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High-Resolution Vacuum Ultraviolet Photoelectron Spectroscopy

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Abstract: The development of narrow bandwidth tunable laser systems in the vacuum ultraviolet region of the electromagnetic spectrum and of new experimental methods has recently enabled a significant improvement in the resolution that can be achieved by photoelectron spectroscopy. This improvement opens new perspectives in fundamental studies of the electronic structure and dynamics of neutral and charged molecular systems.

Keywords: High-resolution spectroscopy · Molecular Rydberg states · Selective field ionization · Vacuum ultraviolet lasers · Zero kinetic energy photoelectron spectroscopy

Photoelectron spectroscopy (PES) was developed 40 years ago [1–3] and has had a profound impact on chemistry for the following reasons: First, by enabling the observation of the ejection of photoelectrons out of *distinct* molecular orbitals, PES has rendered these orbitals, until then perceived by many chemists as abstractions, accessible to experimental studies. PES has thereby stimulated and justified the use of molecular orbitals in the discussion of chemical processes and has strongly influenced models of the structure and reactivity of the main classes of organic and inorganic compounds. Second, PES has established itself as a powerful method for chemical analysis [4]: A photoelectron spectrum is a unique signature of a molecule, and, additionally, inner shell photoelectron spectra provide (potentially time-resolved) information on the chemical environment of individual nuclei within the molecule. Third, PES offers a direct way of measuring the ionization potentials of chemical com-

pounds, which can be linked to other important thermochemical information such as electron affinities and dissociation energies [5]. Finally, because the positions of lines in a photoelectron spectrum correspond to energy differences between the levels of an ionic and a neutral species (see Fig. 1), the technique also provides a means to derive spectroscopic information on molecular ions.

This contribution summarizes recent work of our research group that has enabled a significant improvement of the resolution that can be achieved by photoelectron spectroscopy. Our motivations are a) to study the process of photoionization in detail by characterizing the changes in electronic, vibrational, rotational, electron spin and nuclear spin motions that take place when an electron is photoejected, and b) to extract structural, dynamical and thermochemical information on molecular cations from high-resolution photoelectron spectra. Ions are very difficult to study spectroscopically at high resolution because their high reactivity and the Coulomb repulsion force between ions of the same charge limit the concentration of charged species that can be produced in the gas phase to $<10^{11}$ ions/cm³. The properties of molecular ions are therefore poorly characterized in comparison to those of neutral molecules. The main advantage offered by PES for the study of molecular cations is that photoexcitation is carried out on

neutral molecules, and these can be generated at a much higher concentration than charged species. In our studies of ions by PES, we give particular attention to cations that play an important role in atmospheric chemistry, combustion studies, astrophysics and plasma physics.

The principle of photoelectron spectroscopy is illustrated schematically in Fig. 1 which also highlights the differences between conventional photoelectron spectroscopy (Fig. 1a) and threshold photoelectron spectroscopy (TPES) (Fig. 1b). It is on successive developments of a variant of TPES called pulsed-field-ionization zero-kinetic-energy photoelectron spectroscopy (PFI-ZEKE-PES) [6] that our recent progress relies.

The resolution of conventional PES is limited to ≈ 20 cm⁻¹ by technical difficulties associated with the measurement of electron kinetic energies. This resolution is not sufficient to allow observation of the rotational level structure of molecular ions. In TPES, only electrons of almost zero kinetic energy (so-called threshold electrons) are detected. The measurement of electron kinetic energies is therefore avoided, and a higher resolution can be achieved. The most convenient and effective way to detect such threshold electrons requires field ionization of Rydberg states of high principal quantum number ($n \gg 100$) located just below the successive ionization thresholds using a pulsed electric field of less than 1 V/cm. A PFI-

