# A Unified Mechanism for the Production of ZEKE States

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ZEKE states are highly stabilized Rydberg states which exist below each ionic eigenstate of a molecular system even high up into the continuum. The stability and neutrality of these states is the basis on which the high resolution ZEKE technique for the study of molecular ions is built upon. A new mechanism is proposed for the production of ZEKE states from optically accessible, relatively short lived Rydberg states. The mechanism is based on experimental results for a range of fields and ion concentrations. The experiments were performed with pulsed and static electric fields of different magnitudes at various ion concentrations.

## 1. Introduction

The role of electric fields and ions in the production of long-lived molecular Rydberg states has received much interest in recent years [1 - 30]. The stability and neutrality of these high Rydberg states form the basis on which ZEKE (zero-kinetic energy) spectroscopy is built upon. The number of related experimental observations, however, is relatively small and forms a somewhat fragmented picture with occasional disagreements between different works. The present communication reports on a systematic study of the dependence of benzene ZEKE spectra on varied electric fields and ion densities. The results of these studies and several previously reported observations lead to a unified model for the production of ZEKE states.

## 2. Experimental Setup

The experimental arrangement of the ZEKE spectrometer has been previously reported [5] and involves the inverted long beam configuration [31]. The primary practical benefit of this new configuration is the complete absence of any special electric shielding albeit maintaining complete resolution capability. Here only details pertinent to the present series of experiments are described. In the experiment, benzene at –8 °C seeded in He at 4.5 bar is expanded through a pulsed nozzle with a 200 μm orifice into the vacuum (Figure 1). The supersonic jet is skimmed 5 cm downstream and then again by a second skimmer directly in front of plate P1. The molecules, passing through the skimmers, interact with two counterpropagating pulsed laser beams. The first beam has an intensity between 1 - 10 μJ/pulse, depending on attenuation, and is tuned to excite the resonant $S_1\ 6^1$ intermediate state.

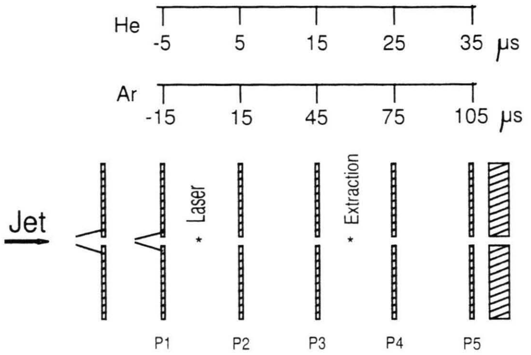

Fig. 1. Schematic of the experimental arrangement: A supersonic molecular beam crosses the two counterpropagating laser beams in the region between plates P1 and P2. The excitation occurs either in a field free space (when both plates P1 and P2 are at the ground potential) or in the presence of a, so called, spoiling field of 0.2 to 3 V/cm (when P2 is at the ground potential and P1 is at –U). In the former case the spoiling field is applied 10 ns to 1μs after laser excitation. The spoiling field, whether static or delayed, serves to separate direct ions from Rydberg (ZEKE neutrals) molecules. To insure a 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 by means of plates P3 and P4. This pulsed delayed field accelerates the now ionized ZEKE molecules towards the detector. The upper part of the figure shows the jet flight time through the ion optics, where He or Ar are used as a carrier gases.

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The resolution of the first laser is 0.1 $cm^{-1}$, which is sufficient to resolve the $J = 1$, $K = 1$ rovibronic level of benzene [32], and the frequency of this laser is monitored using a high resolution wave meter. The transitions from the $S_1$ $6^1$ intermediate state through the Rydberg manifold, accessed by scanning the second laser, having an intensity of 50 - 80 µJ/pulse, always originates from the same $J = 1$ $K = 1$, single rotational level, at the fixed frequency of 38606.5 $cm^{-1}$. The excited molecules drift through the ion optic plates where they are exposed to a number of different weak field and field free conditions. These applied weak fields decelerate the direct ions and thus separate them from the neutrals which pass unhindered through the ion optics. The neutrals drift through the plates at the speed of the jet, which depends on the carrier gas used. The time scale, shown above the optic plates of Fig. 1 illustrates the flight time from laser excitation to pulsed field extraction, approximately 24 µs for He and 66 µs for Ar. These times are fixed by a variable, fast rising positive extraction pulse which is applied to P3 producing an electric field of 200 V/cm. This field ionizes the neutrals which are then extracted into the reflectron time of flight (RETOF) mass spectrometer. The observed ion signal arises solely from field ionized Rydberg states.

