High laser field effects in multiphoton ionization of Na_2. Experiment and quantum calculations

T. Baumert, V. Engel, C. Meier and G. Gerber

Fakultät für Physik, Universität Freiburg, W-7800 Freiburg im Breisgau, Germany

Femtosecond pump/probe multiphoton ionization experiments on Na_2 molecules are performed. The dependence of the total Na_2^+ ion signal on the delay time and the intensity of the femtosecond laser pulses is studied in detail. It is observed that molecular vibrational wavepacket motion in different electronic states dominates the time dependence of the ion signal. For higher laser intensities the relative contributions from the A $^1\Sigma_u^+$ and the 2 $^1\Pi_g$ states change dramatically, indicating the increasing importance of a two-electron versus a one-electron process. For even stronger fields (10^{12} W/cm^2) a vibrational wavepacket in the electronic ground state X $^1\Sigma_g^+$ is formed and its dynamics is also observed in the transient Na_2^+ signal. Time-dependent quantum calculations are presented. The theoretical results agree well with the experiment.

1. Introduction

The availability of short and strong laser pulses has opened a new and exciting field of spectroscopy (for a collection of recent work see refs. [1,2]). It is now possible to detect vibrational and rotational motion of small molecules in real time [3,4]. Experiments are performed which monitor fluorescence from an excited electronic state as a function of delay time between a femtosecond pump and probe laser pulse. By adjusting the laser wavelength properly molecular wavepacket motion can be detected at different internuclear distances. It is also possible to use femtosecond pulses to ionize the molecules under consideration. Then the total ion signal measured as a function of the delay time between pump and probe pulses reflects the molecular dynamics as well. The latter technique has been used to investigate the multiphoton ionization of the sodium dimer [5,6]. It was found that different excitation schemes leading to ionization exist which include several electronic states of the molecule. These experiments were performed with moderate laser intensities (5×10^{10} W/cm^2).

Correspondence to: V. Engel, Fakultät für Physik, Universität Freiburg, W-7800 Freiburg im Breisgau, Germany.

Other recent experiments investigated multiphoton processes in H_2 [7,8] and H_2^+ [9,10]. In these measurements field strengths up to 10^{14} W/cm^2 were employed. New effects like "bond-softening" and "above threshold dissociation" have been discovered [11].

In this Letter, we investigate how the intensity of the laser effects the dynamics of molecular vibrational wavepackets in several electronic states of Na_2 and how that is reflected in the transient Na_2^+ signal, recorded as a function of the delay time between pump and probe laser pulses.

Two major multiphoton processes have been identified when weaker fields (5×10^{10} W/cm^2) and a peak wavelength of 627 nm are employed [5]. The total ion signal contains a strong oscillating contribution with a period of 306 fs. The origin of this periodic variation of the signal is sketched in fig. 1A, which contains the potential energy curves of the electronic states participating in the ionization process. A vibrational wavepacket is prepared by a one-photon transition from the ground electronic X $^1\Sigma_g^+$ state. The packet moves back and forth between the classical turning points of the A $^1\Sigma_u^+$ potential. The two-photon ionization is most probable if the wavepacket is close to the inner turning point and less probable if it is located in the vicinity of the
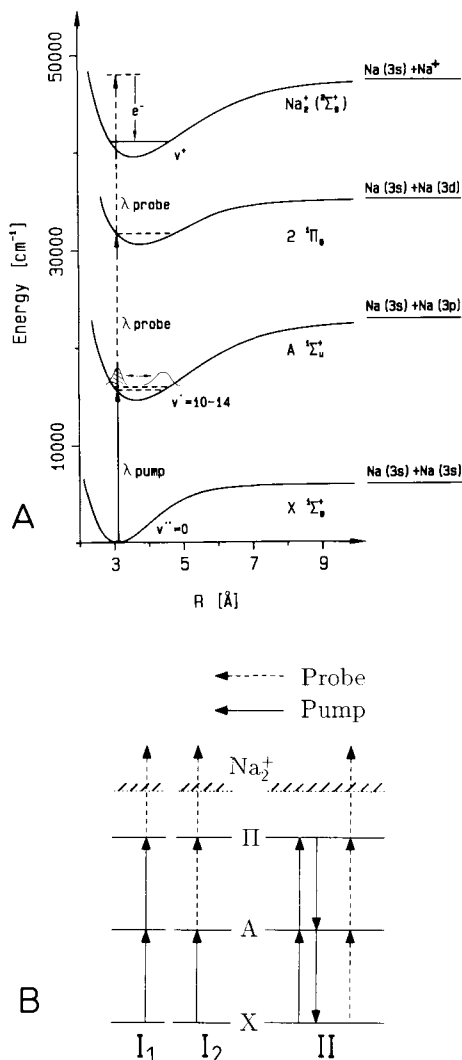
Fig. 1. (A) Potential energy curves of the Na_2 molecule. The one-photon pump and two-photon probe ionization process (I_2) is indicated. (B) Schematic illustration of the multiphoton pump/probe ionization of Na_2. The horizontal lines represent the different electronic states shown in (A). For weak fields (I_1, I_2) two major ionization pathways are shown. In the case of strong fields (II) stimulated emission processes become important. Some of these processes are indicated.

