

Photoelectron Spectroscopy in a New Light: Zero Kinetic Energy (ZEKE) Photoelectron Spectroscopy with Coherent Vacuum Ultraviolet Light

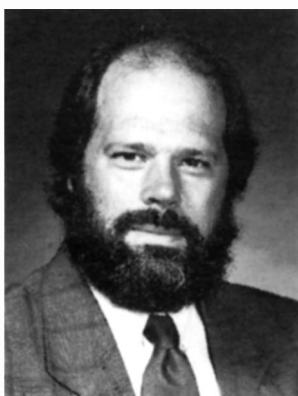
John W. Hepburn

Centre for Molecular Beams and Laser Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

1 Introduction

A great deal of what we know about the electronic structure of molecules and solids has resulted from the study of photoemission. Although studies of the photoelectric effect began in the 19th century, the modern study of photoelectron spectroscopy began with the development of suitable short wavelength light sources in the 1950s and 60s. For gas-phase high-resolution photoelectron spectroscopy (PES), the differentially pumped He discharge lamp was the necessary prerequisite.¹ This light source, along with other rare-gas discharge sources, provides high intensity, reasonably monochromatic light at fixed wavelength in the vacuum ultraviolet (VUV). Not very long after the development of high resolution PES, a different form of photoelectron spectroscopy based on monochromatized continuum or pseudo-continuum radiation evolved out of the field of photoionization mass spectrometry.² This method, called threshold photoelectron spectroscopy (TPES), is based on scanning the photon energy of the ionizing light while detecting only those photoelectrons that have essentially zero kinetic energy. In this way the signal is detected only when the photon energy matches an ionization threshold. The resulting spectrum provides the same information as a conventional photoelectron spectrum, although there are important differences between these two types of spectroscopy. In Fig. 1, both types of photoelectron spectroscopy are illustrated schematically. TPES is ideally suited to synchrotron light sources, which are excellent sources of continuously tunable short-wavelength light. Most of the work in TPES has been done with synchrotrons. The advent of third generation synchrotron sources, such as the Advanced Light Source in Berkeley, California, improves both the resolution and light flux dramatically, compared with previous synchrotrons. Currently, the state of the art for energy resolution in gas-phase photoelectron spectroscopy with rare gas lamps is about 2–4 meV, while TPES can do slightly better. Since the resolution for both techniques is limited largely by the light source, one should be able to gain another factor of five by doing TPES with a high-resolution monochromator with a third generation synchrotron.

John Hepburn is Professor of chemistry and physics at the University of Waterloo. He did his undergraduate studies in chemistry at Waterloo, completing his BSc degree in 1976. He finished his PhD under John Polanyi's supervision at the University of Toronto in 1980, and then spent two years in Yuan Lee's laboratory in Berkeley as a NATO postdoctoral fellow. He returned to Waterloo in 1982 as an NSERC University Research Fellow and became a Professor in



1990. Hepburn's research has focused on photofragment spectroscopy of small molecules, photoionization and photoelectron spectroscopy, and the dynamics of ion-molecule reactions. He has been an A. P. Sloan Foundation Fellow and is currently a Canada Council Killam Fellow. In 1992 he received the Noranda Award from the Canadian Society for Chemistry and the Rutherford Memorial Medal in Physics from the Royal Society of Canada.

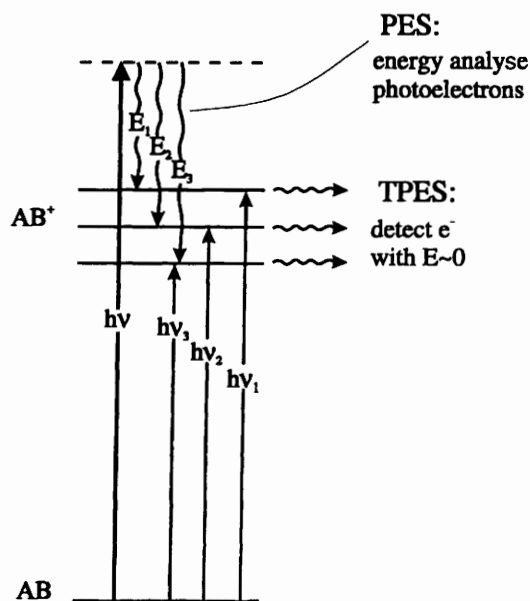


Figure 1 Schematic diagram of conventional PES and threshold PES. Note that since $h\nu - E_1 = h\nu_1$, both measure ionization energies.

In parallel with the development of TPES using synchrotron radiation, the application of coherent light sources to the study of valence-shell photoionization has created a revolution in photoelectron spectroscopy over the past decade and a half. The beginnings of this leap forward came with the development of resonance-enhanced multiphoton ionization (REMPI) by Johnson in the 1970s.³ This technique, based on sequential absorption of visible or ultraviolet photons, allows one to excite to the ionization threshold in molecules with coherent light. Although originally developed as a sensitive method for excitation spectroscopy, REMPI has also been used in elegant and detailed studies of photoionization dynamics.⁴ There are several advantages for photoionization with coherent light. The first, and most important, is energy resolution, as even conventional pulsed laser systems have a resolving power of 200 000, and that can be improved to 4×10^6 with single mode pulsed lasers. The current state of the art in scanning VUV monochromators is less than 150 000 resolving power. Because of the intensity of lasers, very dilute targets such as skimmed supersonic beams of free radicals and clusters can be easily studied. The use of multiple resonance techniques provides a means to photoionize a state-selected, aligned target. Because the excitation is pulsed, sensitive and of high resolution, time of flight techniques can be used for photoelectron spectroscopy following REMPI.⁵

