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Methods and applications of femtosecond time-resolved photoelectron spectroscopy

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Abstract

Femtosecond time-resolved photoelectron spectroscopy is emerging as a new technique for investigating polyatomic excited state dynamics. Due to the sensitivity of photoelectron spectroscopy to both electronic configurations and vibrational dynamics, it is well suited to the study of ultrafast non-adiabatic processes such as internal conversion, often occurring on sub-picosecond time scales. We discuss technical requirements for such experiments, including laser systems, energy and angle resolved photoelectron spectrometers and new detectors for coincidence experiments. We illustrate these methods with examples from diatomic wavepacket dynamics and ultrafast non-adiabatic processes in polyatomic molecules. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The excited state dynamics of polyatomic molecules is dominated by the non-adiabatic coupling of vibrational and electronic degrees of freedom, inducing both charge and energy redistribution in molecules. These dynamics are the primary step in the photochemistry of many polyatomic molecules [1], photobiological processes such as vision and photosynthesis [2] and underlie many concepts in molecular electronics [3]. The initially prepared zeroth order state mixes with a manifold of vibronic levels of a lower electronic state, leading to the radiationless 'decay' of the initial state. This 'decay' represents a conversion of electronic to vibrational energy and is thus often the first step in the ensuing photochemical dynamics. Non-adiabatic coupling [4–8] often leads to complex, broadened absorption spectra due to the high density of nuclear states and strong variations of transition dipole with nuclear coordinate.

In some larger molecules such as pyrazine, high resolution spectroscopy can provide 'exact' solutions to the study of radiationless transitions [9]. In general, however, these problems remain difficult, particularly when the state density becomes high and multi-mode vibronic couplings are involved. The case of greatest import to photochemistry, when the zeroth order excited states are directly or indirectly

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coupled to a true continuum, leading to non-adiabatic photodissociation dynamics [10–14], is especially challenging. Our interest is in developing complementary time-resolved methods for the study of non-adiabatic processes.

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In time-domain studies of molecular dynamics [15] a femtosecond laser pulse is used to prepare an excited state wavepacket, the evolution of which is observed by interaction with a probe laser pulse after some time delay Δt . The probe pulse projects the wavepacket onto a final (e.g. ion) state which acts as a template. The measured signal $S(\Delta t)$ is proportional to this final state population. The choice of the *final state* determines the technique and information content of an experiment. The time-dependence of $S(\Delta t)$ can be generally described by the equation

$$S(\Delta t) = \left| \left\langle \Psi_{f}(\vec{r}) \middle| \vec{\mu}(\vec{r}) \cdot \vec{E} \middle| \phi_{\text{ex}}(\vec{r}, \Delta t) \right\rangle \right|^{2} \tag{1}$$

where $|\phi_{ex}(\Delta t)\rangle$ is the excited state wavepacket of interest, $|\Psi_{f}\rangle$ is the final state onto which the dynamics is projected, and μ is the transition dipole moment, which is in general a function of nuclear coordinates. The first, and still most common probe technique applied in femtosecond experiments is time resolved electronic spectroscopy [16,17] in which the prepared excited state is projected onto a higher lying electronic state and the fluorescence from this final state is collected. Alternatively, as in the case of photoelectron spectroscopy discussed here, the dynamics can be projected onto the ionization continuum by means of photoionization [18,19]. A potential advantage of this latter technique is that the final ion state is often well characterized by independent methods such as high resolution photoelectron or infrared spectroscopy or by ab initio computation.

The particular choice of the molecular ionization continuum as the final state $|\Psi_f\rangle$ in wavepacket experiments has in fact several conceptual and practical advantages [20,21]: (1) charged particle detection is extremely sensitive; (2) Detection of the ion provides mass information; (3) Ionization is always an allowed process, with relaxed selection rules — any molecular state can be ionized (no 'dark' states); (4) Highly detailed, multiplexed information can be obtained by differentially analyzing the outgoing photoelectron as to its kinetic energy [22–33], angular distribution [34–43] and spin polarization. In addition, ZEKE-PFI detection [44] can be used for high sensitivity, state specific detection [20,21,45–48]; (5) Higher order (multiphoton) processes, which can be difficult to avoid in femtosecond experiments, are readily revealed; (6) Ionelectron coincidence measurements allow for studies of environmental effects (i.e. clusters) as a function of cluster size and for detailed studies of correlations in photodissociation dynamics (vide infra).

Photoelectron spectroscopy is particularly well suited to non-adiabatic coupling problems because it is sensitive to both electronic configurations and vibrational structure [49]. An elementary but useful picture is that emission of an independent outer valence electron occurs without simultaneous electronic reorganization of the ion core (the molecular orbital or Koopmans' picture). These simple correlation rules indicate the cation state expected to be formed upon single photon, single active electron ionization of a given molecular orbital. Partial ionization probabilities into specific ion electronic states can differ drastically with respect to the molecular orbital nature of the neutral electronic state. If a given neutral electronic configuration correlates upon removal of a single active outer valence electron - to the ground electronic configuration of the cation, then the photoionization probability is generally higher than if it does not.

