PHYSICAL REVIEW A VOLUME 54, NUMBER 6 DECEMBER 1996

Femtosecond pump-probe photoelectron spectroscopy: Mapping of vibrational wave-packet motion

A. Assion, M. Geisler, J. Helbing, V. Seyfried, and T. Baumert
Physikalisches Institut, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

(Received 3 May 1996; revised manuscript received 10 September 1996)

Energy-resolved photoelectron spectroscopy in combination with femtosecond pump-probe and molecular beam techniques are used to map molecular dynamics along the internuclear coordinate. The capabilities of this method are demonstrated on the one-dimensional wave-packet motion on electronically excited states of the sodium dimer: by recording transient photoelectron spectra in a pump-probe experiment we are able to follow the molecular wave-packet motion on neutral electronic states along all energetically allowed internuclear distances simultaneously. [S1050-2947(96)51312-0]

PACS number(s): 33.60.−q, 33.80.Eh, 33.80.Rv, 31.70.Hq

The exceptional time resolution obtained with femtosecond laser systems is one necessary ingredient for the real-time observation of molecular dynamics as vibrational wave-packet motion, direct dissociation, vibrational energy redistribution, isomerization, and internal conversion. For a review of these topics, see, for example, [1,2] and references therein. In addition, a detailed analysis of molecular dynamics requires well-defined initial and well-defined final states. To achieve well-defined initial states, supersonic molecular beams are widely used to prepare vibrationally and rotationally cold molecules for femtosecond pump-probe studies on molecular dynamics [3–6]. The final states detected in pump-probe experiments, however, are often less well defined. Deriving dynamical information in femtosecond pump-probe experiments, for example, from laser-induced fluorescence (LIF) detection can be complicated by the density of high-lying neutral electronic states usually excited by the probe laser. This often leads to unknown Franck-Condon windows or to a reduced fluorescence yield due to predissociation processes. In comparison, the use of the ionic ground state for detection in femtosecond pump-probe experiments has several advantages: This state is stable and unperturbed and in addition mass and kinetic-energy selectivity in femtosecond time-resolved photodissociation experiments is achieved by detecting ions [7,8]. However, there may be a loss of dynamical information if a large part of internuclear distances is sampled, as, for example, when the probe laser energy reaches the dissociation limit of the ionic ground state [9–11]. In order to resolve molecular dynamics on an intermediate state, sampling of only a small fraction of the internuclear distances is necessary. This can be achieved by tuning the probe laser to low vibrational levels of the ionic ground state, especially if the equilibrium distances in neutral and ionic states are essentially different [12], or by using phase-sensitive pump-probe techniques [13,14] that have recently been applied to study vibrational wave-packet motion on the B state of Cs_2 [6]. Note that by applying these techniques the sampling region cannot be chosen arbitrarily.

In order to map molecular dynamics on neutral intermediate states not only on a limited small fraction of internuclear distances, we combine molecular-beam techniques with femtosecond pump-probe techniques and kinetic-energy photoelectron detection. By the Franck-Condon principle the kinetic photoelectron distribution resulting from direct ionization depends sensitively on the nuclear configuration. Therefore it is ideally suited to follow the intermediate dynamics along all energetically allowed internuclear distances in a pump-probe experiment simultaneously. This advantage of time-resolved photoelectron spectroscopy has already been demonstrated in the picosecond time domain [15–18]. It exhibits its full potential in the femtosecond regime as important molecular dynamics (see above) are on this time scale. Recently femtosecond time-delayed photoelectron spectra on intramolecular vibrational redistribution (IVR) in hexatriene have been reported [19].

Mapping a vibrational wave packet with the help of femtosecond pump-probe techniques and energy-resolved photoelectron spectroscopy was simulated by Meier and Engel in a theoretical publication [20]. This contribution is an experimental proof of the feasibility of this kind of experiment. We show experimentally that energy-resolved photoelectron spectroscopy on a femtosecond time scale allows us to monitor the evolution of a vibrational wave packet along the internuclear distance in real time.

In comparison with another method, the zero kinetic energy (ZEKE) photoelectron spectroscopy [21] detection, which has already been extended from picosecond time scales [22] to femtosecond time resolution [23,24], this approach has a major advantage: a complete mapping of, for example, vibrational wave-packet motion can be achieved with a fixed probe laser wavelength, whereas to map the wave-packet motion at different internuclear distances with the ZEKE detection technique the probe laser has to be tuned [25].

