A Neutral ZEKE Beam: An Approach for Measuring ZEKE Spectra

Andrew Held, Heinrich L. Selzle, and Edward W. Schlag*

Institut für Physikalische und Theoretische Chemie, Technische Universität München,
D-85747 Garching, Germany

Received: June 27, 1996; In Final Form: September 18, 1996⊗

A technique is proposed for zero kinetic energy (ZEKE) spectroscopy that makes use of the long lifetime of neutral ZEKE states lasting for some 100 μs in a long beam. Ionization of the ZEKE states is delayed downstream until just in front of the detector. As such, it eliminates the need for μ-metal shielding and will provide both highly resolved mass and ZEKE electron resolution. When ion detection techniques are used to obtain ZEKE spectra, the ions arising from the ZEKE states of interest must be separated from ions produced directly (background ions). However, the same spoiling fields necessarily used to discriminate ZEKE states also destroys them, via field induced ionization, and thus reduces signal. In the very long beam we demonstrate that the use of extremely small electric fields suffices to separate the ZEKE neutral states from the background ions. This is of crucial importance for large masses. This now will permit the analysis of very large molecules and electrons, both at high resolution.

ZEKE (zero kinetic energy) spectroscopy has its beginnings in 1984,[1] based on and complementing threshold ionization spectroscopy.[2] This is a new high-resolution spectroscopy for the measurement of molecular cation[3,4] and anion[5,6] spectra and hence also neutral spectra in the ground state.[7] ZEKE spectroscopy is generally practiced as a delayed pulsed field ionization technique which relies on the time delay between laser excitation and pulsed field extraction to separate ZEKE state species from "direct" ions/electrons.[8] The spectral resolution in modern ZEKE experiments is, in general, only limited by the light source, typically a laser.[4]

ZEKE states are described as high n Rydberg states which contain a significant amount of high l character. These states are typically produced through electric field induced Stark mixing of optically pumped high n, low l Rydberg states to yield optically inaccessible high n, high l, m_l Rydberg states,[9,10] referred to as ZEKE states. Small Stark fields are ubiquitous in all laboratories and only affect very high values of n ($n > 100$), to produce high l states. The ZEKE state electron for high l states no longer penetrates the core and as such becomes a spectator to the core. Classically, such ZEKE states are field ionized 1−2 μs after laser excitation. The resulting electrons or ions then drift within a μ-metal shield and are finally detected by a multichannel plate detector.

Although the longevity of ZEKE states was known,[8] we now know that such neutral ZEKE states, in the presence of a small constant field, live up to some 100 μs; i.e., these ZEKE states survive a long time prior to decay.[11,12] This long time has the practical consequence that a beam of photoexcited molecules still has nearly all the ZEKE states intact after some 100 μs. Low fields are of paramount importance in these experiments since fields not only reject the unwanted ions but also destroy the ZEKE states of interest. As a practical matter, the width of the ZEKE band is some 8 cm^{-1}; this is the so-called "magic region". The density of ZEKE states, which scales as n^3, is dramatically reduced some 8 cm^{-1} below the ionization threshold. States below this 8 cm^{-1} limit are low n Rydberg states and thus have fast decay rates. Hence, high spoiling fields, which penetrate deep into this 8 cm^{-1} region, will destroy nearly all the ZEKE states and therefore eliminate the desired ZEKE signal.

The entire ZEKE "magic region" of 8 cm^{-1} permits a maximum spoiling field of 4 V/cm before the signal begins to decrease substantially. We therefore assign an arbitrary limit of 1.5 V/cm as an upper limit for spoiling fields to assure reasonable ZEKE signal strength. This limit is especially important when separating direct ions, which are much less mobile than electrons and therefore require higher spoiling fields for separation. The first mass measurements of the ZEKE states of pyrazine employed a field of 0.8 V/cm,[3] which for the above reasons led to a measurable reduction in signal strength. If 0.8 V/cm sufficed for pyrazine at mass 80 Da, then the 1.5 V/cm limit would produce a similar effect near mass 150 Da, this effect scaling roughly linearly with the mass. This indicates a practical limit to the size of the molecules which were studied using ZEKE spectroscopy. One should note that high fields (greater than 1.5 V/cm) have been used to obtain mass analyzed ZEKE spectra; however, these spectra gain their intensity from the wings of the ZEKE band which are inherently sparsely populated. An example of the effects of high spoiling fields on ZEKE spectra is the recently published spectra of NO where a spoiling field of 20 V/cm was used.[13] The field in this experiment not only destroys much of the spectral intensity but also shifts the spectrum in such a way that interferences with lower lying Rydberg states makes the spectra itself more complicated.

