

A Novel Method Capable of Resolving Rotational Ionic States by the Detection of Threshold Photoelectrons with a Resolution of 1.2 cm^{-1}

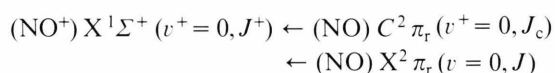
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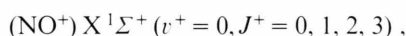
A novel method for the unambiguous direct determination of ionization potentials is presented. This is done by combining a pulsed field technique with a steradiancy analyser for the detection of threshold electrons. For now a resolution of better than 0.15 meV is demonstrated by resolving the first three rotational states of NO^+ .

I. Introduction

In photoelectron spectroscopy (PES) the detection of photoelectrons from atomic or molecular photoionization process by conventional methods [1, 2] suffers from the problem that it is not possible to achieve a substantially better energy resolution than 10 meV . Often this is sufficient to resolve vibronic states of molecular ions but except for the case of H_2^+ or D_2^+ [3, 4] or transitions from very high rotational states of NO into high rotational states of NO^+ (which then are sufficiently separated to be resolved with an analyser of about 10 meV resolution) [5] ionic rotational states cannot be studied by the conventional methods. In order to make possible the study of rotational fine structure of molecular ions and to take advantage of the availability of laser sources with a linewidth of the order of 0.1 cm^{-1} it is evident that a much better photoelectron energy resolution than 10 meV (80 cm^{-1}) is demanded. For this goal, we have in previous work [6] employed a steradiancy analyser with static potentials [7, 8] for the detection of threshold photoelectrons in the



ionizing transition and achieved an energy resolution for threshold electrons of 1.5 meV (12 cm^{-1}). This resolution was sufficient to observe a convolution of transitions from the $\text{C}-\text{T}_y(3/2)$ level [9, 10] into the rotational states of



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but a complete separation of rotational ionic states was not achieved.

A complete separation of the rotational states at the ionization threshold of NO^+ [11] has now been made possible by the new method to be presented here. This method is based on the following indeed very simple principle: If an ion is produced in the absence of electric and magnetic fields and the detuning between photon energy and the energy difference between the selected ionic and molecular level is exactly zero, a photoelectron of exact zero energy is produced (limited by the linewidth of the light source, of course). If, however, the detuning is say 0.1 meV above the discrete ionic level the photoelectron will carry this energy and hence have a velocity. Here we have to remember that an electron of 0.1 meV kinetic energy travels in field free space the distance of 6 mm within $1 \mu\text{s}$. So, if a suitable electric field is switched on a certain time after the ionization event, the kinetic electron will appear on a potential rather different from that if the field was already present at the time of the ionization event. Provided a suitable accelerating and drift stage are used in the apparatus, the time of flight of those kinetic electrons which flew (before the field pulse) towards the detector or in opposite direction will be very different, even if the kinetic energy is small, e.g. 0.1 meV (here we have neglected electrons flying in other directions because these are easily discriminated against by apertures near the test volume). Hence the detector will measure these two groups of kinetic electrons as two peaks well resolved in time. Switching back to our problem of detection of exact threshold electrons it is quite obvious now that an electron of zero kinetic energy

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will remain at the same point where it was produced at the time of the ionization event until the electric field is switched on (except for the movement in the molecular beam $v \approx 1 \text{ mm}/\mu\text{s}$). Hence it will be detected at a rather different time than a kinetic electron.

We have gone one further step in refining the method developed above by combining it with the steradiancy analyser technique [6–8]. Here we have to recall one problem associated with the steradiancy analyser. Those kinetic electrons which travel exactly in the direction of the small solid angle defined by the aperture in front of the detector will also be detected. Usually, this only constitutes a problem when highest resolution is to be achieved because the fraction of kinetic electrons transmitted rapidly decreases with energy. It is clear that by using our pulsed electric field method together with a steradiancy analyser this problem is overcome completely. The steradiancy analyser discriminates against all kinetic electrons which are not confined to the defined solid angle and the pulsed field allows for time discrimination against the two groups of kinetic electrons inside the solid angle.

In a few words the recipe for the detection of threshold photoelectrons can be put as “Wait as long as possible, apply a small electric field and detect at the proper time what is transmitted through a small aperture”.