The experimental setup is described in detail in Ref. [26] and will only be outlined briefly. To generate the femtosecond pulses at 618 nm for our experiments we used a home-built Ti:sapphire oscillator combined with a modified commercial regenerative amplifier that delivered 90-fs, 800-μJ pulses of Gaussian shape at a wavelength of 790 nm and a bandwidth of 22 nm (full width at half maximum) with a repetition rate of 1 kHz. These were converted into transform-limited 40-fs, 20-μJ pulses at 618 nm for the pump-probe measurements by an optical parametric generator and a prism compressor. In a Michelson-type setup the beam was split into equal parts and realigned with a variable time delay between the two pulses. By weakly focusing with

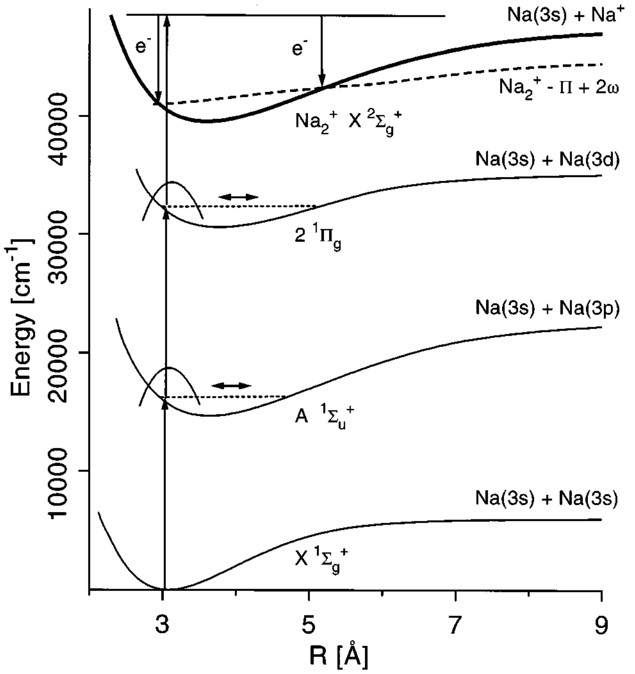

FIG. 1. Excitation scheme of the experiment. The pump laser at 618 nm prepares vibrational wave packets at the inner turning point of the $A\ ^1\Sigma_u^+$ and $2\ ^1\Pi_g$ states of the sodium dimer. The difference potential ($\mathrm{Na}_2{}^+ - 2\ ^1\Pi_g + 2\omega$; ω is the photon energy, dashed line) indicates that upon direct ionization out of the $2\ ^1\Pi_g$ state into the $\mathrm{Na}_2{}^+ X\ ^2\Sigma_g^+$ state the kinetic energy of the photoelectrons depends on the internuclear distance. The propagation of vibrational wave-packet motion can therefore be monitored along the internuclear distance by detecting energy-resolved photoelectrons in pump-probe experiments.

a 300-mm achromatic lens, peak intensities of approximately 10^{11} W/cm^2 were reached. In order to observe the wave-packet motion on the electronic states without coherently coupling the electronic states in the intense laser field [26,27], we attenuated pump and probe lasers properly. The experiments were performed on a cold sodium molecular beam. Na_2 was produced vibrationally cold in its electronic $X\ ^1\Sigma_g^+$ ground state by expanding pure sodium from an oven operated at 1000 K. A μ-metal shielded linear time-of-flight (TOF) spectrometer was used for electron detection. When ionized via different resonances by a ns laser, the sodium atoms in the beam produce several photoelectron peaks of well-defined energies, which served to calibrate the spectrometer. Its resolution is about 50 meV for electrons of kinetic energy in the range 0.8–1 eV. The calibration TOF spectra and the pump-probe spectra were recorded with a 1-GHz, 2-gigasample digital oscilloscope and averaged over several thousand laser shots per time step.