A very important new technique for extremely high-resolution photoelectron spectroscopy, which combines REMPI and threshold photoelectron spectroscopy, was developed about a decade ago by Schlag and Müller-Dethlefs.⁶ The technique has come to be known by the acronym PFI-ZEKE (for pulsed-field ionization zero kinetic energy) photoelectron spectroscopy, or the simpler, and more euphonious, ZEKE (/zi:ki:/) spectroscopy.⁷ The ZEKE method takes advantage of both the high photon energy resolution and the pulsed excitation provided by tunable pulsed-dye lasers. As with conventional TPES, the photon energy is scanned through the

various ionization thresholds, and the signal is detected only from threshold ionization. The key to the high photoelectron energy resolution is the technique used for threshold detection, which is delayed pulsed field ionization. Although it was not realized until a few years after the initial development of ZEKE, the detection of ionization thresholds is based on the excitation and subsequent field ionization of high principal quantum number Rydberg states lying just below the ionization thresholds. Since there are Rydberg series converging to every quantum state of every ion, the ZEKE method is quite universal. The use of optimized ionizing pulse sequences has led to 'photoelectron' energy resolutions of 0.1 cm^{-1} , or *ca.* 0.01 meV . This spectacular energy resolution is sufficient to fully resolve rotational structure in small and medium sized molecules, and can easily resolve very low frequency vibrational structure in larger systems. Furthermore, because the threshold detection is based on pulsed field ionization, one can monitor either the field ionized electrons, as in ZEKE spectroscopy, or the corresponding positive ions. This latter type of threshold spectroscopy, first developed by Phil Johnson,⁸ has come to be known as MATI (*m*ass-analysed *t*hreshold ionization) spectroscopy. The spectroscopic information is the same for ZEKE and MATI, although MATI is typically of somewhat lower resolution. MATI has the enormous advantage that, because one can mass-analyse the product ions, the carrier of the photoelectron spectrum is unambiguously identified. For studies of unstable species, such as molecular clusters, this is a major advance, since it is impossible to make pure clusters of one type for spectroscopic study, and it can be quite difficult to tell them apart spectroscopically.

Most of the work in ZEKE and MATI spectroscopy up until now has been done using multiple resonance with pulsed ultraviolet lasers. While there are many significant advantages to this approach, not the least of which is large signals, one must have an intermediate resonant state to step from to get to the ionization thresholds. In systems where the neutral spectroscopy is unknown, or where potential intermediate states are dissociative, there is some advantage in exciting to the ionization threshold in one step, using short wavelength coherent light. The combination of coherent VUV with the ZEKE or MATI detection creates a universally applicable method for doing ultrahigh-resolution threshold photoelectron spectroscopy at ionization energies up to 19 eV. This review will discuss the use of coherent VUV in ZEKE photoelectron spectroscopy, focusing on a few unique features of this type of photoelectron spectroscopy. The next four sections will describe the generation of coherent VUV, the principles of ZEKE spectroscopy, and two examples of unusual features of ZEKE spectroscopy with coherent VUV.

2 Generation of Coherent VUV

Since there are currently no suitable broadband gain media for amplifying light at wavelengths shorter than 190 nm, coherent VUV must be generated by frequency-mixing longer-wavelength coherent light. This is routinely done to generate coherent light in the ultraviolet region of the spectrum, using birefringent crystals to mix light from visible dye lasers. The current tuning limit for commercially available crystals is the 189 nm limit of β -barium borate (BBO), meaning that photon energies up to 6.5 eV can be reached with current tunable pulsed-laser systems. Beyond this photon energy, gaseous media must be used for frequency mixing. Since symmetry restrictions forbid second-order non-linear processes in materials which have a centre of inversion, gases cannot be used for second-order frequency mixing (*e.g.* second harmonic generation) under normal circumstances. The first non-linear term for gases is the third-order term, which leads to frequency mixing between three input frequencies, resulting in sum and difference mixing of the applied frequencies. Because this third-order non-linear process involves four different waves, three input (fundamental) and one generated, it is called four-wave frequency mixing. The theory of four-wave mixing is described in several places,⁹⁻¹¹ so it will not be considered here. What will be discussed is some of the practical details about generation of tunable coherent VUV, and the current capabilities of coherent sources.

There are two general types of four-wave mixing in gases used for coherent VUV generation, and two wavelength ranges, which need to be considered. The simplest kind of four-wave mixing, and probably the most commonly used, is non-resonant third-harmonic generation, where a single colour is focused into a gaseous medium, and coherent light at three times the fundamental frequency is generated. The second type of four-wave mixing is two-photon resonant sum and difference frequency mixing, in which two different colours are used to generate coherent light at the sum and difference frequencies $\nu_{\text{OUT}} = 2\nu_1 \pm \nu_2$. The two wavelength ranges are based on purely practical considerations: wavelengths above and below the LiF transmission cut-off at about 105 nm. For coherent VUV at wavelengths transmitted by LiF, the non-linear medium can be contained in a gas cell with an LiF output window, while below the cut-off, windowless designs, typically pulsed gas jets, must be used. While any gaseous medium can be used for frequency mixing, atomic gases have the best characteristics and tend to be the most efficient non-linear media. For simplicity, we shall restrict our discussions to rare gases, although in some cases metal vapours, such as Hg or Mg, may be better media. In any case, the general principles of frequency mixing are the same, no matter what gas is employed.

The easiest way to generate coherent VUV is by third-harmonic generation in gas cells. All that is required is to focus the fundamental light fairly tightly (with a 15–30 cm focal length lens) into a cell containing rare gas, and VUV is generated at the focus. Although the process is quite inefficient, under ideal conditions one can convert one part in 10^5 of the input light into VUV. This means that by using 10 mJ, 5 ns pulses of 365 nm light, one can generate up to 10^{11} photons/pulses of Lyman α radiation, with typical yields being one or two orders of magnitude lower. The major drawback to third-harmonic generation is the need to phase-match,⁹ which requires that the index of refraction be lower in the VUV than at the fundamental frequency. Such behaviour, called anomalous dispersion, occurs when the third harmonic frequency is just to the blue of a strong absorption line. Phase matching requires a certain relationship between the refractive indices, depending on focusing conditions, which means that only a certain range of nonlinear medium pressures will be phase matched. Since the refractive index is a strong function of frequency near a resonance, phase matching is also very wavelength sensitive. All this combines to make third harmonic generation useful over small tuning ranges, within windows of frequency close to absorption lines. Furthermore, to increase conversion efficiency up to the one part in 10^5 level, one must increase the density of nonlinear gas, and maintain phase matching with a balancing pressure of normally dispersive rare gas (*i.e.* a mixture of Kr and Ar for 121.6 nm generation). This makes phase matching very frequency dependent, limiting the tuning range to tens of wavenumbers for a given gas mixture. However, for essentially fixed-frequency applications, such as detection of atomic hydrogen, this is not a serious limitation, and third-harmonic generation can be very useful.

