Resolution enhancement in the magnetic bottle photoelectron spectrometer by impulse electron deceleration

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We present a modified time of flight magnetic bottle photoelectron spectrometer (MBPES), designed to operate with mass-selected ion beams. It is based on a configuration in which the ion beam is coaxial with the electron flight tube. High resolution combined with high efficiency is achieved by applying impulse deceleration at the electron detachment zone immediately after detachment. The main effect of the impulse is to improve the resolution of the spectrometer by subtracting the ion velocity from the electron velocity. The impulse can also counteract the spread in the flight times caused by the alignment of the electrons in the magnetic bottle. Unlike previous designs of the MBPES, ultimate resolution is achieved without any loss in signal intensity. Resolutions of 8, 25, and 48 meV were obtained for 0.28, 1.22, and 2.11 eV electrons, respectively, with 60% collection efficiency. This design also allows easy switching between high-resolution high-yield and polarization-sensitive photoelectron spectroscopy modes. Our simulations indicate that, with careful attention to details, sub-meV resolution can be obtained using this approach. © 2001 American Institute of Physics. [DOI: 10.1063/1.1367364]

I. INTRODUCTION

Photoelectron spectroscopy (PES) of anionic clusters is well established now in studying the electronic structure of clusters.¹ This technique seems appealing for several reasons. It enables the assignment of excited energy levels in the neutral final state of mass-selected clusters relative to their ground state. Due to the low values of electron affinities in anionic clusters deep energy levels can be accessed. The pioneering works of Bowen and co-workers² and of Lineberger and co-workers³ utilized continuous wave (cw) cluster sources and lasers. The evolution of versatile pulsed cluster sources and good pulsed lasers in the vacuum ultraviolet (VUV) stimulated the advent of time of flight (TOF) PES. Currently, two main approaches to time of flight PES govern in cluster research, the field free drift and the magnetic bottle. The recently introduced imaging photoelectron spectroscopy⁴ is inferior in resolution, but excels in providing a detailed polarization image of the detached electrons. In the field-free drift approach electrons are detached at a given point in space and are collected at the end of a fieldfree flight tube, carefully masked against magnetic fields and electrostatic potentials. Johnson and co-workers were the first to introduce the field-free approach to cluster research⁵ in 1986. The main disadvantage of this approach is the small collection efficiency of electrons, amounting to $\sim 10^{-4}$, for a typical 1 m long flight tube. The major advantage of the field-free TOF PES is its very high resolution, approaching presently 1–3 meV.⁶

In a remarkable paper in 1983, Kruit and Read⁷ introduced the magnetic bottle time of the flight photoelectron spectrometer (MBPES). They utilized the ability of highly divergent magnetic field to adiabatically direct electrons along its field lines, and to guide them into a long TOF flight tube maintaining a weak longitudinal magnetic field. Their design allowed 2π solid angle collection of electrons, about three to four orders of magnitude higher than drift-free time of flight PES. The main practical constraint on the resolution in the Kruit and Read spectrometer originates from the spread in the alignment times of the photoelectrons along the flight tube. Electrons, ejected in the direction of the flight tube, propagate to the detector with their full velocity ν_{e} . Electrons ejected at some angle θ to the flight tube start to propagate with the longitudinal velocity of $\nu_e \cos \theta$. They are aligned to achieve their full longitudinal velocity only after some distance (typically 1-2 cm). This effect creates a spread in the arrival times of monoenergetic electrons at the detector. The values of the "alignment time" spread can be calculated by numerical integration of the flight time along the direction of the flight tube.⁸ It depends on details of the divergent magnetic field as well as on the kinetic energy of the electrons. The apparent deterioration in resolution due to this effect is inversely proportional to the flight tube length.

The main obstacle in direct application of the Kruit and Read design to charged clusters has been the Doppler energy broadening of the PES by the high velocity of the ion beam, $\nu_{\rm I}$. For the case of 4π collection efficiency, the velocity spread of the electron within the laboratory framework amounts to $2\nu_{\rm I}$. The resulting electron energy broadening, dE, can then be approximated by⁸

$$dE = m_e \nu_e d \nu_e \approx 2m_e \nu_e \nu_I, \tag{1}$$

where m_{ρ} is the electron mass.