To reduce these fields, we propose here to go to the long beam technique where the necessary spoiling field can be kept very low. Using the above upper limit of 1.5 V/cm, this allows one to extend mass detection by some 60 fold into the kilodalton range without seriously interfering with the 8 cm^{-1} magic region of the ZEKE band. We show here measurements demonstrating the feasibility of this new long beam technique for obtaining ZEKE spectra making use of the fact that ZEKE states are extremely robust and survive these 100 μs, hence permitting extremely low spoiling fields and no shielding. We show that the intensity in an attached mass spectrometer survives fully at the end of this long beam, even in an unshielded configuration.

This method now greatly simplifies construction and expense. At the end of the 100 μs one still has the original neutral ZEKE states imbedded only in neutral molecules. When these neutral

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⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1996.

S1089-5639(96)01914-7 CCC: $14.00

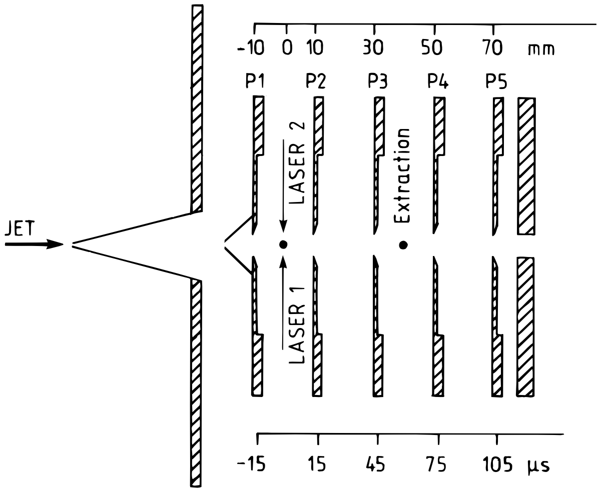

Figure 1. Schematic of the experimental arrangement: a supersonic molecular beam crosses the two propagating lasers in the region between plates P1 and P2. The excitation occurs under field-free conditions (both plates P1 and P2 are at the ground potential). A spoiling field can be produced by applying a voltage $-U$ to plate P1 and holding plate P2 at ground potential. A constant applied field throughout the ion optics is produced by applying voltages U, $2U$, and $3U$ to plates P3, P4, and P5, respectively. When all plates are at ground potential, only a stray field is present (<40 mV/cm). Extraction of ZEKE neutrals, and in some cases the direct ions, into the RETOF mass spectrometer can occur between plates P2 and P3 or between plates P3 and P4, 33 and 66 μs, respectively, after laser excitation via a fast rising 200 V/cm electric pulse.

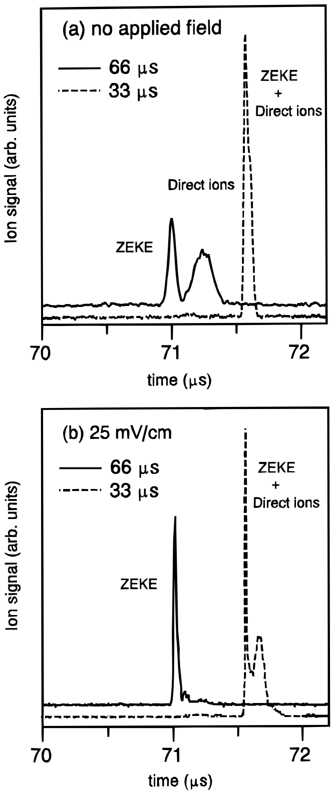

Figure 2. Time-of-flight spectrum monitored via the $S_1\ 6^1$ ($J' = 4$, $K' = 4$, $+l$) intermediate state of the 0^{0+} mode of the benzene cation. Part a shows the ion pattern detected when extraction occurs 33 μs after laser excitation (dashed line) and 66 μs after laser excitation (solid line) *where no external field is applied.* Part b shows the ion pattern detected when extraction occurs 33 μs after laser excitation (dashed line) and 66 μs after laser excitation (solid line) *where a constant external field of 25 mV/cm is applied throughout the ion optic.* Mass resolution, determined from peak widths and flight times, is approximately 1000.

ZEKE states pass in the proximity of an electron detector, they could be field ionized by a counter electrode to record the ZEKE spectrum. Similarly we show that the simultaneously produced ions can be ejected into a time-of-flight (TOF) mass spectrometer. These ions are now not just counted[14] but also mass analyzed to obtain mass resolved ZEKE spectra. Now, one must consider one additional point. The total signal of electrons and ions is always equal by charge neutrality. As the energy increases, the electron signal remains intact, but the ions can fragment. Hence, a given fragment in the mass spectrometer reflects only a part of the ZEKE spectrum.