The spoiling field used to discriminate the direct ions from the ZEKE neutrals is produced by applying a small negative voltage to plate P1 and holding plate P2 at ground potential. The field is pulsed with respect to the laser pulse using an EH pulse generator. Excitation in the presence of the electric field is accomplished by applying a very long field pulse before the laser pulse. Field free photoexcitation is accomplished by delaying this pulse until after the laser pulse. The minimum delay between the pulsed field and the laser pulse is 10 ns. The rise time of the spoiling field is 10 ns. In all experiments a constant field is applied till the point of extraction. It was recently discovered that in the presence of a constant electric field the ZEKE state decay rate is significantly reduced [26]. The application of the constant field, therefore, greatly enhances the signal collected tens of microseconds after photoexcitation. This constant field, applied over a long time (a long beam) also allows to separate large ions, produced through direct ionization, from ZEKE neutrals, using very small spoiling fields.

It should be noted that no special attempts were made to shield the instrument from stray fields. The stray fields present in the experiments were directly measured to be 40 mV/cm or less. The stray field was determined by recording both the direct ion signal and the neutral ZEKE signal with and without an applied spoiling field. In the absence of an applied spoiling field, the flight-time separation of the direct ions, produced at the point of laser excitation, with respect to ions produced from ZEKE neutrals, at the extraction point, is a measure of the strength (retarding force) of the stray field. An applied field, of opposite polarity to the stray field, is applied until the signal from the direct ions and that from the ZEKE neutrals overlaps in time. This additional field is now a direct experimental measure of the stray field.

## 3. Results and Discussion

It is well know that the ionization threshold is lowered by applied fields and that this lowering, for diabatic ionization, goes as $E = 4\sqrt{F}$, where $F$ is in volts/cm and $E$ is in $cm^{-1}$. Energy shifts of the high frequency edge of the PFI spectra presented here fit well to this relation, however the low frequency portion, where fields large enough to ionize all Rydberg states are applied, does not fit this simple relation. The width from the red edge is typically too narrow. Hence, the ZEKE states capable of surviving the delay period from photoionization to pulsed field ionization are not produced from all Rydberg states. The production of ZEKE states from Rydberg states is shown here to be strongly dependent on electric fields and ion concentrations.

It should be noted that many of the spectra resulting from the many sets of experiments reported here are not illustrated in figures but are rather simply described in words in order to concisely relate our overall experimental findings. An extensive and detailed description of all experimental spectra is presented in [33].

### *3.1. ZEKE Signal Dependence on Electric Fields*

In this first set of experiments we examine the dependence of the ZEKE signal on initial conditions. Namely, the dependence of the signal on whether laser excitation takes place in the presence of a spoiling field or under field free conditions where the spoiling field is applied shortly after laser excitation (ca. 100 ns). Figure 2 shows the pulsed field ionization (PFI) spectrum of benzene, pumped via the $S_1$ $6^1$

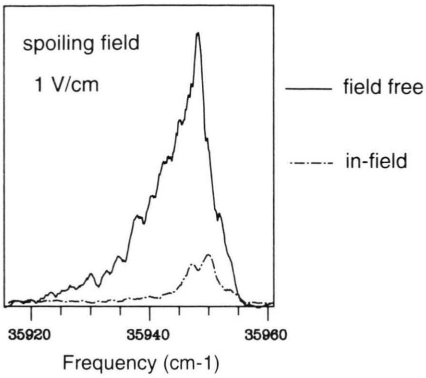

Fig. 2. Effect of static and delayed dc electric fields on the pulsed field ionization spectra near the $0^{0+}$ transition of benzene via the $S_1$ $6^1$ $J = 1$ $K = 1$ intermediate state. The dashed spectrum was recorded where a dc field of 1 V/cm was present during laser excitation. The solid spectrum was recorded where the same 1 V/cm field was applied 100 ns after laser excitation.

$J = 1$ $K = 1$ intermediate state level, where laser excitation occurs under in-field conditions and under field free/delayed field conditions. The spoiling field in both cases is 1 V/cm. A significant loss in signal is observed when laser excitation occurs in-field compared to that when the field is delayed by 100 ns. The 1 V/cm applied field cannot produce such a large signal loss due to field ionization alone. Additional measurements, made at various field strengths, show that signal losses, where photoexcitation occurs in-field, increase dramatically with increasing applied fields compared to those where photoexcitation occurs under field free conditions.

The shape of the spectra, in general, is asymmetric, having a sharp rising blue (high frequency) edge and a long trailing red (low frequency) edge. High resolution studies of the benzene PFI spectra, pumped via the $S_1$ $6^1$ $J = 4$ $K = 4$ intermediate state, demonstrate empirically that the blue portion of the ZEKE spectrum corresponds to transitions from selected intermediate state levels to high-n Rydberg states built on the appropriate rotational level of the $0^{0+}$ ion state [33]. The red edge of the spectrum corresponds to the lower-n Rydberg states converging on these $0^{0+}$ rotational levels. The overall ZEKE spectral contour is produced through the ionization of all surviving ZEKE Rydberg states below each ionic rotational level. Hence, the energy overlap of the Rydberg level series below different rotational levels of the cation precludes rotational resolution. No sharp spectral structure, arising from these Rydberg levels, is expected to be resolved in these experiments due to the limiting resolution of the excitation lasers and due to the spectral congestion of the rotational levels of the ion. Figure 3 shows the same field free (top) and in-field (bottom) spectra as shown in Fig. 2, but here their intensities have been scaled. Simulated spectra, calculated for transitions from the $J = 1$ $K = 1$ intermediate state to the allowed ionic rotational states are superimposed on the blue edges of both spectra. The relative positions of the rotational states are calculated from rotational constants given in the paper of Lindner et al. [32]. The contour simulation was performed by convoluting the rotational transitions using

