

## Femtosecond time-resolved observation of above-threshold ionization in Na<sub>2</sub>

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Femtosecond pump-probe techniques are applied to the measurement of above-threshold ionization (ATI) electrons to observe the influence of vibrational wave-packet dynamics on molecular above threshold ionization in real time. When ionized by a single laser pulse structural changes in the ATI electron spectra map the changes of the vibrational wave-packet evolution in the resonant intermediate electronic states as a function of laser intensity. Molecular vibrational motion in the coherently coupled electronic states dominates the electron energy distribution rather than the energy splitting induced by Rabi oscillations. [S1050-2947(97)06703-6]

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Since its first observation in 1979 [1], 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 [2,3] and references therein). The multiple ionization of atoms in strong laser fields is under detailed investigation [4], and progress has been made to establish the connection between ATI and other intense field effects, such as high harmonic generation [5]. When molecules interact with laser fields, an additional degree of freedom is given 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 Na<sub>2</sub> using nanosecond and femtosecond laser pulses [6]. Under strong field conditions energy partition among fragments and electrons has been investigated in Cl<sub>2</sub> [7]. Using H<sub>2</sub> 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) [8]. In the study of molecular above threshold ionization, however, in spite of its observation in some diatomics [7,9–11], molecule-specific effects have so far only played a minor role. Most data can be fully explained within the concepts developed for atoms, and the additional internal degrees of freedom have not been fully explored. Only an indirect sign of the importance of vibrational motion in the ATI process in molecules has been found in the case of H<sub>2</sub>, where energy transfer to the nuclei is considered a possible explanation for the observed anomalous energy spacing of the ATI electron peaks [9]. The difficulty of detecting such 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 period of the molecule under investigation. In H<sub>2</sub>, for example, vibrational periods of approximately 15 fs correspond to pulse durations that are still difficult to produce at very high laser intensities. In Na<sub>2</sub> with vibrational periods of the order of 300 fs, on the other hand, an ultrashort, intrinsically broad laser pulse can coherently couple vibrational levels to form a wave packet 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. In this publication, we present a time-resolved observation of molecular above-threshold ionization with femtosecond pulses, and we show that the 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 wave function is reflected by a change of the electron kinetic energies. 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 zero kinetic energy (ZEKE) photoelectron spectroscopy were introduced by us [12] to study the Na<sub>3</sub> threshold ionization dynamics. Only very recently has kinetic electron detection together with fs time resolution been applied to study molecular dynamics [13,14]. Here we demonstrate that this technique allows us to follow directly the influence of the molecular vibrational motion on above threshold ionization in real time.

The experimental setup is described in detail in Ref. [15] and will only be outlined briefly. To generate the femtosecond pulses for our experiments we used two different laser systems. Bandwidth limited pump and probe pulses of 40 fs at 618 nm were derived from a regenerative amplified 1 kHz Ti:sapphire system followed by optical parametric generation and pulse compression in a prism compressor. The beam was split into two equal parts in a Michelson-type setup with a variable time delay between the two pulses. By weakly focusing with a 300 mm achromatic lens, peak intensities of approximately 10<sup>11</sup> W/cm<sup>2</sup> were obtained. More energetic 80 fs pulses for the single pulse experiments were provided by an amplified colliding pulse mode-locked (CPM) laser. The sodium dimers were produced predominantly in the  $v''=0$  vibrational level of the  $X^1\Sigma_g^+$  ground state in a supersonic molecular beam. A linear time-of-flight (TOF) mass spectrometer was used for both electron and ion spectroscopy. The energy resolution of the electron spectrometer (50 meV for 1 eV and 500 meV for 5 eV electrons) was sufficient to resolve the vibrational effects discussed in this paper. However, ponderomotive shifts could not be detected, as the ionization threshold at  $I=10^{12}$  W/cm<sup>2</sup> lies less than 0.04 eV above its zero field value. Ion and electron time-of-flight spectra were recorded under similar conditions and averaged over several thousand laser shots. The ion signal consists of