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In 1987 Cheshnovsky et al. introduced a design which is based on the magnetic bottle principle,⁸ that is suitable for working with high kinetic energy charged ions or clusters and high photon energies. This design incorporated pulsed deceleration of the mass-selected cluster ions to low kinetic energies, prior to photodetachment. In this deceleration scheme, the original kinetic energy spread of the ions, generated in the time of flight mass spectrometer, was maintained ($\sim 100 \text{ eV}$). Unlike the Kruit and Read design, it was open structured in order to minimize stray electrons detached by laser light hitting surfaces, thus enabling the use of VUV photons. The highly divergent magnetic field was generated by a pulsed solenoid. Electron detachment occurred between the solenoid and the flight tube, allowing 98% electron collection efficiency. Somewhat later Meiwes-Broer and co-workers9 introduced a similar design based on a permanent magnet as the source of the highly divergent magnetic field in the MBPES.

Further developments in MBPES focused on improving the deceleration of the mass-selected ions prior to detachment. In 1990, Cheshnovsky and co-workers introduced impulse deceleration of the ions.¹⁰ In this approach a given momentum is subtracted from the original momentum of the ion using a short high voltage impulse. It allows a better decrease in the ion-velocity spread prior to detachment, as explained in detail by Wang and co-workers.¹¹ In the realization of this approach both groups used a deceleration stack, located about 1-2 cm in front of the detachment zone, thus making it practical to use VUV photons in the MBPES. In 1995 Ganteför and co-workers¹² introduced a refined impulse deceleration scheme that achieved routine resolution of 10 meV at electron kinetic energy of 0.3 eV. The only drawback in this exquisite deceleration scheme is the proximity of metal structures to the detachment zone, making it unfavorable for PES at VUV energies. Recently, Wang and co-workers¹³ described a MBPES based on impulse deceleration. Its careful design and its long flight tube (4 m) enabled the achievement of 9 meV resolution at 0.5 eV electron kinetic energy.

To summarize, using the MBPES technique, resolution values of $\sim 10 \text{ meV}$ at 0.5 eV electron kinetic energy can be obtained, worse by about a factor of 3 from the best drift field-free PES of charged ions. It is blessed, though, with high collection efficiency, up to $\sim 98\%$ (as opposed to $\sim 0.01\%$ in the drift-free approach). Due to its high solid angle collection, polarization effects cannot be observed with the MBPES. Finally, the photoelectron signal drops by about one order of magnitude when the ions are decelerated so as to achieve the best resolution in the MBPES. This is caused by the longitudinal and transversal spread in the decelerated ion packet at the detachment zone, which leads to poor overlap between the ion packet and the detachment laser. Recall that electron alignment in the MBPES and the laser pulse duration introduce a finite time spread in the TOF of monoenergetic electrons. Extending the length of the flight tube can reduce the effect of this time spread on the resolution. In contrast, the ion velocity introduces a real kinetic energy spread within the laboratory framework, and should be re-

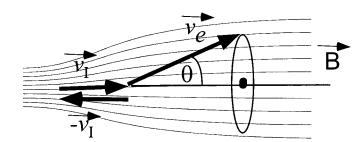


FIG. 1. Vector superposition of the ion velocity and the detached electron velocity, ν_e , results in a Doppler shifted electron velocity within the laboratory framework. θ is the angle between the symmetry axis and the electron velocity. In a coaxial MBPES the velocity of the ion, ν_1 , prior to detachment is coaxial with the flight tube and the symmetry axis of the magnetic field lines. In coaxial geometry, the ion velocity component is fixed in space and can be removed by a decelerating electric pulse.

duced as much as possible in order to achieve the ultimate resolution with the MBPES.

The possible benefits of coaxial ion–electron flight tube geometry in the MBPES were advocated by Cheshnovsky *et al.*⁸ Here we introduce an advanced version of the coaxial geometry. We describe a coaxial MBPES in which we use an electric impulse, immediately after detachment, to remove the ion velocity from the electrons. This design enables in principle the *complete* removal of the ion velocity from the electron with no signal loss. We also show that the same electrical impulse can be used to compensate for the alignment time spread of the electrons. Finally, we show how we combine this new spectrometer with a polarization sensitive MBPES. We present a MBPES system which can be operated in two easily interchangeable modes, regular and polarization sensitive modes, with 60% or 4% collection efficiencies, respectively.