The excitation scheme of the experiment is depicted in Fig. 1. Three photons at 618 nm are needed to ionize the Na_2 molecule from its neutral ground state $X\ ^1\Sigma_g^+$ into its ionic ground state $^2\Sigma_g^+$. The dynamical aspect of this multiphoton excitation has been investigated in this wavelength regime in detail with ion detection [3]. Due to the spectral width of the 40-fs laser pulse and due to the Franck-Condon principle one-photon excitation prepares a wave packet at the inner turning point of the $A\ ^1\Sigma_u^+$ state potential by coherent superposition of the vibrational levels $v' = 12–16$, which correspond to vibrational energy spacings ranging from 108.1 to 106.0 cm^{-1}. Two-photon excitation leads to preparation of a wave packet at the inner turning point of the $2\ ^1\Pi_g$ state potential, being composed of vibrational levels $v^* = 15–23$, which correspond to vibrational energy spacings ranging from 91.2 to 85.9 cm^{-1}. In [3] it was found that the $A\ ^1\Sigma_u^+$ state wave-packet motion is reflected in the total $\mathrm{Na}_2{}^+$ ion yield due to a resonance-enhanced "direct" photoionization process via the $2\ ^1\Pi_g$ state into the $\mathrm{Na}_2{}^+(X\ ^2\Sigma_g^+)$ state at the inner turning point of the molecular potential curves involved. In those experiments the $2\ ^1\Pi_g$ state wave-packet motion could only be detected in the $\mathrm{Na}_2{}^+$ and Na^+ fragment signal due to the excitation of a doubly excited neutral state of the Na_2 molecule near the outer turning point of the $2\ ^1\Pi_g$ state potential and its subsequent decay channels as autoionization (indirect photoionization) and autoionization-induced fragmentation [3,7]. Note that direct photoionization out of the $2\ ^1\Pi_g$ state into the $\mathrm{Na}_2{}^+(X\ ^2\Sigma_g^+)$ state cannot provide the dynamical information on the wave packet prepared on this state when detected by the total $\mathrm{Na}_2{}^+$-ion yield, since a large part of internuclear distances is sampled in a pump-probe experiment [9,10].

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 photoionization process the released kinetic energy of the photoelectrons can be determined by a difference potential analysis [9,28]. The dashed line in Fig. 1 displays the difference potential $^2\Sigma_g^+\ (\mathrm{Na}_2{}^+) - 2\ ^1\Pi_g + 2\omega$, where ω is the photon energy. Within this concept, the expected photoelectron energy in this photoionization process out of the $2\ ^1\Pi_g$ state is decreasing with increasing internuclear distance. At the inner turning point of the potential curve photoelectrons of about 0.94 eV are formed, whereas at the outer turning point photoelectrons of about 0.78 eV are released. By recording transient photoelectron spectra we are able to probe molecular wave-packet motion on neutral electronic states along all energetically allowed internuclear distances simultaneously. Note that the autoionization processes of the doubly excited state lead to photoelectrons with less than 0.5 eV kinetic energy [7], and are therefore separated from the electrons released in the direct photoionization process.

In Fig. 2 the measured TOF photoelectron distribution is shown as a function of pump-probe delay. The TOF range from 250 to 290 ns corresponds to an energy interval from 1.2 to 0.6 eV of photoelectrons released. At earlier TOFs photoelectrons with higher kinetic energies are released and therefore in our experiment smaller internuclear distances are probed. Later TOFs correspond to photoelectrons with lower kinetic energies, which in this case are generated at larger internuclear distances. The dynamics of vibrational wave-packet motion on the neutral electronic states is beautifully resolved and can be followed in great detail along all energetically allowed internuclear distances simultaneously. By taking cuts along a constant TOF the dynamics at a specific internuclear distance can be analyzed. The insets give two examples. The power spectrum density (PSD) of a fast-Fourier transformation (FFT) is displayed for a "fast" pho-