In Fig. 1, we show a picture of excited state polyatomic wavepacket dynamics probed via timeresolved photoelectron spectroscopy. A zeroth order bright state α is coherently prepared with a femtosecond pump pulse. According to the molecular orbital picture, it ionizes into the α^+ continuum, the electronic state of the ion obtained upon removal of the outermost valence electron (here chosen to be the ground electronic state of the ion). This process produces a photoelectron band ε_1 . We now consider a non-adiabatic coupling process which transforms the zeroth order bright state α into a lower lying zeroth order dark state β , as induced by promoting vibrational modes of appropriate symmetry. According to the molecular orbital picture, the β state should ionize into the β^+ ionization continuum (here assumed to be an electronically excited state of the ion), producing a photoelectron band ε_2 . Therefore, for a sufficiently energetic probe photon, we expect a



Fig. 1. Time-resolved photoelectron spectroscopy of excited state dynamics in polyatomic molecules. An electronic state α is prepared by a fs pump pulse. Via a non-adiabatic process, it converts to a vibrationally hot lower lying state, β . Electronic correlations upon ionization suggest that these two states should ionize into different ion electronic continua, α^+ and β^+ , respectively. This will have a large effect on the photoelectron spectra as a function of time and allows for the monitoring of both electronic and vibrational excited state dynamics.

switching of the electronic photoionization channel from ε_1 to ε_2 during the non-adiabatic process. This simple picture suggests that one might be able to monitor directly the evolving excited state electronic configurations (i.e. the electronic population dynamics) during non-adiabatic processes while simultaneously following the coupled nuclear dynamics via the vibrational structure within each photoelectron band. This disentangling of electronic from vibrational dynamics has recently been demonstrated via a time-resolved photoelectron spectroscopy study of internal conversion dynamics in the all-*trans* decatetraene [33].

We now consider the other component of an ionization continuum final state, that of the free electron. The symmetry of the outgoing electron partial waves are likewise highly sensitive to the symmetry of the electronic state undergoing ionization. This is due to the requirement that the product of the symmetry species of the prepared excited state, the dipole operator, the ion state and the free electron wavefunction must equal (or contain) the totally symmetric irreducible representation of the molecular point group, in order that the transition be allowed

$$\Gamma_{\rm ex} \otimes \Gamma_{\mu} \otimes \Gamma_{+} \otimes \Gamma_{\rm e^{-}} \supseteq \Gamma_{\rm TS}. \tag{2}$$

It can be seen that if, due to a non-adiabatic process, the symmetry species of the initial zeroth order state Γ_{ex} changes, then the symmetry species of the outgoing electron Γ_{e^-} must also change in order that the product remain (or contain) the totally symmetric species Γ_{TS} . Hence, measurement of time-resolved photoelectron angular distributions could provide a sensitive probe of electronically non-adiabatic processes [33,42], which are almost invariably accompanied by a change in electronic symmetry. This could be particularly valuable when such processes are not discernable from photoelectron kinetic energy analysis alone (as could be the case when Koopmans-type correlations do not separate the electronic states involved).

The extension of the photoelectron-photoion-coincidence (PEPICO) technique to the femtosecond time-resolved domain has recently been demonstrated [31,50]. This technique is particularly advantageous in cluster studies because clusters of many different sizes may be present and the coincidence measurement allows a detected electron to be associated with a particular mass and hence cluster size. Femtosecond PEPICO experiments have used a timeof-flight mass spectrometer coupled with a magnetic bottle time-of-flight photoelectron spectrometer, providing high collection efficiencies for both particles. Coincidence measurements of this type have become feasible with the availability of amplified femtosecond Ti:Sapphire laser systems that provide UV pulses with μJ energies at kilohertz repetition rates.

Time and angle-resolved PEPICO measurements yielding ion-electron kinetic energy and angular correlations will shed new light on photodissociation dynamics in polyatomic molecules. Correlated photofragment and photoelectron velocities can provide a complete probe of the dissociation process [51,52]. The photofragment recoil measurement defines the energetics of the dissociation process and the orientation of the molecular axis in the lab frame, the photoelectron energy provides spectroscopic identification of the products and the photoelectron angular distribution can be transformed to the recoil

frame in order to extract vector correlations such as the photofragment angular momentum polarization. The integration of photoion-photoelectron energy and angular correlation measurements with femtosecond laser technology has recently been demonstrated by Hayden et al. at Sandia National Labs and allows the time evolution of complex dissociation processes to be studied [53].