outer turning point [6,12]. This results in a periodic variation of the ion signal as a function of the delay time between the pump and probe pulse.

The pump pulse simultaneously prepares another wavepacket in the $2\,{}^1\Pi_g$ electronic state via a two-photon excitation process. Direct photoionization out

of this excited electronic state results in a time-dependent ion signal [6,13]. An indirect ionization process out of the Π state takes place by excitation of a second electron and formation of a doubly excited Rydberg state Na_2^{**} (nl, $n'l'$) which decays via electronic autoionization and autoionization induced fragmentation. This Π-state contribution is 180° out of phase with respect to the contribution originating in the A state and has a period of about 370 fs. The two contributions obtained for weak laser fields (designated as I_1 and I_2, are illustrated in fig. 1B. The experimental results in this situation were successfully interpreted by quantum calculations which used time-dependent perturbation theory [12]. However for higher laser intensity perturbation theory breaks down and a non-perturbative approach has to be taken. In this case stimulated emission processes and direct three- (or even higher order) photon transitions become important during the time the ultrashort pulses interact with the molecules. This is indicated (as case II) in fig. 1B. During the pump process the population in the $X\,{}^1\Sigma_g^+$, $A\,{}^1\Sigma_u^+$ and $2\,{}^1\Pi_g$ electronic states changes essentially. The shapes and phases of the corresponding wavepackets depend critically on the laser pulse parameters (width, intensity and wavelength). An intense probe pulse is able to ionize the molecule out of each of the relevant electronic states. The stimulated emission processes induced by the probe pulse are not shown in fig. 1B.

Below we will present time-dependent quantum calculations to interpret the features observed in the femtosecond experiments on Na_2.

2. Experiment

The experimental apparatus is described in detail in ref. [6]. We employ a supersonic beam of sodium dimers which is produced by expanding pure sodium from an oven operated at 1000 K. Na_2 is produced in its electronic $X\,{}^1\Sigma_g^+$ ground state and predominantly in the vibrational ground state $v''=0$ and small rotational states J''. Molecular ions are formed by a pump and a time delayed probe femtosecond laser pulse interacting with the Na_2 molecular beam. The femtosecond pulses are generated in a colliding pulse mode-locked (CPM) ring dye laser. Since the CPM

pulse energies are only ≈ 100 pJ we employed a bow-tie amplifier pumped by a 308 nm excimer laser synchronized to the CPM. The pump and probe pulses enter the interaction region collinearly with the same intensity and polarization and perpendicular to the molecular beam. Molecular ions are detected with a TOF spectrometer arranged perpendicular to the beam. The experiments were performed with pulses of 80 fs duration and a central wavelength of 624 nm. The maximum intensity I_0 used in these experiments was $\approx 10^{12}$ W/cm^2. The pump/probe delay was varied in steps of 22 fs and a boxcar integration over 300 laser shots was taken at each delay time.

3. Theory

To simulate the experiment we have integrated the time-dependent Schrödinger equation numerically. The time evolution of the wavefunctions in the three relevant electronic states (the X $^1\Sigma_g^+$, A $^1\Sigma_u^+$ and 2 $^1\Pi_g$ states, henceforth simply denoted by X, A and Π) is calculated by solving

$$\begin{pmatrix} H_X & W_{XA} & 0 \\ W_{AX} & H_A & W_{A\Pi} \\ 0 & W_{\Pi A} & H_\Pi \end{pmatrix} |\psi(t)\rangle$$

$$= i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle . \tag{1}$$

The field–matter interaction was taken to be

$$W_{nm} = \lambda \mu_{nm} f(t) \cos(\omega t) , \tag{2}$$

where μ_{nm} denotes the component of the X–A (A–Π) transition dipole moments [14] along the polarization vector of the field. $f(t)$ is a Gaussian envelope function of 80 fs width (fwhm) and ω was chosen to match the experimental wavelength of 624 nm. The parameter λ controls the intensity of the laser. Eq. (1) was solved exactly with the split-operator technique [15,16] as described elsewhere [17]. At $t=0$ the wavefunction is the vibrational ground state $v''=0$ in the electronic ground state of Na$_2$. The potential curves of the neutral molecule were taken from refs. [18–21]. We applied the rotating-wave approximation which was not essential for the results presented below but reduces the numerical effort.