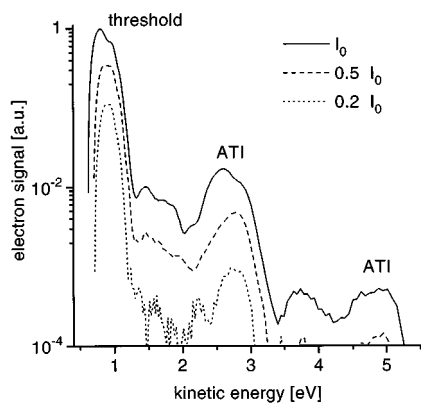


FIG. 1. Threshold and above threshold ionization (ATI) electron spectra of  $\text{Na}_2$  for three different laser intensities ( $I_0 \approx 10^{12}$   $\text{W}/\text{cm}^2$ ).

atomic and molecular ions. The  $\text{Na}^+$  signal is dominated by ionic fragments having kinetic energy from photodissociation processes [6] and is an order of magnitude smaller than the  $\text{Na}_2^+$  signal. Photoelectrons arising from photoionization of sodium atoms can thus only lead to minor substructures in our ATI spectra. Multiphoton excitation of  $\text{Na}_2$  has been investigated in detail in the 620 nm wavelength regime and a complete discussion of the excitation scheme can be found in Refs. [6] and [16]. Starting from the ground state  $X^1\Sigma_g^+(v''=0)$  the ionic ground state  $2\Sigma_g^+$  is reached via the two resonant neutral electronic states  $A^1\Sigma_u^+(v'=11-15)$  and  $2^1\Pi_g(v^*=16-20)$ . Using the split-operator FFT method, previously employed to study the interaction of the  $\text{Na}_2$  molecule with fs pulses [17], we calculated the time evolution of vibrational wave functions in these electronic states nonperturbatively, by numerically integrating the time-dependent Schrödinger equation. To obtain photoelectron spectra, the three neutral bound states were coupled perturbatively to the discretized ionization continuum. Up to the highest intensities used in our calculations this yields the same results as more involved continuum coupling techniques [18], which were applied to the  $\text{Na}_2$  molecule by Meier and Engel [19].

Figure 1 shows the ATI spectra of  $\text{Na}_2$  at three different intensities recorded with 80 fs pulses centered at 618 nm (8 nm bandwidth, FWHM). Clearly visible are three peaks at 0.9 eV, 2.9 eV, and 4.9 eV separated by the photon energy. These energies correspond to ionization with three (threshold), four, and five photons of the molecule in the  $v''=0$  level of the electronic ground state. In addition, electrons of slightly lower kinetic energy are formed with increasing laser intensity. An enlarged view of the threshold electron peak shows this behavior in more detail (left-hand side of Fig. 2). While the fast electrons (0.9 eV) are present at every laser intensity, slower electrons appear, and their contribution to the total signal increases as the intensity increases. The same is also observed for the ATI peaks. This behavior is well reproduced by our quantum mechanical calculations for which a maximum intensity of  $I_0 = 3 \times 10^{11}$   $\text{W}/\text{cm}^2$  was chosen to best fit our experimental data (right-hand side of Fig. 2). An electron distribution peaked at 810 meV and 940 meV has also been observed in previous low intensity experiments [6] and was explained by the two Franck-Condon

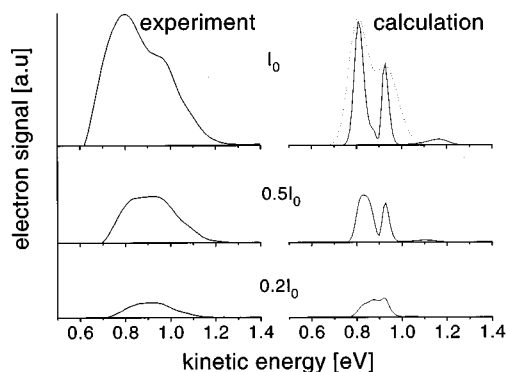


FIG. 2. Enlarged view of the threshold ionization peak (left) and results of quantum-mechanical calculations (right). The dotted line is obtained by taking into account the resolution of the spectrometer.