For wavelengths less than 105 nm, a pulsed jet is used in place of the gas cell. Although the phase matching conditions are somewhat different in pulsed jets, because of the short length of the nonlinear medium relative to the confocal parameter, roughly the same wavelength limitations exist for jets and gas cells. Furthermore, one cannot obtain the same densities in a jet that are possible in a cell, which makes the conversion efficiency substantially lower. Nevertheless, one can still generate useful amounts of VUV, of the order of 10^9 photons/pulse, by this method. A good description of an apparatus employing third-harmonic generation in gas jets is given by Tonkyn and White.¹²

To obtain higher conversion efficiency, and a much broader tuning range, resonant-enhanced four-wave frequency mixing must be used. The expression for the third-order nonlinear susceptibility ($\chi^{(3)}$), which determines the strength of the generated nonlinear response, has resonance terms at one, two and three photon energies.³ Since one-photon and three photon resonances will lead to one-photon absorption of the fundamental or generated radiation, two photon resonance is used to enhance the value of $\chi^{(3)}$ by orders

of magnitude. What this means in practical terms is that one uses two independently tunable lasers, at frequencies ν_1 and ν_2 , to generate coherent VUV. The first frequency is fixed on an allowed two-photon resonance for the atom being used as the nonlinear medium, and the second laser is tunable. While phase matching still applies for the sum mixing ($\nu_{\text{OUT}} = 2\nu_1 + \nu_2$), one can achieve negative dispersion over a very broad spectral range by choosing a medium such that ν_{OUT} is above the lowest ionization limit. Below the ionization limit, or in regions of strong autoionizing resonances, the conversion efficiency will vary quite markedly with frequency, but one can obtain quite spectacular conversion efficiencies near Rydberg resonances. In our own laboratory, we have used Mg, Hg, Kr and Xe for this type of sum mixing, and they all work very well, with routine conversion efficiencies of one part in 10^4 being obtainable. The combination of Hg, Kr and Xe provides continuous coverage of the 10 to 19 eV spectral range for sum mixing.

For photon energies below 11 eV, the best way to generate coherent light is by difference-mixing using Kr or Xe in a gas cell. The phase matching conditions for difference-mixing are very much less restrictive than in sum-mixing, which means that just about any output wavelength can be generated efficiently within the tuning range of the ν_2 laser. For example, an efficient way to generate Lyman α is to use difference-mixing in Kr, with the ν_1 laser set at 212.5 nm, and the ν_2 laser at 842 nm. A summary of the tuning ranges available for different choices of media and ν_1 is shown in Fig. 2. For more information, readers are referred to refs. 10 and 11.

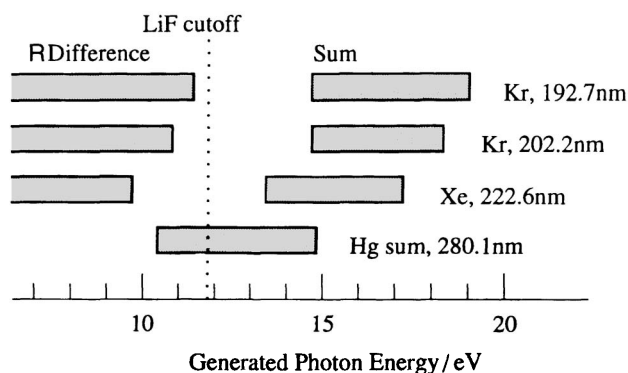


Figure 2 Continuous tuning ranges for two photon resonant frequency mixing in Hg, Kr and Xe. The wavelengths corresponding to ν_1 are given. For sum-mixing, only the tuning range above the ionization limit ($^2P_{1/2}$ in Kr, Xe) is shown.

For this review, it is sufficient to understand the practical end result. Using standard nanosecond dye lasers and frequency-mixing crystals, one can generate between 10^9 and 10^{11} photons/pulse of VUV, continuously tunable from 6.5 eV, where frequency-mixing crystals currently cut off, to 19 eV. This VUV has the coherence properties of the input fundamental light, meaning that photon energy resolutions of a fraction of a wavenumber at $100,000 \text{ cm}^{-1}$ are easily achievable. The data discussed in the following sections were recorded using light generated by sum-mixing in pulsed jets of Kr or Xe.

3 The ZEKE Process

Because ZEKE spectroscopy has created such excitement, there have been numerous recent reviews which have treated many different aspects in great detail. Probably the best single source of general information about several aspects of ZEKE is the book edited by Powis, Baer and Ng.¹³ The intention of this review is to draw attention to some unusual features of ZEKE spectroscopy with coherent VUV light sources, so we shall begin with a recap of what is currently understood about this type of spectroscopy.

ZEKE spectroscopy was originally developed as a very high resolution version of TPES, exploiting the pulsed nature of REMPI to introduce a long (of the order of a microsecond) delay between excitation to the ionization threshold under field-free conditions and extraction of the resulting threshold electrons with a small pulsed

electric field. The basic idea was that during this long delay, any electrons formed with small amounts of kinetic energy (even just a few wavenumbers) would drift away from the excitation volume, leaving only those with zero kinetic energy to await extraction and detection. This explains the ZEKE acronym, which remains despite the true nature of this spectroscopy. The first hint that something was wrong in this interpretation was that the directly measured ionization energy of NO was found to be 74717.2 cm^{-1} ,⁶ later revised to $74719.0 \pm 0.5 \text{ cm}^{-1}$,¹⁴ substantially below the then accepted value of $74721.5 \pm 0.5 \text{ cm}^{-1}$, determined by extrapolation of very well understood Rydberg series.¹⁵ The explanation of this significant discrepancy was that the signal detected in ZEKE spectroscopy came, not from electrons formed by ionization at photon energies just above threshold, but instead was the result of field ionization of very high lying Rydberg states just below the ionization threshold.¹⁶ This difference in signal source is actually good news from an experimental standpoint, as the care and feeding of extremely low energy electrons is a substantial chore, while field ionization detection of Rydberg states is a relatively straightforward task. Furthermore, because of continuity of oscillator strength through the ionization limit of any Rydberg series, the information available from field ionization is, in principle, the same as from threshold ionization. The ZEKE process is shown schematically in Fig. 3.