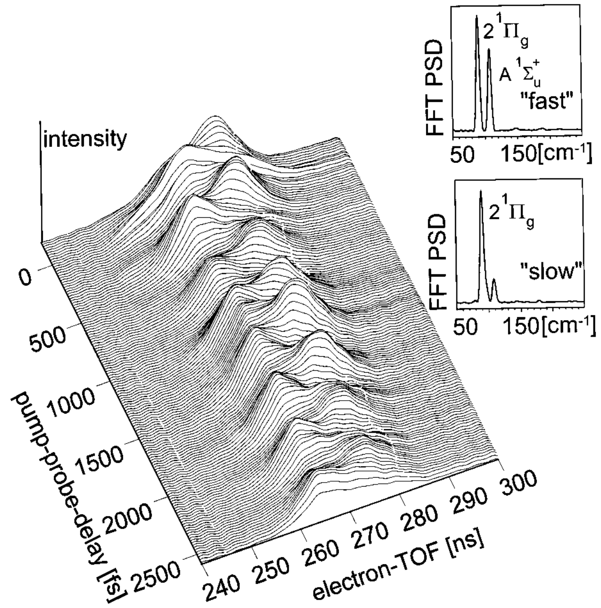

FIG. 2. The measured time-of-flight (TOF) photoelectron distribution as a function of pump-probe delay is shown. This femtosecond time-resolved photoelectron signal shows the vibrational wave-packet motion on the neutral electronic states. Cuts at a constant TOF reveal the wave-packet dynamics at a specific internuclear distance. The insets display the Fourier transform of transient photoelectron signals obtained at two different cuts. At an earlier TOF, photoelectrons with higher kinetic energy are released (''fast'' photoelectrons) and therefore the inner turning point is probed, whereas at a later TOF the outer turning point is probed and ''slow'' photoelectrons are released. Consequently the Fourier transform of the ''fast'' photoelectron transient reflects wave-packet motion in the $A\,^1\Sigma_u^+$ and $2\,^1\Pi_g$ state, whereas the Fourier transform of the ''slow'' photoelectron transient reflects mainly the wave-packet motion in the $2\,^1\Pi_g$ state.

toelectron 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 can be seen in the insets, one around 90 cm^{-1} and the other around 107 cm^{-1}. These are the frequencies of oscillating wave packets in the $2\,^1\Pi_g$ and $A\,^1\Sigma_u^+$ states, respectively. As stated above the direct photoionization out of the $2\,^1\Pi_g$ state into the $\mathrm{Na}_2{}^+(X\,^2\Sigma_g^+)$ state does indeed provide the dynamical information on the wave packet prepared on this state when detected via kinetic-energy-resolved photoelectrons. According to the excitation scheme, at the inner turning point the $A\,^1\Sigma_u^+$ state wave packet contributes, in addition to the $2\,^1\Pi_g$ state wave packet, to the fast photoelectron transient. This is why the frequencies of both wave packets 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 $2\,^1\Pi_g$ state wave packet dominate the spectrum. The small contribution of the $A\,^1\Sigma_u^+$ state frequencies in that FFT is attributed to the limited resolution of our spectrometer.

This experiment demonstrates that by means of transient kinetic photoelectron spectroscopy a vibrational wave-packet motion can be mapped simultaneously over a wide range of internuclear distances. Therefore this method should be suited to follow structural changes of molecules upon excitation with an ultrashort laser pulse in real time. In cases of monotonically decreasing or increasing difference potentials between an intermediate state and the ionic ground state the interpretation of the data is straightforward, as in the example demonstrated here. Several exciting experiments can now be performed directly. The detailed determination of the quantum state of a wave packet from position probability distributions measured during the wave-packet motion on the potential [29] should be possible with this technique and it should be an alternative route to molecular emission tomography [30]. The influence of phase-modulated laser pulses on the evolution of vibrational wave packets can also be monitored directly by this means [31,32]. We performed single-pulse experiments using phase-shaped femtosecond laser pulses on this molecule in order to control the efficiency of the multiphoton ionization process described here [33]. Dynamical aspects of high laser field effects in molecular physics, as, for example, above-threshold ionization (ATI), are often difficult to investigate in an ion detection scheme. With the help of transient photoelectron spectroscopy we were recently able to follow the dynamics of molecular ATI in real time [34].

In summary we have combined molecular-beam photoelectron spectroscopy with femtosecond pump-probe techniques in order to follow structural changes in a molecule upon excitation with an ultrashort laser pulse in real time along the internuclear coordinate(s). The one-dimensional wave-packet motion on electronically excited states of the sodium dimer has been chosen to demonstrate the capabilities of this method. We show experimentally that energy-resolved photoelectron spectroscopy on a femtosecond time scale allows us to monitor the evolution of vibrational wave packets along the internuclear distance in real time.

We would like to thank G. Gerber and V. Engel for help and fruitful discussions. Help from M. Bergt and D. Woessner in handling large data files is gratefully acknowledged. This work was supported by the DFG.

---

[1] *Femtosecond Chemistry,* edited by J. Manz and L. Wöste (VCH, Weinheim, 1995).

[2] *Ultrafast Phenomena IX,* edited by P.F. Barbara *et al.* (Springer-Verlag, Berlin, 1994).