maxima for the neutral-free transition from the  $2^1\Pi_g$  state ( $v^*=20$ ) to the  $v^+=14,15$  and  $v^+=24,25$  vibrational levels of the ionic ground state. The spectra in Figs. 1 and 2 can best be understood by making use of the Franck-Condon principle. Since the nuclear kinetic energy is conserved during electronic transitions, the transition from the  $2^1\Pi_g$  electronic state to the ionic ground state yields decreasing electron energies with increasing internuclear separation. At the internuclear distance of the neutral ground state ( $v''=0$ ) fast electrons (0.94 eV) are formed, while slow electrons (0.80 eV) are formed at the outer classical turning point of the  $2^1\Pi_g$  potential. Consequently, the electron kinetic energy can serve as a measure of the internuclear distance at which ionization takes place, as has been discussed theoretically in [18] and [20]. Excitation with an ultrashort laser pulse of low intensity ( $6 \times 10^{10}$   $\text{W}/\text{cm}^2$ ) leaves the nuclei in the molecule essentially fixed. They have no time to move apart before the laser is turned off. Ionization takes place with the nuclear wave function peaked at the nuclear separation of the ground state ( $v''=0$ ) yielding electrons of 0.9 eV, and 2.9 eV or 4.9 eV. In an intense ultrashort laser field a considerable amount of population is transferred to the excited states already during the leading edge of the laser pulse. The nuclear wave function can start to spread earlier and ionization and above threshold ionization can take place over a wider range of internuclear distances leading to the appearance of slow photoelectrons in the electron spectra in Fig. 1. This interpretation is supported by looking at the population in the excited  $2^1\Pi_g$  electronic state calculated as a function of time and nuclear separation  $R$  (Fig. 3). In the upper graph the maximum  $\Pi$ -state population is at small internuclear distances during the time of interaction. When the intensity is increased by a factor of 5 (lower graph) a vibrational wave packet is seen to form and propagate to almost its outer turning point before the laser of 80 fs pulse duration is turned off. This is a nonperturbative effect due to the strong coupling of the bound states by the intense laser field. The population maximum in an excited state of the molecule can only start to move to larger internuclear distances, when the rate of population transfer from the ground state is beginning to decrease. In the perturbative regime this will always happen at the laser pulse maximum, independent of the intensity. In a strongly coupled system, however, a depleting ground state

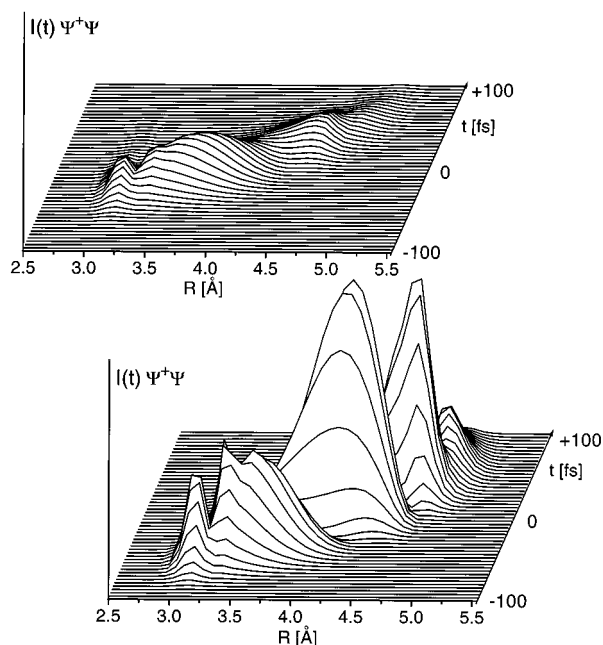


FIG. 3. Wave-packet evolution in the  $2^1\Pi_g$  state during the interaction with an 80 fs laser pulse. Top:  $I=6\times 10^{10}$  W/cm $^2$ ; bottom:  $I=3\times 10^{11}$  W/cm $^2$ . The plots have been multiplied by the pulse envelope  $I(t)$ , in order to relate them directly to the ionization probability as a function of  $R$ .

can cause a wave packet in an excited state to propagate long before the molecule is exposed to the maximum laser intensity. Coherent coupling of the neutral states also causes the amplitude variations in Fig. 3, which reflect Rabi oscillations between the  $2^1\Pi_g$  and the  $A^1\Sigma_u^+$  electronic states. These Rabi cycles lead to a splitting in the calculated electron spectra of Fig. 2 and give rise to the small peak at 1.18 eV [19]. The interferences which cause this splitting are, however, very sensitive to spatial intensity variations over the focused laser beam [21] and only the dynamical effect discussed above can give rise to the dominance of slow photoelectrons in the ATI spectra at the highest intensity. The small double structure (1.5 eV and 1.8 eV) repeated at about 3.7 eV (not resolved) for high laser intensities in Fig. 1 is tentatively attributed to ionization via high-lying doubly excited neutral states.

