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A new detection scheme for synchronous, high resolution ZEKE and MATI spectroscopy demonstrated on the Phenol · Ar complex

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Abstract

We present a new detection scheme for high resolution mass analyzed threshold ionization (MATI) spectroscopy which utilizes fractional Stark state selective electric field ionization of high-*n* Rydberg states. The method represents a significant advance over previous approaches to MATI spectroscopy, which have been characterized by their low resolution compared to zero kinetic energy (ZEKE) photoelectron spectroscopy. In addition, the scheme can be used to synchronously obtain electrons and ions originating from the same Rydberg states, facilitating the acquisition of synchronous, high resolution ZEKE and MATI spectra. We demonstrate the technique by obtaining MATI dissociation spectra of the phenol · Ar complex, which provide dissociation energies of 364 ± 13, 397 ± 13, and 535 ± 3 cm^{-1} for the S_0, S_1 and D_0 states, respectively. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Since its introduction in 1984 [1], ZEKE photoelectron spectroscopy has advanced considerably to become a high resolution technique that is widely applicable for studies of molecules and clusters [2–6]. One of the most significant innovations of recent years has been the realisation that fractional Stark state selection via electric field ionization (FSSFI) allows a noteable improvement in ZEKE spectral resolution [7]. In this approach, an offset pulse selectively ionizes the more fragile 'red' Stark states, while the more resilient 'blue' Stark states survive and are shifted down in energy upon application of a second pulse of opposite direction. Dietrich et al. [7] demonstrated that the spectral resolution of peaks in the ZEKE spectrum of benzene could be improved by more than a factor of eight using FSSFI.

MATI spectroscopy was introduced by Zhu and Johnson as a variation of the ZEKE method that allows mass analysis of ions produced by pulsed field ionization (PFI) [8]. The technique is particularly useful for cluster studies where it facilitates unambiguous identification of the ionized species, and can be used to follow cluster fragmentation [9–12]. The major drawback with the MATI technique has been obtaining spectral resolution that can compete with ZEKE resolution since relatively large separation fields and field ionization pulses have been employed to separate PFI ions from ions spontaneously produced by the laser pulse [13]. In this Letter, we report a new scheme for the synchronous detection of high resolution ZEKE and MATI spec-

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tra. While a relatively high resolution approach to MATI spectroscopy has been suggested previously [13], this is the first time that FSSFI has been used to maximize the experimental resolution. Our strategy for obtaining high resolution MATI spectra can be readily extended to allow the synchronous detection of a high resolution ZEKE photoelectron spectrum. We demonstrate the technique by presenting a MATI dissociation [9,11,12] spectrum of the phenol · Ar cluster, to show that the approach is not only useful in the high signal regime of molecular spectroscopy, but can readily be used to obtain spectra of complexes where lower signal intensities are the rule.

2. Experimental

The apparatus used has been described in detail in a recent paper [14]. Briefly, phenol · Ar clusters were produced in a skimmed supersonic expansion by passing argon gas over a heated phenol sample. The excitation and ionization region consisted of a mutually perpendicular arrangement of the jet, two counter-propagating frequency-doubled dye lasers (Excimer pumped Radiant Narrowscan for $S_1 \leftarrow S_0$ excitation and Lambda Physik FL 3002 for $D_0 \leftarrow S_1$ excitation) and μ-metal shielded extraction plates. The ZEKE electron and threshold ion signals were obtained using electric field pulses generated by an arbitrary function generator (Le Croy, AFG 9100), which produces pulses with rise times of less than 5 ns. The pulses used are described in detail in Section 3. Electrons were post-accelerated onto the electron microchannel plate detector and ions were extracted in the opposite direction into the reflectron time-of-flight analyser with a high voltage pulse of 290 V/cm applied 3 μs after the AFG pulse. ZEKE spectra were recorded with an SRS boxcar integrator while MATI signals were simultaneously detected by a digitising oscilloscope. Laser frequencies were calibrated by comparison to iodine absorption spectra [15], to ensure an accuracy in the laser energy of ± 0.02 cm^{-1}. All ZEKE and MATI spectra presented in this paper were obtained via the phenol · Ar $S_1 0^0$ transition at 36 323 cm^{-1} [16].

