

# LETTERS TO THE EDITOR

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## COMMUNICATIONS

### Femtosecond wave-packet dynamics studied by time-resolved zero-kinetic energy photoelectron spectroscopy

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Femtosecond pump-probe zero-kinetic-energy (ZEKE) photoelectron spectroscopy is studied using the known wave-packet dynamics of  $I_2$  (B state). The 340 fs wave-packet period, wave-packet dephasing and rephasing are observed in the ZEKE signal. The effect of various laser and ZEKE parameters on the wave-packet dynamics is discussed.

Recent developments in laser technology have allowed for real-time femtosecond (fs) pump-probe studies of gas phase chemical reactions using a variety of very elegant techniques.<sup>1</sup> An emerging important goal of fs pump-probe spectroscopy is the chemical reaction dynamics of polyatomic molecules.<sup>1-5</sup> We might describe such an experiment by the equation

$$S(t) = |\langle f | \mu(Q) | ex(t) \rangle|^2, \quad (1)$$

where  $S(t)$  is the measurement,  $|f\rangle$  is the final state, used as a "screen" onto which we project the dynamics,  $\mu(Q)$  is the coordinate dependent dipole coupling and  $|ex(t)\rangle$  is the evolving state that we wish to study. A range of techniques using different kinds of final states  $|f\rangle$  have been implemented: time-resolved fluorescence spectroscopy;<sup>1,5,6</sup> ionization/mass spectroscopy;<sup>1,7,8</sup> stimulated emission pumping;<sup>2</sup> and direct absorption.<sup>9</sup>

In general, the choice of the final state must take into consideration several effects: (1) In order to decompose the evolving wave packet in the basis of the final states,  $|f\rangle$  must be well known. In general, however, higher excited states of polyatomic molecules are poorly known; (2) variation of the dipole coupling between electronic states during the wave-packet evolution will have a strong effect on the measured signals. It is important to choose a technique that "follows" the reaction dynamics, even to "dark" states. (3) Polyatomic reaction dynamics implies multidimensional wave packets with many frequency components. An *integrated* detection technique which simultaneously collects all components (e.g., total fluorescence, total ion yield) may not resolve the complicated underlying dynamics. It is important to develop a *differential* detection technique<sup>10</sup> that "disperses" or "isolates" the various components, if possible. This was demonstrated successfully using the dispersed fluorescence technique.<sup>1,10</sup>

Time-resolved ionization is a general approach to addressing these issues. Aside from technical advantages such as extreme sensitivity, ionization presents certain conceptual advantages: (1) The ground state of the ion is often the best known excited state of a polyatomic molecule and can there-

fore serve as a useful "template" for the reaction dynamics; (2) ionization is a universal detection scheme: Any atom, radical, or molecule in any state may be ionized. There are no "dark" states and symmetry selection rules are relaxed—due to the range of symmetries of the outgoing electron<sup>11</sup>—in comparison with electronic spectroscopy; (3) ionization provides two species for analysis, the ion and the electron. Detection of the ion corresponds to an integrated detection scheme. Detection of the electron can be a differential technique, as discussed above, because the electrons may be *further* analyzed, as to their kinetic energy distribution for example.<sup>12,13</sup> We will discuss, below, the possible use of different final vibrational states of the ion as "Franck-Condon filters" of the wave-packet dynamics.

The first studies of time-resolved photoelectron spectroscopy were published some time ago.<sup>14</sup> More recently, these studies were brought into the picosecond domain.<sup>15,16</sup> In a seminal experiment,<sup>15</sup> zero-kinetic-energy (ZEKE) photoelectron spectroscopy<sup>17</sup> was combined with picosecond pump-probe techniques, showing that excited state phenomena such as picosecond quantum beats and intramolecular vibrational energy redistribution (IVR) can be observed and investigated using ZEKE detection. In order to study the dynamics of many interesting chemical reactions, however, the time resolution needs to be brought into the femtosecond domain.<sup>1</sup> The technique of fs pump-probe ZEKE is relatively unexplored, demonstrated recently on the  $Na_3$  system.<sup>3</sup> We note that in photoelectron spectroscopy, there is always the danger that the amplified fs pump and probe lasers can individually produce background signals due to higher order processes. ZEKE detection has the advantage of being insensitive to background (i.e., kinetic) electrons produced by other channels.