2. Experimental methods

2.1. Laser techniques

The recent progress in femtosecond time-resolved photoelectron spectroscopy derives from prior developments in femtosecond laser technology, since techniques for photoelectron spectroscopy have been highly developed for some time. There are several general requirements for such a femtosecond laser system. Most of the processes of interest are initiated by absorption of a photon in the wavelength range from ~200 to 350 nm, produced via non-linear optical processes such as harmonic generation, frequency mixing and parametric generation. Thus the output pulse energy of the laser system must be high enough for efficient use of nonlinear optical techniques and ideally would be tunable over a wide wavelength range. Another important consideration in a femtosecond laser system for time-resolved photoelectron spectroscopy is the repetition rate. To avoid domination of the signal by multiphoton processes, the laser pulse intensity must be limited, thus also limiting the available signal per laser pulse. This aspect is discussed in more detail in a following section. As a result, for many experiments a high pulse repetition rate can be more beneficial than high energy per pulse. Finally, the signal level in photoelectron spectroscopy is often low in any case and, for time-resolved experiments, spectra must be obtained at many time delays. This requires that any practical laser system must run very reliably for many hours at a time.

Modern Ti:Sapphire-based femtosecond laser oscillators have been the most important technical advance for performing almost all types of femtosecond time-resolved measurements. Ti:Sapphire oscillators are tunable over a 725–1000 nm wavelength range, have an average output power of several hundred mW and produce pulses as short as 8 fs, but more commonly 80–130 fs, at repetition rates of 80–100 MHz. A tunable femtosecond pulse can be derived directly from amplification and frequency conversion of the fundamental laser frequency.

The development of chirped-pulse amplification and Ti:Sapphire regenerative amplifier technology now provides mJ pulse energies at repetition rates of greater than 1 kHz with <100 fs pulse widths. Chirped pulse amplification uses a grating pulse stretcher to dispersively stretch fs pulses from a Ti:Sapphire oscillator to several hundred picoseconds. This longer pulse can now be efficiently amplified in a Ti:Sapphire regenerative amplifier to energies of several mJ while avoiding nonlinear propagation effects in the solid-state gain medium. The amplified pulse is recompressed in a grating pulse compressor similar to the pulse stretcher.

The most successful approach for generating tunable output is optical parametric amplification of spontaneous parametric fluorescence or a white light continuum, using the Ti:Sapphire fundamental or second harmonic as a pump source. Typically, an 800-nm pumped fs OPA can provide a continuous tuning range of 1200–2400 nm [54]. Non-collinear OPAs (NOPAs) [55] pumped at 400 nm provide μ J-level ~15 fs pulses which are continuously tunable within a range of 480–750 nm, allowing for extremely high time resolution measurements.

In Fig. 2, we show a schematic layout of the present NRC femtosecond laser system. A fs Ti:Sa oscillator (Spectra-Physics Tsunami) and a ps Nd:YAG oscillator (Lightwave Electronics 131) are each electronically phase locked to an 80-MHz external reference oscillator. This synchronizes the optical pulse trains from the two oscillators to within 1-2 ps. The Ti:Sa oscillator is pumped by a diodepumped Nd:YVO₄ laser (Spectra Physics Millenia). The ps Nd:YAG oscillator is directly diode-pumped. The ~80 fs, 800 nm Ti:Sa pulses are stretched to a few hundred ps and then regeneratively amplified (Positive Light, Spitfire) using a 10 mJ, 1 kHz Nd:YLF laser (Positive Light, Merlin) as the pump source. Upon switch-out, this produces ~ 2 mJ pulses which can be recompressed to yield ~1 mJ, 80 fs pulses at 1 kHz. Alternatively, these pulses can be passed through a linear Ti:Sa amplifier before com-

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Fig. 2. The NRC femtosecond laser system; fs Ti:Sa and ps Nd:YAG oscillators are electronically synchronized and each amplified at 1 kHz. The Ti:Sa laser is stretched, regeneratively amplified, linearly amplified and subsequently compressed for output. The ps YAG pulses are amplified in an NRC-design diode-pumped Nd:YVO₄ cavity. The amplified Ti:Sa output at 800 nm is used to pump two multi-pass OPAs (OPA1, OPA2), producing fs near-IR tunable pulses. Pulses (400 nm) from second harmonic generation of the Ti:Sa output are used to pump two non-collinear OPAs (NOPA1, NOPA2), producing broadly tunable, very short (~15 fs) pulses throughout the visible region. For a detailed discussion, see the text.

pression, pumped by another 10 mJ, 1 kHz Nd:YLF laser. This yields ~ 5 mJ/pulse at 1 kHz. Upon compression, about 2.5 mJ, 80 fs pulses at 1 kHz are obtainable. The 150 ps 1064 nm pulses from the Nd:YAG oscillator can be amplified to ~1.5 mJ/ pulse in an NRC-design 1 kHz diode-pumped $Nd:YVO_4$ grazing incidence slab laser (GISL) [56]. Alternatively, the Nd:YVO4 GISL can be operated as a Q-switched laser, producing ~1.5 mJ, 2.5 ns 1064 nm pulses at 1 kHz. In either case, ~50% doubling efficiency to 532 nm is obtained. This laser and its harmonics can be used for many purposes, including: (1) laser ablation of metal or semiconductor clusters at 1 kHz; (2) pumping an OPA to give high resolution tunable radiation for synchronized quantum state pre-selection or post-detection; (3) prism dye cell post-amplification ($\sim 10 \times$) at 1 kHz of fs visible pulses from doubling of the fs OPA output.