Fig. 3 shows the limits to electron energy resolution, or more correctly threshold resolution, in ZEKE spectroscopy. One can obviously do no better than the bandwidth of the exciting light, but

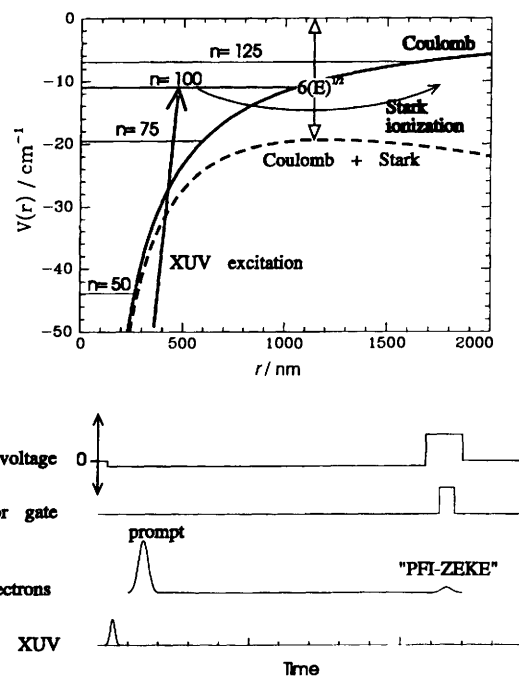


Figure 3 Schematic of the ZEKE process. Rydberg states around $n = 100$ are excited at $t = 0$, in the absence of applied fields. Prompt electrons are formed by excitation of degenerate ionization continua. After a delay, the remaining $n \approx 100$ Rydberg states are Stark ionized, and the resulting PFI-ZEKE signal is detected.

that is generally not what limits ZEKE resolution. Resolution is normally determined by the pulsed ionizing field. In the presence of a pulsed electric field, the ionization limit is lowered by between $4\sqrt{E}$ and $6\sqrt{E} \text{ cm}^{-1}$ (where E is in cm^{-1}), depending on whether the Stark ionization is diabatic or adiabatic.^{17,18} This means that for even fairly modest pulsed fields, a wide range of Rydberg states will be detected at each threshold. Because of stray DC fields present in any apparatus, and the fields caused by ions formed simultaneously with the Rydberg molecules, one cannot decrease the pulsed ionizing field arbitrarily, since there is a pre-existing reduction of the ionization threshold. To get higher resolution, combinations of pulsed fields must be used to create an energy

window of Rydberg states for detection. As an example, if one uses a 0.5 V cm^{-1} pulse, followed by a 0.6 V cm^{-1} pulse, and detects the electrons formed by the second pulse, the band of Rydberg states between 2.8 and 3.1 eV below threshold will be detected. It turns out that the time evolution of the Stark states formed in the presence of the pulsed ionizing field means that the best strategy is to apply two pulses of roughly equal magnitude, but opposite polarity.[†]

While the mechanism of Stark ionization leading to a ZEKE spectrum explains the observed shifts in thresholds, it introduces a new conceptual problem: how do the originally excited Rydberg states survive for several microseconds? In the case of NO, one would expect the Rydberg states to decay by predissociation, as was pointed out by Muller-Dethlefs, Schlag and co-workers.¹⁶ In many cases, especially for ionization limits above the lowest, one would expect even high- n Rydberg states to decay through autoionization or predissociation on a timescale much shorter than the delay time. The solution, first pointed out by Chupka a few years ago,¹⁸ was that the initially excited low- l , high- n Rydberg states could be rapidly mixed with energy-degenerate high- l , high- m_l Rydberg states because of the perturbing effects of weak stray electrical fields and the inhomogeneous fields caused by nearby ions created with the Rydberg states. These high- l, m_l states interact very weakly with the ion core, and thus decay very slowly. The effects of electric fields on autoionization rates had been previously noted in a study of nd Rydberg states of Na_2 ,¹⁹ and the lengthening of the nd state lifetimes was interpreted in terms of Stark-mixing with high- l states. The idea of optically exciting a particular 'state,' whose lifetime properties are modified by coupling to optically inaccessible states, is very familiar in photophysics, and the analogy between radiationless transitions and suppression of Rydberg state decay is made in some recent articles by Bixon and Jortner.²⁰ These articles also have a comprehensive bibliography, and readers are referred to them for a more detailed discussion of the stabilization of the Rydberg states involved in ZEKE spectroscopy.