II. THE DESIGN CONCEPT

So far, in all MBPES designs, coupled with TOF mass spectrometers, the flight tube of the electrons, and thus the symmetry axis of the magnetic field lines, have been perpendicular to the ion velocity. This choice was made for experimental convenience. The electron velocity after detachment is a superposition of the ion velocity and the center of mass electron velocity (Fig. 1). The magnetic field at the detachment zone is typically 0.1 T. Consequently, the velocity component of the electron, contributed by the ion, undergoes precession with a subnanosecond period. In contrast, when using a coaxial geometry, the same velocity component remains fixed in space over a much longer time, determined by the alignment time (\sim 20 ns), and could be subtracted by an electric impulse (see Fig. 1).

Ideally, an infinitely short impulse applied immediately after detachment could completely cancel the ion velocity component, provided that the ion packet velocity is uniform. In practice, a finite time impulse should compete with the adiabatic alignment of the electron in the diverging magnetic field. A typical time of alignment in a MBPES is 20 ns. This time is long enough for the application of a voltage impulse to remove $\nu_{\rm I}$ from the velocity of the electron. Unlike in ion deceleration, this impulse is of low magnitude (~1 V ns cm⁻¹) and does not induce residual stray electrical

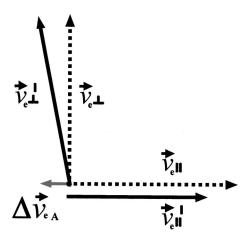


FIG. 2. Schematic illustration demonstrating that a small electric impulse decelerates mainly a coaxially ejected electron. The velocity of a perpendicularly ejected electron hardly changes.

fields in the detachment zone. Since the impulse deceleration is performed in the detachment zone, the full population of detached electrons is preserved.

The idea of removing the ion velocity component from the laboratory electron velocity has recently been introduced by Bosel and co-workers¹⁴ in a threshold electron spectrometer (ZEKE¹⁵) designed to operate with negatively charged ion beams. Their experiment was performed in a shielded zero magnetic field regime. Therefore, it was possible in their case to apply the deceleration impulse perpendicular to the flight direction of the electrons.

We use the decelerating electric pulse also to suppress the time spread caused by the alignment of the electrons, ejected at different angles, θ , relative to the flight tube axis. Consider an electron with a velocity ν_e , ejected from a stationary ion, perpendicular to the flight tube of length L. Its flight time to the detector, t_{\perp} , is longer than the flight time of the coaxial ($\theta = 0$) electron, t_{\parallel} , by the alignment time t_A . We slightly decelerate the axially detached electron to compensate for this time difference. An electrical impulse collinear with the flight tube, applied immediately after detachment, can decelerate the axially detached electrons by Δv_{eA} . The same impulse hardly influences the perpendicularly detached electrons¹⁶ (see Fig. 2). The axial and perpendicular electron velocities $\nu_{e\parallel}$ and $\nu_{e\perp}$ (equal in magnitude to ν_e) will change after the impulse to $\nu'_{e\parallel}$ and $\nu'_{e\perp}$, respectively. Therefore, the following relation defines the Δv_{eA} necessary to achieve arrival time focusing:

$$t_{A} + L/\nu'_{e\perp} = L/\nu'_{e\parallel},$$

$$t_{A} = L(1/\nu'_{e\parallel} - 1/\nu'_{e\perp}) \approx L\Delta\nu_{eA}/\nu^{2}_{e},$$
 (2)

$$\Delta\nu_{eA} \approx \nu^{2}_{e}t_{A}/L.$$

Since t_A is inversely proportional to ν_e , ⁸ $\Delta \nu_{eA}$ should be proportional to ν_e .

It can be shown that electrons ejected $\theta < 90^{\circ}$ will have shorter alignment times than t_A and will be decelerated less by the electric impulse. Consequently, the same impulse will practically time focus electrons detached in all intermediate angles. A given velocity compensation impulse is valid in principle only for a single electron velocity, ν_e . In practice, however, $\Delta \nu_{eA}$, which is suitable for an electron velocity ν_e , improves the alignment time dispersion for all electron velocities larger than ν_e and starts to spoil the resolution only for velocities smaller than $\nu_e/2$. There is a wide dynamic range of electron energies for which a given $\Delta \nu_{eA}$ impulse is useful. Both voltage impulses described above are applied immediately after detachment and are additive. A single voltage impulse can be used to subtract from the electron velocity,