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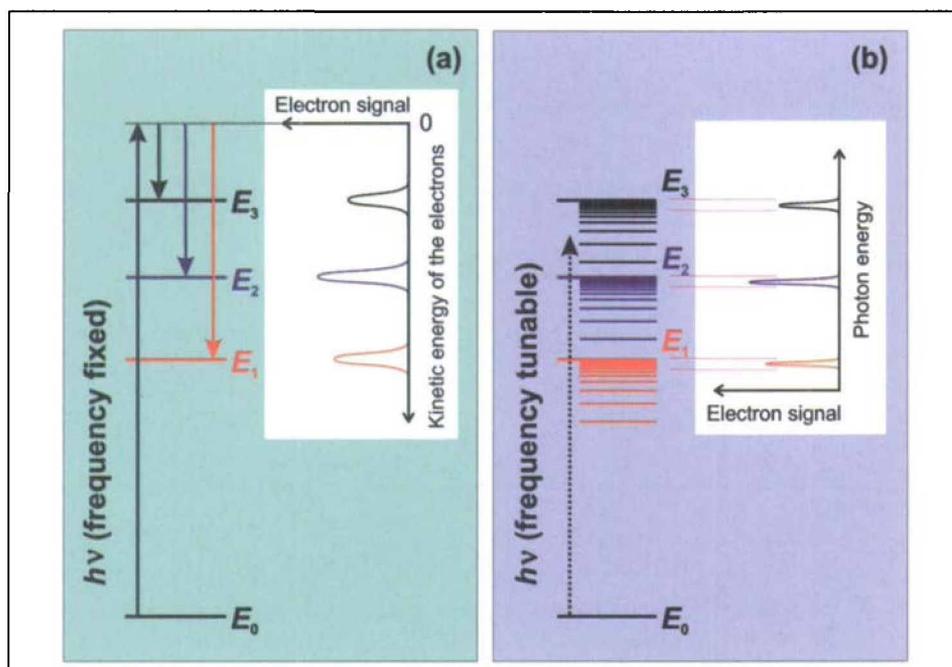


Fig. 1. (a) Principle of conventional PES. Ionization of molecules with monochromatic radiation of fixed frequency leads to the photoejection of electrons. From the measurement of the electron kinetic energy distribution, the positions of ionic energy levels E_1 , E_2 , E_3 , ... can be determined with respect to an energy level E_0 of the neutral molecule. (b) Principle of TPES and PFI-ZEKE-PES. The emission of electrons of near zero kinetic energy are detected as a function of the frequency of a tunable radiation source. Peaks are observed at each ionization threshold, which also correspond to the convergence limit of Rydberg series. In PFI-ZEKE-PES high Rydberg states located just below each ionization threshold are detected by pulsed field ionization.

ZEKE photoelectron spectrum thus represents the field ionization yield of high Rydberg states as a function of the frequency of a tunable light source. Like a conventional photoelectron spectrum, it shows a line at each ionization threshold, at a position that is shifted with respect to the position of the ionic energy levels by the binding energy of the field ionized Rydberg states. The resolution of a PFI-ZEKE-PE spectrum is limited by the selectivity of the field ionization process (*i.e.* the ability to field ionize high Rydberg states over a narrow range of n -values, see Fig. 1b) and typically amounts to 1 cm^{-1} . Improving the resolution beyond this limit is difficult, and only a handful of PFI-ZEKE photoelectron spectra have so far been reported at a resolution better than 0.5 cm^{-1} , the best resolution achieved until this work being 0.2 cm^{-1} [7][8].

Fig. 2 illustrates the respective advantages of conventional and PFI-ZEKE photoelectron spectroscopy with the examples of N_2 and CO. The advantage of the conventional photoelectron spectra (from [9]) is that they give a survey of the dominant ionization channels and reveal vibrationally resolved transitions to the electronic ground (X) and first excited (A and B) states of N_2^+ (trace (a)) and CO^+ (trace (b)). The PFI-ZEKE photoelectron spectra (from our own work) show the rotationally resolved structure of the transitions to individual vibrational levels of the ground electronic state of N_2^+ (trace (c), $v^+ = 0$) and CO^+ (trace (d), $v^+ = 1$). Both PFI-ZEKE-PE spectra were recorded

under very similar experimental conditions ($T \cong 5 \text{ K}$ and resolution of 0.3 cm^{-1}). The rotational structure in these spectra, already discussed in [10], reflects striking differences in the photoionization dynamics of these two isoelectronic molecules. In CO, photoionization is accompanied by a much larger change in rotational motion than in N_2 , a fact that has its origin in the absence of a center of symmetry in CO. The high resolution of the PFI-ZEKE photoelectron spectra renders possible the observation of many spectral features which contain detailed information on the photoionization dynamics, the energy level structure of the ion and the electronic structure of the neutral.