The extensive literature discussion from over the past three years can be summarized in the following way. The optical excitation is to a band of high- n Rydberg states which lie within the bandwidth of the exciting laser. These states have low- l character, typically with $l \leq 3$, and in many cases are expected to have relatively short lifetimes (sometimes sub-nanosecond) because of autoionization or predissociation. The unperturbed decay lifetimes for the typical states involved in ZEKE spectroscopy ($150 < n < 300$) can be estimated by scaling the measured lifetimes for lower nl states using the n^3 scaling law for lifetimes.⁷ During the initial period after excitation, there is a competition between decay

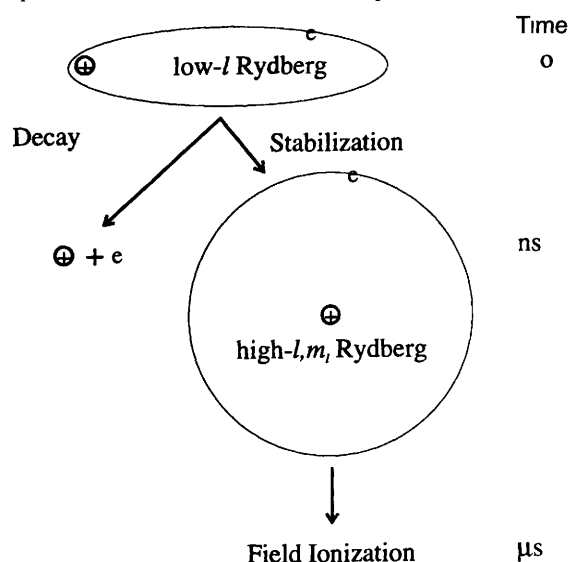


Figure 4 Mechanism for ZEKE spectroscopy. Initially excited low- l state can decay by autoionization or predissociation.

[†] H. J. Dietrich and K. Muller-Dethlefs, *Phys. Rev. Lett.* 1996, **70**, 3530.

of the initially excited low- l Rydberg state and stabilization by l, m_l mixing. This stabilization occurs by two different mechanisms: l mixing, which is caused by Stark mixing due to weak DC fields present in the excitation volume, and m_l mixing, which requires the inhomogeneous electric fields created by nearby ions.²¹ Both l and m_l mixing lead to an increase in lifetime by a factor of roughly n , about two orders of magnitude increase for each type of mixing. This means that if the unperturbed lifetime of the initially excited low- l states is significantly less than one microsecond, both l and m_l mixing will have to occur to observe a ZEKE spectrum. The significance of this is that in some cases, there may be a requirement of an ion density of the order of 10^4 – 10^5 cm^{-3} in the excitation volume for ZEKE spectroscopy, or observed line strengths may be ion density-dependent. Recent experiments have probed ion density effects on ZEKE spectra^{23, 24} and we have observed these effects in ZEKE spectroscopy on H_2 .²² While these ion densities are easily achieved under REMPI conditions, they may not be present when VUV excitation is employed, especially if the VUV is from a synchrotron light source.

For coherent VUV, if one assumes a light flux of 10^9 photons/pulse in a spot of 1 mm^2 , with a target density of 10^{12} cm^{-3} , about 10^6 ions cm^{-3} are formed for a typical 10 Mb ionization cross section. With more dilute targets, such as a radical beam, it may be necessary to seed an easily ionized molecule into the beam to achieve the ion densities necessary for stabilization. Finally, for synchrotron sources, which are discussed in more detail in the final section, the greatly reduced instantaneous light flux will reduce the ion density by four or five orders of magnitude, which may have strong effects on Rydberg state stabilization. While understanding the detailed Rydberg state dynamics behind ZEKE spectroscopy can provide important new information about interpretation of spectral intensities or lead to technical advances such as resolution improvement, one should not lose sight of the experimental fact that ZEKE has proved to be a very generally applicable technique. In our own experience, we have never failed to find the ZEKE signal at any threshold where we have looked for it. In fact, one of the surprises of ZEKE spectroscopy is that the signal can be found even where you may not expect to find it, as shall be described in the next section.

4 ZEKE and the Franck–Condon Principle

In conventional photoelectron spectroscopy with 21.22 eV photons from a He I resonance lamp, the band intensities observed in the spectrum are generally well described by Franck–Condon factors between the starting neutral ground state and the final vibrational levels of the ion.²⁵ However, when lower-energy resonance lines are used for PES, such as the 16.85 eV Ne I resonance line, one can observe dramatic changes in the band intensities in PES. An example is provided by oxygen, shown schematically in Fig. 5. The

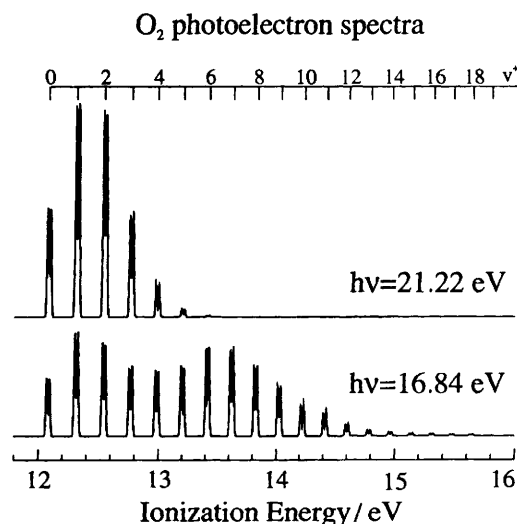


Figure 5 Schematic of oxygen PES with He I and Ne I resonance lines. Adapted from spectra shown in ref. 9.

band intensities seen in the He I spectrum (21 22 eV) are the same as the Franck–Condon factors, while the relative intensities for Ne I photionization (16 84 eV) are bimodal, with substantial intensity for high vibrational levels of O_2^+ . The reason for the change in band intensities is autoionization: there is a broad autoionizing resonance at 16 84 eV, and the intensities of the high vibrational levels reflect the Franck–Condon factors between the autoionizing Rydberg state and the vibrational levels of the ion.²⁶ In TPES, the observation of Franck–Condon forbidden peaks (meaning the Franck–Condon factor to the starting neutral state is zero) is very common, and can produce ions in highly vibrationally excited states. In oxygen, the TPES spectrum shows significant intensity for vibrational levels up to $v^+ = 24$ of the $X^2\Pi_g$ state of O_2^+ .²⁷

In the case of TPES, the reason for this breakdown of the Franck–Condon approximation is not the same as in the Ne I PES of O_2 . For TPES, the ionizing light is tuned continuously, and bands are observed in TPES whether or not there is a coinciding autoionizing Rydberg state. While there is some ambiguity about this last statement if one examines (relatively) low-resolution TPE and PIE spectra, there is none if one looks at the high-resolution ZEKE and PIE spectra of jet-cooled oxygen recorded with coherent VUV. In the spectra shown in Fig. 6, part of a much larger data set that has

