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Bálint Sztáray and Tomas Baer

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Suppression of hot electrons in threshold photoelectron photoion coincidence spectroscopy using velocity focusing optics

Balint Sztarayab and Tomas Baerb)

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

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Velocity focusing of electrons is combined with photoelectron photoion coincidence (PEPICO) spectroscopy to achieve a true threshold PEPICO signal without contributions from energetic electrons. Ions are generated by a continuous vacuum ultraviolet light source. Electrons, extracted by a field of 20 V/cm, pass through a 13 cm drift region and are dispersed in space on a multichannel plate detector by velocity focusing optics. The ions are extracted in the opposite direction by the same electric field, further accelerated by a second field, and collected after passing through a 30 cm drift region. Ions are measured in coincidence with electrons collected from the central 3.2 mm electrode as well as a ring electrode (inner and outer diameters of 5.6 and 8.1 mm). The central ring electrode contains mostly true threshold electrons along with a background of “hot” electrons, whereas the outer ring electrode collects only hot electrons. By subtracting the latter from the former, true threshold photoelectron photoion coincidence spectra are obtained. The major advantages of this approach are the high electron energy resolution with the use of high direct current extraction fields, and the complete suppression of energetic electrons. © 2003 American Institute of Physics. [DOI: 10.1063/1.1593788]

I. INTRODUCTION

The study of energy selected ions by photoelectron photoion coincidence (PEPICO) spectrometry has a long history.1–4 The principle is based on the collection of ions in coincidence with energy selected electrons so that the ion internal energy is given by conservation of energy. Two versions of PEPICO have been developed. In one, a fixed energy light source is used and the ions measured in coincidence with energy selected electrons using a dispersive energy analyzer. In the other approach (TPEPICO), a variable energy light source is used so that initially zero energy electrons, so-called threshold electrons, can be detected in coincidence with the ions. Because the threshold electron approach has the advantage of a much higher collection efficiency for electrons and because of its higher electron energy resolution (<0.5 meV), most coincidence experiments today use a variable energy light source with collection of threshold electrons, i.e., TPEPICO.3–10 A very high resolution version of TPEPICO involves the use of pulsed field ionization of high-\(n\) Rydberg states to generate zero kinetic energy (ZEKE), electrons and their detection in coincidence with the corresponding ions.11–13

The selection of threshold electrons is based on the high collection efficiency of low energy electrons, which can be passed through small apertures, whereas energetic electrons with perpendicular velocity components are stopped by the small aperture.14,15 One of the major experimental hurdles in all of these TPEPICO studies has been the simultaneous optimization of the electron energy resolution and the ion time-of-flight (TOF) mass resolution. Good electron resolution requires low extraction fields, whereas good ion TOF resolution requires high electric fields. A common approach is to collect and energy analyze the electrons with low electric fields. Once an energy selected electron is detected, the ions are extracted with a large pulsed electric field.16 However, such pulsed ion extraction impedes the accurate determination of ion dissociation rates from the ion TOF distribution. It also results in a false coincidence signal that is sometimes difficult to distinguish from the true coincidence signal.

A major problem associated with the selection of threshold electrons by use of this low energy filter is the inability to suppress energetic electrons whose initial velocity vectors are in the direction of the detector. This “hot electron” tail becomes increasingly significant as the photon energy is increased. The use of an electrostatic energy analyzer is of limited value if the ionization region has a width of more than a few microns because the voltage drop across this region generates electrons with a range of energies that is much larger than the desired resolution of 1–10 meV. Hot electrons have been successfully suppressed in synchrotron radiation experiments in which the pulsed photon source permits the selection of true zero energy electrons on the basis of their time of flight.17,18 However, this necessitates the use of small extraction fields (~1 V/cm), which are detrimental for collecting the ions. In addition, electron TOF analysis requires a large time intervals between light pulses, which are only possible during the rare times that third-generation synchrotron sources are operated in single bunch mode.

We have recently reported19 a significant improvement in the collection efficiency and resolution of a threshold electron detector by incorporating velocity focusing optics.20,21 This permits focusing a large photoionization region (5 mm

aOn leave from the Eötvös Loránd University, Budapest, Hungary.

bElectronic mail: baer@unc.edu
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\[ \times 6 \text{ mm} \] to a 1.6 mm aperture. The collection efficiency for electrons and ions was measured to be 49% and 20%, respectively, and the resolution for threshold electrons at the Xe \( 2P_{3/2} \) peak was 13 meV, most of which was limited by the photon monochromator resolution.\(^{19} \) In addition, it solves the ion extraction field problem in that 1 meV electron energy resolution can easily be achieved with large electric fields (>20 V/cm). However, this improved detector still suffers from the “hot electron” tail problem because the velocity focusing optics focus both energetic and slow electrons as long as their velocity in the direction of the detector are the same. In this article, we present a method for eliminating the hot electron tail by collecting and subtracting the hot electron signal from the combined threshold and hot electron signal.