The total ion signal obtained as a function of delay time between pump and probe pulse was calculated as well. For this we coupled the electronic state system (A and Π only, see below) to the ionization continuum associated with the electronic ground state of the molecular ion [22]. This was done using a method introduced by Burkey and Cantrell [23,24] which was successfully applied to molecular pump/probe processes by Seel and Domcke [25]. The method was combined with the split-operator technique. The details of this rather involved calulation will be presented in a separate paper [26].

4. Results

The transient Na$_2^+$ spectrum was measured for three different intensities of our laser pulses. They were chosen to be $I_0=10^{12}$ W/cm^2, $0.3I_0$ and $0.1I_0$, respectively. The results are displayed in the upper part of fig. 2 where we plot the total ion yield as a function of the delay time between pump and probe laser pulses. Because the experiment uses only one laser colour the spectra are symmetric with respect to zero time delay. The curves exhibit periodic oscillations with different periods for different laser intensities. The lower part of fig. 2 contains the Fourier transform of the three spectra. For the lowest intensity the ionization signal and its Fourier transform are similar to the curves obtained for an intensity of 5×10^{10} W/cm^2 which were discussed in section 1 and in refs. [5,6]. The frequency analysis yields two main peaks. The large peak around 110 cm^{-1} is associated with vibrational motion in the A state and the smaller peak around 90 cm^{-1} corresponds to the Π state vibrational period. Thus wavepacket dynamics in two electronic states is probed in the experiment. Two features can be taken from fig. 2:

– the Π-state contribution is enhanced relatively to the A-state contribution if the intensity is increased,

– for the highest intensity another major peak around 156 cm^{-1} appears in the Fourier spectrum. This frequency corresponds to the average vibrational spacing between the $v''=0$–3 vibrational levels in the electronic ground state.

To understand the experimental results in more detail quantum-mechanical calculations were car-
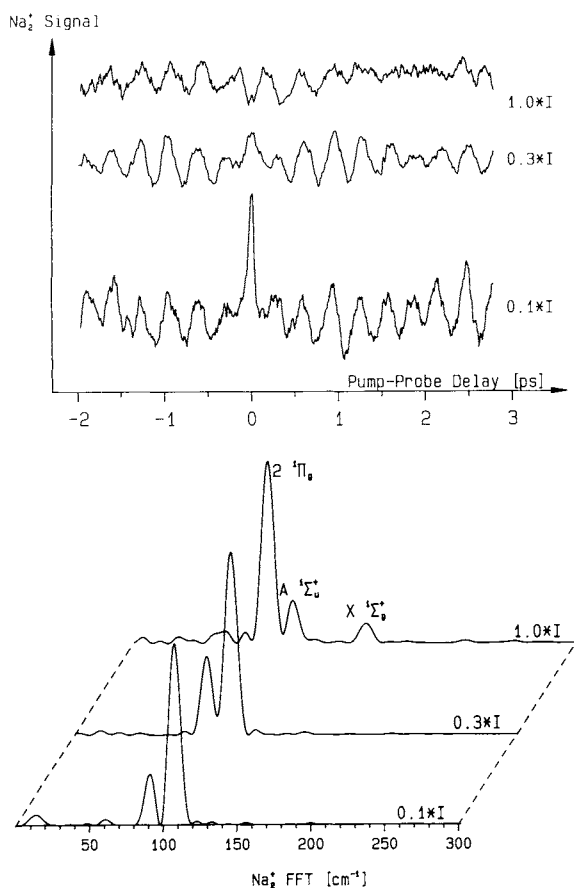
Fig. 2. The upper part of the figure shows transient Na_2^+ spectra as a function of delay time between the femtosecond pump and probe pulses. Different intensities were used, as indicated. Below, the Fourier transforms of the transient spectra are displayed.