$$\Delta \nu = \nu_{\rm I} + \Delta \nu_{eA} \,. \tag{3}$$

For most practical situations ν_{I} is much larger than $\Delta \nu_{eA}$. Note, that ν_{I} depends on the ion acceleration voltage V in the mass spectrometer and on the ion mass m_{I} . Accordingly, the electric deceleration impulse, which relates to ν_{I} , should scale as $(V/m_{I})^{1/2}$. The compensation to the alignment time spread, $\Delta \nu_{eA}$, depends on the magnetic field regime of the MBPES and on the electron energy.⁸ It should be optimized for the chosen electron energy according to the range of photoelectron spectrum desired.

III. SIMULATIONS

We have tested the concept of the new MBPES by simulating¹⁷ the TOF distribution of electrons. Our MBPES is based on a small coil that generates a high diverging magnetic field, and on a long solenoid generating a low guiding magnetic field in the flight tube. In the first stage of the simulation magnetic fields were calculated according to a chosen geometry. Subsequently TOF distributions of the electrons were calculated. In the TOF simulation the initial directional velocity, $\nu_{\rm I}$, was added to the various spatial distributions of electrons of a given kinetic energy. Both random spatial distributions and polarization dependent distributions were simulated. TOF histograms were calculated using 1.5° increments of θ with appropriate weighting of $\sin \theta$. We have assumed adiabatic alignment¹⁸ of the electrons along their flight. Electric fields of deceleration were introduced for a predetermined intensity and duration in order to study their influence on the time of flight distribution. Typical physical parameters of the simulated apparatus included a 4 mm long, 18 mm inner diameter (i.d.) and 26 mm outer diameter (o.d.) solenoid with ~4000 A · turns and a 150 cm long flight tube with a typical magnetic field of 10^{-4} T. Electrons are excited 13 mm downstream of the center of the high field solenoid. In Sec. III we describe the electric impulse applied in terms of the formal change of the electron velocity, Δv_{imp} , namely, $\Delta v_{imp} = eEt_{imp}/m_e$; where E is the electric field and $t_{\rm imp}$ is the pulse duration and m_e is the electron mass. We define Δt , the spread in the arrival times of the electrons, as the half height width of the electron arrival time histogram. The resolution, ΔE , is related to Δt by $\Delta E = 2E\Delta t/t$, where t is the average arrival time for an electron of energy E.

The following cases were studied. The results of the simulations are summarized in Table I.

(1) First, TOF histograms of 1.22 eV electrons were calculated, assuming stationary ions. This simulation gener-

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TABLE I. Simulated and experimental resolutions (in meV) of our MBPES utilizing an electrical impulse for electron deceleration. In both simulations and experiments electrons are detached from 400 eV I⁻ ions.

| Electron kinetic energy | Resolution in meV | | |
|---|-------------------|---------|---------|
| | 0.28 eV | 1.22 eV | 2.11 eV |
| Simulation for 1 ns impulse, optimized for each energy, δ laser | 0.5 | 2 | 4 |
| Simulation for 4 ns impulse, optimized for each energy, δ laser | 0.5 | 8 | 12 |
| Simulation for 4 ns impulse optimized for 1 eV, δ laser | 5 | 10 | 23 |
| Simulation for 4 ns impulse, optimized for 1 eV, 5 ns laser | 7 | 17 | 35 |
| Experimental resolution optimized for 1 eV electrons, 5 ns laser | 8 | 25 | 48 |

ated $\Delta t \sim 15$ ns and collection efficiency of about 60%. The time spread results from the spread in the alignment times. The simulation shows that, by applying a short (4 ns) deceleration impulse, resulting in Δv_{imp} of 4500 m s⁻¹, the TOF distribution is reduced to 2 ns ($\Delta E = 2$ meV for the 150 cm flight tube). Similar simulations performed on 0.28 and 2.11 eV electrons resulted in 0.5 and 4 meV resolution, respectively.

