are needed to ionize Fe(CO)₅. As the laser power is increased, the different fragments start to appear. Only at very high intensities, the CO fragment is observed. In a MPI description, at least sixteen photons of 800 nm are needed to produce CO⁺ via dissociative ionisation (10 photons of 800 nm are necessary to ionize CO). In addition, that mass peak could be the combination of CO⁺ and doubly charged Fe⁺⁺, as they will appear at practically the same flight time in the TOF spectrometer. The other doubly charged species clearly observed are $Fe(CO)_3^{++}$ and $Fe(CO)^{++}$. The doubly charged $Fe(CO)_4^{++}$ and $Fe(CO)_2^{++}$ fragments would appear at practically the same time as the $Fe(CO)^{\dagger}$ and Fe^{\dagger} ions, respectively. Therefore, the $Fe(CO)^{\dagger}$



Fig. 22 Time-of-flight spectra obtained for different femtosecond laser wavelenghts and intensities on Fe(CO)₅. Top: $\lambda = 400$ nm; I_{400} approx. $5 \cdot 10^{13}$ W/cm². Bottom: $\lambda = 800$ nm; I_{800} approx 10^{14} W/cm². The mass peaks corresponding to the parent molecule and different fragment ions are labeled in the spectra.

and Fe⁺ mass peaks in the TOF spectra may show some contribution from such doubly charged species at the highest laser intensities. In a discussion based upon arguments relevant in the MPI regime, these results obtained from single pulse excitation indicate that multiphoton induced fragmentation of the parent molecule is occurring most likely in the ionization continuum, i.e. ionization precedes fragmentation. There are interesting differences between the two sets of TOF spectra taken at both wavelengths. In the 800 nm series, $Fe(CO)_2^+$ is the most favoured fragment from middle to high laser intensities (with the only exception of very high laser intensities where Fe^{\dagger} is the most prominent ion). In contrast, Fe⁺ is the dominant ion for a similar range of laser intensities in the 400 nm series as indicated in the figure caption of Fig.22. The intensities of the $Fe(CO)_4^+$ and $Fe(CO)_3^+$ fragments are larger than the one of the parent molecule when $\lambda = 800$ nm, whereas in the 400 nm series the signals of these two largest fragments are very small. In a MPI approach the different fragmentation patterns observed experimentally are most likely due to the fact that additional fragmentation channels are open by using 800 nm radiation compared to 400 nm excitation. Within this context a possible explanation for the $Fe(CO)_2^+$ to be favoured with the 800 nm laser is, that the available energy after absorption of seven photons of 800 nm will be enough for the parent ion to fragment up to $Fe(CO)_2^+$ (see Fig.21). This intermediate excitation is not possible for the 400 nm laser. On the other hand it is worthwhile to notice, that especially at the highest intensities (approximately 10¹⁴ W/cm²) used to obtain the 800 nm TOF spectra an estimate for Keldysh γ parameter yields values less than one. Therefore the onset of contributions due to ionization mechanisms that have to be attributed to the electric field strength in the focused laser beam cannot be excluded.

Conclusions

In this contribution we discuss the interaction of small molecules (Na₂, Na₃) and large molecules (C₆₀, C₇₀ and Fe(CO)₅) with intense femtosecond laser fields. The experiments are performed by combining molecular beam and femtosecond pump-probe techniques with ion- and photoelectron spectroscopy.

The sodium dimer molecule serves as a prototype molecule in the discussion of the dynamics of molecular multiphoton ionization in weak laser fields. By recording transient Na⁺₂ and Na⁺ signals two different MPI processes are observed. Time resolved photoelectron spectroscopy allows to follow molecular dynamics over a wide range of internuclear distances simultaneously. We have successfully demonstrated that vibrational wavepacket motion can be mapped by applying this combination of techniques. A detailed understanding of the molecular dynamics in the weak field limit-where perturbation theory applies-is important in order to understand changes of the transient ion and -electron spectra as a function of the laser field strength. For higher laser intensities Rabi cycling between different electronic states participating in the MPI processes are deduced from the ionization transients. The onset of Rabi cycling determines the breakdown of perturbative descriptions in MPI of molecular systems. A clear experimental indication of this Rabi cycling is the observation of a vibrational ground state

wavepacket. Additionally we find that threshold and above threshold ionization (ATI) signals are sensitive to vibrational wavepacket dynamics.

Time resolved studies were also performed with the nonlinear triatomic Na₃. In this molecule we observe a similar behaviour of the dynamics of MPI with respect to the laser intensity as seen for the diatomic Na₂. Vibrational and pseudorotational wavepacket motion on the multidimensional excited B-state potential energy surface of Na₃ is observed. In higher laser fields we again observe vibrational wavepacket motion on the electronic ground state.

We report on preliminary results of our experiments on C_{60} , C_{70} and the organometallic molecule $Fe(CO)_5$. The experiments were performed in a laser intensity regime where the generally accepted description of molecular multiphoton excitation has to be changed and recently proposed mechanisms due to the high field strengths have to be taken into account in order to explain the observations.

Acknowledgements

The authors have performed the experiments presented in this contribution together with A. Assion, L. Bañares, M. Bergt, M. Geisler, J. Helbing, B. Kiefer, D. Schulz, V. Seyfried, M. Strehle, R. Thalweiser, V. Weiss and D. Woessner. Discussions with V. Engel were stimulating and motivating. Financial support was given by the Deutsche Forschungsgemeinschaft through SFB 276 "Korrelierte Dynamik hochangeregter atomarer und molekularer Systeme" in Freiburg, through SFB 347 "Selektive Reaktionen Metall-aktivierter Moleküle" in Würzburg and through DFG Schwerpunktprogramm "Femtosekunden-Spektroskopie elementarer Anregungen in Atomen, Molekülen und Cluster" and is gratefully acknowledged.

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