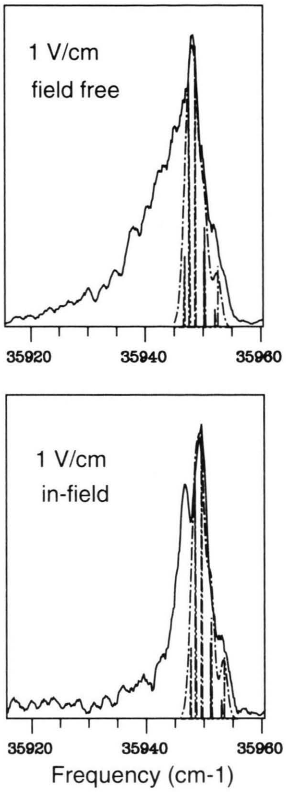

Fig. 3. Effect of electric field on the widths of PFI spectra. The upper figure shows the PFI spectra near the $0^{0+}$ transition of benzene via the $S_1$ $6^1$ $J = 1$ $K = 1$ intermediate state where the 1 V/cm spoiling field is applied 100 ns after photoexcitation. The lower figure shows the benzene PFI spectrum recorded under the same conditions except that the spoiling field was present during excitation. The intensities of the spectra in both figures are normalized. The simulated spectra (dashed) show the relative positions of the rotational states calculated from rotational constants determined by Lindner et al. [32].

a Gaussian lineshape of 1.5 $\mathrm{cm}^{-1}$ fwhm. The overlay of the simulated rotational ionic transitions onto the experimental spectra (obtained under field free and in-field excitation conditions) clearly illustrates that, in addition to the overall loss in signal, when excitation occurs in-field, there is also a relatively stronger erosion of the red edge of the spectrum (compared to that where excitation takes place under field free/delayed field conditions).

The red edge in our ZEKE spectra arises from lower-n Rydberg levels converging to several different rotational levels. The presence of an electric field does not change the total crossection of the optical absorption into Rydberg states. *Therefore, excitation in the presence of an electric field provides a parallel process for the disappearance of the optical Rydberg states rather than their conversion into ZEKE states which then live long enough to be ionized by a delayed pulsed field and detected. In particular, an intentionally applied electric field may reduce the longer lifetimes in the distribution of lifetimes describing the optically accessible Stark Rydberg states. Firstly, at higher fields, more short-lived lowest-l states merge into the Stark manifold, as was seen by Vrakking in NO [22, 23] and by Neuhauser and Neusser in benzene [34] (see also theoretical works by Bixon Jortner, NO, Ar [35], and Vrakking NO [23]). Secondly, field-assisted rotational channel coupling [36 - 38] may increase the predissociation/internal conversion rates of the optical Rydberg states via multi-step couplings to increasingly lower-n states built on higher rotational levels of cations.*

*The stronger red-side degradation of in-field signals is not surprising considering that corresponding lower-n states are already at the very boundary of the "magic" region of stability; hence they are particularly sensitive to even small additional field-induced destabilization.*

As indicated above, the losses in signal where excitation occurs in-field increases with increasing field strength relative to the signal losses where excitation occurs under field free/delayed field conditions. The relatively small signal losses, observed in the field free excited spectra, occur only at the blue edge of the spectral contour. This is a field induced ionization effect, where the field ionizes states $4\sqrt{F}$ below the field free ionization threshold. The red edges of the spectra are not eroded when the delayed field strengths are increased. *Thus, ZEKE state formation is not hindered by increasing field strengths when the field is delayed with respect to laser excitation. The delay times of the applied fields were varied from 10 ns to 1 μs with no change in the shape or intensity of the spectra.*

Whereas large signal differences between in-field and field free excited spectra were observed with increasing field strengths, no signal differences, in contour or intensity, were observed when fields below 200 mV/cm were applied. Thus, *at field strengths lower than 200 mV/cm, under our experimental conditions (ion concentrations, stray fields, etc.), ZEKE state formation is not hindered by the presence of the field during excitation or for that matter by the presence of the field later on.* The ZEKE signal intensity, in this low field regime is not affected by a field, whether delayed or not.