II. EXPERIMENTAL APPROACH

A. Velocity focused electrons

Molecules are photoionized by dispersed vacuum ultraviolet light from a hydrogen discharge, which produces the so-called “many-line” emission spectrum. The ionization region consists of dual two-stage acceleration regions for electrons and ions. A 20 V/cm acceleration field extracts the electrons and ions in opposite directions. The electrons travel 6.75 mm through this region before they are accelerated to about 60 V by the second acceleration region. They then drift about 13 cm to the electron detector. The ions travel some 5 cm through the first acceleration region and are further accelerated to 220 V before they pass through a 30 cm drift region terminated with a set of microchannel plates that detect them.

Velocity focusing of charged particles is accomplished by extracting the electrons (or ions) from the ionization region with an electrostatic lens in which the commonly used grids over the extraction apertures are removed. The simplest approach is the use of two apertures and a drift tube, as shown in Fig. 1 (vertical and horizontal scales are not the same). By adjusting the voltages on the first and second apertures, electrons with zero velocity perpendicular to the extraction voltage are focused to a spot at the end of the flight tube, whereas the energetic electrons are focused onto rings around this central spot with radii proportional to their initial velocity perpendicular to the extraction axis. Because small stray electric and magnetic fields can easily deflect the threshold electrons, four steering plates were installed early in the electron drift region. Finally, a 10 mm ID “skimmer” to suppress high energy scattered electrons from reaching the electron detector was installed near the end of the electron drift region.

The effectiveness of the velocity focusing for electrons originating from various positions in the ionization region was determined by SIMION (Ref. 22) calculations that illustrate the focusing properties for electrons with initial energy of 0 and 38 meV directed upward and downward. As shown in Fig. 1, electrons were launched from five vertical locations separated by 1 mm as well as three horizontal locations separated by 1 mm.

With voltages adjusted as indicated in Fig. 1, zero energy electrons are focused within a 1-mm-diam spot located at the center of the collector, the hot electrons are spread uniformly over the whole detector. If we assume that the hot electron signal in a ring around the central spot is proportional to the hot electron contribution in the central spot, a weighted fraction of the outer ring signal can be subtracted from the central electrode signal and thus correct the threshold electron signal for this contribution. To achieve this, the multichannel plate collector was divided into two sections with a central 3.2-mm-diam circle reserved for the threshold electrons and the background hot electrons, whereas an outer ring with inner and outer diameters of 5.6 and 8.1 mm collected the hot electrons. In order to minimize the interference between the classes of electrons, a mask (Fig. 2) was placed in front of the multichannel plate (MCP) detectors. A smaller central electrode collector (such as the 1.6 mm electrode used in the previous study\(^{19} \) is probably better in that the threshold electron detection efficiency remains about the same, whereas the “hot” electron contribution is reduced.

The effectiveness of the hot electron subtraction was tested by collecting a threshold photoelectron spectrum of acetylene in the vicinity of this molecule’s ionization energy at 11.40 eV (Fig. 3). The upper scan (light line) shows the signal collected from the central electrode, which detects the true threshold electrons along with hot electrons. The other light line shows the scan of the outer ring electrode, which
determines only the hot electrons. When the two are subtracted, we obtain the heavy line spectrum, which is devoid of the hot electron tail. The complete subtraction is evident by the signal’s return to the base line prior to each new vibrational state. In order to achieve a full subtraction, it was necessary to multiply the ring electrode signal by a factor of 0.54. It was determined empirically and optimized to achieve a flat and zero electron signal between the acetylene ion vibrational states. This subtraction procedure in the case of molecule with well defined and sharp vibrational structure near its ionization energy is only approximately correct because the hot electron signal on the detector is highly structured. In the case of our detector in which the circle electrode collects electrons with perpendicular energy of 38 meV, the ring electrode does not receive signal until the photon energy is 38 meV above the molecule’s ionization energy. Thus, no hot electrons are subtracted between 0 and 38 meV. Although the use of a constant factor is not really justified, it seems to work remarkably well over the whole range of energies in Fig. 3. This problem becomes progressively less important at higher photon energies where the distribution of hot electrons is much broader. In addition, the problem is expected to be less severe for complex molecules because of their large density of vibrational states and their correspondingly less structured photoelectron spectrum.