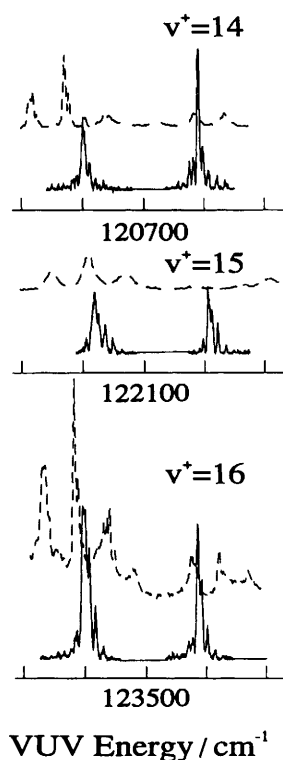


Figure 6 PIE (dashed) and ZEKE (solid) spectra of jet-cooled O_2 . The PIE spectra have been shifted upwards for clarity. All three ZEKE spectra, and all three PIE spectra, have the same relative scales. The VUV energy axis is 100 cm^{-1} per division.

been published,^{28,29} one can see that the peaks in the ZEKE spectra, which can all be assigned to O_2^+ quantum states, are not always coincident with resonances in the PIE spectrum. Furthermore, not only are all the resonances observed in the ZEKE spectra assignable to ionization thresholds in oxygen, but for all the 16 vibrational bands investigated,²⁹ the observed rotational linestrengths can be reproduced using a standard model for photoelectron spectra, called the BOS model.³⁰ These observations can be explained in terms of a modified resonant autoionization mechanism.³¹ In this mechanism, the initial excitation is to a Franck–Condon-allowed Rydberg state, which is coupled through a dissociative valence continuum to Rydberg states converging to a highly vibrationally excited ion core. Vibrational and rotational autoionization from this final Rydberg state produces low-energy electrons, which are detected in TPES. The modification suggested by our ZEKE results

is that it is not necessary to be in resonance with a Franck–Condon-allowed Rydberg state for the excitation to occur. Rather, one excites the valence continuum directly, and it is coupled to the vibrationally excited Rydberg state. The interesting end result is that one obtains at least a partial yield of stabilized Rydberg states, which are subsequently field-ionized, rather than the neutral fragments one might expect. This is similar to the commonly observed ZEKE dynamics, where Rydberg state stabilization competes successfully with predissociation and autoionization. The interesting difference in this case is that the oscillator strength for the initial excitation is not carried by the high- n Rydberg states, but by the valence continuum (or continua). The result, which will be fairly common based on TPES results, is that it will be possible to investigate the spectroscopy of Franck–Condon-forbidden levels by ZEKE, as well as using PFI to state select highly vibrationally excited ions for reaction dynamics studies.

5 ZEKE at Thresholds Corresponding to Unstable States of the Ion

Since, as we have seen, ZEKE spectroscopy seems to work in cases where it is somewhat surprising that it does, we investigated whether there were instances where ZEKE did not work, because the initially excited Rydberg states simply could not survive the subsequent dynamics. One simple example, where it is not really a surprise that ZEKE works, is the ZEKE spectrum at the $N_2O^+ A^2\Sigma^+$ ionization limit.³² Since this excited state of N_2O^+ has a fluorescence lifetime of about 200 ns, the initially excited Rydberg states with the $N_2O^+ A^2\Sigma^+$ ion core would undergo a radiative decay during the microsecond delay before field ionization, resulting in a Rydberg state with an $N_2O^+ X^2\Pi$ ion core. This radiative relaxation of the ion core does not have any effect on the Rydberg electron, as the intensity of the ZEKE spectrum is not a function of time, on the hundreds of nanoseconds timescale. In this particular case, it is not too surprising that the high- l, m_l Rydberg state formed after excitation should be essentially unaffected by the relatively minor change of the ion core relaxing from the $A^2\Sigma$ to the $X^2\Pi$ state. A more dramatic case of core relaxation is provided by the $A^2\Sigma$ state of HBr^+ , which is strongly predissociated for all vibrational levels above $v^+ = 1$.

In this case, the ZEKE spectrum is quite interesting, since for the $v^+ = 0$ and 1 levels, the ion is stable, fluorescing to the ground state with several microseconds lifetime, while for $v^+ = 2$, the lifetime is $ca\ 10^{-10}$ s, and for $v^+ = 3$, the lifetime is 10^{-13} s. In our experiments, we measured ZEKE spectra for all of the vibrational levels from $v^+ = 0$ to 3 for the $HBr^+ A^2\Sigma$ state.³³ The spectra for two of these levels is shown in Fig. 7. The spectrum for the $v^+ = 1$ level is exactly as one would expect, given the high-resolution spectroscopic results for this level. The simulation shown below the spectrum was calculated using the BOS model for rotational linestrengths.³⁰ The spectrum for $v^+ = 2$, shown in the lower panel, is precisely what one would expect, based on the $v^+ = 0$ and 1 ZEKE spectra. This means that the spectral constants obtained from the ZEKE spectrum are what one would expect (there are no high resolution data for this level), and the parameters used for the BOS simulation are the same as those for $v^+ = 1$. In fact, even the relative intensities of the $v^+ = 0, 1$ and 2 ZEKE bands are in reasonable agreement with the Franck–Condon factors. All this, in spite of the fact that the $v^+ = 2$ level predissociates in $ca\ 10^{-10}$ s. How can we explain the observation of a ZEKE spectrum at a threshold where the ion core is unstable? The answer is the same as the N_2O case mentioned above. As long as the decay of the ion core does not affect the Rydberg electron significantly, it will still be available for pulsed-field ionization microseconds later.