- (2) The simulation was extended to include the superposition of the coaxial ion velocity, $\nu_{\rm I}$, with the velocity of the electron. The velocity of a 400 eV I⁻ ion was chosen as $\nu_{\rm I}$. Without any impulse, Δt of 1.22 eV electrons amounted to 180 ns. An infinitely short deceleration impulse $\Delta v_{imp} = \Delta v_{eA} + v_I$ reduces Δt to ~ 2 ns. In the case of a finite time impulse the resolution deteriorates due to partial alignment of the electrons during the impulse. For example, to achieve optimal resolution with a 4 ns impulse, Δv_{imp} has to be somewhat larger than Δv_{eA} $+\nu_{\rm I}$, and the resulting width of the electron packet increases to 8 ns. Somewhat different impulses have to be chosen to achieve the best resolutions for the 0.28 and 2.11 eV electrons. For the 0.28 eV electron a 6% smaller impulse was required, while for the 2.11 eV electron a 3% higher impulse was required to achieve the best resolutions at these energies. There are two reasons for this trend: First, Δv_{eA} , the impulse needed to compensate for the alignment time, is proportional to ν_e . Second, the degree of alignment, which occurs during the finite impulse, is larger for the faster electrons, and a somewhat stronger impulse is needed to compensate for the ion velocity.
- (3) The next step was to simulate a practical situation in which a wide kinetic energy range PES was measured. We have applied an optimal electrical impulse for a 1 eV electron to all simulated electron energies (0.28, 1.22, and 2.11 eV electrons). Note in Table I that the resolutions of the 0.28 and 2.11 eV electrons deteriorate substantially.
- (4) Finally, we wish to refer to the influence of the duration of the laser pulse on the resolution. In the abovementioned simulations, we have turned on the impulse 1 ns after generation of the photoelectrons. In a real ex-

periment, due to the finite duration of the laser pulse, (5 ns) the deceleration impulse acts on the detached electrons with variable delays. Consequently, for the early electrons, partial alignment along the magnetic field lines may occur before the impulse is turned on. We have simulated the influence of the variable delay on the resolution. We conclude that under the conditions of a 5 ns laser pulse further resolution deterioration occurs, as detailed in Table I.

The above simulations indicate that good resolution can be achieved in the MBPES by applying electric impulse deceleration on the detached electrons. The resolution values obtained are 7, 17, and 35 meV for 0.28 1.22, and 2.11 eV electron energies, respectively. These values compare well or exceed the best resolution attainable in MBPES instruments. In particular, our simulations indicate that a sub-meV resolution for electrons with low kinetic energies can be achieved with a \sim 1 ns detachment laser.

We note that the simulations do not include additional experimental factors, which could further deteriorate the resolution. The most annoying one is the finite velocity distribution of the parent ions; it prevents the use of a unique deceleration pulse appropriate for all electrons. Also, due to practical constraints, the impulse field might be inhomogeneous in space, leading to nonuniform deceleration of the electrons.

IV. EXPERIMENTAL DETAILS

The experimental system was built in accordance with the design principles outlined above and the results of the simulations. In the source chamber, methyl iodide (background pressure of 10^{-6} mbar) is "picked up" ¹⁹ into the supersonic expansion of a 10 Hz pulsed nozzle.²⁰ The expansion consists of 3-4 bar of Ar. Negatively charged I⁻ ions are produced by dissociative attachment²¹ of the methyliodide molecules using a 500 eV electron beam. The resulting anion beam is skimmed into a chamber where it is mass separated by a Wiley-McLaren TOF mass spectrometer²² (TOFMS). A few cm in front of the ion detector of the mass spectrometer the ions can be mass gated and decelerated. Coupling of the ion beam to the photoelectron spectrometer is shown schematically in Fig. 3. An electrostatic mirror (2), consisting of two high-transmission (92%) meshes, can reflect the ions coaxially into the MBPES. To record mass spectra the mirror is turned off, transmitting the ions to the multisphere plate (MSP®) detector.²³ To record the PES the reflected ions pass through a hole in a plate, which carries a hollow solenoid (3). This pulsed solenoid (18 mm i.d., 26 mm o.d.) provides a magnetic field of ~ 0.4 T at its center for a period of about 80 μ s during detachment. It serves as the high diverging magnetic source in the magnetic bottle. 12 mm downstream the solenoid anions are intersected by a tunable pulsed laser beam (4) \sim 5 ns long.²⁴ At this point, the magnetic field, generated by the pulsed solenoid, equals \sim 0.04 T. A hollow permanent magnet can replace the solenoid and serve equally well as the source of the high diverging magnetic field. About 1 ns after termination of the laser pulse, a deceleration pulse of ~ 1 V, lasting 4 ns,²⁵ is applied