In this Communication, we study fs pump-probe ZEKE by applying it to wave-packet dynamics in a simple diatomic system. The example of the  $I_2$ (B) state was chosen because it has been studied in great detail using fluorescence (and ion<sup>8</sup>) detection.<sup>18</sup> For this experiment, a single photon prepared the B state, followed by a *tunable* two-photon projection onto the ground state of the ion. We show here that information

similar to the fluorescence experiments can be obtained using ZEKE detection and we investigate the effects of laser and ZEKE parameters on the fs pump-probe scans, as well as showing the effect of varying the final state.

Our broadly tunable fs pump-probe laser system is based upon phase-lock synchronization<sup>19</sup> of a fs Ti:sapphire (Ti:Sa) laser with a regeneratively amplified picosecond (ps) Nd:YAG laser, the details of which will be presented in a future publication. This synchronization allows for a variety of efficient wavelength conversion schemes based upon sum- or difference-frequency mixing<sup>19</sup> of amplified fs Ti:Sa pulses with the high power ps Nd:YAG pulses (and harmonics). Briefly, the pump pulse in this experiment had a wavelength of 580 nm and a pulse duration of 95 fs (1–30  $\mu$ J,  $\cong$  2 mm spot diam.). This corresponds to exciting vibrational levels around  $v'=14-17$  of  $I_2(B)$ . The probe pulse was tuned between 300–350 nm and had a pulse duration of 100 fs (1–25  $\mu$ J,  $f/40$ ). This allowed us to tune from below the ionization potential (IP) up to high vibrational levels of the ground state of the ion. The pump and probe pulses were combined in a Michelson arrangement with a computer controlled delay stage.

The second component of this experiment is a molecular beam tandem photoelectron/photoion spectrometer. Photoelectron detection (usually ZEKE detection) and ion time-of-flight mass spectrometry (TOFMS), both using static and/or pulsed fields, can be done simultaneously or independently due to the use of the two flight tubes. Magnetic shielding reduces the stray fields to the microGauss level, allowing for efficient electron collection and time-of-flight studies. Background signals are negligible due to the ultrahigh vacuum environment in the spectrometer ( $2 \times 10^{-10}$  Torr). A universal differentially pumped molecular beam chamber can be used with a variety of pulsed or continuous sources. For this experiment, we used a skimmed, pulsed seeded beam (0.04%  $I_2$  in 1000 Torr He). Femtosecond pump and probe laser pulses propagate perpendicular to both the molecular beam axis and the TOFMS and ZEKE spectrometer axes. The absolute laser  $\Delta t=0$  and cross-correlation were determined in two independent ways: nonresonant ionization of nitric oxide (at the interaction point of the spectrometer) and sum-frequency mixing in an external 0.1 mm BBO crystal. A computer collected mass-selected ion and ZEKE signals as a function of pump-probe time delay,  $\Delta t$ .

In Fig. 1 we present fs pump-probe scans of  $I_2(B)$  state wave-packet dynamics using both  $I_2^+$  ion TOFMS (top) and ZEKE (bottom) detection. The wavelength of the probe laser was 345 nm for excitation of  $v^+=0-1$  in the ion. A modulation period of 340 fs is observed, corresponding to the average vibrational frequency of  $I_2(B)$ ,  $v'=14-17$  that is expected for 580 nm excitation. The modulation is due to the *interferences between transitions* from a set of vibrational levels in the B state to a final state of the ion. The ion and ZEKE scans are exactly in phase. Both decay after about ten vibrational periods due to quantum mechanical spreading (dephasing) of the wave packet.