In this extreme case, the dissociation of the HBr^+ core into $H + Br^+$ has little effect on the Rydberg electron, which continues orbiting the Br^+ ion core after the H atom has departed. Since the signal obtained after field ionization is larger than at the $v^+ = 1$ threshold, where the ion core is stable, we can conclude that in this particular case the dissociation of the ion core has essentially no effect on the Rydberg electron. For the $v^+ = 3$ level, the results are even more striking, as shown in Fig. 8. In this case, the lifetime of the ion core is extremely short, orders of magnitude shorter than the period of the

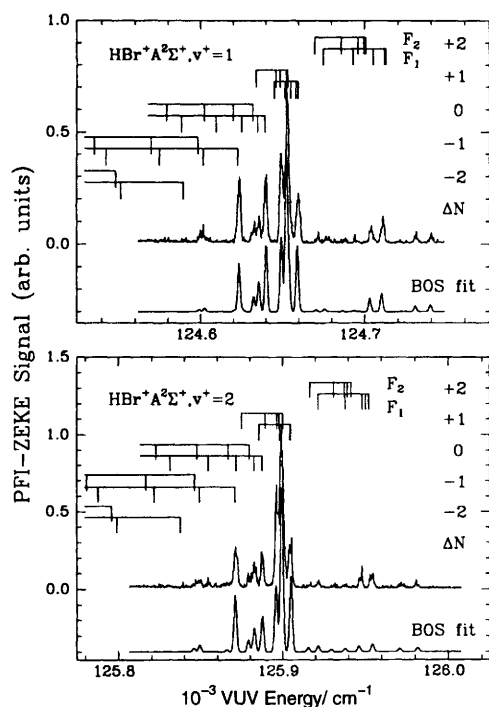


Figure 7 ZEKE spectra at the $\text{HBr}^+ \text{A}^2\Sigma^+ \nu^+ = 1$ and 2 thresholds. Assignments are given on the spectra, as are the results of a simulation using the BOS model. Adapted from ref. 33.

Rydberg orbit for the $n = 200$ state. However, even for this level, we observe a ZEKE spectrum, with an integrated intensity that is comparable with that for the $\nu^+ = 1$ and 2 levels, in agreement with Franck–Condon factors. The solid line drawn through the data in Fig. 8 is the result of taking the $\nu^+ = 2$ ZEKE spectrum shown in

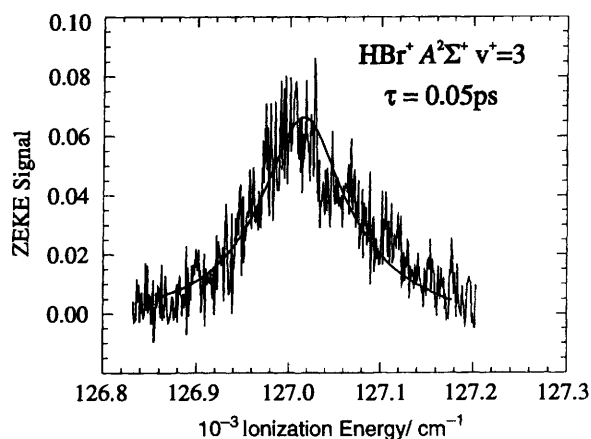


Figure 8 PFI-ZEKE spectrum at the $\text{HBr}^+ \text{A}^2\Sigma^+ \nu^+ = 3$ threshold. The line drawn through the data is the result of convoluting the shifted $\nu^+ = 2$ ZEKE spectrum with a Lorentzian line corresponding to a 0.05 ps lifetime.

Fig. 7, and convoluting it with a Lorentzian lineshape corresponding to a lifetime of 5×10^{-14} s. This lifetime is consistent with previous theoretical work, and our measured ZEKE spectrum is the same as high-resolution photoelectron spectra for this band. Because of lifetime broadening, the ionization energy for this level is ‘uncertain’ by $\pm 50 \text{ cm}^{-1}$, yet we are observing the ZEKE spectrum using Rydberg states that are bound by less than 5 cm^{-1} to the ion core.

6 Future Directions

ZEKE photoelectron spectroscopy is now a well-established field, with many different systems studied. Although this article has

focused on ZEKE spectroscopy of small molecules, there has been quite extensive work done on large molecules, and molecular clusters, as well as metal clusters and metal compounds. It would appear that ZEKE is an essentially universally applicable technique, which can even be used to probe quantum states of ions that cannot be reached through Franck–Condon allowed transitions. Improvements in resolution can still be made, and it is conceivable that the transform limit for pulsed-dye lasers may be achieved in the near future. There is beginning to be some interest in using PFI to create state-selected ions for reaction dynamics studies, although to date only preliminary work has been done.³⁴ Given the high state-selectivity provided by PFI, it is easy to predict that this will become a method of choice for creation of state-selected molecular ions.

From the point of view of this review, we can look forward to developments in two areas of technology. The current maximum photon energy of coherent VUV sources is 19 eV, a limit established by frequency-mixing crystals. As this technology improves, making it possible to generate millijoule pulses of tunable light at wavelengths shorter than 189 nm, the maximum photon energy will increase accordingly. However, to achieve a substantial increase in tuning range, the best currently available solution is provided by third generation synchrotron light sources. As mentioned in the introduction, a long period undulator with a high-resolution monochromator can produce 10^{10} to 10^{11} photons/ s^{-1} at a resolution of 2 cm^{-1} (0.25 meV) at 20 eV.³⁵ While the resolution is somewhat inferior to that of a coherent source, the photon flux is comparable, and the upper limit of photon energy can be above 30 eV. Furthermore, the synchrotron source can be easily tuned over very broad photon energy ranges, and the flux can be increased at the expense of energy resolution. Efforts have just begun at the Advanced Light Source in Berkeley, California, to utilize third generation synchrotron radiation for threshold ionization experiments. If these efforts are successful, the resulting threshold ionization mass spectrometer will be a powerful addition to this field, enabling us to carry out experiments at much higher photon energies, and allowing for very broad survey spectra, which will be extremely useful for systems where little is known, such as free radicals and clusters.

Acknowledgements The data from our lab which are discussed in this review were produced by the hard work of my collaborators: Profs W. Kong and D. Rogers, Drs A. Mank and C. Alcaraz and T. Nguyen and J. D. D. Martin. Funding for the research was provided by the NSERC (Canada), and the Canadian Federal Networks of Centres of Excellence program, administered by the NSERC. I thank the Canada Council for a Killam Research Fellowship.

