

# Zero Kinetic Energy Spectroscopy

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## Introduction

The structure and spectra of ionized molecules are often very different from those of the corresponding neutral species and are much more difficult to obtain using conventional spectroscopic techniques. The removal of a single electron from a molecule can produce dramatic changes in its reactivity and sometimes induces instabilities large enough to dissociate the molecule itself. While the spectra of neutral molecules, even in electronically excited states, are now obtainable at resolutions better than  $0.0001\text{ cm}^{-1}$ ,<sup>1</sup> the high-resolution spectroscopy of ions has proven to be much more difficult. The fundamental difficulty comes from the uncertainty in the transition energies to ionic states compared to those within a neutral molecule. To clarify this difficulty, let us compare the transitions that take place within a neutral molecule (change of rotation, vibration, and/or electronic state) to those that produce an ion from a neutral species

Andrew Held was born in Erie, PA, on October 9, 1961. He received his B.Sc. in chemistry from the University of Pittsburgh in 1984 and then moved to Cleveland, OH, where he worked as a ceramist. Three years later, he returned to the University of Pittsburgh, where in 1993 he received his Ph.D. in physical chemistry under the supervision of Professor David W. Pratt; his thesis work concerned the rotationally resolved optical spectroscopy of hydrogen-bonded complexes. He spent the following year working as an invited research fellow of the Communauté française de Belgique in Brussels, Belgium. In 1995, he was awarded an Alexander von Humboldt Fellowship and moved to the Technical University in Munich, Germany, where he was introduced to the field of ZEKE spectroscopy working with Professor E. W. Schlag. He is presently working as a Chateaubriand Fellow at the University of Pairs-Sud in Orsay. His research interests include the chemical and physical properties of hydrogen-bonded neutral and ionic clusters, the physical properties and dynamics of high Rydberg states, and the development of ZEKE spectroscopy.

Edward W. Schlag was born in Los Angeles, CA, on January 12, 1932. He received his B.A. from Occidental College and his Ph.D. in 1958 at the University of Washington in Seattle. His thesis demonstrated the geometrical isomerization of cyclopropane to which he applied the new Marcus version of unimolecular theory. He developed early methods of state counting and master equation approaches for this theory. In 1960 he joined the chemistry department of Northwestern University in Evanston, IL, as an assistant professor. In 1969, he advanced to full professor and in 1971 he moved to the chair of physical chemistry at the Technische Universität München. He has been involved in unimolecular reactions of small rings and of very large molecules. He was involved in the earliest work on REMPI (in 1978) and in early direct timing measurements of radiationless processes in 1969, and since 1984 he has been involved in the development of the new ZEKE spectroscopy. Besides this he has worked in molecular sub-Doppler spectroscopy, laser ionization and mass spectrometry of clusters using RETOF techniques, and most recently charge migration in tailor-made polypeptides. He is a member of the Bayerische Akademie der Wissenschaften and serves on numerous editorial boards.

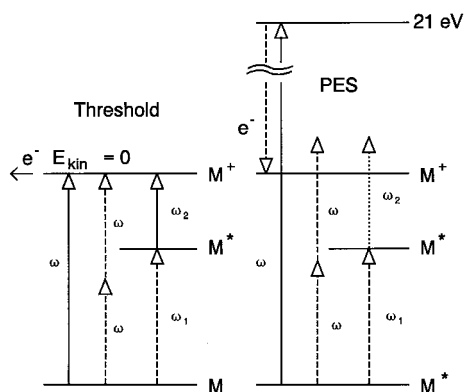
(ionization). We define a transition simply as a change in a system from one condition to another under the influence of a perturbation. Such transitions occur in neutral molecules when a discrete amount of energy, equal to the energy difference between two stationary states, is absorbed. In the case of a laser absorption experiment, light of an appropriate frequency can cause an upward transition between two energy levels subject to selection rules and Franck–Condon factors. This energy is very well defined or “quantized” by the energy levels. If an amount of energy is introduced that does not correspond to any transition energy of the molecule, a transition simply does not occur. This situation is significantly different for transitions leading to ionization. The energy states of an ion are also quantized; however, the ionization process allows the release of excess energy through the kinetic energy of the ejected electron. Energy absorbed that exceeds the energy gap between the two stationary levels can still result in a transition. The uncertainty arises from the fact that the observed transition energy can be equal to the energy gap *or* can be larger given by the sum of the gap energy plus the energy of the ejected electron. An electron or ion signal is therefore observed everywhere above the lowest ionization threshold (the ionization potential) and is cumulative for all transitions and generally without structure. Removing this background signal and seeing only the signal due to the eigenstates of the ions proved to be somewhat tricky.