Our current research in PES aims at improving the resolution of PFI-ZEKE photoelectron spectroscopy further. This requires a) the development of narrow bandwidth tunable laser sources in the vacuum ($\lambda < 200 \text{ nm}$) and extreme ($\lambda < 105 \text{ nm}$) ultraviolet range of the electromagnetic spectrum, a spectral region where no commercial laser systems are available, and b) fundamental investigations of the properties of high Rydberg states [11] and the design of experimental methods that enable a very selective ionization of these high Rydberg states. Both objectives are pursued by our research group as part of a research program on extreme ultraviolet photochemistry and photophysics.

Inset (a) in Fig. 3 shows an electric field pulse sequence with which photoelectron spectra can be recorded at an un-

precedented resolution. The body of the figure describes schematically the effect of the pulse sequence on high Rydberg states. The full lines in Fig. 3 depict the energy paths followed by selected Rydberg states during the pulse sequence, the Stark energies being calculated using fourth order perturbation theory, and the circles indicate the fields at which ionization occurs. The outcome of a pulse sequence can be predicted on the basis of the following properties of Rydberg states in the presence of electric fields (see [7][11][12] for additional details):

- The electric field required to ionize Rydberg states scales as $1/n^4$;
- Rydberg states that are shifted toward lower energies (red-shifted states) by the field ionize at lower fields than those shifted toward higher energies (blue-shifted states);
- Rapid inversion of the polarity of the field between F_1 and F_2 converts red-shifted states into blue-shifted states and *vice versa*.

Inspection of Fig. 3 shows that after application of a first pulse of positive polarity (F_1) subsequent negative field pulses of smaller amplitude can be used to induce ionization of Rydberg states over a very restricted range of n values. The field ionization from these negative field pulses becomes highly n -selective and the resolution of the PFI-ZEKE spectrum improves. Inset (b) in Fig. 3 shows a high-resolution PFI-ZEKE spectrum of the central line in Fig. 2c recorded using a pulse sequence such as shown in inset