7 References

- 1 F. I. Vilesov, B. L. Kurbatov and A. N. Terenin, *Sovi. Phys. (Dokl.)*, 1961, **6**, 490; M. I. Al-Joboury and D. W. Turner, *J. Chem. Phys.*, 1962, **37**, 3007.
- 2 D. Villarejo, R. R. Herm and M. G. Inghram, *J. Chem. Phys.*, 1967, **46**, 4995; W. B. Peatman, T. B. Borne and E. W. Schlag, *Chem. Phys. Lett.*, 1969, **3**, 492.
- 3 P. M. Johnson and C. E. Otis, *Acc. Chem. Res.*, 1980, **32**, 20; *Annu. Rev. Phys. Chem.*, 1981, **32**, 139.
- 4 D. J. Leahy, K. L. Reid, H. Park and R. N. Zare, *J. Chem. Phys.*, 1992, **97**, 4948; H. Park, D. J. Leahy and R. N. Zare, *Phys. Rev. Lett.*, 1996, **76**, 1591; J. B. Milan, W. J. Buma, C. A. de Lange, K. Wang and V. McKoy, *J. Chem. Phys.*, 1995, **103**, 3262.
- 5 P. Kruit and F. H. Read, *J. Phys. E: Sci. Instrum.*, 1983, **16**, 313.
- 6 K. Muller-Dethlefs and E. W. Schlag, *Chem. Phys. Lett.*, 1984, **112**, 291.
- 7 K. Muller-Dethlefs and E. W. Schlag, *Annu. Rev. Phys. Chem.*, 1991, **42**, 109.
- 8 L. Zhu and P. M. Johnson, *J. Chem. Phys.*, 1991, **94**, 5769.
- 9 D. C. Hanna, M. A. Yuratich and D. Cotter, *Nonlinear Optics of Free Atoms and Molecules*, Springer-Verlag, Berlin, 1979.
- 10 R. Hilbig, G. Hilber, A. Lago, B. Wolff and R. Wallenstein, *Comments At. Mol. Phys.*, 1986, **18**, 157; A. Lago, in *Half Collision Resonance Phenomena in Molecules; Proceedings of the Escuela Latinoamericana de Fisica*, ed. M. Gacia-Sucre, G. Raseev, and S. C. Ross, AIP Proc. No. 225, AIP, New York, 1990.

- 11 J W Hepburn, in *Laser Techniques in Chemistry*, ed A B Meyers and T R Rizzo, Wiley, New York, 1995, pp 149–183
- 12 R G Tonkyn and M G White, *Rev Sci Instrum*, 1989, **60**, 1245
- 13 *High Resolution Laser Photoionization and Photoelectron Studies*, ed I Powis, T Baer and C Y Ng, Wiley, New York, 1995
- 14 M Sander, L A Chewter, K Muller-Dethlefs and E W Schlag, *Phys Rev A*, 1987, **36**, 4543
- 15 E Meischer, *Can J Phys*, 1976, **54**, 2074
- 16 G Reiser, W Habenicht, K Muller-Dethlefs and E W Schlag, *Chem Phys Lett*, 1988, **152**, 119
- 17 T F Gallagher, *Rydberg Atoms*, Cambridge University Press, Cambridge, 1994
- 18 W A Chupka, *J Chem Phys*, 1993, **98**, 4520
- 19 C Bordas, P F Brevet, M Broyer, J Chevalere, P Labastie and J P Perrot, *Phys Rev Lett*, 1988, **60**, 917
- 20 J Jortner and M Bixon, *J Chem Phys*, 1995, **102**, 5636, 1995, **103**, 4431
- 21 F Merkt and R N Zare, *J Chem Phys*, 1994, **101**, 3495
- 22 J D D Martin, C Alcaraz, W Koz and J W Hepburn, in 'Laser Techniques for State-Selected and State-to-State Chemistry III', ed J W Hepburn, SPIE Proc 1995, **74**, 2548, J D D Martin, C Alcaraz and J W Hepburn, to be published
- 23 M J J Vrakking and Y T Lee, *J Chem Phys*, 1995, **102**, 8833
- 24 M J J Vrakking, I Fischer, D M Villeneuve and A Stolow, *J Chem Phys*, 1995, **103**, 4538
- 25 J H D Eland, *Photoelectron Spectroscopy*, Butterworth, London, 1984
- 26 J N Bardsley, *Chem Phys Lett*, 1968, **2**, 329, A L Smith, *Phil Trans Roy Soc Lond A*, 1970, **268**, 169
- 27 F Merkt, P M Guyon and J W Hepburn, *Chem Phys*, 1993, **173**, 479
- 28 W Kong, D Rodgers and J W Hepburn, *Chem Phys Lett*, 1993, **203**, 497
- 29 W Kong and J W Hepburn, *Can J Chem*, 1994, **72**, 1284
- 30 A D Buckingham, B J Orr and J M Sichel, *Philos Trans Roy Soc London, A*, 1970, **268**, 147
- 31 P M Guyon, T Baer and I Nenner, *J Chem Phys*, 1983, **78**, 3665
- 32 W Kong, D Rodgers and J W Hepburn, *Chem Phys Lett*, 1994, **221**, 301
- 33 A Mank, T Nguyen, J D D Martin and J W Hepburn, *Phys Rev A*, 1995, **51**, RI
- 34 S R Mackenzie and T P Softley, *J Chem Phys*, 1994, **101**, 10 609, S R Mackenzie, E J Halse, F Merkt and T P Softley, in *Laser techniques for State-Selected and State-to-State Chemistry III*, ed J W Hepburn, SPIE Proc **2548**, SPIE, 1995, p 293
- 35 M Koike, P A Heimann, A H Kung, T Namioka, R DiGennaro, B Gee and N Yu, *Nucl Instrum Meth Phys Res A*, 1994, **347**, 282, P A Heimann, personal communication of unpublished data