Femtosecond Time-Resolved Molecular Multiphoton Ionization: The Na2 System

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We report here the first experimental study of femtosecond time-resolved molecular multiphoton ionization. Femtosecond pump-probe techniques are combined with time-of-flight spectroscopy to measure transient ionization spectra of Na_2 in a molecular-beam experiment. The wave-packet motions in different molecular potentials show that incoherent contributions from direct photoionization of a singly excited state and from excitation and autoionization of a bound doubly excited molecular state determine the observed transient ionization signal.

Multiphoton ionization of diatomic molecules has been studied recently by a variety of techniques and is well understood [1]. The ionization is predominantly due to resonance-enhanced multiphoton processes. Dynamical aspects of the interaction of laser radiation with molecules have been studied by several groups in great detail [2]. The ionization and fragmentation of H_2 via unbound doubly excited states is a particularly interesting example [3]. We recently performed femtosecond spectroscopy of molecular autoionization and fragmentation of Na_2 [4].

Here, we report novel time-resolved studies of molecular (Na_2) multiphoton ionization using femtosecond pump-probe techniques. In an independent study, Dantus, Janssen, and Zewail have resolved the femtosecond dynamics of wave-packet motion in I_2 using multiphoton-ionization mass spectrometry in a molecular beam [5]. Our results reveal unexpected features of the dynamics of the absorption of many photons by a diatomic molecule. The time-resolved motion of wave packets in different molecular potentials clearly shows two different multiphoton-ionization processes rather than two different internal ionization pathways. The direct photoionization of a singly excited Rydberg state and the two-electron excitation of bound molecular states with subsequent electronic autoionization result in different final ionic states. The measured transient ionization spectra (Fig. 1) show that both processes determine the time evolution of molecular photoionization. For the first study of the time-resolved dynamics of molecular multiphoton ionization in a molecular-beam experiment applying femtosecond-laser pump-probe techniques, we have chosen the spectroscopically well-studied Na_2 [6] as a prototype.

Femtosecond pump-probe studies in the gas phase have been pioneered by Khundkar and Zewail [7]. Relevant to this work, they investigated the motion of wave packets in molecular potentials for a variety of neutral molecules (e.g., NaI, I_2) by detecting the emitted fluorescence from excited states.

In our femtosecond-laser–molecular-beam studies of multiphoton ionization of Na_2, we combined several experimental techniques. Femtosecond laser pulses were used to induce and probe the molecular transitions. A supersonic molecular beam generated the Na_2 molecules

and restricted the initial states to $v''=0, J''$. Time-of-flight (TOF) spectroscopy was used to determine the mass of the ions and the released kinetic energy of the ionic fragments. Femtosecond pulses were generated in a home-built colliding-pulse mode-locked ring dye laser and amplified in a two-stage dye amplifier, pumped by an excimer laser (Lambda Physik LPX 120). A Michelson arrangement delayed the probe laser relative to the pump laser. Both the pump and probe laser beams enter the interaction region collinearly, with the same polarization, and perpendicular to the molecular beam. We used recompressed laser pulses of 70-fs duration, of about 100-Å spectral width centered at 627 nm, and of 0.2-μJ energy ($I \approx 50$ GW/cm^2) for both the pump and the probe. The laser pulse energy was kept this low to simplify the study of the basic physical processes. The laser system and the experimental arrangement are discussed in detail elsewhere [8]. The ion TOF spectrum we obtain from the interaction of the femtosecond laser pulses with a supersonic sodium molecular beam consists of "slow" and "fast" Na ionic fragments, a strong $Na_2{}^+$ signal, and cluster ions $Na_n{}^+$ up to $n=8$.

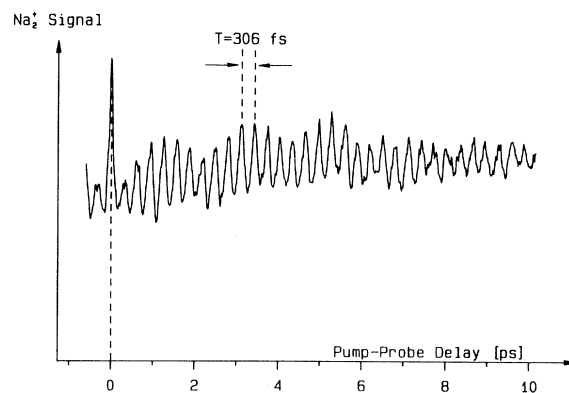The observed femtosecond pump-probe delay spectrum

FIG. 1. Transient multiphoton-ionization spectrum of Na_2. The envelope intensity variation and the oscillatory structure of the $Na_2{}^+$-ion signal reveal two contributions out of phase by 180° related to wave-packet motions with 306- and 363-fs oscillation periods.