### *3.2. ZEKE Signal Dependence on Ion Concentration*

The experiments presented thus far were carried out under conditions where the ion concentrations in the laser excitation region were kept very low. This is accomplished by reducing the intensity of the intermediate state laser beam which can produce benzene ions through direct one-color two photon ionization. The experiments carried out with a 1 V/cm spoiling field, applied during and after laser excitation, at low ion densities were repeated at higher ion density. The ion density was increased by increasing the intensity of the intermediate state laser beam. Spectra obtained at high ion densities under in-field and field free excitation conditions are shown in Figure 4. Comparing the spectra recorded at higher ion density with those at low ion density (see Figs. 2 and 3), we see that for in-field experiments, the losses, due to field enhanced decay can be restored by increasing the ion concentration. When the in-field spectrum is normalized (see bottom of Fig. 4) to the intensity of the delayed field spectrum we see that the spectral widths are nearly identical. *These results indicate that, at least for the typical conditions employed here, the addition of ions at the point of laser excitation, where laser excitation occurs in the presence of a field, enhances the formation of ZEKE states.* This result is less clear for field free/delayed field experiments since there the field does not dramatically affect the ZEKE intensity. Also, as the intermediate state laser intensity is increased, both the in-field and delayed field signals increase due to the increased population of the $S_1$ intermediate state of benzene.

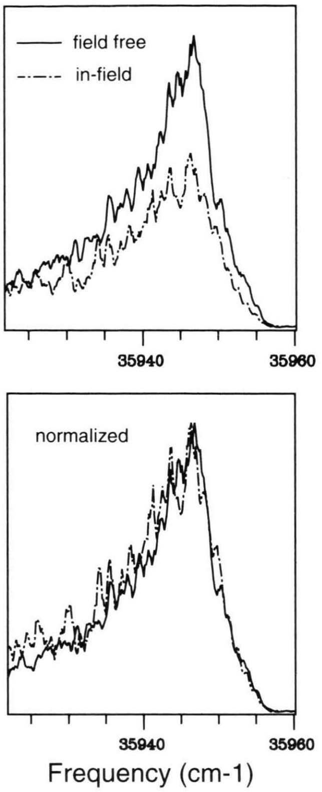

Fig. 4. Effect of high ion concentration on the pulsed field ionization spectra near the $0^{0+}$ transition of benzene via the $S_1$ $6^1$ $J = 1$ $K = 1$ intermediate state. The dashed spectra were recorded where a dc field of 1 V/cm was present during laser excitation. The solid spectra were recorded where the same 1 V/cm field was applied 100 ns after laser excitation. The spectra shown in the lower figur are the same as those in the uper figure but here their intensities are normalized.

In an attempt to decouple increases in signal due to ion induced enhancement of the ZEKE formation process from increases in signal simply due to an increase in the population in the $S_1$ intermediate state, a third laser was used to independently produce additional ions. The third laser comes from doubling part of the second harmonic of the YAG laser. The fixed frequency of the third laser at 37,594 cm$^{-1}$ ($\lambda =$ 266 nm) ionizes states from the intermediate $S_1$ level populated by the first laser. This laser is not resonant with any ionic eigenstate of benzene and thus produces additional ions but no additional ZEKE states. Both the intermediate state laser and the scanning laser intensities were kept low and hence the ion concentration, without the third laser, was very low. The spectrum with the third laser is more intense and has a more extensive red edge than that recorded without the third laser, that is, without additional ions produced by the third laser. This shows that even under field free conditions, where only our experimental stray field (40 mV/cm) is present, ions enhance ZEKE state formation.

### *3.3. Reciprocal Effect of Field Strength and Ion Concentration*

The experiments described above demonstrate that the presence of an electric field (> 200 mV/cm) during laser excitation hinders the production of ZEKE states and that the addition of ions enhances the formation of ZEKE states. To investigate whether there is a true reciprocal effect between field strength and ion concentration on ZEKE state formation a series of measurements were made at higher ion concentration with increasing field strengths. The ion concentration was augmented by increasing the intermediate state laser power until the in-field spectrum, where 1 V/cm spoiling field is applied, had the same intensity and width as that where the field is delayed. The spoiling field was then increased to 2 V/cm and then to 3 V/cm. The resulting spectra show similar losses in signal strength and spectral width (losses from red edge) with increasing field strengths, as those where the ion concentrations were kept low. This demonstrates that the attrition due to external fields can be compensated for by added ions and vice versa. This effect, however, has its limits, as seen below.

### *3.4. Saturation Limit of the Ion Enhanced ZEKE State Formation Process*

We have shown in Sec. 3.1 that fields below 200 mV/cm do not affect ZEKE intensities. Hence here we have no attrition of signal due to fields. In addition we have clearly shown that ions enhance the ZEKE signal intensity. Clearly this latter effect is limited since the ZEKE signal cannot exceed the number of optically absorbing high-n Rydberg states, which are the precursors to these Rydberg states. In fact we can say that under these conditions the production of ZEKE states is "saturated". Above this saturation limit, the introduction of additional ions will not further enhance the ZEKE signal and may even reduce it through an ion induced lowering of the ionization threshold.