In this Account, we describe some of the recent advances made in the spectroscopy of ions, focusing on the development of a new high-resolution technique called ZERo Kinetic Energy (ZEKE) spectroscopy.<sup>2</sup> The ZEKE technique has successfully overcome the pitfalls hindering previous photoelectron spectroscopies and produces spectra of ions with unprecedented resolution and with the same quality and ease of those produced in neutral spectroscopy. Although the field of ZEKE spectroscopy is less than 15 years old, ZEKE spectrometers can be found in laboratories around the world. The ZEKE high-resolution technique is being used to study cations, anions, and, indirectly through these species, neutrals of atoms, molecules, and clusters of chemical and biological interest. It has even yielded the first direct spectroscopic data on the elusive transition states of chemical reactions.<sup>3</sup>

## A Bit of Background

The first breakthrough in discerning the true energy levels of ions and thus indirectly the first measurements of the energy of molecular orbitals was made by Turner *et al.*,<sup>4</sup> Terenin *et al.*,<sup>5</sup> and Siegbahn *et al.*<sup>6</sup> in the 1960s using a technique known as photoelectron spectroscopy (PES). In PES, electrons are ejected from molecules by a high-energy photon (from a short-wavelength source). The kinetic energy of the emitted photoelectron is the energy of the incident photon,  $h\nu$ , less the ionization energy of

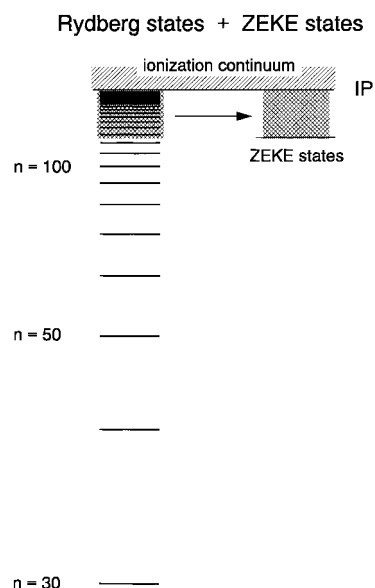
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**FIGURE 1.** Photoelectron measurements. Photoelectron spectroscopy is shown on the right-hand side, typically employing the sharp He I resonance lamp fixed at 21 eV, "back-titrating" the hot electrons from the various molecular states. Threshold experiments are shown on the left-hand side, excited with one photon excitation or resonance or nonresonance multiphoton ionization. Also shown for both cases are one-photon and multiphoton excitations.

the photoelectron, as illustrated in Figure 1. The latter is usually determined by the energy of the ionic state and by the one-electron orbital states of the neutral molecule (Koopman's rule) and thus the molecular orbital. Hence, by measuring the kinetic energies of the photoelectrons, the lowest-lying ionic eigenstates can be determined. Unfortunately, measuring the kinetic energy of light particles such as electrons interacting with metal spectrometers is difficult due to surface potentials, and thus the resolution in PES is limited. For many years, resolution much better than  $100\text{ cm}^{-1}$  proved to be very difficult to achieve, although resolution down to  $\sim 16\text{ cm}^{-1}$  has been reported in a few instances,<sup>7</sup> and very recently Lehrer et al.<sup>8</sup> have recorded PES spectra at  $3\text{ cm}^{-1}$  resolution.

In an effort to overcome the seemingly inherent limitations in spectral resolution of PES, threshold photoelectron spectroscopy (TPES) was developed.<sup>9</sup> Figure 1 illustrates how photon energies are selected such that only electrons emitted at the threshold of an ionic eigenstate are specified. In the case that the complete photon energy is absorbed in the transition, the ejected electron is left with zero kinetic energy. As the photon energy is increased beyond an ionization threshold, electrons with nonzero kinetic energy are produced. At photon energies greater than the transition energy, absorption still occurs during the transition into the eigenstate with the remaining energy imparted to the ejected electron as kinetic energy. Recall, this "heat bath" does not exist for neutral molecules. The resulting "hot" electrons can, however, be discriminated from the zero kinetic energy electrons simply through the fact that they are moving and the electrons with zero kinetic energy are not. The zero kinetic energy threshold electrons remain in the interaction region while the hotter electrons spread out. A small electric field can be applied to extract the zero kinetic energy electrons through a narrow pathway leading to a detector. The hotter electrons will follow a different trajectory and miss the detector entrance. The advancements that led to TPES were logical precursors to the development of ZEKE spectroscopy. Like TPES, ZEKE