of the molecular-ion signal Na_2^+ is shown in Fig. 1. The spectrum shows a beat structure superimposed on a strong modulation of the ionization signal. Because pump and probe are identical, the signal is symmetric around zero time delay. The modulation period estimated from the peak-to-peak separation is $T_A \approx 306$ fs. Evident from the beat structure in Fig. 1, there are two frequencies involved and therefore there are two contributions to the transient-ionization spectrum, and the envelope intensity variation reveals them to be 180° out of phase. These are the most important findings of this experiment. With the given experimental parameters, the dynamics can best be understood in terms of the motion of wave packets in bound molecular potentials. Phase-shifted oscillatory motion of a wave packet has also been observed by Bowman, Dantus, and Zewail [9] in multiphoton excitation and depletion experiments with molecular iodine.

A Fourier analysis of the spectrum in Fig. 1 yields two major groups of frequencies, one centered at 108.7 cm^{-1}, from 106.9 to 110.5 cm^{-1}, and a second centered at 92.0 cm^{-1}, from 90.2 to 93.9 cm^{-1}.

From the transient-ionization spectrum (Fig. 1) and the Fourier frequencies, we identify two major contributions to the multiphoton ionization of Na_2. The Na_2 molecules in the ground state $X\,^1\Sigma_g^+$ and $v''=0$ are pumped into excited electronic states by a laser pulse whose 70-fs duration is much shorter than the vibrational period of Na_2. The classical vibrational period for the $v'=10-14$ states of the excited electronic A state are $T_A \approx 304.6-310.6$ fs. Thus, the pump laser forms a coherent superposition of the vibrational eigenstates $v'=10-14$ in the $A\,^1\Sigma_u^+$ state. The vibrational wave packet so created at the inner turning point oscillates between the classical turning points of the A-state potential well. The motion of the wave packet is determined by the vibrational energy spacings of the A state [10], which are 109.5, 108.8, 108.1, and 107.4 cm^{-1} for the levels $v'=10$ to $v'=14$. These values agree with the frequency components derived from the Fourier analysis. The A-state wave packet is transferred via the $2\,^1\Pi_g(3s,3d)$ Rydberg state into the Na_2^+ $X\,^2\Sigma_g^+$ ionization continuum by the time-delayed probe pulse. From the oscillatory Na_2^+ signal (period $T_A \approx 306$ fs) which is in phase with the preparation of the wave packet at the inner turning point at $t=0$, the motion of the wave packet in the A state is evidently probed only near the inner turning point. Probing at the outer turning point would result in a 180° phase shift, which, however, is not observed with the 306-fs motion. Note that a direct transition from the A state into the Na_2^+ $X\,^2\Sigma_g^+$ ionization continuum results in a time-independent ionization signal, because the shapes of the potentials are so similar. Analysis based on difference potentials shows that only through the resonant intermediate $2\,^1\Pi_g$ state, which acts as a "window" for the two-photon-probe transition, can the time-dependent motion of the wave packet be seen [11]. The relevant Rydberg-

Klein-Rees potential curves and the preparation and probing of the A-state wave-packet motion are shown in Fig. 2. The two-photon-probe process occurs periodically at the inner turning point after each round trip.

Based on the derived second set of Fourier components of about 92 cm^{-1} ($T_\Pi \approx 363$ fs) and the fs-laser wavelengths around 627 nm, we conclude that in the second ionization channel the pump laser creates a coherent superposition of vibrational levels in the $2\,^1\Pi_g$ state by a two-photon transition. The absorption of two laser photons induces transitions from $v''=0$ to vibrational levels $v^*=11$ to $v^*=18$. Using the known spectroscopic constants of the $2\,^1\Pi_g$ state [12], the vibrational spacings of these coherently excited levels are calculated. They range from 89.7 to 94.1 cm^{-1} and agree with the frequencies 90.2 to 93.9 cm^{-1}, obtained in the Fourier analysis. From a difference-potential analysis [11] we know that this vibrational wave packet is formed at the inner turning point of the $2\,^1\Pi_g$ state. The time-delayed fs-probe pulse transfers this wave-packet motion into the ionization continuum, but only, as the 180° phase shift of the $T_\Pi \approx 363$ fs period clearly shows, at the outer turning point. Using only Franck-Condon arguments, there is no reason why direct photoionization of the Rydberg electron should take place only at the outer turning point for
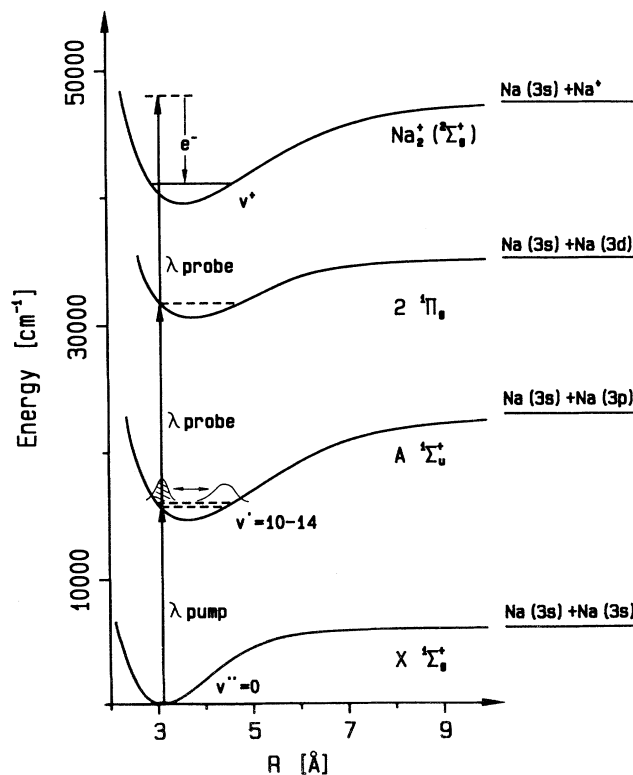