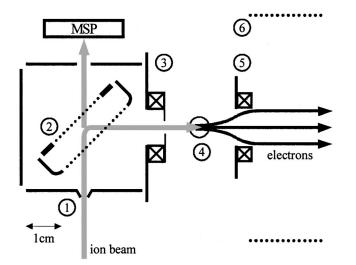


FIG. 3. Schematic of the MBPES: (1) input ion beam skimmer; (2) electrostatic mesh mirror; (3) isolated impulse plate, carrying a pulsed solenoid (activated only in the high collection-high resolution mode); (4) laser interaction zone; (5) counterground electrode carrying the second solenoid (activated only in the polarization sensitive mode); (6) solenoid of the electron flight tube, 150 cm long; MSP represents the ion detector.

to the plate carrying the pulsed solenoid. 2 cm further along the flight path of the detached electrons, an additional hollow plate serves as the counter electrode (5). The detached electrons are directed by the "magnetic bottle" into a 150 cm flight tube (6) with a static low magnetic field of ~0.0001 T, shielded by two μ -metal layers.

In an alternative operational mode, the high diverging field is generated by a second pulsed solenoid situated on the counterelectrode of the impulse (5). This solenoid is 28 mm i.d. and 36 mm o.d. In this mode, the electrons detached at ~ 0.04 T pass through a higher 0.4 T magnetic field (at the center of the second solenoid) on their way to the electron detector. Only the electrons which are ejected at an angle smaller than ϑ_{max} off the flight axis are collected, where ϑ_{max} is given by $\sin^{-1}(B_d/B_s)$. B_d and B_s are the magnetic fields at the detachment point and the center of the second solenoid, respectively. Accordingly, the collection efficiency is reduced and is given by

yield =
$$0.5\{1 - [1 - (B_d/B_s)]^{0.5}\}.$$
 (4)

It amounts in our geometry to 4%. ϑ_{max} is determined by the ratio of B_d/B_s , that is, the geometry of the detachment zone of the MBPES. In this alternative mode, the MBPES can be operated in a polarization sensitive mode, since only electrons ejected in the direction close to the flight axis are collected. The deceleration impulse is still useful to remove the ion velocity in this geometry, but will not compensate for the alignment time. The reason is that, at the detachment zone, all electrons, which are transmitted, are initially aligned along the flight tube. The spread in the alignment times and angles relative to the flight tube evolve in the flying electron packet only in the vicinity close to the second solenoid (5).

V. RESULTS AND DISCUSSION

Figure 4 displays photoelectron spectra of I^- recorded in our MBPES at 290 nm (4.28 eV). The broad peak (180 meV

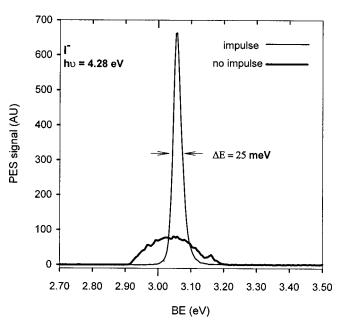


FIG. 4. Effect of a 10 ns electric impulse on the PES resolution of a 1.22 eV electron detached from a 400 eV I^- . Note the dramatic improvement in resolution and the full conservation of the electron signal.

half width) of a 1.22 eV electron is generated by the detachment of electrons from 400 eV ions. The narrow peak is recorded under the same conditions but subjected to a 10 ns pulse of 0.97 V applied ~1 ns after the end of detachment. Note the dramatic improvement in the resolution (25 meV) and no loss of signal. For 2.11 eV electrons at 400 eV ion energy, a resolution of 48 meV was recorded with the same impulse. Figure 5 presents the full PES of I⁻ taken at 290 nm with a deceleration impulse of 4 ns. We have reached 25 meV resolution at 1.22 eV kinetic energy (j=3/2). At 0.28

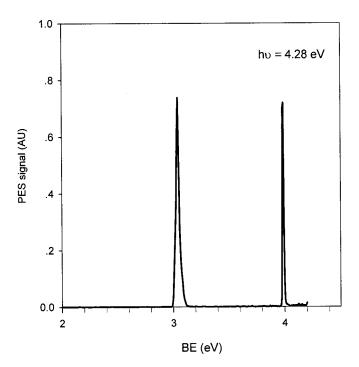


FIG. 5. Photoelectron spectrum of 400 eV I^- taken with 4.28 eV photons. The resolution obtained is 25 and 8 meV for the 1.22 and the 0.28 eV electrons, respectively.