**FIGURE 2.** Schematic representation of a Rydberg progression converging toward an ionization threshold and extending into the ionization continuum. The shaded area indicates the narrow band of very stable high- $n$  Rydberg states (ZEKE states). Such a Rydberg series exists beneath each rotational, vibrational, and electronic eigenstate of an ion.

spectroscopy detects zero kinetic energy electrons, but whereas TPES techniques produces ions/electrons from just above the ionic eigenstates, ZEKE spectroscopy relies on ions/electrons produced through ionization of high Rydberg states existing in a very narrow band just below the ionization limit of each ionic eigenstate. Use of the unique properties of these "special" weakly bound high- $n$  Rydberg states below the ionization limit rather than the unbound states above the limit led to an improvement in resolution of about 2 orders of magnitude.

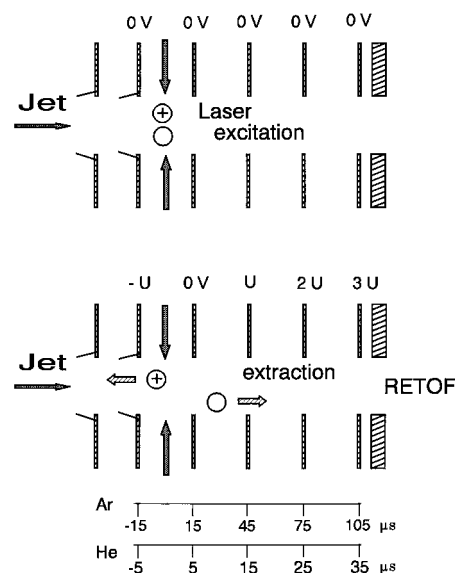
Central to the understanding of ZEKE spectroscopy is some basic notion concerning Rydberg states.<sup>10</sup> Rydberg states are formed through the excitation of an electron into an orbital that is best described by atomic orbitals belonging to shells well outside the valence shells of the atom(s). As illustrated in Figure 2, the bound electronic Rydberg levels become closer together as the energy is increased and eventually merge into an ionization continuum. The Rydberg states that converge on the lowest ionization threshold of an atom or molecule constitute its ionization potential, IP. In addition to this lowest-lying series, each electronic, vibrational, and rotational eigenstate of the molecular ion, i.e., those above the IP, has its own Rydberg series. The unexpected new effect discovered was that the high- $n$  Rydberg states ( $n > 100$ ) in each series were observed to have a surprising stability and can now be thought of as "islands of stability" lying in the ionization continuum. These high Rydberg states are so closely spaced that they are transformed to specially stabilized Rydberg states, which we here call ZEKE states. The two unique properties of these high- $n$  Rydberg ZEKE states that make the ZEKE technique possible are the following: first, the transformation produces an electron in this ZEKE state that is several thousand times further

from the ionic molecular core than those electrons remaining in valence states. The electron–ionic core interactions are therefore strongly reduced. The core finds itself in an *ionic eigenstate*, the electron now acting solely as a slowly orbiting spectator. This electron, once separated from the molecular core, is on the threshold of escaping the high- $n$  Rydberg orbit with zero energy remaining. The selection of these states from completely ionized states depends on the fact that, despite their respective distances, the ionic core and the orbiting electron remain together as a neutral species. Second, high- $n$  Rydberg states are very stable with respect to decay and thus live for a very long time. Separation of these long-lived states from the fast-decaying low- $n$  Rydberg states is simply accomplished using a delay period. The long lifetimes, first discovered by Reiser et al. in 1988,<sup>11</sup> were unanticipated since they deviate by nearly 2 orders of magnitude from what one would expect on the basis of the lifetimes of lower- $n$  Rydberg states by means of an  $n^3$  scaling law and thus constitute a new effect. The stability of these states turns out to be due to external perturbations that operate only on the high- $n$  Rydberg states, that is, those lying extremely close to the ionization threshold. Selection of this narrow band of states is what produces the high resolution in ZEKE spectroscopy.