FIG. 2. Potential curve diagram illustrating the preparation of the wave packet in the A state and the two-photon-probe process transferring the motion of the wave packet into the Na_2^+ ($^2\Sigma_g^+$) ionization continuum.

the given vibrational levels v^*. Moreover, a difference-potential analysis [11] and wave-packet calculations by Engel [13] show that direct photoionization of the $2\,^1\Pi_g$ state results in a time-independent contribution to the observed Na_2^+ signal.

Are these two contributions to the oscillating Na_2^+ ionization signal just two different ionization pathways whose amplitudes have to be added coherently, or do they come from two independent ionization processes resulting in distinguishable final states, to require incoherent addition of intensities? The fs-pump pulse coherently excites wave-packet motions in the A state and in the $^2\Pi_g$ state. Both are transferred by the fs-probe pulse into the ionization continuum. The total ionic population is given by $P_{tot} = P(A) + P(\Pi) + P(A,\Pi)$, where the first two terms describe the independent (incoherent) ionizing transitions of the A and Π wave packets, respectively, while the last term—the coherence term $P(A,\Pi)$ $= 2\,\mathrm{Re}(\langle \Psi(A)|\Psi(\Pi)\rangle)$—describes the interference effect. Strong interference is expected whenever the probe-pulse ionization of the A and of the Π wave packet populates the same final ionic states. However, if there are distinguishable ionic states populated in these ionizing transitions, the interference term becomes zero and the total ionic population consists only of the periodic (incoherent) signals $P(A)$ and $P(\Pi)$. From the analysis of the transient-ionization spectrum (Fig. 1) it is clear we only observe the superposition of the two periodic signals $P(A)$, $T_A \approx 306$ fs, and $P(\Pi)$, $T_\Pi \approx 363$ fs. Of course, the important question now is what is the nature of the "second" independent ionization process.

In order to clarify the situation we performed another time-resolved experiment where we measured the time dependence of the slow Na^+-ionic-fragment signal. The
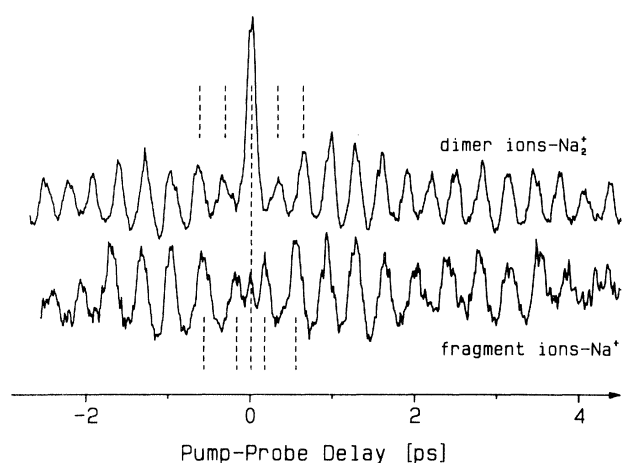
observed Na^+ fragmentation spectrum, displayed in Fig. 3 together with the Na_2^+ ionization spectrum, shows a striking result. The oscillation period of the transient Na^+ signal is T_Π, which is determined by the wave-packet motion in the $2\,^1\Pi_g$ state. This oscillation T_Π shows again the phase shift of 180° with respect to zero delay time. These results strongly suggest that the molecular ion Na_2^+ and the slow Na^+ ionic fragments, which are both formed via the outer turning point of the $2\,^1\Pi_g$ state, have a common origin. Details of the Na^+ photofragmentation process are discussed elsewhere [8].