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eV kinetic energy (j = 1/2) the resolution is 8 meV. Note that according to our simulation the resolution (finite impulse and laser pulse widths) should have been 17 and 7 meV for the 1.22 and 0.28 eV electrons, respectively. When the TOFMS is operated with 1600 V (4 × the kinetic energy), and the impulses scaled up accordingly ($\sim 2\times$), the best resolutions obtained were 29 and 12 meV, respectively.

We note that the experimental resolution achieved is as good as the best MBPES, which uses ion deceleration to improve resolution, with the added benefit of complete conservation of the signal. However, the resolution achieved in the experiment is worse than the simulated resolution, and deteriorates with an increase in the kinetic energy of the ions. Three major factors contribute to these observations.

- (1) The partial alignment of the electrons during the impulse deteriorates the resolution.
- (2) Due to design constraints the deceleration field is not uniform: For a 2 mm finite size of the detached electron packet the field inhomogeneity amounts to 3%.
- (3) The velocity of the ion packet is not uniform. This is an intrinsic property of a TOFMS that accelerates a finite volume of the ion packet. Therefore, there is no impulse which is appropriate for all ion velocities. In our TOFMS the velocity distribution amounts to 5%.

To fight the resolution deterioration described in observations (1) and (2) it is desirable to partially decelerate the ions prior to detachment. By doing so, the required impulse to decelerate the electrons is smaller, and so is the deterioration in resolution due to the inhomogeneous impulse field or the partial alignment of the electrons. In order to improve the resolution beyond the value determined by the ion velocity distribution [observation (3)], one can pick a subgroup of ions with a smaller velocity spread, as described by Ganteför and co-workers.¹² We are currently developing a deceleration scheme that will decelerate the ions to an almost uniform kinetic energy. Such a scheme will substantially reduce the effect described in observation (3). We wish to emphasize that partial deceleration of the ions prior to detachment very often increases the photoelectron signal in the MBPES due to bunching of the ion packet. For the best combination of resolution and signal it is probably useful to combine partial ion deceleration prior to detachment with additional impulse deceleration of electrons at the detachment zone.

In the case of detachment lasers with relatively long pulses (>10 ns) and in cases where the electron deceleration impulse cannot be precisely synchronized with the detachment laser, the conventional method of ion deceleration is superior. In such a case we recommend the use of electron deceleration as a complementary method for further improvement in resolution. On the other hand, in the case of an ultrafast laser PES the benefits of the electron impulse deceleration method, in which no signal is lost, are obvious.

We can replace the first solenoid in our MBPES [(3) in Fig. 3] with a hollow stack of permanent magnets. The stack, 5 mm i.d., 14 mm o.d., and 6 mm long, produces 0.03 T at the detachment zone. The same photoelectron spectra quality is achieved with this stack. However, we prefer to use a

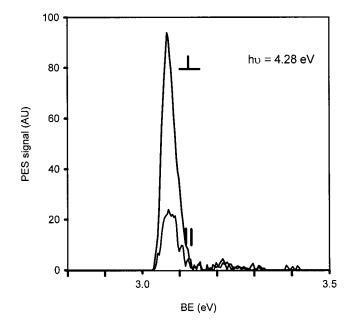


FIG. 6. Photoelectron spectrum of the j=3/2 final state of iodine in the polarization sensitive mode. The polarization ratio recorded is 1: 3.5.

pulsed solenoid to produce the magnetic field. This choice enables easy switching between the high collection efficiency and the polarization sensitive modes.

In Fig. 6 we present PES spectrum of I^- taken in the polarization sensitive mode. The spectra were collected with a laser polarized 0° and 90° relative to the symmetry axis of the flight tube. In this mode we have achieved 40 meV resolution and a 1:3.5 contrast ratio of the two polarizations for 1.22 eV electrons. The substantially poorer resolution achieved in this mode results from the much longer alignment time in this configuration, which cannot be compensated for by using an electric impulse.

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