The  $I_2(B)$  state excited at 580 nm is a bound state and therefore the dephased wave packet must *rephase*, as shown in Fig. 2, beginning around 15 ps. For this single mode prob-

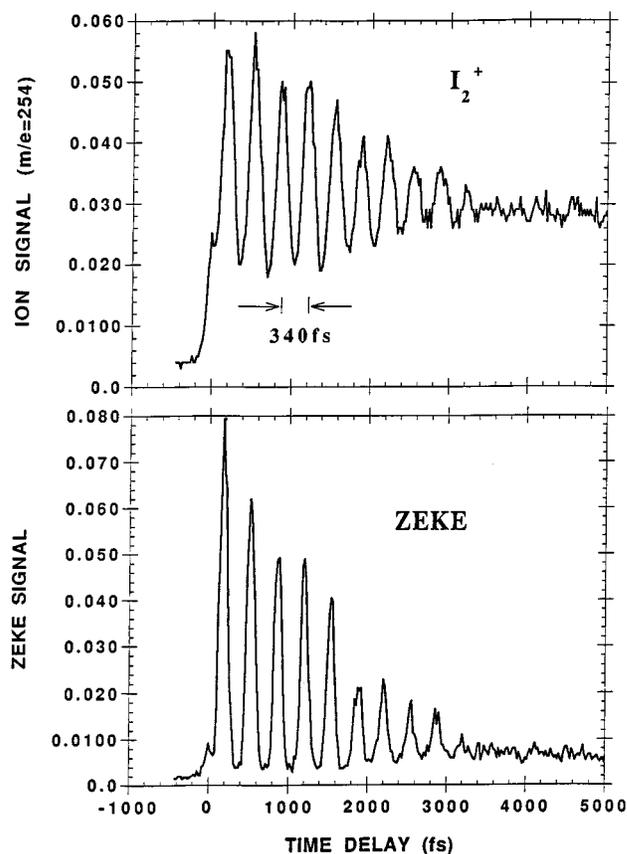


FIG. 1. Femtosecond pump-probe ion (top) and ZEKE (bottom) scans of  $I_2(B)$  state wave-packet dynamics, showing the 340 fs vibrational period expected for 580 nm excitation. The probe laser (345 nm) projected the wave packet onto  $v^+=0-1$  of the ion. The ZEKE signals shown in this Communication were recorded with a pulsed field of 1.5 V/cm applied after a 1  $\mu$ s delay. The time delay zero point was determined by nonlinear cross correlation using a small amount of nitric oxide in the molecular beam. The ion and ZEKE signals are exactly in phase. The ZEKE scan exhibits a deeper modulation depth.

lem we expect that the threshold ion and ZEKE time delay scans should be similar and that the information content should be comparable to the previously reported fluorescence time delay scans.<sup>18</sup> We show as insets in Fig. 2 Fourier transform power spectra (FFT) of each data set, revealing the similar information content of the ion and ZEKE scans. The three large peaks in the FFT near  $100 \text{ cm}^{-1}$  correspond to nearest-neighbor coherences between vibrational levels  $v'=14-15$ ,  $15-16$ ,  $16-17$  in the B state. A slight contribution at the second harmonic (near  $200 \text{ cm}^{-1}$ ) is due to *next-nearest-neighbor* coherences and can be related to several effects, discussed briefly below. The spectral content of time delay scans of  $I_2(B)$  wave packets and their relationship to the potential have been discussed in great detail.<sup>18</sup>

The ZEKE scans, interestingly, have deeper modulation depths. It is the interference between transitions that gives the modulation and if many final ion states are allowed, there will always be some transitions for which there can be no interference, leading to a “background” which reduces the modulation depth; the ZEKE detection is more restrictive of the final state than is ionization. However, there are also several experimental parameters that affect the ZEKE sig-