The excitation of a neutral electronically doubly excited Na_2 molecule is such a process. A doubly excited molecule $Na_2^{**}(nl,n'l')$ may electronically autoionize, to form Na_2^+ as well as the fragments $Na^+ + Na$ $+ e^-\,(E_{kin})$. The reasons that such an excitation occurs only at the outer turning point of the $2\,^1\Pi_g$ state could be the relative location of the two potentials involved and a strong R dependence of the electronic transition moment. No calculations have yet been reported for doubly excited states in this energy range [14].

Figure 4 illustrates the two-photon-pump and one-photon-probe ionization process which involves excitation and decay of doubly excited states. The pump laser prepares a wave packet at the inner turning point, which
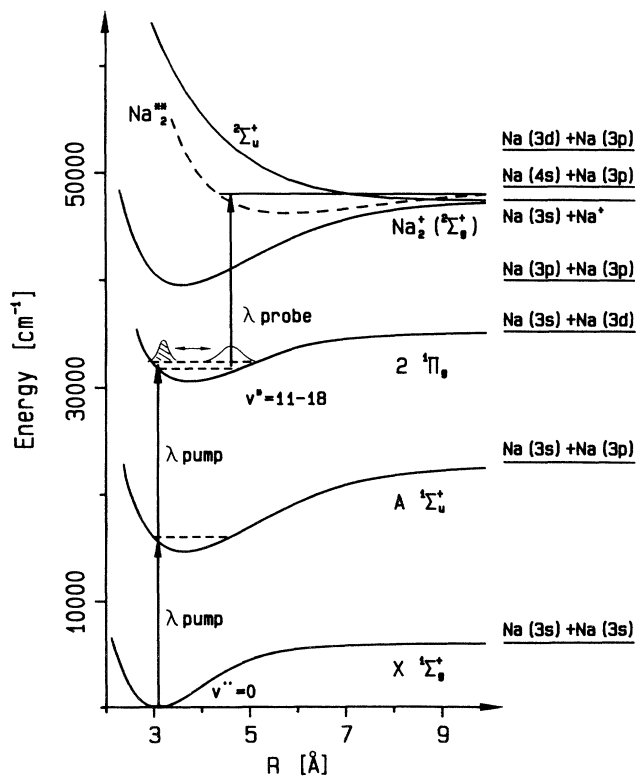

FIG. 3. Na_2^+ ionization spectrum and Na^+ fragmentation spectrum. The period T_A with no phase shift with respect to the zero delay time is the main structure in the Na_2^+ signal. The period T_Π with the 180° phase shift dominates the Na^+ signal.

FIG. 4. Potential curve diagram illustrating the preparation of the wave packet in the $2\,^1\Pi_g$ state and the one-photon-probe process occurring at the outer turning point with excitation of $Na_2^{**}(nl,n'l')$.

then propagates to the outer turning point, where the probe laser transfers the motion into the continuum by exciting a second electron, forming doubly excited Na_2 molecules. The decay of these molecules by electronic autoionization and autoionization-induced fragmentation accounts for the time structure T_Π and the phase shift of 180° seen in the Na_2^+ ionization and in the Na^+ fragmentation spectra.

Another interesting result is obtained at laser intensities of ≈ 500 GW/cm^2, where we found that excitation of two electrons with subsequent autoionization is more important than direct photoionization of a singly excited electronic state.

In conclusion, this is the first study in a molecular-beam experiment to use femtosecond pump-probe techniques in combination with ion spectroscopy to study the dynamics of molecular multiphoton ionization. The analysis of transient Na_2^+ ionization and Na^+ photofragmentation spectra measured with 70-fs pump and probe pulses shows that wave-packet oscillations in the $A\,^1\Sigma_u^+$ and the $2\,^1\Pi_g$ potentials occur. From the observed two oscillation periods T_A and T_Π, the 180° phase shift of T_Π, and the Na^+ fragmentation spectrum, we conclude that for Na_2 two different multiphoton-ionization processes exist, to require incoherent addition of the intensities to account for the measured signal. The direct photoionization of an excited electron, where one pump photon creates a wave packet in the $A\,^1\Sigma_u^+$ state and two probe photons transfer that motion via the $2\,^1\Pi_g$ state into the ionization continuum, is one process. The second involves excitation of two electrons and subsequent autoionization. Here two pump photons create a wave packet in the $2\,^1\Pi_g$ state and one probe photon transfers its motion into the ionization and fragmentation continuum, but this happens only at the outer turning point of the $2\,^1\Pi_g$ state periodically after each round trip. In this case the probe photon is absorbed at the earliest about 180 fs after the pump photons were absorbed.

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