## How ZEKE Spectroscopy Works

ZEKE spectroscopy differs from other photoelectron spectroscopic techniques in that it is a two (sometimes many) step technique. The successive steps are applied in order to isolate the narrow band of long-lived high- $n$  Rydberg neutrals from the background hot electrons/ions and the short-lived (autoionizing) low- $n$  Rydberg states. Here, we mention electrons and ions together since they are formed as a pair and hence the separation and detection of ZEKE electrons is essentially equivalent to the separation and detection of ions produced through the ejection of a ZEKE electron.<sup>12</sup> The latter technique, first developed by Johnson et al.,<sup>13</sup> has the added advantage of mass selectivity (Mass-Analyzed Threshold Ionization, MATI), but usually at lower resolution.

A schematic of the ion optics system of the spectrometer, used in the Munich experiments,<sup>14,15</sup> is shown in Figure 3. Although the apparatus is specifically designed to separate cations from the neutrals of relatively large molecular species, the principles illustrated in Figure 3 are the basis of all ZEKE experiments. The neutral molecular beam (here benzene seeded in He or Ar) enters the region between the first two ion optic plates, where either a static or delayed pulsed electric field is applied. This allows for laser excitation in the presence or absence of an electric field. In the case of benzene, excitation occurs through a two-color, two-photon process: the first laser excites the molecules into an electronic intermediate state and the second laser is used to scan through the Rydberg manifold. Ions can be produced directly, in the excitation region, by two-photon, one-color absorptions from the first laser, which has an energy greater than half

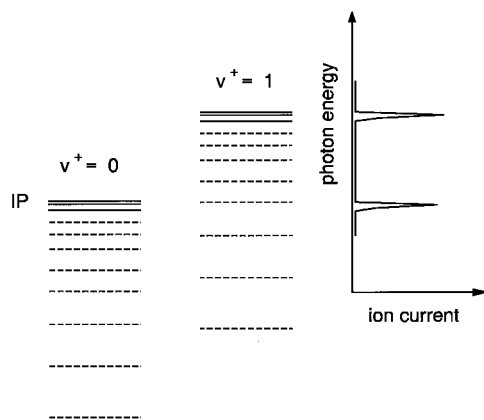


**FIGURE 3.** Schematic of the experimental arrangement: A supersonic molecular beam crosses the two counterpropagating lasers in the region between plates P1 and P2 (top). The excitation occurs either under field-free conditions (when both plates are at ground potential) or in the presence of a separating field of 0.2–3 V/cm (when P2 is at ground potential and P1 is at  $-U$ ). In the former case the separating field is applied 10 ns–1  $\mu$ s after laser excitation. The separating field, whether static or delayed, retards the direct ions with respect to the Rydberg (ZEKE neutrals) molecules (bottom). To ensure proper separation and signal, the field is applied through the ion optics up to the point of extraction. The molecules are ionized by a 200 V/cm field applied to the last two sets of plates. This pulsed delayed field accelerates the now ionized ZEKE molecules toward the detector. The very bottom part of the figure shows the jet flight time through the ion optics where He or Ar is used as a carrier gas.

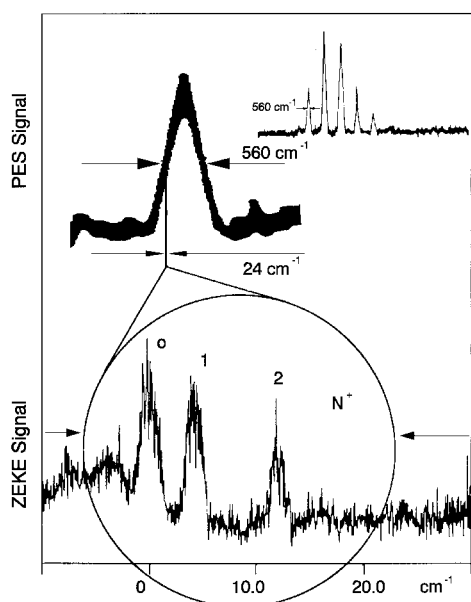
the ionization energy of benzene. Direct ions are also produced through autoionization processes, which will be discussed later.