ried out. The excitation process initiated by the first laser pulse was simulated by solving eq. (1) for different intensities of the pump pulse. We have used an intensity of $I_0 = 3.0 \times 10^{10}$ W/cm^2 in the calculation. It is not the intensity alone but also the transition dipole moment which enters in the interactions W_{nm} (eq. (2)). Since the absolute value of the transition dipole moment for the Π-ion transition is not known we have set it to be a factor of 10 lower than the transition dipole moment μ_{AX} at a distance of $R = 4$ Å. Therefore there is an arbitrariness in choosing the strength of the molecule–laser interaction which however does not change the main results. We adjusted the parameter λ in such a way that the A-state peak, which is obtained by taking the

Fourier transform of the calculated time-dependent ion signal in the $0.1I_0$ case, dominates the Π-state contribution, as is seen in the experiment. In fig. 3a we plot the change of the populations in the electronic A and Π states during the time the 80 fs pump pulse interacts with the molecule. Note that the sum of the X-, A- and Π-state populations adds up to one. Also shown is the Gaussian envelope function $f(t)$ of the pulse. For an intensity of $0.1I_0$ the A state is populated preferentially. As one would expect from perturbation theory, transitions to the higher electronic state (Π), which can be reached by the absorption of two photons are less probable. This changes with increasing intensity: for $0.3I_0$ A and Π states are almost equally populated. For even higher intensities (lower panel) one obtains inversion and finds a higher population in the Π state. The same effects are obtained by fixing the intensity and changing the length of the laser pulse since it is the product of interaction time and field strength which determines the relative population of the different states. The whole process is a reminisence of the Rabi two- (or three-) level problem, however more complicated since the vibrational degree of freedom is present and finite pulse durations are under consideration.

The ratio with which the A and Π states are populated when different intensities are employed seems to explain the experimental findings: with increasing intensity the Π state is preferentially populated and the dynamics of the Π-state wavepacket dominates the time variation of the transient ionization signal. To confirm this we have calculated the total ionic population as a function of delay time up to 5 ps and Fourier transformed the calculated curves to compare them with the experimental results. We coupled the X, A and Π states for the pump process and took only the latter two to calculate the ion signal. If the X state is included in the probe process, the signal shows a rich interference structure resulting from the coherent sum of the different ionization pathways. The details of these interferences are not understood properly yet and they are currently under investigation [26]. Figs. 3b and 3c compare the experimental frequency spectra with the theoretical results. Note that the ionization process which includes the doubly-excited Rydberg state mentioned in section 1 is not included in our theoretical model. As men-
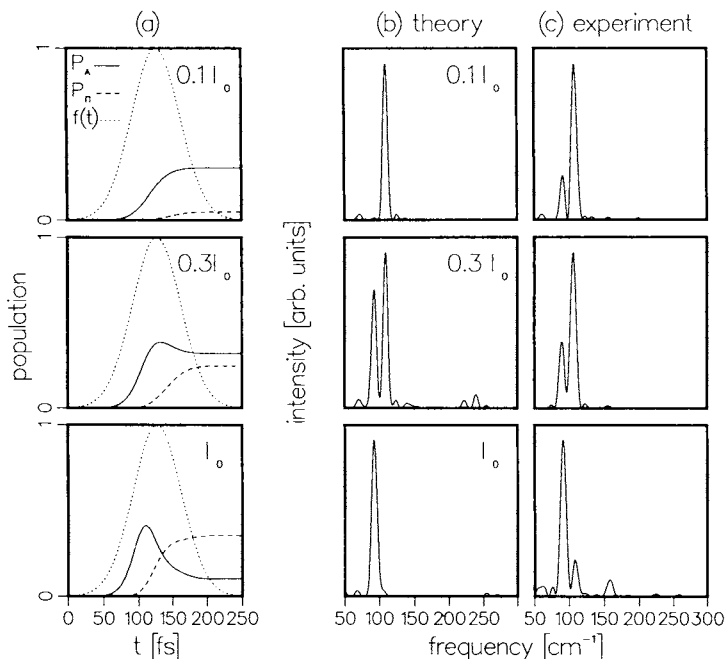
Fig. 3. (a) Time evolution of the populations in the electronic A state (straight line) and the Π state (dashed line). The envelope of the 80 fs Gaussian pulse is shown as a dotted curve. The Fourier spectra of the calculated ionic populations (b) and of the measured transient ion signals (c) are shown for different intensities.

tioned, the direct photoionization out of the Π state as a single process does not yield a time-dependent ion signal [13]. For strong fields however the calculations show that a time dependence is introduced by stimulated emission processes down to the A state at times, when the wavepacket is close to the inner turning point of the Π-state potential. This is the region where resonant transitions are possible [6,13]. Nevertheless, the fact that the Π state is more populated with increasing field strength is reflected in the (incomplete) ion signal. The theoretical and experimental Fourier spectra in fig. 3 show the same trend although the relative heights of the signals are slightly different. With increasing intensity the Π-state contribution dominates the ionization signal. Of course the theoretical curve does not show any contribution from the electronic ground state which was decoupled in calculating the ion signal.