The experimental arrangement of the ZEKE spectrometer has been previously reported,[15] and so only details pertinent to the described modifications will be presented here. In the experiment (Figure 1), benzene at −8 °C in Ar at 3 bar is expanded through a pulsed nozzle with a 200 μm diameter into the vacuum. The supersonic jet is skimmed 5 cm downstream and then again by another skimmer directly in front of plate P1 to form a well-collimated beam. The molecules, passing through the skimmers, interact with two counterpropagating lasers. The first laser is tuned to excite the resonant $S_1\ 6^1$ intermediate state. The resolution of this laser is 0.1 cm^{-1}. The transitions from the S_1 intermediate state through the Rydberg manifold, accessed by scanning the second laser, originate from selected sets of intermediate state rovibronic levels. The excited molecules pass through the ion optic plates which can be fixed to a certain potential, which produces an additional constant field throughout the ion optics, or set to ground potential. The neutrals and direct ions drift through the plates at the speed of the jet, arriving at fixed points between plates P2 and P3 and plates P3 and P4, ~33 and ~66 μs after laser excitation, respectively. These times are fixed by a variable, fast rising extraction pulse which is applied to either P2 or P3 leading to an electric field of 200 V/cm. This field ionizes the ZEKE states, and the resulting ions are extracted into the reflectron time-of-flight (RETOF) mass spectrometer. The measured mass spectra, where extraction occurs 33 and 66 μs after laser excitation and where all ion optic plates are set to ground potential, are shown in Figure 2a. Separation of the neutrals from the direct ions is accomplished after 66 μs using only stray fields, however, when extraction occurs 33 μs after excitation the direct ions and ZEKE state ions reach the detector at nearly the same time and are therefore indistinguishable. Figure 2b shows the mass spectra measured, again with an unshielded stray field, but also with an additional 25 mV/cm applied field. Extraction 33 μs after laser excitation produces a spectrum where the direct ions are now separated from the ZEKE ions. Complete spoiling of the direct ions occurs 66 μs after laser excitation. The fact that we only observe signal from ZEKE states and no longer from direct ions means that our mass resolution is conserved. One should note that the ZEKE ion signal intensity at 66 μs compared to 33 μs is still significant (Figure 2b). This is consistent with the results of our earlier experiments[11] where we found that, in the presence of a constant electric field, the ZEKE state decay rate is extremely slow. The slow ZEKE state decay rate and the in-line construction of our spectrometer make it possible to separate neutrals from direct ions with little or no applied field and retain mass resolution. This eliminates the need for complicated ion optics and, because the neutrals are ionized well after separation from direct ions, this technique also eliminates the need for μ-metal shielding. Proof that the peaks, shown in Figure 2, labeled “ZEKE” and “direct ions” arise from neutral ZEKE states and direct ion states, respectively, comes from comparing the ZEKE and direct ion mass peak positions at two different spoiling fields (Figure 2, a and b). The ZEKE neutrals are immune to the effects of the electric field, whereas the direct ions are retarded by the field. The direct ion peaks are shifted, in flight time, with increasing field strength while the ZEKE peaks are not. One could also simply record frequency scans where the detector is gated on the ZEKE and/or on the direct ion mass peak.

An interesting question which remains is, what is the stray field in our experiments? We propose to answer this question not with an estimate but with a direct measurement. We return to Figure 2a where both ion signal from the ZEKE neutrals and from direct ions are observed. The delay of the direct ions in the time-of-flight mass spectrum by ∼200 ns with respect to the ions produced from the ZEKE neutrals indicates the stray fields have a net retarding tendency. The application of a small positive voltage to plate P1 should accelerate the retarded ions. The applied voltage was increased until the mass spectral peaks arising from the direct ions and ZEKE neutrals overlapped. This occurs at 40 mV/cm. This measured stray field is the upper limit since it was applied only between the first two plates. The stray field which produces separation may be present throughout the entire ion optics. This constitutes one of the first direct measurements of these stray fields without the necessity of using Rydberg extrapolation from high-resolution laser experiments.[16]

The recipe for this long supersonic ZEKE beam then is quite simple: construct an in-line configuration of a beam with the molecules of interest heading into a RETOF mass spectrometer. Excite with a laser at right angles at the start of the beam. Employ an unshielded configuration allowing the laboratory stray field augmented by up to 200 mV/cm if required to reject the direct ions and electrons. After 100 μs at the end of the beam the neutral ZEKE states enter a field in front of a RETOF for mass analysis or an electron detector. The apparatus involves a considerable simplification of existing ZEKE techniques in that it eliminates the need for μ-metal shielding. We demonstrate that the total ZEKE signal is maintained in the long beam. At the same time one can significantly extend the mass limits for ZEKE detection. Further work is in process with this new apparatus with a laser of still better resolution.

Acknowledgment. A.H. acknowledges the Alexander von Humboldt Foundation for support through a research fellowship.

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