The validity of the subtraction assumes an isotropic distribution of ejected electrons. Because threshold electrons have an isotropic distribution, any anisotropy in the energetic electron distribution will have an effect on the subtraction. The anisotropy of ejected electrons can be described by a single parameter, \( \beta \), which varies from \(-1\) to \(+2\). We have calculated this effect on the factor by which the ring electrode signal must be multiplied. For \( \beta = -1 \), the additional factor would be 0.8, whereas for the maximum \( \beta \) value of \(+2\), the additional factor would be 1.32. These are not insignificant corrections for the electron anisotropy and would certainly need to be applied in the case of small molecules where electron angular distributions deviate most from isotropic. On the other hand, larger molecules with closely lying electronic states tend to have rather isotropic electron angular distributions so that this correction may not be necessary.

### B. Threshold photoelectron photoion coincidence (TPEPICO)

Photoelectron photoion coincidence experiments permit the study of energy selected ions. The ion energy is given by

\[
E_{\text{ion}} = h\nu - IE + E_{\text{th}} - E_{\text{el}},
\]

in which \( h\nu \) is the photon energy, \( IE \) is the molecule’s ionization energy, \( E_{\text{th}} \) is the thermal energy of the molecule, and \( E_{\text{el}} \) is the kinetic energy of the departing electron. In the case of threshold PEPICO the last term is zero. The electrons, either from the central electrode or the ring electrode, provide start signals for measuring the ion time of flight. The TOF spectra generated by photoionization of the CHFCl\(_2\) sample at 11.95 eV with the two electron electrodes are shown in Fig. 4. This energy is just above the dissociation limit, all parent ion signal is associated with energetic electrons. In the case of threshold PEPICO the coincidence spectrum associated with the ring electrode (energetic electrons and thus lower energy ions) has a much larger fraction of parent ions than the central electrode PEPICO data. When the hot PEPICO TOF spectrum is subtracted from the central one, it effectively eliminates the parent ion signal.
FIG. 5. Breakdown diagram of CHFCl₂ (fractional abundance of parent and daughter ion signal) with various fractions of the ring electrode signal subtracted from the central electrode. The factors are: 0.0, 0.05, 0.10,..., 0.30, the last one being the optimum factor.

By collecting pairs of spectra at many photon energies, we can generate a breakdown diagram, which is a plot of the fractional abundance of the parent and daughter ions as a function of the ion internal energy. This is one of the most useful pieces of information from PEPICO experiments because it provides a very precise measure of the ion dissociation limit. Figure 5 shows the breakdown diagram for a CHFCl₂ in which the fractional abundance of the ions plotted as a function of the photon energy. The seven breakdown diagrams are corrected by subtracting various fractions of the ring electrode signal from the central electrode signal. These factors are: 0, 0.05, 0.10,..., 0.30, the last one being the optimum factor because beyond f = 0.30, the signal above 11.95 eV would go negative. This factor is universal (for our electrodes) in that it is optimum for the breakdown diagram of all molecules that we have tested (about five in number). However, the factor is slightly different from the one used in the acetylene TPES because of the reasons pointed out previously.

This freon molecule was chosen because the CHFCl₂ ion dissociates immediately when its internal energy is in excess of the dissociation limit. The breakdown diagram, in the limit of a delta function resolution, and a 0 K sample, takes the form of a step function in which the parent ion signal drops from 1 to 0 while the daughter ion signal jumps from 0 to 1 at the dissociation limit. However, because of the finite resolution of our spectrometer (photon and electron) and the molecule’s thermal distribution of internal energies, the breakdown diagram in Fig. 5 deviates significantly from a step function. The breakdown diagram can be modeled with the molecule’s normalized thermal energy distribution, P(E), as shown in Fig. 6 and Eqs. (2)–(4):

\[ \text{Parent}(h\nu) = \int_{0}^{AE-h\nu} P(E) dE \quad \text{for} \quad h\nu < AE, \quad (2) \]

\[ \text{Daughter}(h\nu) = \int_{AE-h\nu}^{\infty} P(E) dE \quad \text{for} \quad h\nu < AE, \quad (3) \]

\[ \text{Parent}(h\nu) = 0, \quad \text{Daughter}(h\nu) = 1, \quad \text{for} \quad h\nu > AE. \quad (4) \]

In which AE is the 0 K dissociation limit (appearance energy). When the photon energy exceeds the AE, the parent ion signal is 1 and daughter ion signal is 0. This calculated breakdown diagram is then convoluted with the instrumental resolution, which in our case is about 25 meV. A fundamental assumption implied in Fig. 6 is that photoionization simply shifts the thermal energy distribution from the neutral to the ionic manifold. The validity of this assumption rests on an ionizing transition probability that is independent of the molecule’s initial internal energy. It is born out by numerous successful fits to the experimental data for a variety of molecules.