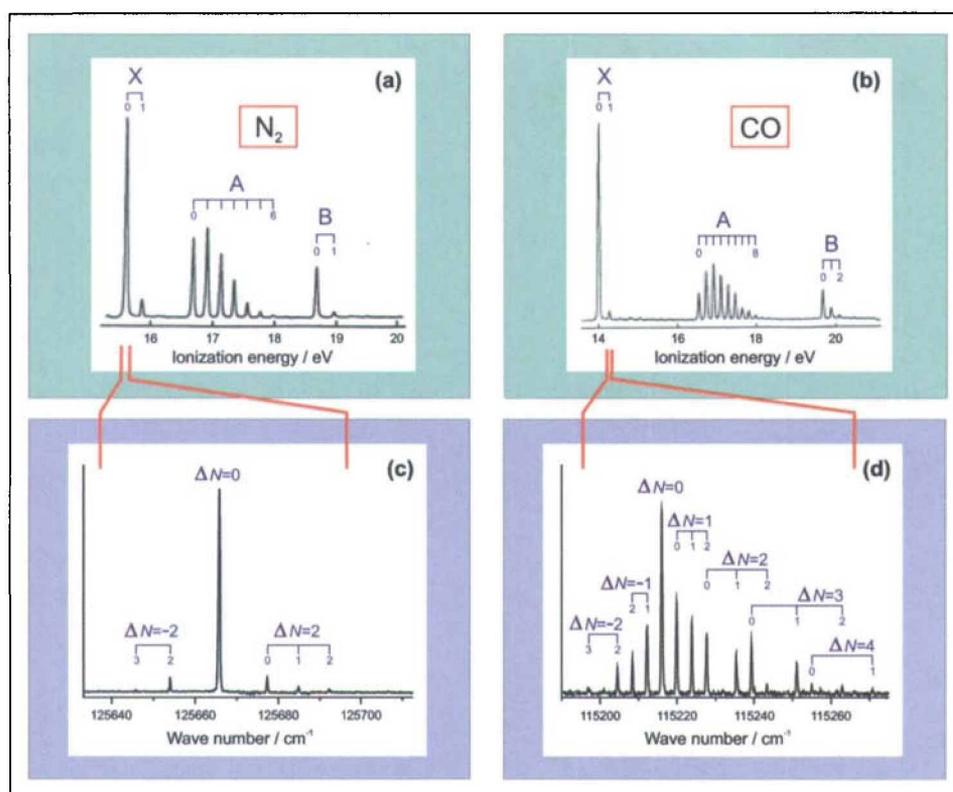


Fig. 2. Conventional PE spectra of N_2 (a) and CO (b) recorded using HeI radiation of $\lambda = 58.4$ nm (21.2 eV). PFI-ZEKE-PE spectra of N_2 (c) and CO (d). In (a) and (b) the X, A, B labels refer to the ground and first two excited electronic states of the cation and the assignment bars give the positions of the vibrational levels. In (c) and (d) the rotational branches are labeled by the value of $\Delta N = N^+ - J''$ where N^+ and J'' represent the rotational quantum numbers of the ion and the neutral, respectively. The assignment bars give the positions of transitions from the rotational level J'' of the neutral ground state.

(a). At the higher resolution (Fig. 3b), the spectrum reveals three lines (full width at half maximum of 0.055 cm^{-1}) where Fig. 2c shows only one. At a resolution of 0.055 cm^{-1} , PES becomes an attractive method for the study of larger molecular ions.

An even higher precision in the determination of the position of ionic energy levels can be reached if the individual Rydberg states can be resolved within each line of a PFI-ZEKE photoelectron spectrum [13]. Because the spacing between adjacent members of a Rydberg series scales as $\frac{2R}{n^3}$ (R is the Rydberg

constant and this spacing amounts to 0.027 cm^{-1} at $n = 200$), resolving adjacent Rydberg states at $n = 200$ necessitates the use of a pulsed laser with a very narrow bandwidth. Fig. 4 shows a Rydberg-state-resolved PFI-ZEKE photoelectron spectrum of argon recorded using a home-built near-Fourier-transform-limited VUV laser system (0.008 cm^{-1} bandwidth at 125000 cm^{-1}) [14]. The spectrum, which was recorded using a sequence of two pulsed fields of $+0.5$ V/cm and -1 V/cm, shows two Rydberg series of atomic argon between $n = 140$ and 200 that are well resolved within the 2.5 cm^{-1}

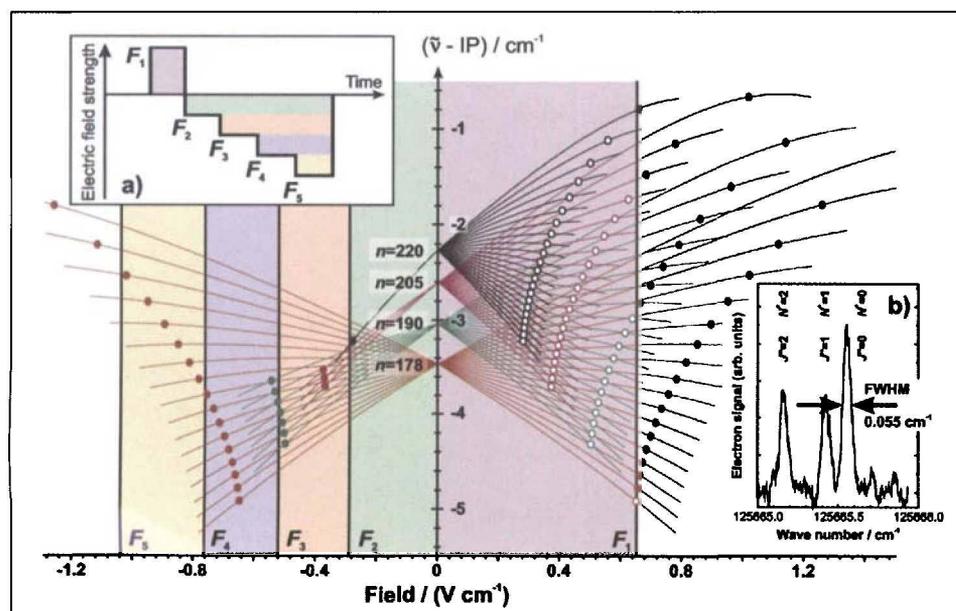


Fig. 3. High-resolution PFI-ZEKE-PES. The body of the figure is an energy level diagram showing the energy paths followed by Rydberg states of selected principal quantum number when exposed to the electric field pulse sequence displayed in inset (a). The dots indicate at which point in the field sequence the Rydberg states ionize. Inset (b) shows part of the high-resolution PFI-ZEKE photoelectron spectrum of the $X(v^+ = 0) \leftarrow X(v'' = 0)$ transition of N_2^+ .