In the past, we have introduced the technique of recording transient threshold ionization signals by femtosecond ion and ZEKE electron spectroscopy [16,12]. We have applied the femtosecond pump-probe technique to time-resolved measurements of energetic electrons from threshold and above threshold ionization using 40 fs pulses at 618 nm. The transient signal of electrons from threshold ionization can be seen in the lower part of Fig. 4. The transient shows an oscillatory behavior, which is dominated by two frequencies of approximately  $110\text{ cm}^{-1}$  and  $90\text{ cm}^{-1}$  with a smaller contribution at  $157\text{ cm}^{-1}$ . The origin of these frequencies has already been discussed and assigned in the context of our previous measurements of ions [17]. The intense pump pulse is preparing vibrational wave packets in the  $A^1\Sigma_u^+$  ( $110\text{ cm}^{-1}$ ) and  $2^1\Pi_g$  ( $90\text{ cm}^{-1}$ ) excited states as well as in the  $X^1\Sigma_g^+$  ( $157\text{ cm}^{-1}$ ) state. At five times higher pump and

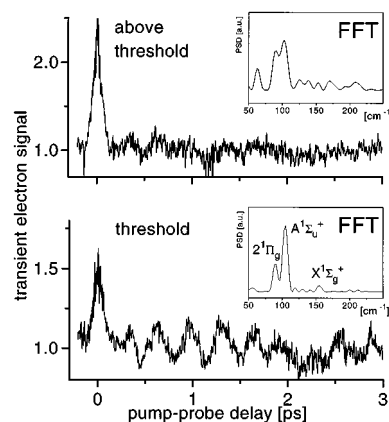


FIG. 4. Transient electron signal of electrons with energies between 2.7 eV and 3.1 eV (first order ATI) obtained with 40 fs pulses of approximately  $10^{11}$  W/cm $^2$  (top) and for energies between 0.6 and 1.1 eV (threshold ionization) at a five times lower intensity (bottom).

probe pulse intensities it is possible to record the transient electron signal even for electrons from above threshold ionization, shown in the upper part of Fig. 4. Again, the observed pump-probe signal is composed of the vibrational frequencies of wave packets propagating in the electronic  $A^1\Sigma_u^+$  ( $90\text{ cm}^{-1}$ ) and  $2^1\Pi_g$  ( $110\text{ cm}^{-1}$ ) states. This is a clear confirmation of our findings in the single pulse experiments, that the molecular ATI is directly sensitive to the vibrational motion of the nuclei. Deformation of the potential curves in more intense laser fields may cause the wave packet dynamics to be probed over a wider range of internuclear distances and can be made responsible for the relatively small modulation depth of the transient ATI signal. The contribution of the  $60\text{ cm}^{-1}$  frequency to the transient ATI signal is believed to be due to vibrational wave packet motion in the  $4^1\Sigma_g^+$  shelf state of  $\text{Na}_2$  [22], which may be reached with two 618 nm photons. Slightly lower frequencies have already been observed in earlier time-resolved measurements of ions produced via this state in higher laser fields [23].

In summary, we have presented electron spectra obtained with single laser pulses of 80 fs duration which show a dramatic change in structure when the laser intensity is increased beyond a regime, where the coherent coupling of the resonantly excited neutral electronic states becomes important. These changes in the electron spectra are directly related to changes in the vibrational motion of the  $\text{Na}_2$  molecule because the electron kinetic energy depends on the internuclear distance at which ionization occurs. ATI electron signal and electrons from threshold photoionization exhibit the same change in structure as a function of laser intensity and are thus shown to be equally affected by the vibrational wave packet motion. Supported by time-dependent calculations, we can assign the formation of the fast electrons to the leading edge of the ultrashort laser pulse, when the nuclear wave function is peaked at the ground state equilibrium position. Lower energy electrons are formed at later times during the pulse, when the vibrational wave packet has propagated to larger internuclear distances. This demonstrates that the vibrational degree of freedom in a mol-

ecule can yield time-resolved information about the ATI process even in experiments with single femtosecond laser pulses. When we apply femtosecond pump-probe techniques to the measurement of ATI electrons, we observe the vibrational frequencies of the resonant intermediate states in the transient ATI signal and thus show directly that molecular above threshold ionization depends on the vibrational motion

of the molecule.

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