We can now take this signal as a normalization for all other experiments, at increased ion concentrations or decreased fields. We now introduce this concept of relative signals to define a quasi quantum yield for ZEKE formation $\Phi(z)$. This then becomes the fraction of originally available states that have survived to finally become ZEKE states. When this value of $\Phi(z)$ is plotted against low ion concentrations we have a near linear relation that extrapolates to zero, within our experimental uncertainty. This suggests that ions are required under our experimental conditions to produce ZEKE states. Nevertheless, this process is seen to saturate for the small fields and at the typical ion concentrations found in most ZEKE experiments.

Saturation of the ion induced ZEKE formation process provides an explanation as to why the experiments of Alt et al. [4] and Bahatt et al. [12] show no dependence between ZEKE signal and ion density, whereas we and others [24, 25, 29] report a very strong dependence. A reasonable explanation as to where from the differences arise is important since these experiments (Alt et al. [4] and Bahatt et al. [12]) create an apparent gap in series of experimental results which would otherwise point to universal effects of external conditions on ZEKE states, regardless of the nature of the ionic core (e. g. molecular or atomic).

In the experiments conducted by Alt et al. [4], three lasers were used to excite a mixture of benzene-$h_6$ and benzene-$d_6$. The first laser L1, at fixed frequency, excites benzene-$h_6$ to the $S_1$ $6^1$ vibronic intermediate state, whereas the second laser L2, also at a fixed frequency but different from that of L1, excites benzene-$d_6$ to its $S_1$ $6^1$ intermediate state. The third laser is then scanned in the ionization region. The intermediate state of benzene- $h_6$ is lower than that of benzene-$d_6$ and therefore, when L3 is scanned through the upper Rydberg states of benzene-$h_6$ it is already producing direct benzene-$d_6$ ions above the ionization threshold. The laser excitation of benzene-$h_6$ and benzene-$d_6$ occurred under field free conditions, and after 50 ns a spoiling field of 1V/cm was applied. This three laser/two species experiment was designed to study the effect of the presence of independently injected ions on ZEKE state formation. The results and conclusions reached in these experiments were that the injection of additional ions had no effect on the ZEKE signal and thus no effect on ZEKE state production. In the light of the new experimental results presented here, the experiments of Alt et al. [4] were most probably performed under the more typical conditions where the ion densities were already in the saturation limit described here. Recall that this saturation limit is defined by the field present at excitation. The "reciprocal effect" experiments showed that this *saturation limit scales with the electric field strength when excitation occurs in the presence of the field.* Therefore, the ion density needed to saturate the enhanced ZEKE state formation process under field free excitation, where only the stray field is present, is very small. Under normal ZEKE experimental conditions, where excitation occurs under field free conditions in order to avoid large signal losses, the ion densities produced through direct 1+1 ionization from the intermediate state laser or through multiphoton direct ionization from the intermediate state and scanning lasers are most likely always near or above the saturation limit. Further evidence that the Alt et al. [4] experiments were conducted above the critical ion density limit come from the widths of the spectra, which are comparable to the widths of the experimental spectra reported here, where ion enhanced ZEKE state formation is observed. The saturation limit may differ between atomic and molecular species.

In an attempt to reproduce the results of Alt et al. [4] we return to the experiments described in Sect. 3.3 where a third laser is used to introduce additional ions into the excitation region. Recall that in this experiment the intermediate state laser and the scanning laser where kept at low intensity in order to reduce the production of direct ions. The ions produced in the excitation region, by the third laser, *under nearly field free condition where the field is delayed by 100 ns*, enhanced and broadened the red edge of the ZEKE signal compared to the same ZEKE signal where the third laser was not present. This suggests that, when the third laser is not present, the ion density at excitation is too low to enhance the formation of ZEKE states, in other words the ion density is below what is needed, at this specific field strength (here the field strength is that of the stray field), to saturate the enhanced ZEKE states formation process. The experiment was repeated where the intermediate state laser and the scanning laser intensities were increased. The intermediate state laser produces direct ions which have been shown to enhance ZEKE state formation. Spectra were recorded with the above mentioned higher laser intensities, with and without the third laser. The resulting spectra are nearly identical with respect to intensity and width, suggesting that the ion density is already sufficient to saturate the enhanced ZEKE state formation process and that the introduction of additional ions has no effect.

## 4. Theoretical considerations concerning the effect of ions

The conclusions of this paper as well as independent experiments [23 - 25] leave no doubt that, *as a matter of principle*, ions *will* enhance the yield of long-lived Rydberg states and that quite often they do so under the conditions typical of ZEKE experiments. The next task is to understand this interplay between the properties of a Rydberg system and the density of ions and, eventually, to establish general conditions under which ion-induced perturbations become an important factor controlling Rydberg kinetics. The literature appears to give no guide-lines to date, concerning the ion effect dependence on the density of ions and the principle quantum number $n$ of the Rydberg electron, or the conditions of the onset of the ion-induced $m$-mixing. In this section, we present the elementary physics of the ion-induced $m$-mixing and show that even the simplest scaling considerations can lead to very important general conclusions.