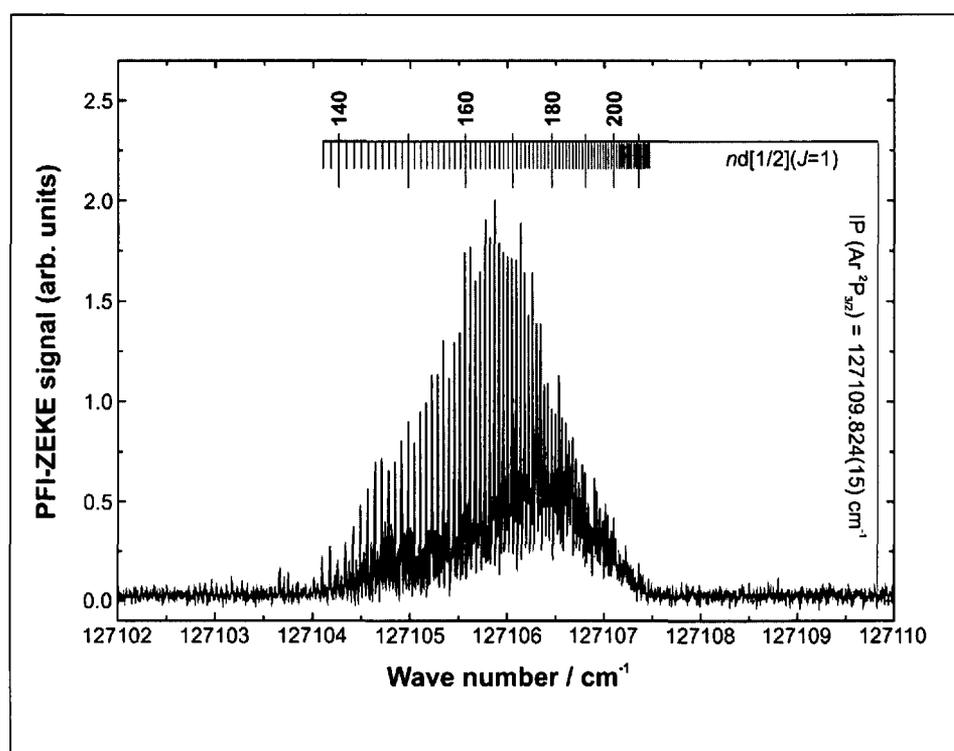


Fig. 4. Rydberg-state-resolved PFI-ZEKE-PE spectrum of Ar. The spectrum shows resolved transitions to individual Rydberg states within the $\text{Ar}^+ 2P_{3/2} \leftarrow \text{Ar} 1S_0$ line of the PFI-ZEKE spectrum. Extrapolation of the Rydberg series to $n = \infty$ gives the ionization potential marked by a vertical line at the right of the figure. The assignment bars designate the main series.

wide envelope of the PFI-ZEKE line. Extrapolation of these series to $n = \infty$ using Rydberg's formula enables the determination of the ionization potential of argon ($\text{IP} = 127109.824(15) \text{ cm}^{-1}$) at a precision close to the bandwidth of the VUV radiation. A PFI-ZEKE photoelectron spectrum such as that shown in Fig. 4 combines for the first time the advantage of PFI-ZEKE photoelectron spectroscopy with that of Rydberg series extrapolation and enables the determination of highly accurate ionization potentials.

The new generation of experiments described above and illustrated in Figs. 3 and 4 open new perspectives for the study of molecular cations by photoelectron spectroscopy and for the fundamental investigation of molecular photoionization dynamics. In particular the high resolution renders possible the study of larger molecular systems.

Acknowledgements

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