3. Results and discussion

3.1. Synchronous high resolution ZEKE and MATI spectroscopy

The key to our method of improving MATI spectral resolution lies in utilizing FSSFI which has

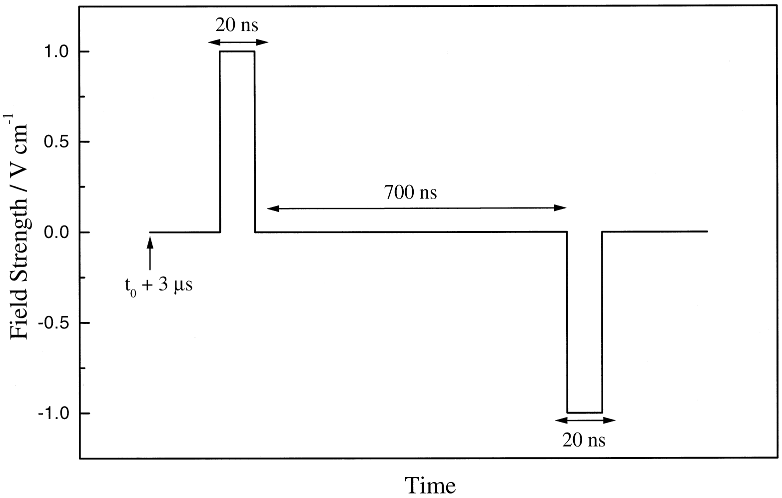

Fig. 1. Schematic of a typical field ionization pulse used in a FSSFI ZEKE experiment. The pulse is applied 3 μs after photoexcitation (t_0).

produced significant improvements in ZEKE spectral resolution [7]. The general procedure for effecting Stark state inversion in ZEKE spectroscopy involves the application of a short (~ 20 ns) electric pulse in the positive z direction, followed several hundred nanoseconds later by one in the negative z direction. (In this Letter, negative and positive z direction are used to indicate a field accelerating the electrons onto or opposite to the microchannel plate detector). A schematic of a typical pulse employed in experiments in our laboratory is displayed in Fig. 1. In a ZEKE experiment, photoelectrons produced by the initial laser interaction will rapidly separate from the neutral, long-lived Rydberg states in the ionization region. This process is repeated upon application of the first ionizing pulse (positive z) in the FSSFI experiment, so that when the negative z pulse is applied several hundred nanoseconds later only electrons from original 'blue' Stark states are detected. While this procedure readily produced high resolution ZEKE spectra, it will entirely fail as a scheme for MATI spectroscopy since in FSSFI, PFI ions produced by the positive z pulse would begin to spatially disperse from the remaining Rydberg excited molecules in one direction only to be 're-focused' by the negative z pulse.

Fig. 2a displays the tailored pulse we have employed to combine FSSFI with MATI spectroscopy. The excitation lasers fire at $t = 0$, followed by the application of a $+1$ V/cm pulse 200 ns later (t_a). This pulse can be considered to be equivalent to the separation pulse employed in a typical MATI experiment (Fig. 2b), but will also ionize the more fragile 'red' Stark states. The more resilient 'blue' states survive, and the spontaneous ions spatially separate from the neutral Rydberg states for 3 μs before the electric field is rapidly inverted to -1 V/cm for 20 ns at t_b. Stark state inversion occurs, and the original 'blue' states are now ionized, producing high resolution ZEKE electrons and MATI ions. The polarity of the electric field is now reversed again to continue the spatial separation of spontaneous ions from both the high resolution MATI ions, and the remaining Rydberg states which will be ionized to produce low resolution MATI signal by the substantial pulsed field (290 V/cm) used to extract ions into the reflectron time-of-flight analyzer. The time-of-flight distribution of ions produced at different points in the pulse sequence is presented with the pulse scheme in Fig. 2a. This time-of-flight profile can be compared to one obtained using a traditional MATI separation pulse in Fig. 2b. Although the inverted pulse (t_b) reverses the field experienced by the spontaneous ions, and therefore counteracts the spatial separation achieved during the first 3 μs, the effect is minimized by the shortness of this pulse. The pulse displayed in Fig. 2a was tailored to optimize the separation of the spontaneous, high resolution and low resolution ion signals in the time-of-flight spectrum and will be dependent on parameters such as the experimental configuration, the mass of the system being studied and the molecular beam velocity. The greater ion separation achieved by increasing the magnitude of the pulse in the positive z