In order to obtain tunable fs radiation, the amplified Ti:Sa output is used to pump several OPAs. High power pulses at 800 nm pump two OPAs (Quantronix, TOPAS), each producing 40–80 fs pulses continuously tunable within the range of 1200–2400 nm. These can each be doubled or summixed with the pump and subsequently doubled again to produce tunable fs UV pulses. Second harmonic generation of the amplified Ti:Sa laser yields 400-nm pulses which are used to pump two non-collinear OPAs (NOPAs). These produce very short (10–20 fs) pulses with a few μ J of energy, continuously tunable in the range of 480–750 nm. A

computer controlled stepper motor is used to control the time delay between the pump and probe laser systems. Typically, the pump and probe laser pulse energies are recorded on a shot-to-shot basis and used as a real-time data collection filter.

2.2. Intensity effects

Laser field-matter couplings are often assumed to be sufficiently weak that they are only perturbative with respect to the matter Hamiltonian. However, amplified femtosecond laser pulses are inherently intense and experimentalists and theorists alike must be aware of this. The neglect of intensity effects can lead to misinterpretation of results. Even moderate focusing (f/40) of a 100 fs pulse (e.g. $\lambda = 300$ nm) yields an intensity of 10^{12} W/cm² with a pulse energy of only 1 µJ. It can be seen that amplified femtosecond pulse experiments will be very difficult to carry out in the perturbation theory (Golden rule) limit of $10^6 - 10^8$ W/cm². As the strong laser field physics of molecules is amply discussed elsewhere [57], we consider here only briefly some potential consequences of the non-perturbative fields that can appear in almost any femtosecond experiment using amplified pulses.

From a very practical point of view, it is often difficult to use one-photon preparation of an excited state wavepacket unless the absorption cross-section for this step is large. The reason for this is that femtosecond pulses generally favour non-linear over linear processes. Since the ratio of one- to twophoton cross-sections is fixed for a given material system, the only possibility is to reduce the laser intensity until the one-photon process dominates. The signal levels at this point, however, may be very small and very sensitive detection techniques are required.

An important consequence of non-perturbative intensities is the AC Stark effect — the shifting and modification of potential energy surfaces due to the strong electric field of the laser pulse. This leads to an alteration of the molecular dynamical evolution and to sweeping field-induced resonances which may introduce phase-shifts in the probe laser signal. In the photoionization continuum, the AC Stark effect manifests itself in terms of the ponderomotive potential U_p , well known in strong field atomic physics

[58]. Classically, the ponderomotive potential of an electron in a laser field of strength *E* and frequency ω is given by the time-averaged 'wiggling' energy:

$$U_{\rm p} = \frac{e^2 E^2}{4m_{\rm e}\omega^2}.$$
(3)

A convenient rule of thumb is that the ponderomotive shift is 10 meV per TW/cm² at 0.330 μ m. U_p scales linearly with laser intensity and quadratically with wavelength. Due to the spatio-temporal averaging of intensity in the pulse, the effect is observed as a blue shift and broadening of the photoelectron spectrum [59].

Non-perturbative intensities can have a particularly pronounced effect on the measurement of photoelectron angular distributions (PADS). The anisotropic nature of the photoexcitation pump process results in an alignment of both the angular momentum and molecular axis distributions of the excited state in the laboratory frame (defined by the polarization direction of the pump laser field). In the Golden rule limit, for a single photon pump excitation, a $\cos^2\theta$ distribution of excited state molecular axes in the lab frame results from a parallel transition $(\sin^2\theta$ from a perpendicular transition). Non-perturbative intensities will, due to Rabi cycling [60,61], give rise to higher than expected alignment and can be used to align the molecular ground state [62]. This alignment of the molecular axis distribution in the lab frame *directly* affects the observed PADS since the relative contributions of parallel and perpendicular ionization channels and the interferences between them depends upon the degree of alignment [37]. This can be exploited to follow the evolution of molecular axis alignment as a probe of rotationvibration coupling in polyatomic molecules [38,63], as well as to enhance the sensitivity of PAD measurements to non-adiabatic processes which result in a change of symmetry of the allowed photoelectron partial waves, as discussed above.

The study of non-linear optical phenomena is often complicated by fluctuations in laser energy and intensity. One way to make accurate constant intensity measurements is via the use of the autocorrelation ratio (ACR) as a pulse filter [59]. This involves splitting off a small portion of the fs laser pulse and subsequent second harmonic generation in a thin crystal. Both the fundamental and second harmonic are recorded on a shot-by-shot basis with photodiodes. The ratio of the second harmonic signal to the square of the fundamental signal (this ratio is the ACR) is calculated on a shot-by-shot basis. The ACR is constant if the laser intensity is constant. Therefore, the ionization signals may be filtered on a shot-by-shot basis according to the limits (e.g. $\pm 10\%$) set on the ACR. We note that pulse filtering via energy measurements alone do not account for fluctuations in pulse duration or spatial mode distribution.