As far as fast time scales are concerned (shorter then some 100 ns) the ions can be taken to be at rest so that the inhomogeneity of their field is the only cause of $m$-mixing. Assuming a random uniform distribution of molecules, the number of Rydberg molecules $N(R)$ which have a nearest-neighbor ion at a distance *shorter* than $R$ is $N(R)/N = [1 - (1 - 4\pi R^3/3V)^{N_I}] \approx [1 - \exp(-4\pi R^3 \rho/3)]$, where $N$ is the total number of Rydberg molecules, $N_I$ the number of ions, $V$ the excitation volume, and $\rho = N_I/V$ the density of ions. Hence, 50% of the Rydberg molecules have a nearest-neighbor ion at a distance shorter than $0.55\rho^{-1/3}$. There is a finite probability to find a Rydberg molecule in closer proximity to an ion, however the number of such molecules decreases rapidly with $R$. For instance, only 10% of the molecules are at a distance of less than $0.29\rho^{-1/3}$ from a nearest ion. For reference we choose a standard example where we shall use $n = 120$ (which is close to the low-n side of a typical "magic region" of longevity) and a density of 1000 ions/mm$^3$ (in various ZEKE experiments, the reported densities were from about 30 [39] up to 30000 [25] ions/mm$^3$, while the most typical densities are, probably, 100 - 1000 ions/mm$^3$). Hence, the radius of a Rydberg state ($< 2n^2$ [a. u.] = 1.5 µm at $n = 120$) is typically much smaller than the Rydberg-ion separation (55 µm (50%) and 29 µm (10%) under conditions of the standard example), so that the field of the ion can be well approximated by several first terms of the multipolar expansion: $\mathbf{F}(\mathbf{r}) = -\mathbf{R}/R^3 - (\mathbf{r} - 3\mathbf{R}(\mathbf{Rr})/R^2)/R^3 + \ldots$ This field consists of a homogeneous part $\mathbf{F}_0 = -\mathbf{R}/R^3$ and an inhomogeneous correction $\delta\mathbf{F}(\mathbf{r}) \approx -(\mathbf{r} - 3\mathbf{R}(\mathbf{Rr})/R^2)/R^3$ which depends on the location $\mathbf{r}$ of the Rydberg electron and varies across the volume of the Rydberg orbital. The first part is larger than the second one, $|\mathbf{F}_0| = 1/R^2$ (4.8 mV/cm (50%) and 17 mV/cm (10%)), but it does not induce any additional $l$-dilution beyond the ordinary Stark effect because it adds vectorially to the stray field to form a total homogeneous field, $\mathbf{F}^{\text{total}}_{\text{homo}} = \mathbf{F}_{\text{stray}} + \mathbf{F}_0$, which defines the physical quantization axis for the Stark states. Only the inhomogeneous part of the field can break the cylindrical symmetry which is required to make the ions effective in producing ZEKE states. Though this field is small, $|\delta\,\mathbf{F}| < 2(2n^2)/R^3$ (0.26 mV/cm (50%) and 1.8 mV/cm (50%)), it is not as innocent as it's magnitude suggests. Inhomogeneity of the field introduces coupling $Q \approx (r^2 - 3(\mathbf{rR})^2/R^2)/(2R^3)$ between zero order Stark states of different $m$. The magnitude of this coupling, $\langle Q\rangle \sim n^4/R^3$, strongly depends on the principle quantum number $n$ and Rydberg-ion separation $R$.

Consider now an optically accessed low-$m$ Stark Rydberg state which is coupled via inhomogeneity to a dense $m$-mixed manifold formed by higher-$m$ magnetic sublevels of a nearest Stark level(s). This initial state can either decay at a rate characteristic of low-$m$ optical states, $\sim \Gamma_0/n^4$, or it can first escape into the $m$-mixed manifold of ZEKE states which then decay at a slower rate. Extensive $m$-mixing is possible *only if* the coupling strength, $\sim n^4/R^3$, exceeds the core perturbations manifested as non-hydrogenic energy shifts of the zero order low-$m$ levels ($\sim \mu/n^4$, $\mu$ is a quantum defect) and as finite decay rates ($\sim \Gamma_0/n^4$, $\Gamma_0$ is a reduced rate) of these states. Hence, in the high-$n$ Stark states (typically formed in presence of a stray field) the $m$-mixing starts when $n^4/R^3 \simeq f(\mu, \Gamma_0)/n^4$, where $f$ is a factor on the order of unity or less depending on the strength of the core perturbations. Correspondingly, the cross-section of the $m$-mixing collisions scales as $n^{16/3}$.