[3] T. Baumert, M. Grosser, R. Thalweiser, and G. Gerber, Phys. Rev. Lett. **67**, 3753 (1991).

[4] M. Dantus, M.H.M. Janssen, and A.H. Zewail, Chem. Phys. Lett. **181**, 281 (1991).

[5] R. de Vivie-Riedle, B. Reischl, S. Rutz, and E. Schreiber, J. Phys. Chem. **99**, 16 829 (1995).

[6] V. Blanchet, M.A. Bouchene, O. Cabrol, and B. Girard, Chem. Phys. Lett. **233**, 491 (1995).

[7] T. Baumert, B. Buehler, R. Thalweiser, and G. Gerber, Phys. Rev. Lett. **64**, 733 (1990).

[8] T. Baumert, S. Pedersen, and A.H. Zewail, J. Phys. Chem. **97**, 12 447 (1993).

[9] T. Baumert, B. Buehler, M. Grosser, R. Thalweiser, V. Weiss, E. Wiedenmann, and G. Gerber, J. Phys. Chem. **95**, 8103 (1991).

[10] V. Engel, Chem. Phys. Lett. **178**, 130 (1991).

[11] M. Seel and W. Domcke, J. Chem. Phys. **95**, 7806 (1991).

[12] G. Rodriguez, P.C. John, and J.G. Eden, J. Chem. Phys. **103**, 10 473 (1995).

[13] N.F. Scherer, A.J. Ruggiero, M. Du, and G.R. Fleming, J. Chem. Phys. **93**, 856 (1990).

[14] J.F. Christian, B. Broers, J.H. Hoogenrad, W.J. van der Zande, and L.D. Noordam, Opt. Commun. **103**, 79 (1993).

[15] X. Song, C.W. Wilkerson, J. Lucia, S. Pauls, and J.P. Reilly, Chem. Phys. Lett. **174**, 377 (1990).

[16] P.M. Weber and N. Thantu, Chem. Phys. Lett. **197**, 556 (1992).

[17] J.A. Syage, Z. Phys. D **30**, 1 (1994).

[18] M.R. Dobber, W.J. Buma, and C.A. deLange, J. Chem. Phys. **99**, 836 (1993).

[19] D.R. Cyr and C.C. Hayden, J. Chem. Phys. **104**, 771 (1996).

[20] C. Meier and V. Engel, Chem. Phys. Lett. **212**, 691 (1993).

[21] K. Müller-Dethlefs and E.W. Schlag, Annu. Rev. Phys. Chem. **42**, 109 (1991).

[22] J.M. Smith, X. Zhang, and J.L. Knee, J. Chem. Phys. **99**, 2550 (1993).

[23] T. Baumert, R. Thalweiser, and G. Gerber, Chem. Phys. Lett. **209**, 29 (1993).

[24] I. Fischer, D.M. Villeneuve, M.J.J. Vrakking, and A. Stolow, J. Chem. Phys. **102**, 5566 (1995).

[25] I. Fischer, M.J.J. Vrakking, D.M. Villeneuve, and A. Stolow, Chem. Phys. **207**, 331 (1996).

[26] T. Baumert and G. Gerber, Adv. At. Mol. Phys. **35**, 163 (1995).

[27] T. Baumert, V. Engel, C. Meier, and G. Gerber, Chem. Phys. Lett. **200**, 488 (1992).

[28] R.S. Mulliken, J. Chem. Phys. **55**, 309 (1971).

[29] U. Leonhardt and M.G. Raymer, Phys. Rev. Lett. **76**, 1985 (1996).

[30] T.J. Dunn and I.A. Walmsley, Phys. Rev. Lett. **74**, 884 (1995).

[31] B. Kohler, V.V. Yakolev, J. Che, J.L. Krause, M. Messina, and K.R. Wilson, Phys. Rev. Lett. **74**, 3360 (1995).

[32] C.J. Bardeen, Q. Wang, and C.V. Shank, Phys. Rev. Lett. **75**, 3410 (1995).

[33] A. Assion, T. Baumert, J. Helbing, V. Seyfried, and G. Gerber, Chem. Phys. Lett. **259,** 488 (1996).

[34] A. Assion, T. Baumert, J. Helbing, V. Seyfried, and G. Gerber, Phys. Rev. A (to be published).