The separation of the direct ions from the long-lived ZEKE Rydberg neutrals begins between the first two ion optic plates when the field is applied. The field retards the direct ions while the neutrals pass through holes, centered on each plate, at the speed of the carrier gas. The time scales, shown below the ion optic plates in Figure 3, illustrate the flight time from laser excitation to pulsed field extraction, approximately 24  $\mu$ s for He and 66  $\mu$ s for Ar. These times are fixed by a variable, fast-rising positive extraction pulse that is applied to the last two sets of extraction plates, producing an electric field of 200 V/cm. This field ionizes the neutrals, which are then extracted into a reflectron time-of-flight (RETOF) mass spectrometer. The observed ion signal arises solely from the field-ionized Rydberg states that are stable enough to survive the relatively long drift time through the ion optics, i.e., the modified high- $n$  Rydberg states (ZEKE states).

The Rydberg energy levels and the corresponding schematic spectrum, shown in Figure 4, illustrate how state selectivity is used in ZEKE spectroscopy. Scanning the laser from below the ionization threshold through a series of ionization limits and applying the delayed pulsed-



**FIGURE 4.** Schematic ZEKE spectrum. Only the highest long-lived ZEKE states below a specific threshold contribute to the ZEKE spectrum. States above the threshold (ionic) are removed by small applied fields and the short-lived low- $n$  states (dashed lines) decay before pulsed field ionization.



**FIGURE 5.** PES and ZEKE spectra. A comparison of the VUV–PES spectrum and the first rotationally resolved ZEKE spectrum of NO is shown.  $N^+$  denotes the total angular momentum quantum number.

field ionization scheme outlined above, a spectrum similar to the one shown in Figure 4 will be obtained. Whenever long-lived high- $n$  Rydberg states are populated, they will be field-ionized some 10  $\mu\text{s}$  after laser excitation and detected. Lower- $n$  states (dashed lines) decay during this delay time and ions produced above the IP are removed by the applied electric field. The first experiment in 1984 produced rotational resolution at the onset of ionization, and hence rotational structure of the  $\text{NO}^+$  ion at threshold could be observed for the first time.<sup>16</sup> Rotational states that are separated only by 4  $\text{cm}^{-1}$  (0.5 meV) were completely separated in the initial experiment. To demonstrate the dramatic improvement in resolution, a comparison of the first ZEKE spectrum with the PES spectrum of  $\text{NO}$ <sup>17</sup> is shown in Figure 5. Since the first ZEKE experiments, the technique has been further improved to produce resolution less than 0.2  $\text{cm}^{-1}$ <sup>18</sup> and

has been applied to resolve states as high as  $\sim 11$  eV above the ionization threshold of  $\text{N}_2$ .<sup>19</sup>

## Why High- $n$ Rydberg (ZEKE) States Live So Long

Until recently the very long lifetimes of high- $n$  Rydberg states were an enigma when compared to the conventional wisdom concerning the expected decay rate dependence extrapolated from low- $n$  to high- $n$  Rydberg states and the previously assumed rapid rate of autoionization. The most prevalent mechanisms for the decay of these states are autoionization and predissociation from internal conversion. Decay via these channels occurs as a second step, which follows the initial excitation of the molecule into a state above the IP and produces a de-excitation from this state to give a positive ion with lower energy and an ejected electron (autoionization) or two lower energy fragments (predissociation). Interactions that cause Rydberg states to decay through autoionization and/or predissociation can only take place near the ionic core; since the probability of finding a Rydberg electron near the core scales as  $1/n^3$ , interactions that lead to autoionization or predissociation also will scale as  $n^{-3}$  and a scaling law of  $n^3$  for the lifetimes is expected. The high- $n$  Rydberg states detected in ZEKE experiments have a new scaling law with much longer lifetimes that scale as  $\sim n^5$ ! The orbital describing the long-lived high- $n$  Rydberg state must therefore be significantly modified in order to avoid electron–core interactions. The answer lies in the fact that the previously disregarded  $l$  and  $m_l$  quantum numbers are, *in addition to*  $n$ , important determinants in the stabilization of these states.