2.3. Time-of-flight and ZEKE photoelectron spectroscopy

Spectrometers for femtosecond time-resolved photoelectron spectroscopy have modest requirements compared to modern standards for photoelectron spectrometers. The bandwidth (FWHM) of a Gaussian 100 fs pulse is $\sim 150 \text{ cm}^{-1}$. A pump-probe measurement involves the convolution of two such pulses, leading to an effective bandwidth of ~ 25 meV. The same measurement with 50 fs pulses would have an effective bandwidth of about ~50 meV. This limits the energy resolution required in measuring the energy of the photoelectrons. For many experiments, a UHV (10^{-10} Torr) time-of-flight photoelectron spectrometer of the type shown in Fig. 3 is sufficient. This consists of a magnetically shielded (7) 20 cm long time-of-flight tube (5) with a cathode-ground microchannel plate (MCP) detector (6). Fast risetime electron pulses from the MCP anode (typically at 3 kV) are coupled out by an in vacuo GHz bandwidth coaxial decoupling capacitor [64]. A molecular beam source (a) and skimmer (b) provide an intense beam of jet-cooled molecules for study. A low profile (<1'') UHV gate valve is used to isolate the source from the UHV chamber [65]. Ionization occurs at the laser focus (x). A collinear 50-cm ion time-of-flight tube (8) with a second MCP detector (9) is used to determine mass spectra and operates in the Wiley-McLaren configuration by grounding electrode (1), applying +500 V to (3) and -1500 V to the flight tube (8). The guard rings (2) parallelize the electric field lines. The main interaction chamber is differentially pumped by a 400 1/s maglev turbo pump, as are each of the two flight tubes. Time-of-flight photoelectron and mass spectrometers have the advantage of measuring the entire spectrum on every laser shot, effectively self-normalizing the measurement. In addition, the timeresolved time-of-flight photoelectron spectrum provides a spectrum of the evolving molecular excited state over a very wide energy range without the need to tune the frequency of the femtosecond laser.

In time-resolved ZEKE spectroscopy the probe pulse does not directly ionize the molecules excited by the pump pulse but rather excites them to high lying Rydberg states. After a time interval (typically 1 µs) to allow kinetic electrons to leave the ionization region, a pulsed electric field of typically 0.5-1V/cm ionizes the high Rydberg states and accelerates them towards a detector. In ZEKE mode, electrode (3) is grounded and a ns risetime voltage pulse is applied to electrode (1), with the guard rings (2) parallelizing this pulsed field. A 10-ns voltage pulse on the tube electrode (4) is used as a post-acceleration stage to kick the ZEKE electrons up to 10 eV drift energy, improving their transmission and separating them in time from any stray electrons. The technique provides essentially unit collection efficiency for the ZEKE electrons and hence very high signal-to-noise ratios are obtained.

2.4. Magnetic bottle photoelectron spectroscopy

A large improvement in electron collection efficiency while retaining the advantages of the timeof-flight measurement can be obtained by using a magnetic bottle spectrometer [66], as shown in Fig. 4. This technique uses a strong inhomogeneous magnetic field (1 T) to rapidly parallelize electron trajectories in the upper half plane, followed by a constant magnetic field (10 G) to guide the electrons to the detector. With careful design, the collection efficiency of magnetic bottle spectrometers can approach 50%, while maintaining an energy resolution essentially equivalent to the fs laser bandwidth. Highest resolution is obtained for electrons created within a small volume ($\phi < 100 \mu m$) at the very center of the interaction region. In contrast with ns laser experiments, however, it is not desirable to focus fs lasers to small spot sizes due to the inherently high intensity of such pulses, leading to multiphoton ionization. Longer focal lengths mean



Fig. 3. A photoelectron-photoion collinear time-of-flight spectrometer. A high intensity molecular beam (a) from a high throughput source chamber (10^4 l/s) is skimmed (b) before entering the spectrometer interaction region (x). The ion time-of-flight mass spectrometer (8) points upwards, whereas the electron spectrometer (5) points downwards. Both electron time-of-flight and ZEKE modes of detection are possible. The interaction region and the two flight tubes are each pumped by a 400 l/s turbo pump. The base pressure of the spectrometer is 10^{-10} Torr. For a detailed discussion, see the text.



Fig. 4. The NRC magnetic bottle photoelectron spectrometer. The bottle uses a 1 T parallelizing field which leads into a 10 Gauss guiding field in the electron drift tube. The geometry is optimized for high intensity molecular beam throughput. The source chamber (10^4 I/s) houses a continuous or 1 kHz pulsed variable temperature molecular beam nozzle. The interaction chamber and electron drift tube are each pumped by a 400 l/s turbo pump. The base pressure of the spectrometer is 10^{-10} Torr. For a detailed discussion, see the text.

that the Rayleigh range (the 'length' of the focus) extends well beyond the favourable region, leading to an overall lower resolution. In order to minimize surface potentials, we use in vacuo quartz bake-out lamps to keep the interior surfaces of the spectrometer hot at all times, keeping a constant energy calibration over extended periods of time.