It is also interesting to estimate how fast the ion-induced $m$-mixing sets in so that afterwards the experimentally measured decay rates of the Rydberg population can no longer be rationalized on the basis of intramolecular interactions only. The above mentioned escape rate of the initial low-$m$ optical Stark state into the $m$-mixed manifold can be shown to scale as $\Gamma_{\text{esc}}/(2\pi) \simeq n^4/R^3$. Under conditions of the standard example, this means that 50% of the optical $n = 120$ states undergo onset of $m$-mixing faster than in 20 ns while 10% in 3 ns.

The above estimates are only a rough approximation which can be inaccurate well within an order of magnitude. Scaling properties showing strong dependence of the onset of $m$-mixing on the principle quantum number $n$ and on the Rydberg-ion separation $R$ are the main result of this section having important implications for ZEKE experiments. It is clear in particular, that:

1. Just as in the case of the $l$-mixing in the presence of a homogeneous field, for similar reasons there exists a sharp onset above which optical states can undergo step-like ion-induced enhancement of the lifetimes. Sufficiently high-$n$ states inevitably undergo $m$-mixing. On the other hand there always exist lower-$n$ optical states below the onset of $m$-mixing whose decay is unperturbed by the presence of ions. The location of the transitional region of $n$'s is determined by the competition between ion-induced perturbations (dependent on the density of ions and on $n$) and the non-hydrogenic core perturbations, whose strength depends on the nature of particular Rydberg system and generally decreases fast at higher $n$'s. Signal variation on the red (lower-$n$) side of a ZEKE peak which is caused by a change in the ion density and/or electric field during excitation (which controls the natural life-times of the optically accessed states) is the most direct manifestation of the presence of ion effect and of the competition between intramolecular and external factors;
2. At densities of $10^3$ ions/mm$^3$ or higher, an extensive $m$-mixing can be expected to occur throughout a typical region of longevity ($n > 100$ - $150$) where the optical (low-$m$) Rydberg Stark states can survive until the onset of $m$-mixing;
3. At lower densities, say, $10^2$ ions/mm$^3$ or less, very fast $m$-mixing (on the order of 10 ns) is very unlikely, especially at the red edge of a ZEKE band, $n < 100$;
4. On the other hand, even at these low densities, at least some collisional stabilization appears inevitable on a time scale longer than 1 µs, provided some optical states survived. Residual thermal motion of the ions (typical rms velocity of about 50 m/s) increases the chances of the closer range Rydberg-ion interaction. Hence, it can be expected that in most of the experiments with tens of µs delays there is always a considerable effect due to ion-induced stabilization.

## 5. Concluding Discussion

The systematic study of the benzene ZEKE spectra dependence on varied electric fields and ion densities presented here along with the results reported by others form the basis for an emerging unified picture of the mechanisms affecting the formation of the long lived Rydberg states probed by ZEKE spectroscopy. There is growing experimental evidence that, under conditions found in most experiments, the delayed ionization signal usually carries a signature of competition between intramolecular decay of optical Rydberg states and ion induced stabilization via m-mixing. The lifetimes of the optical states determine the interval of time during which these states are available for m-mixing, while the density of ions controls the rate and extent of m-mixing leading to the formation of longer lived m-mixed states.

More specifically, excitation typically takes place in the presence of small residual fields sufficient to provide extensive $l$-mixing of the near-threshold Rydberg states. Hence, optical states are low-$m$ Stark states with lifetimes strongly dependent on their principle quantum number, $n^4$ on average. Experimental and theoretical results from the last years for real non-hydrogenic systems, in the presence of optimal small fields, show that actual $l$-mixing is not uniform and that there is a wide distribution of lifetimes with large deviations from the average, both in direction of much shorter and much longer lived optical states. Couplings between Rydberg series built on different states of a molecular core further enhance non-uniformity. The resulting "long" lifetimes of the optical near-threshold states are strongly dependent on the nature of the core and can vary from tens of ns (e. g. in Xe) up to well above microseconds (e. g. in benzene).

The presence of an increased field (more than 200 mV/cm in case of benzene) during excitation enhances the decay rates of the optical states and results in a considerable loss of delayed ionization signal. *An interesting practical consequence of this experimental observation is that in-field excitation can be used as a method to vary the lifetime and hence availability of the optical states for the slower processes occurring later.* Several mechanisms contribute to the field-enhanced decay. At fields which exceed several times the Inglis-Teller field for a given $n$, all low-$l$ states, including the shortest lived ones, merge into the hydrogenic-like Stark manifold. This process results in the reduction of the long time component in the life times distribution. Field assisted rotational channel coupling is another mechanism allowing mixing with the increasingly lower-n states converging to higher rotational levels of the ion. These states can efficiently decay by predissociation and/or internal conversion. Fields applied after the laser pulse, even those with delays as short as 10 ns, do not enhance the decay of the states excited in field-free conditions. Hence, these states are immune towards post-excitation fields.