In ZEKE spectroscopy, an electric (or magnetic) field is requisite for the ion–neutral separation process; however, in addition to its practical applications, the field is now realized to have a more subtle and profound consequence. In 1993 Chupka outlined a proposal suggesting that the long lifetimes of ZEKE states have their origins at least in part as a result of Stark mixing of different orbital angular momentum states ( $l$  states) induced by electric fields.<sup>20</sup> Electric fields induce Stark splittings in the  $n$ -Rydberg manifold, which for a given  $n$  leads to new, nondegenerate Stark eigenstates. The presence of a DC field breaks the spherical symmetry of the Coulombic potential, thus distorting the electron's orbit, which means  $l$  is no longer a good quantum number. The eigenstates in the presence of an electric field are Stark states, characterized by quantum numbers  $n$ ,  $k$  (defined by parabolic quantum numbers  $n_1$  and  $n_2$ , which can take on values from 0 to  $n - 1$ ) and  $m$ .<sup>10</sup> When these Stark states are described in terms of field-free eigenstates characterized by  $n$ ,  $l$ , and  $m$ , one finds that a large range of  $l$  values contributes to a given single Stark state. The decay rates of Rydberg states are strongly dependent on the interactions between the Rydberg electron and the ionic core; thus electrons in orbitals that avoid interactions with the ionic core, that is, orbitals with high  $l$  character, have slower decay rates compared to those that can



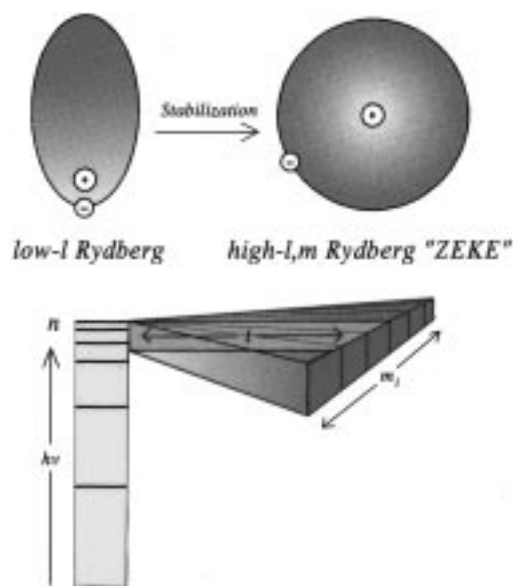
penetrate into the ionic core, i.e., orbitals with low  $l$  character. The centrifugal barrier prevents an electron of given angular momentum  $l$  from approaching the core closer than a distance of  $r \sim l(l+1)/2$ . This modification of the Rydberg orbital provides a vanishing probability of finding the ZEKE electron near the core and is the commonly accepted element of most models explaining the stability of these states.

When the above-mentioned angular momentum state coupling occurs ( $l$  mixing), in the presence of a small electric field, the field-free low- $l$  lifetimes are greatly enhanced by mixing with the longer living high- $l$  states. However, whatever the precise origin of all couplings between low- $l$  and high- $l$  states is, we must remember that these processes are subject to microscopic reversibility (i.e., low- $l$  states  $\leftrightarrow$  high- $l$  states). Hence, any mechanism that enables the production of high- $l$  states from low- $l$  states also favors the production of low- $l$  states from high- $l$  states. Further dilution of the low- $l$  content of the eigenstates can be realized when the Rydberg neutrals experience the inhomogeneous electric field of nearby ions; here, in addition to the spherical symmetry, also the cylindrical symmetry of the homogeneous electric field is broken. Under these conditions the magnetic quantum number  $m$  is no longer conserved. Mixing between optically accessible low- $m$  states and “dark” higher- $m$  Stark states, which have zero low- $l$  content, greatly enhances dilution of the decay rates.

Figure 6 illustrates pictorially how the electric field lifts the degeneracy of orbitals within a given  $n$  Rydberg state and changes its geometry. The electric field breaks the  $n$ -fold  $l$  degeneracy of each  $n$ -Rydberg level and the presence of ions breaks the  $(n - |k|)$ -fold  $m$  degeneracy of each  $l$  state. The result is a phase space that favors the population of states which have a high degree of high- $l$  character. The above-described model has recently been experimentally verified by several groups.<sup>18,21–29</sup> It has been clearly shown that the transformation of the optically accessible low- $l$  Rydberg states into high- $l$  Rydberg states (ZEKE states) depends in a competitive manner on the field strength and the ion concentration present during excitation. By controlling these parameters it is possible to control the shape of the Rydberg orbitals (see top of Figure 6) and thus the interaction of the electron with the ionic core. Very recently, a new technique was discovered that uses externally applied pulsed fields to control the lifetime and stability of high- and low- $n$  Rydberg states in ZEKE experiments.<sup>30</sup> The newly found ability to control the production, lifetime, and stability of Rydberg-ZEKE states is progressing rapidly and will ultimately lead to obtaining optimal ZEKE spectra.