We emphasize that in fs pump-probe experiments, the laser intensity must be kept below multiphoton ionization thresholds. This simply requires a reduction of the intensity until one-photon processes dominate. In order to recover acceptable signal levels, the target density must be increased. Hence, we implement a high intensity molecular beam source as shown in Fig. 4. The source chamber has ~10,000 l/s pumping speed, backed by a large booster pump. A doubly skimmed beam passes through the main interaction chamber, which is differentially pumped by a 400 l/s maglev turbo. The electron time-of-flight tube is differentially pumped by another 400 1/s maglev turbo. Even with intense molecular beams, the pressure in the drift tube does not exceed 10^{-6} Torr.

The time-of-flight of photoelectrons in a magnetic bottle spectrometer is expected to follow the kinetic energy equation $E_{kin}(t) = (1/2)m_e x^2/t^2$ with x being the length of the flight tube. The strong influence of stray electric fields, however, necessitates a calibration of the photoelectron energies, using established electron energies and times-of-flight in wellknown molecules (e.g. NO). The equation is simplified to $E_{kin} = IC/(t - t_0)^2 + E_0$ and the instrument constant IC, the pump-probe overlap time t_0 and an energy offset E_0 are determined in a nonlinear least squares fit. The resolution of the spectrometer depends on the kinetic energy of the electrons. Fast electron signals are often broadened by the limited bandwidth of the detection electronics and slow electrons are very sensitive to stray fields. To obtain the best possible energy resolution, an accelerating or retarding voltage can be applied to the flight tube and only a time-of-flight window with the best resolution (e.g. 0.5 eV electrons) is recorded. By scanning the retarding voltage, all electron signals can be brought into the high resolution region and the complete spectrum can be reconstructed. The simple addition of the retarding potential $V_{\rm ret}$ however does not satisfactorily describe the effect of the retarding voltage. A use of a simple power series [66]

$$E_{\rm kin} = \sum_{n} \frac{b_n}{T_n} + V_{\rm ret} \sum_{n} c_n T_n \text{ with } n = 0-4$$
(4)

with fitting parameters $b_1 - b_n$ and $c_1 - c_n$ suffices to describe the dependence on the retarding voltage. For a fixed retarding voltage, the use of the power series is not distinguishable from a calibration via $E_{\rm kin} = {\rm IC}/(t - t_0)^2 + E_0$. In femtosecond experiments, the resolution is usually limited by the laser bandwidth (e.g. 50 meV) and voltage scans are seldom necessary.

2.5. Photoelectron imaging

Measurements of photoelectron angular distributions (PADs) usually involve control of the light polarization vector with respect to the electron timeof-flight axis, using optical elements such as double Fresnel rhombs or waveplates. The use of such optical components in conjunction with femtosecond light pulses is impractical because they often introduce either dispersion, leading to pulse broadening, or have small bandwidth, leading to varying polarization states across the spectrum of the femtosecond pulse. Better suited to fs pulses is the use of a UV-grade crystalline quartz Berek's compensator which can act as a very thin (2 mm) broad band, variable zeroth order waveplate, analogous to a Soleil-Babinet compensator. However, a disadvantage of all methods relying on the rotation of polarization vectors is that it can be difficult to avoid systematic deviations in the temporal and spatial overlaps of the pump and probe beams as the polarization is rotated. Femtosecond photoelectron imaging techniques [39] using CCD cameras overcome these problems by recording all electron

emission angles simultaneously, eliminating the need for rotation of the polarization vector with respect to the electron time-of-flight axis and, due to multiplexing, significantly reduce the signal averaging required. In this case a two dimensional projection of the three dimensional distribution of recoil velocity vectors is measured, and inverse-Abel transform techniques are then used to recover the full three dimensional distribution [67]. This approach however may only be used when the image is a projection of a cylindrically symmetric distribution whose symmetry axis lies parallel to the two-dimensional detector surface. This requirement precludes the use of non-coincident pump and probe laser reference frames (i.e. non-parallel laser polarizations), a situation which may provide detailed information on intramolecular dynamics through the alignment dependence of the PAD discussed above. Additionally, the mathematical techniques used for the reconstruction of the three dimensional distribution from the projection are inherently noisy. It is therefore preferable to adopt fully three dimensional imaging techniques based upon time-and-position sensitive detection, where the full three dimensional distribution is obtained directly without the introduction of mathematical reconstruction.

2.6. Recent developments in coincidence spectroscopy

The use of coincidence-imaging technology in fs pump-probe experiments was successfully demonstrated by Hayden [53]. In collaboration, we are developing a similar methodology, based on crossed delay line anodes, in our laboratory [68]. An illustration of a generic coincidence-imaging spectrometer is shown in Fig. 5. First the electrons, which are fast compared to the ions, are pulsed out of the interaction region and accelerated towards a time-andposition sensitive detector. After the electrons have cleared the interaction region and/or hit the electron detector, the ions may be pulsed towards a second time-and-position sensitive detector at the end of the ion flight tube. The important figure of merit for an imaging spectrometer is the energy resolution as a percentage of the maximum recoil energy viewed by the detector. The most important factors in this figure of merit are the molecular beam diameter (which