In our experiments we clearly show that the presence of ions is instrumental in the ZEKE states formation process. Ion induced $m$-mixing converts optical Rydberg states into longer lived $m$-mixed ZEKE states. This process competes with the decay of the optical states. The ratio of the two rates, $m$-mixing and decay, respectively, determines branching between two parallel processes leading to two different product states formed from the same optical (reactant) states. We have experimentally verified that both rates can be varied. Decay can be accelerated by increasing the field during excitation, while $m$-mixing is faster at higher densities of ions. If the optical states are relatively long lived, as they are in benzene when the spoiling field is delayed, then, even at low ion densities saturation of the ZEKE yield can be reached such that all optical states are converted into ZEKE. The intensity of the ZEKE signal in this case is a quantitative measure of how many states were available originally for the conversion. The ratio of the intensity of the signal produced where the field is present during photoexcitation to the intensity of the signal obtained under delayed field conditions is a direct measure of the fraction of these states that survive the attrition produced by the field. The ratio of signal intensities can be termed a quantum yield for ZEKE state formation in the presence of a field, $\Phi(z)$. The experiments presented here indicate that ions are requisite to counter the effects of field enhanced Rydberg state decay and that without ions the ZEKE signal would nearly completely disappear or, in other words, the ZEKE state quantum yield would go to zero.

Red side degradation of the in-field signal and its restoration in presence of higher densities of ions is another manifestation of the competition between field-enhanced decay and ion induced stabilization. The lower-$n$ states on the red side of a ZEKE peak are the shortest lived among all states within the "magic region" of longevity. At the same time, the $m$-mixing rate is the slowest in these states, considering the strong $n^4$ dependence of this rate. Hence, this region is most sensitive to field/ion dependent variations of the decay/stabilization rates.

The field assisted rotational channel coupling and concomitant enhancement of the predissociation rate does not apply to atomic species. Yet, Merkt has observed both in-field degradation and immunity with respect to post-excitation field in ZEKE spectra of atomic Argon. He explained the degradation in terms of direct suppression of the ion induced $m$-mixing in presence of an intentional field which may increase undesirable splittings between otherwise near degenerate magnetic sublevels. The latter effect was attributed by Merkt and Zare to the increasing importance of the avoided crossings in non-hydrogenic systems in presence of above Inglis-Teller fields. Second order Stark effect is another possible direct suppression mechanism. The immunity was attributed to the fast m-mixing occuring prior to delayed field application, which in these experiments was pulsed with delay of 50 ns. This is a viable explanation in case of Ar, where m-mixing needs to be fast in order to stabilize optical states subject to very fast spin-orbital autoionization.

Finally, the above picture of the combined field/ion effect can be schematically cast into the form of a kinetical description of ZEKE formation in the following way:

$$\text{benzene} \xrightarrow{h\nu} \begin{matrix}\text{Rydberg (M)}\\ \text{optical low-m states}\end{matrix} \xrightarrow{k_1[M^+]} \begin{matrix}\text{ZEKE}\\ \text{Stark states}\end{matrix}$$

$$\xrightarrow{(F)} \text{non-Rydberg states.}$$

The fraction of in-field ZEKE states is given by

$$\frac{I_{\text{in-field}}}{I_{\text{fieldfree}}} = \Phi(z) = \frac{k_1[M^+]}{k_1[M^+] + \alpha F}. \tag{1}$$

This can be recast into standard Stern-Vollmer or Hinshelwood kinetics so that

$$\frac{1}{\Phi(z)} = 1 + \frac{\alpha F}{k_1[M^+]} \tag{2}$$

or

$$\left[\frac{1}{\Phi(z)} - 1\right][M^+] = \frac{\alpha}{k_1}F. \tag{3}$$

Equation (3) gives a mechanistic description of the ZEKE yield as a function of in-field strength $F$ and ion concentration $[M+]$. It assumes linear dependence of

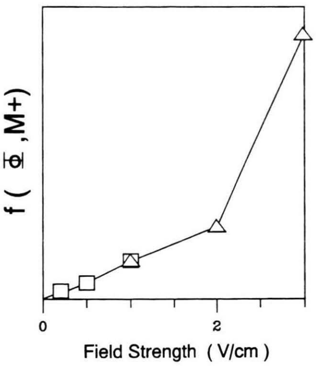

Fig. 5. Quantum yield function (see left half of (3) in text) versus electric field strength.

the *m*-mixing rate on [$M$+] and some, generally non-linear, dependence of the effective decay rate $\alpha(F)$ on field. Our measurements at various concentrations and series of fields fit well with (3), as shown in Figure 5. The curve is linear at lower fields and exhibits stronger non-linear signal loss at higher fields, which is what one would expect when direct in-field suppression of m-mixing is added to the simple decay/stabilization competition.

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