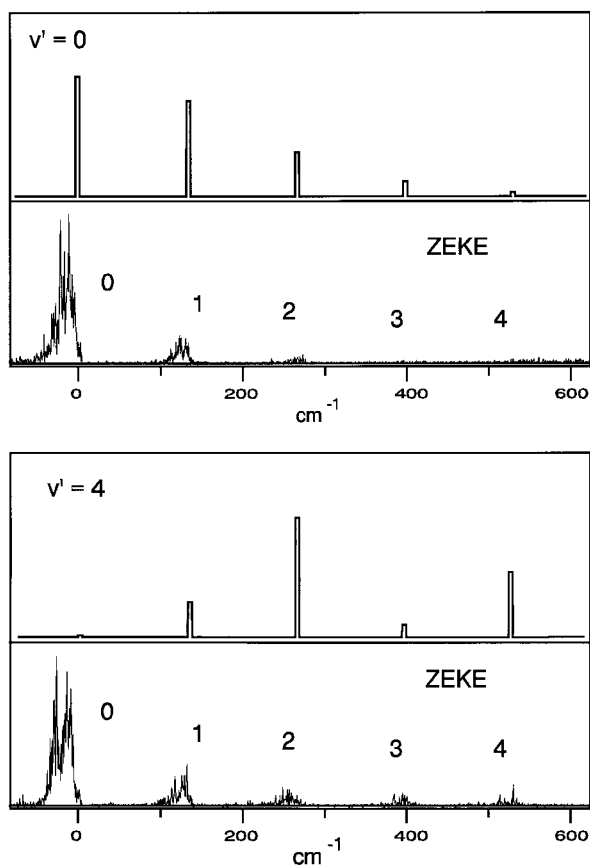
## Breakdown in the Born–Oppenheimer Approximation

It is well-known from early atomic physics studies that Rydberg states from different series can interact with each other.<sup>31,32</sup> The dynamics of very high molecular Rydberg states also exhibits these couplings<sup>33–36</sup> and have been



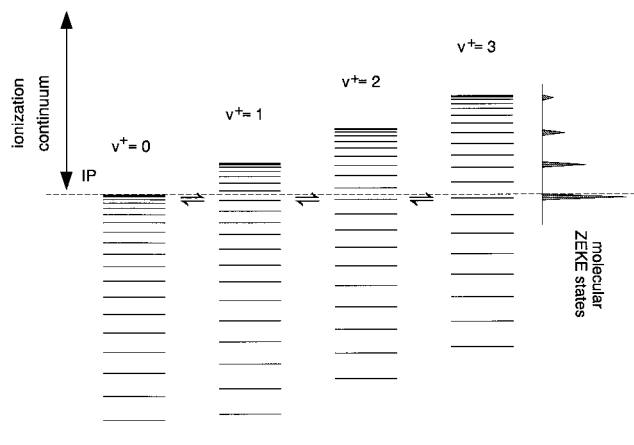
**FIGURE 6.** The Rydberg series on the left-hand side (in yellow) is that under field-free conditions where excitation takes place into low- $l$ , low- $m$  states. The horizontal orange bar, extending from the upper- $n$  Rydberg states, represents a single, field-induced,  $l$ -mixed, Stark state. The loss of  $m$  degeneracy within this  $l$ -mixed state is produced by inhomogeneous effects on the field often produced by nearby ions and is represented here by a series of red blocks. The phase space for higher  $l$  states is favored by the break in  $m$  degeneracy since the number of  $m$  states increases with increasing  $l$ . The orbitals, illustrated in the upper portion of the figure, correspond to the optically excited low- $l$  states (left) and the transformed “high- $l$  character” ZEKE states (right).