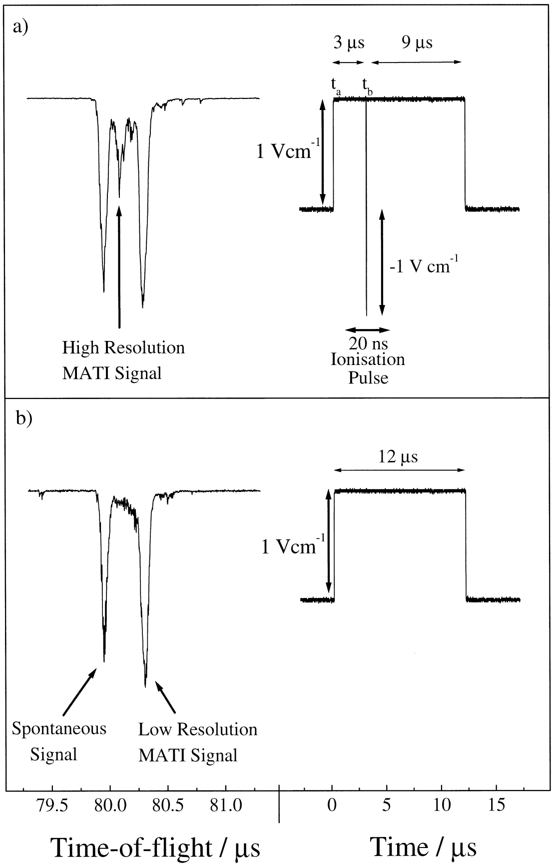

Fig. 2. Pulse detection schemes and resulting ion time-of-flight spectra involved in (a) the new high resolution detection scheme and (b) low resolution MATI spectroscopy.

direction must be offset against the lower ZEKE resolution obtained for larger ionizing fields, and as demonstrated in the FSSFI ZEKE experiment [7], the ratio of the positive/negative z field must also be balanced with regard to high resolution signal intensity versus spectral resolution.

The high resolution MATI technique described above can be straightforwardly extended to obtain synchronous, high resolution ZEKE spectra in our apparatus since electrons are extracted into a flight tube perpendicular to the reflectron time-of-flight spectrometer used to detect cations [14]. Examples of simultaneously recorded ZEKE and MATI spectra of phenol · Ar are presented in Section 3.2.

3.2. MATI dissociation spectroscopy of phenol · Ar $^+$

The synchronous ZEKE and MATI spectra recorded using the new detection scheme are presented in Fig. 3. The spectra consist of two groups of peaks with the lower energy region corresponding to the adiabatic ionization energy (IE) region, while the second group corresponds to excitation of the 6a intramolecular mode (518 cm^{-1} ion internal energy). Each group is composed of low frequency intermolecular vibrations, which have been analyzed as part of a new investigation of the ZEKE spectroscopy of phenol · Ar [17]. The spectra are in good agreement with a previous spectrum which was recorded over the IE region [18].

The low resolution MATI spectrum presented in Fig. 3c can be regarded as a rather typical example and clearly illustrates the poor resolution of the method compared with ZEKE spectroscopy (Fig. 3a). The doublet feature centred at 29 cm^{-1} ion internal energy merges into a single feature, while the peak at 37 cm^{-1} ion internal energy is entirely obscured compared to the ZEKE spectrum. However, the resolution of the MATI spectrum produced by ionization at t_b (Fig. 3b) compares extremely well with the ZEKE spectrum, a result which is entirely expected since *the two spectra arise from ionization of the same Rydberg states*. The FWHM of the IE peak in the low resolution MATI spectrum (Fig. 3c) is 6 cm^{-1} while the FWHM of the corresponding peak in the high resolution MATI spectrum (Fig. 3b) is 3 cm^{-1}. This value is indeed equal to the FWHM of the IE peak in the ZEKE spectrum (Fig. 3a) which is also 3 cm^{-1}.

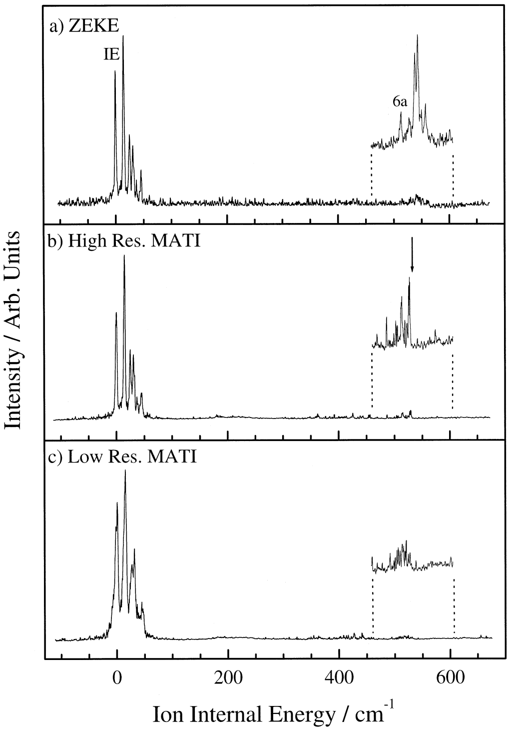

Fig. 3. Synchronously recorded (a) ZEKE, (b) high resolution MATI, and (c) low resolution MATI spectra of phenol · Ar recorded via the $S_1 0^0$ band origin. The spectra are enlarged over the region of the 6a intramolecular vibration, with the arrow indicating the dissociation energy of [phenol · Ar]$^+$. The adiabatic ionization energy (IE) is labelled on the figure.