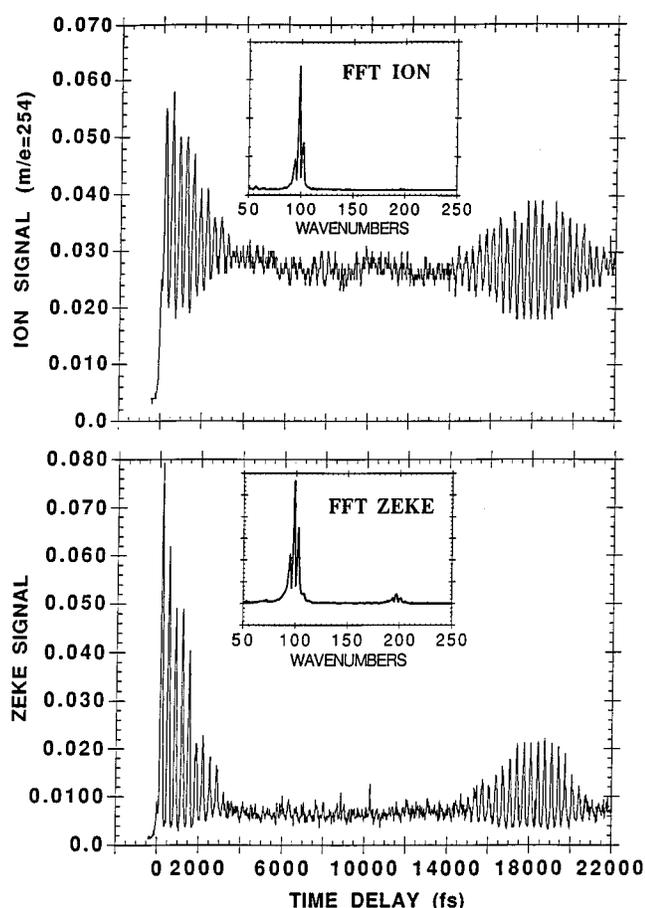


FIG. 2. Long fs pump-probe ion (top) and ZEKE (bottom) scans of the 580 nm  $I_2(B)$  wave-packet dynamics using 345 nm probe (final state,  $v^+=0,1$ ) showing 340 fs modulations. Dephasing and recurrence of the wave packet is seen. The Fourier transform power spectra, inset, show that coherences between vibrational levels  $v'=14-15$ ,  $15-16$ ,  $16-17$  are involved and that the ion and ZEKE scans contain similar information.

nals. We studied the modulation depths as a function of pulsed extraction field delay, pulsed extraction field strength and laser powers. We observed that the modulation depth increases with increasing extraction field delay. There is increasing evidence that Rydberg lifetimes are enhanced by ( $l,m$ )-changing collisions with free charged particles.<sup>20-22</sup> In our experiment, the ion concentration is *modulated* (see Fig. 1, top). This suggests that, at the 1  $\mu$ s extraction delay used in these scans, the peaks of the ZEKE spectrum are enhanced (through ion collisions which increase Rydberg lifetimes) by the higher ion concentration at the peaks of the ion spectrum. To check this idea in another manner, we introduced excess ions with an independent laser (266 nm, 80 ps, 0.1–1.0 mJ) approximately 40 ns *before* the fs pump-probe experiment. In this case, the modulations were less pronounced and the overall magnitude of the ZEKE signal was considerably larger, consistent with our speculation.

In experiments using amplified fs lasers, intensities can be quite high. Strong fields can promote undesirable processes such as higher order transitions to other states, loss of selectivity in ZEKE experiments due to ponderomotive broadening<sup>23</sup> and generation of “false ZEKE” signals due to