successfully modeled using multichannel quantum defect methods involving breakdowns in the Born–Oppenheimer approximation (Hund’s case D).<sup>36–40</sup> In ion spectroscopy these lateral interactions often result in unexpected transition intensities where lines are observed that are apparently Franck–Condon forbidden. The population of Franck–Condon forbidden states is also observed in ZEKE spectroscopy, as it was in TPES, where the resulting intensity anomalies can be used to great benefit at high resolution, leading to a greatly enriched spectrum. In fact, one can explain this apparent anomaly by recognizing that each vibrationally populated ground state can be excited into its own Rydberg ladder. The finally excited states of all these Rydberg ladders couple together to produce spectra that appear to violate the Franck–Condon principle. This channel coupling is a very important tool in ZEKE spectroscopy. A dramatic example illustrating such a breakdown is found in the ZEKE spectrum of  $\text{Ag}_2^+$ .<sup>34</sup> The vibrationally resolved spectra of the ionic ground-state  $X^2\Sigma_g^+$  of  $\text{Ag}_2^+$  were recorded using multiphoton excitation through different intermediate  $B^1\pi_u$  states. The spectra shown in Figure 7 correspond to mass-analyzed ZEKE spectra of  $^{107,109}\text{Ag}_2^+$ , excited via  $v' = 0$  and  $v' = 4$ , of the intermediate  $B^1\pi_u$  state. The numbering of the ZEKE peaks corresponds to the vibrational quanta in the ionic ground state. Irrespective of the selected vibration  $v'$  in the intermediate state, all vibrational progressions were found to have an intense  $v^+ = 0$  band followed by progressively decreasing intensities for higher vibrational



**FIGURE 7.** Vibrationally resolved mass-analyzed ZEKE spectra for  $^{107,109}\text{Ag}_2^+$  using resonant two-color excitation scheme (lower trace) together with the spectral intensities calculated with standard Franck–Condon factors. The top spectrum was recorded with the pump laser fixed on  $v' = 0$  of the  $B^1\Pi_u$  intermediate state, whereas the lower spectrum was recorded via  $v' = 4$ . The spectra illustrate how deviations from the standard Franck–Condon principle can occur in ZEKE spectroscopy.

states  $v^+$  of the ion. The intensity pattern of the spectrum, excited via  $v' = 4$ , is apparently in strong disagreement with that calculated with standard Franck–Condon factors.<sup>35</sup> The vibrationally excited ground-state geometry is expected to have stronger overlap with the vibrationally excited ion state; hence higher vibrational states of the ion should be more intense. An explanation for these anomalous intensities is realized when one examines the many isoenergetic Rydberg levels found in different Rydberg manifolds (see Figure 8). The initial optical excitation proceeds within the Franck–Condon scheme; thereafter, the slowly orbiting electron allows mixing between isoenergetic Rydberg vibronic states. Intensity is gained at transition energies into the  $v^+ = 0$  state through isoenergetic population transfer from low- $n$ , short-lived Rydberg states of higher vibrational states (e.g., the  $v^+ = 4$  state in Figure 8) to high- $n$ , long-lived Rydberg states of lower vibrational states (e.g., the  $v^+ = 0$  state in Figure 8). This “channel coupling” can occur through several horizontal steps. In the absence of channel coupling, the optically excited low- $n$  state would quickly decay and not be detected by the delayed pulsed-field ionization. An important implication of this spectroscopic breakdown of



**FIGURE 8.** Series of Rydberg manifolds built on several different rotational levels illustrates how couplings between these levels (channel coupling) can produce the anomalous intensity patterns seen in Figure 7.

the Born–Oppenheimer approximation is that the ZEKE technique can now be used to examine highly resolved Franck–Condon forbidden states that are not accessible in conventional photoelectron spectroscopy.

## Conclusion

ZEKE spectroscopy is a spectroscopy based on a newly observed molecular effect of long-lived states below any ionic eigenstate that provides information about ionic systems at unprecedented resolution. The rotational structure of molecular ions and low-frequency vibrations of molecular cluster ions can thus now be obtained in a routine manner. ZEKE spectroscopy has also provided a means for studying the physics of high- $n$  Rydberg states, the knowledge of which is being used to further improve the technique itself. The properties of the states probed by ZEKE spectroscopy are unique to the eigenstates of the system and thus provide unique spectroscopic conditions. The extreme stability of ZEKE states and the breakdown in Franck–Condon restrictions are new observations for which two examples are presented here and which give this spectroscopy a unique direction in spectroscopic techniques. ZEKE spectroscopy is finding new directions in applications to synchrotron radiation,<sup>41</sup> radical chemistry and other chemical intermediate states, and even transition states of chemical reactions!<sup>3</sup> Studies of ZEKE states promise to open new areas of chemical physics as well as further understanding of the spectra and structure of ions, both positive and negative—and even neutrals produced from anions and under mass selection in mixtures. It is a rich new form of spectroscopy.

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