Fig. 5. A depiction of a time-resolved photoelectron-photoion coincidence-imaging experiment (Hayden et al. [53]). Without coincidence, photofragment energy-angular distributions and photoelectron energy-angular distributions may be measured as a function of time. With coincident mass detection, a time-resolved PEPICO technique obtains. With energy and angular resolution for both ion and electron distributions in coincidence, highly detailed information about the dynamics is obtained as a function of time. For a discussion, see the text.

determines the ionization volume since fs lasers cannot be tightly focused in pump-probe experiments), the laser bandwidth and the timing errors in the electronics. (In principle, velocity map imaging [69] may be used to counteract the finite size of the source and improve the resolution of the spectrometer.) The position-sensitive detector must be capable of time-of-flight measurements at sufficient resolution to resolve the three dimensional recoil velocity vectors of the particles.

There are two basic architectures for time-andposition sensitive detectors. In the direct readout method, each detector cell is read out individually.

This method is ideal for true multi-hit detection since dead time issues concern only hits on the same detector cell. Such methods, however, may be expensive, difficult to calibrate and complicated to implement. A second method, more attractive for large area detectors, is referred to as an interpolating readout. This type is designed such that some measurement parameter is sensitive to time and position on the detector surface. Examples of such detectors are charge division or delay line readout anodes. Charge division (e.g. wedge-and-strip) anodes are critically sensitive to scattered light and background signals since they inherently cannot tolerate multiple hits. Delay line detectors, by contrast, allow for multiple hits and achieve both timing and spatial resolution with a minimum of electronics [51,52]. The position is determined by measuring the difference in propagation times between the point of signal incidence (i.e. the 'hit') on the anode and the two different ends of the transmission line (or transmission lines). For example, along the x('horizontal') delay line, the propagation times are $t_1 = x/v_g$ and $t_2 = (l - x)/v_g$ where x is the position, *l* is the length of the transmission line and $v_{g} = c/\sqrt{\varepsilon}$ is the group velocity on this transmission line of dielectric constant ε . The x-position obtains as x = $(l - (t_2 - t_1)v_g)/2$. The same arguments apply for the y position (the 'vertical' delay line): y = (l - l) $(t_4 - t_3)v_{g}/2$. The position resolution depends on the measurement of these propagation time differences. The sum of the propagation times in the two directions is a constant and allows determination of the time-of-flight. The signal amplifiers should have an RC time constant, t_a , which matches the rise time of the pulse coming off of the transmission line, $t_{\rm p}$, maximizing the slope to noise ratio required for maximum timing resolution. In this case the time resolution is

$$\Delta t = \frac{C\nu_n}{2Q}\sqrt{t_a} = \frac{\varepsilon C_0\nu_n}{2Q}\sqrt{t_a}$$
(5)

where ν_n is the spectral noise density of the amplifier, Q is signal charge, C is the capacitance of the transmission line and C_0 is the capacitance of the transmission line for $\varepsilon = 1$. This uncertainty in the time results in a position resolution

$$\Delta x = \frac{cC_0 \nu_n}{2Q} \sqrt{\varepsilon t_a}.$$
(6)

The position resolution is improved by decreasing the delay line capacitance, the amplifier noise, and the signal rise time and by increasing the signal charge Q. Using this technique, a position resolution of $<50 \ \mu\text{m}$ in combination with a time resolution of $<300 \ \text{ps}$ is readily achievable [70].

2.7. Some example applications

The use of time-resolved ZEKE photoelectron detection is shown in Fig. 6, using $I_2(B)$ vibrational wavepacket dynamics as an example [20,21]. A femtosecond pump pulse at 580 nm prepared a vibrational wavepacket in the B-state. As a function of time delay, a two-photon probe at 345 nm projected this wavepacket onto the ground vibra-

tional state of the ion. After a time delay of 1 µs in which all free electrons escaped, a 2 V/cm pulsed field ionized the high-lying Rydberg states and pushed the ZEKE-PFI electrons towards the detector. The collected electron signal, plotted in Fig. 6, oscillates as a function of time delay. This modulation simply reflects the wavepacket vibrational motion in the excited state with a period of 340 fs. The wavepacket can only be detected in the region where the overlap with the final state is high (i.e. at the Condon point of the transition, the inner turning point). Therefore as the wavepacket evolves, it passes this region, leading to a modulated signal. As the vibrational states dephase, the classical-like oscillation disappears. Eventually, they recover their initial phases and the wavepacket revives [71], in



Fig. 6. Time-resolved ZEKE photoelectron spectroscopy of wavepacket dynamics in a diatomic molecule, $I_2(B)$. Well resolved 340 fs modulations can be seen, corresponding to classical-like vibrational motion in the excited B-state. The wavepacket undergoes quantum mechanical dephasing in ~3 ps and exhibits a revival at ~18 ps. Inset is the power Fourier transform of this time domain data, showing the vibrational coherences responsible for the modulated signal. Very high signal-to-noise ratios are obtainable with the ZEKE technique. For a discussion, see the text.

this case around 20 ps. In the frequency domain picture, the modulations are due to interferences between the individual transitions from different eigenstates terminating in the same final ionic state and are described by nearest-neighbour coherences as well as higher order coherences (e.g. next-nearest-neighbour). The power Fourier transform of the time domain data is inset in Fig. 6, showing the vibrational level spacings (e.g. v = 15/v = 16) responsible for the time-domain signal. These results show the high, background free signal-to-noise ratios obtainable with ZEKE detection.