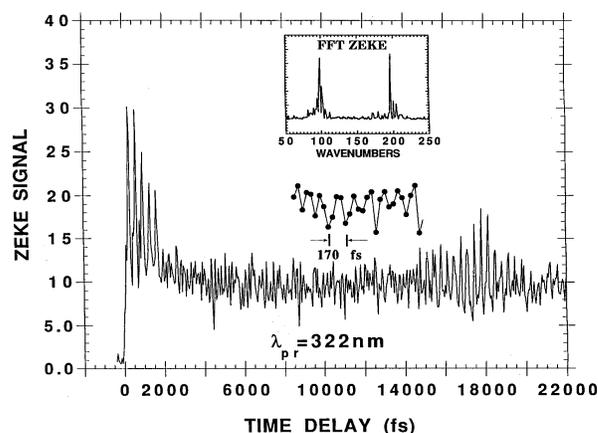


FIG. 3. Long fs pump-probe ZEKE scan of the  $I_2(B)$  wave-packet dynamics using 322 nm probe (final state around  $v^+=20$ ). The complicated pattern contains 170 fs modulations which can be seen on an expanded scale. The Fourier transform power spectrum, inset, shows the significant second harmonic contribution to the signal. Factors affecting the second harmonic are discussed in the text.

plasma effects.<sup>24</sup> In order to confirm that our measured signals are due to single photon preparation of and two photon ionization from the B state, we studied the wavelength threshold behavior of the ion and ZEKE spectra. The modulations in the spectra (and their Fourier transforms, see below) are proof that the detected state is indeed the B state. By tuning the probe laser through the IP, we confirmed that the measured signals (both ion and ZEKE) are due to two photon excitation from the B state and not a higher order process: the onset of the signal occurs exactly at the IP, as expected. Studies of the ZEKE signal as a function of pulsed valve delay, extraction time delay, extraction field strength, and the effects of a dc offset field confirm that the detected ZEKE signals are due to molecular high- $n$  Rydberg states.

In Fig. 3 we show the fs ZEKE signal when the probe laser is tuned to 322 nm (i.e., around  $v^+=20$ ). It can be seen that the modulation is much more complex and, as seen on an expanded scale, there are many small 170 fs modulations throughout the spectrum. This is evident in the FFT of the scan, inset. Additionally, we observed that there is a variation in the phase shift of the signal with probe wavelength. There are several effects which can alter the phase shifts and the ratio of fundamental to second harmonic contributions, such as fractional revivals,<sup>1,25</sup> the location of the Condon point for ionization and the occurrence of intermediate resonances.<sup>26</sup> For example, if the Condon point is located in the middle of a potential, then the wave packet will pass it *twice* upon each vibration.<sup>1</sup> These issues will be discussed in a forthcoming publication.

Although we have observed detailed wave-packet dynamics in a diatomic molecule using femtosecond pump-probe ZEKE detection, we believe that the method will be most powerful when applied to polyatomic molecules. As an example, we consider an excited state triatomic wave packet which is composed of bending and stretching components. In a chemical reaction, these modes are strongly coupled and energy will flow between degrees of freedom as the molecule dissociates. The final state of the ion can also be considered

as composed of bending and stretching states. A particularly interesting aspect of the ZEKE technique is the ability to *select* the final state. Due to the nature of Franck–Condon factors, it may be possible to use final states of the ion as *filters* of the dynamics, i.e., there may be a *propensity* for the bending state of the ion to “project out” the bending components of the wave packet, etc. In this idealization we could use Franck–Condon factors for different vibrational states of the ion to filter different components of an evolving multidimensional wave packet and relate these to the flow of energy in the excited state of the molecule. The extent to which this picture is correct will depend on vibrational level spacings in the ion as compared with laser bandwidths, geometry changes upon ionization, non-Franck–Condon effects,<sup>27</sup> etc., and will be a subject of our future experimental and theoretical investigations.

In conclusion, we have used the well understood wavepacket dynamics of the I<sub>2</sub>(B) state to study the femtosecond pump–probe ZEKE technique and suggested that ZEKE detection may be useful in investigating polyatomic molecular reaction dynamics. We discussed the dependence of the observed ZEKE signals on various experimental and molecular parameters. Details of this experiment will be discussed in a forthcoming publication. Our future studies will involve the application of this technique to excited state polyatomic reaction dynamics, with a particular interest in excited state nonadiabatic effects.

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