II. Experimental

The experimental arrangement is shown in Figure 1. The acceleration region consists of 16 molybdenum apertures (without grids) of 50 mm o.d. and 1 mm thickness. The central apertures with holes of 6 mm i.d. are separated by 10 mm. The other apertures of 20 mm i.d. are separated by 5 mm.

The two central apertures 2, 3 are connected by a 480 k Ω resistor. All other apertures are connected by 240 k Ω resistors. The field free drift tube (i.d. 20 mm) is made of stainless steel of 30 cm length and followed by four tube segments cut at 90°, the steradiancy aperture (i.d. 3 mm), the electron lens and the fast rise-time box and grid electron multiplier (pulse width < 10 ns). All connections (marked by numbers) to the BNC type UHV sockets are made by 50 Ω Teflon coaxial cable. This is absolutely essential in order to reduce parasitic pulses from the detector when electric fields are pulsed. Earth-

ing was very carefully optimized to minimize parasitic pulses. After decoupling by a 10 nF capacitor and amplification the signal was measured by a boxcar integrator fitted to a microcomputer (Microcomputers for Research, Compdata).

Common VMOS electronics is used for the circuit to switch the voltages (typical rise times < 10 ns). A trigger pulse from a photodiode illuminated by the laser pulse triggers the circuit. The voltages can be adjusted from 0 to $\pm 10 \text{ V}$ and the time delay between laser pulse and electric field pulses can be varied from 60 ns to several μs .

In our experiments good results were obtained with a time delay of 1.1 μs . Photoionization in the supersonic skimmed jet [further details in 11] is carried out with earth potential on apertures 1, 2, 3, 4 and the drift tube. After 1.1 μs the potential of aperture 2 is switched to -0.5 V and the potential of aperture 4 and the drift tube $+4.0 \text{ V}$. The constant potentials applied are: 5, 6 a, b, c, d, 7: $+25 \text{ V}$; 8: $+100 \text{ V}$; first dynode of electron multiplier: $+100 \text{ V}$; supply voltage of 20 stage EM: $+3100 \text{ V}$.

Great care was taken in excluding Coulomb effects which would in an ion electron cloud perturb the measurement. For this reason the maximum event rate was limited to below one electron count per laser shot (laser repetition rate: 50 Hz).

A demonstration of the resolving power of our technique is given in Fig. 2. The first rotational

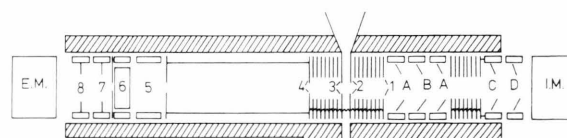


Fig. 1

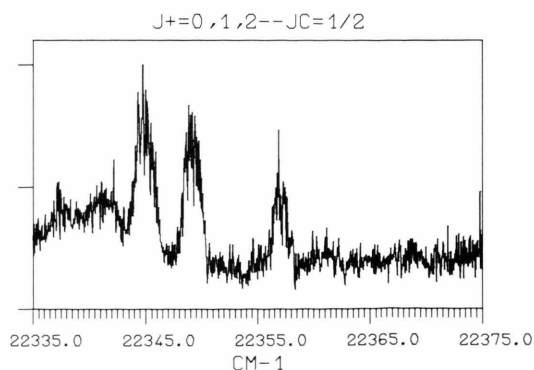


Fig. 2

levels of NO^+ which are separated by $F(1) - F(0) = 4 \text{ cm}^{-1}$ and $F(2) - F(0) = 8 \text{ cm}^{-1}$ are clearly resolved. Thus our technique allows for the unambiguous direct determinations of molecular ionization potentials. This is fully discussed in [11].

III. Conclusion

We have provided what we think is the method of choice for direct observation of the lowest states of molecular ions and hence the precise measurement of ionization potentials. Perturbations, e.g.

field and collisional ionization are completely excluded by our method. Because detection efficiency is high, also Coulomb interactions can be excluded by reducing the number of ion electron pairs to 1–3 per laser shot.

In the future we hope to increase resolution even further towards the limit given by the laser bandwidth ($\approx 0.1 \text{ cm}^{-1}$).

Acknowledgements

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