The corrected breakdown diagram is compared to the calculated diagram in Fig. 7 in which the solid lines are obtained from Eqs. (2)–(4). The error limits on the data points arise from an assumed uncertainty in the subtraction in which the hot electrode signal from the central electrode signal. These diagrams are corrected by subtracting various fractions of the ring electrode signal from the central electrode. The factors are: 0.0, 0.05, 0.10,..., 0.30, the last one being the optimum factor.

FIG. 6. Diagram showing the effect of thermal energy on the expected breakdown diagram. We assume that the neutral thermal energy is transported to the ionic manifold without change. At the given photon energy, which is below the 0 K appearance energy, AE₀K, shaded part of the thermal energy distribution results in daughter ion signal, whereas the part below the dissociation limit leads to parent ions.

FIG. 7. Corrected breakdown diagram of CHCl₃F⁺ in which the hot electron contamination has been eliminated. The solid lines are the calculated breakdown diagram in which ab initio calculated vibrational frequencies were used to calculate the thermal energy distribution of the neutral molecule. This distribution was convoluted with the instrument analyzer function, given by the TPES acetylene spectrum (Fig. 1). The arrow shows the 0 K dissociation limit, which is calculated to be 11.92±0.010 eV.
factor of 0.30±0.005. The arrow at 11.920±0.010 eV shows the derived 0 K dissociation limit. The gentle approach to the base line for the parent ion signal near 11.92 eV is the result of the finite photon/electron resolution. With better photon and electron resolution, the 0 K AE would be characterized by a discontinuity in the slope, as has been demonstrated by a number of high resolution pulsed field ionization PEPICO experiments. 24–26

The complete suppression of the hot electrons greatly simplifies the identification of the 0 K dissociation limit. In the absence of complete hot electron suppression, it is necessary to model the whole breakdown diagram with assumed electron resolution functions, a procedure that is difficult to apply in all cases. For instance, the TPEPICO data collected in Franck–Condon gap regions have much smaller fractions of true threshold electrons to hot electrons so that the hot electron signal represents a correspondingly larger fraction of the TPEPICO signal. As a result, the fitting of the data requires a hot electron tail function that must be adjusted as a function of the photon energy. 27 By eliminating the hot electron tail through subtraction, these difficulties in modeling are avoided. The major negative consequence of hot electron subtraction in Franck–Condon regions is the larger noise level resulting from the subtraction of a larger background signal from the central electrode TPEPICO signal.

C. Comparison with PFI–PEPICO

The previously mentioned pulsed field ionization (PFI–PEPICO) version of this experiment does not suffer from the detection of hot electrons. In that experiment high-n Rydberg states are isolated by gently removing the direct electrons from the ionization region by a small electric field (0.3 V/cm). When the field ionizing electrical pulse (2–10 V/cm) is applied, only energy selected ions are present in the ionization region. Normally, PFI is carried out with 10 Hz lasers. However, low repetition rate lasers cannot be used for coincidence experiments because too many ions are created in a single laser shot. Instead, PFI–PEPICO experiments are carried out with quasicontinuous synchrotron radiation. To achieve good suppression of hot electrons, it is important to field ionize the Rydberg states during a dark period when no photons are ionizing the sample. Thus, the experiment can be run either in few bunch modes (light pulses separated by 300–1000 ns) or by the use of a 100 ns dark gap in an otherwise quasicontinuous source of light pulses. 28 In either case, the field ionizing pulse cannot be applied over a sufficiently long time to extract the ion from the ionization region. As a result, the ions experience several of these pulses and the average extraction field is sufficiently low that the mass resolution offered by time of flight analysis suffers.

A second problem with PFI–PEPICO is associated with the relatively low signal levels for ZEKE electrons. This is partly a result of the very high resolution (typically, 0.1 meV) and partly because the high-n Rydberg states appear to have a short lifetime when generated by a weak continuous light source, so that the fraction of ionization events leading to stable Rydberg states is rather low. 29 Increasing signal levels by reducing the photon resolution does not help because the pulsed field ionization method only works by exciting Rydberg states in a very narrow band of energies. This is in contrast to the present TPEPICO experiment in which photon resolution and signal levels can easily be traded off. The velocity imaging PEPICO experiment will be especially useful for larger molecules where high signal levels are more important than the high resolution capability offered by the PFI–PEPICO approach.

III. FUTURE DIRECTION: USE OF ELECTRON IMAGING DETECTION

The current experiment collects ions in coincidence with electrons from only two electrodes. In fact, it is possible to use an imaging detector for the electrons and thus to collect the ions in coincidence with position selected electrons. 21,30 This approach has the advantage that the whole photoelectron spectrum (at least from 0 to ~1 eV) is collected and can be visualized in order to optimize the subtraction procedure. Such a setup is currently being developed at the Advanced Light Source (ALS) synchrotron in which a photon resolution of 1 meV will also increase the resolution of this experiment by at least a factor of 10.

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