As an example of typical results obtained via time-resolved magnetic bottle photoelectron spectroscopy, we show a raw pump-probe photoelectron time-of-flight spectrum of NO in Fig. 7. The pump and probe laser wavelengths were set to 277 and 207.5 nm, respectively. These time-resolved spectra

show a set of time-independent peaks, between 400 and 600 ns, due to non-resonant two-photon ionization by the probe laser alone. These are assigned to lowest vibrational levels in the ground state of the ion. The relative intensities depend on the Franck– Condon overlap factors of those vibronic levels with the ground state of molecular NO. Between 700 and 1200 ns, a time-dependent signal is observed which is due to non-resonant two-photon absorption of one 277 nm pump and one 207.5 nm probe photon. These results illustrate the power of the technique as a time and frequency resolved spectroscopy and the high signal-to-noise ratios obtainable with only a few minutes of signal averaging.

In the NO case above, a time-dependent signal can only be observed when pump and probe pulses are overlapped in time and decays with the laser crosscorrelation. Therefore this data set also gives us the



Fig. 7. Time-resolved magnetic bottle photoelectron spectroscopy, showing raw, unprocessed time-of-flight data for non-resonant ionization of nitric oxide. The peaks are assigned to the corresponding vibrational state of the cation. A signal which depends only on the 207-nm probe laser (500–600 ns) does not vary with time delay. A 277-nm pump–207-nm probe signal appears at zero time delay, as expected. For a discussion, see the text. In this data set, the accumulation period was 100 s per time step, illustrating the high signal-to-noise ratios obtainable in this time- and energy-resolved spectroscopy.

absolute pump-probe $\Delta t = 0$, the instrumental time response function and accurate energy calibration of the photoelectron spectrometer. We note that the energy of two pump photons (277 nm) is below the ionization potential and the intensity of the pump pulse was insufficient for non-resonant three photon ionization.

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As an example of ultrafast non-adiabatic dynamics, in Fig. 8 we show calibrated femtosecond timeresolved photoelectron kinetic energy spectra of naphthalene recorded with the magnetic bottle spectrometer. The first and the second excited singlet states of naphthalene, S_1 and S_2 , are strongly coupled via ultrafast internal conversion. The vibrationless origin of the S_2 state was prepared with a fs pump pulse at 277 nm. The excited molecules are then ionized after a delay time Δt using a 207.5-nm probe photon. The ultrafast S_2-S_1 internal conversion process leads to the time-resolved photoelectron spectra shown. These spectra have had pump only and probe only spectra subtracted. The spectra show a band at 2.3 eV which is due to ionization of the S_2 state to the D_0 ground state of the ion. They also show a band at 1.8 eV arising from photoionization of vibrationally hot S_1 molecules, formed by the internal conversion process, into the ionic ground state of the cation. The signal between 1.2 eV and 1.7 eV corresponds to a transition between the S_2 state and the first excited state of the ion. The timedependent behavior of the S2 band closely follows the cross correlation of the pump and the probe lasers. This observation means the S_2-S_1 internal conversion time must be faster than 100 fs. For time delays outside the cross correlation we find a constant signal between 0.6 eV and 1.8 eV which is mainly due to ionization out of the S_1 state. This



Fig. 8. Time-resolved magnetic bottle photoelectron spectroscopy of ultrafast non-adiabatic dynamics in naphthalene. The 277-nm pump pulse prepared the S_2 state at its origin. Upon photoionization with the 207-nm probe pulse, the photoelectron band near 2.4 eV obtains. This band decays extremely quickly, well within the ~130 fs laser cross-correlation. The vibrationally hot S_1 state formed by the internal conversion produces a broad photoelectron band, centered at 1.5 eV. Only this band is observed at longer delay times. These results illustrate the capability of observing both electron population dynamics and vibrational dynamics in an excited molecule.

shows for non-overlapping lasers that only the S_1 state is populated. The combination of a high intensity molecular beam together with the magnetic bottle spectrometer makes it possible to record such a spectrum in only $\sim 1-2$ min.

3. Conclusions

Time-resolved photoelectron spectroscopy is emerging as a promising technique for the study of ultrafast excited state dynamics in polyatomic molecules. Existing femtosecond laser and photoelectron spectroscopy techniques of the kind discussed here are sufficient for these investigations. The examples discussed above illustrate its applicability to problems ranging from detailed diatomic wavepacket dynamics to vibrational/nonadiabatic intramolecular dynamics in polyatomic systems. Our present research directions include the study of excited state proton and electron transfer reactions, ultrafast molecular electronic switches, photoelectron angular distribution measurements and coincidence techniques. We look forward to exciting developments in time-resolved photoelectron spectroscopy in many laboratories around the world.

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