How do we understand the origin of the ground state peak in the experimental spectrum? The most straightforward explanation is that a vibrational wavepacket in the electronic ground state of Na_2 is

built by a stimulated emission process. This possibility has been studied for a diatomic molecule theoretically before [27] and it remains to be shown that this occurs in the present case. Therefore we have calculated the ground state vibrational populations:

$$f_{v''} = | \langle \phi_{v''} | \psi(t_1) \rangle |^2 , \qquad (3)$$

where $\phi_{v''}$ are the vibrational eigenfunctions in the electronic X state and $\psi(t_1)$ is the X-state component of the total wavefunction appearing in eq. (1), calculated at a time t_1 after the pump pulse has passed the molecular sample. The ratio f_1/f_0 for a pump pulse intensity of $0.1I_0$ is 0.009. Thus only the vibrational ground state is populated. For $0.3I_0$ one finds the ratios $f_{v''}/f_0$ to be 1, 0.452, 0.036 and 0.001 and in the case of the highest intensity one obtains 1, 0.833, 0.063 and 0.018 for $v'' = 0$, 1, 2 and 3, respectively. With increasing intensity the distribution becomes broader and the $v'' = 1$ state becomes almost equally populated for the full intensity I_0. To estimate if this is sufficient to see any molecular motion the coordinate expectation value in the X state as a function
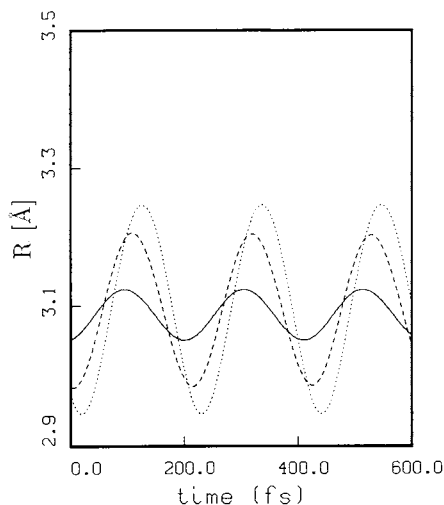
Fig. 4. Bond-length expectation value in the electronic ground state as a function of time. The curves were calculated with the time-dependent X-state wavefunction after pulses of intensity $0.1I_0$ (straight line), $0.3I_0$ (dashed line) and I_0 (dotted line) interacted with the Na_2 molecules.

of time was calculated. The results are plotted in fig. 4. Fig. 4 illustrates that for all intensities one sees a periodic motion with a period of 210 fs. The amplitude of the oscillation increases with increasing intensity and is about 0.3 Å in the case of the strongest pulses. Obviously this spatial variation of the ground state wavepacket is strong enough to be seen in the ion signal. Note also that the equilibrium distance around which the periodic variation occurs shifts to larger internuclear distances with increasing laser intensity. This reflects the anharmonicity of the ground state potential.

The formation of the X-state wavepacket observed in the present experiment is similar to the preparation of "Rydberg anti-wavepackets" observed in atomic barium [28]. In the latter case a linear combination of atomic Rydberg states is prepared by a stimulated Raman process initiated by intense picosecond laser pulses.

5. Summary

In conclusion we have shown that for different field strengths of the femtosecond laser pulses various electronic states of the sodium dimer are populated differently. This is clearly seen in the pump/probe ionization signal. For lower intensities the A state is preferentially populated by the pump pulse and the A-state wavepacket motion dominates the ion signal. For the highest intensity used in this experiment, the contribution of the Π-state motion is strongest. The reason for this is that the pump pulse populates the Π state more than the A state. Thus by changing the intensity of the laser one may selectively control the relative strength of the direct one-electron photoionization versus the two-electron excitation and electronic autoionization process.

For strong enough fields it is possible to prepare a wavepacket within the electronic ground state via stimulated emission. Its dynamical behaviour is also seen in the ion signal. Although the latter effect has been predicted theoretically [27] it is, to our knowledge, the first time that it has been observed in molecular physics.

Acknowledgement

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