The tailored pulse scheme for obtaining high resolution MATI spectra described in this work is fully equivalent to the FSSFI pulse scheme used previously to obtain fully rotationally resolved ZEKE spectra of benzene with linewidths of ~ 0.15 cm^{-1} [7]. This also represents the inherent resolution of the present experiment since the TOF spectra shown in Fig. 2 clearly illustrate that the high resolution MATI signal can be resolved from the low resolution MATI signal, and the linewidths in the high resolution ZEKE and MATI spectra are equivalent. The spectral resolution observed in the phenol · Ar spectra presented here is not limited by the inherent ZEKE/MATI resolution but due to the pump laser selecting a group of rotational levels in the S_1 state. In future work, this high resolution MATI technique will be used to partially resolve the rotational structure of the molecular cluster cation and to apply a fitting procedure to determine the rotational constants [19]. This requires the determination of the rotational state population in S_1 as a function of $S_1 \leftarrow S_0$ transition wavenumber [19].

Inspection of the expanded spectra over the region 450–600 cm^{-1} ion internal energy reveals that while the MATI signal ends abruptly above ~ 530 cm^{-1} due to dissociation of the ionic core, the ZEKE signal continues. The high resolution MATI spectrum of $[phenol \cdot Ar]^+$ is reproduced in Fig. 4 along with the spectrum of its daughter fragment, $phenol^+$. The insert presents an expanded view of the dissociation region, illustrating that the last peak in the parent channel occurs at 532 cm^{-1}, while the first peak in the daughter channel occurs at 543 cm^{-1}. Signal in the parent channel goes abruptly to zero at 535 cm^{-1}, and since the breakdown of signal in the parent channel has been shown to represent the field-free dissociation threshold [12], we are led to assign the dissociation energy of $[phenol \cdot Ar]^+$ as 535 ± 3 cm^{-1}. Note that unlike previous MATI dissociation spectra [9,12], there is *no overlap of signal between the parent and daughter mass channels*, probably due to the small electric field employed to ionize the Rydberg states in this experiment (1 V/cm versus ~ 500 V/cm) [12]. This experiment illustrates that there is no reason to believe that the signal will always overlap between the two channels due to energy transfer from electronically excited high *n*-Rydberg electrons to the vibrational degrees of freedom of the ionic core, as suggested previously [12]. This observation, in the light of the present results, can now be understood as an artifact due to the lower-*n* Rydberg states employed in that high field experiment. For those lower-*n* Rydberg states the electron still interacts with the ion core and the field can influence the electron-core coupling.

The $[phenol \cdot Ar]^+$ dissociation energy obtained in this work is in line with dissociation energies of other aromatic-noble gas complexes [11,12]. The dissociation energies of the S_0, and S_1 states of phenol · Ar can be calculated using the cation binding energy and the red-shifts of the $S_1 \leftarrow S_0$ and $D_0 \leftarrow S_0$ transitions of the complex relative to the phenol monomer [14], giving values of 364 ± 13 and 397 ± 13 cm^{-1}, respectively. The binding energies illustrate that the interaction energy increases significantly upon ionization of the phenol moiety due to the introduction of the charge–dispersion interaction.

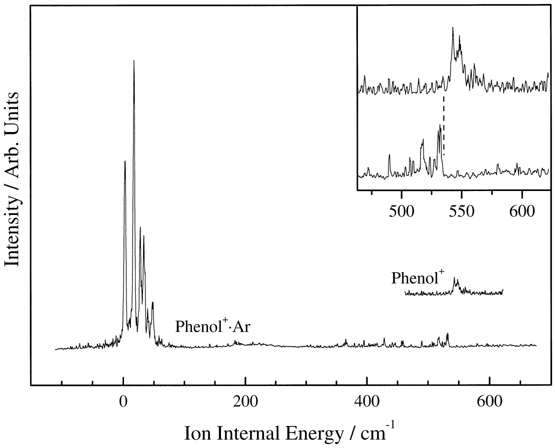

Fig. 4. MATI spectrum of $[phenol \cdot Ar]^+$ at mass channels 134 amu ($[phenol \cdot Ar]^+$) and 94 amu ($phenol^+$) recorded via the $S_1 0^0$ band origin. The inserts show expanded plots of the dissociation region with the dashed line indicating the position of the field-free ionic dissociation threshold.

4. Concluding remarks

In their 1991 paper [8], Zhu and Johnson remarked that while MATI and ZEKE spectra should provide the same information, the higher voltages necessary for MATI spectroscopy meant that electron detection should be preferred when the highest optical resolution was required, while MATI would be the method of choice when mass information was required. The new detection scheme for obtaining high resolution MATI spectra presented in this work demonstrates that MATI spectroscopy need not be regarded as a compromise between resolution and mass information. In addition, the new scheme allows high resolution ZEKE and MATI spectra to be obtained synchronously, providing an experimental approach for monitoring interactions between ZEKE electrons and the cationic core.

Acknowledgements

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