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Lifetimes of Rydberg States in ZEKE Experiments I: Electric Field Induced and Collisional Enhancement of NO Predissociation Lifetimes

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ABSTRACT

Lifetime measurements are reported for high principal quantum number (n=40-125) Rydberg states of the NO molecule, prepared using state-selective double resonance excitation with a narrow bandwidth laser. The influence of (i) the application of a DC electric field, and (ii) interactions of the Rydberg states with surrounding ions, were investigated. It is demonstrated that the presence of DC electric fields can lead to enhancements in the lifetimes due to $l$-mixing, and the conclusion is reached that under the conditions existing in a typical Zero Electron Kinetic Energy (ZEKE) PhotoElectron Spectroscopy experiment, the Rydberg states involved are excited in a regime where $l$-mixing is expected to be significant. It is observed that $l$- and $m$-mixing collisional interactions provide a further mechanism to stabilize the optically prepared Rydberg states, beyond the limits which can be achieved by $l$-mixing alone.

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Introduction

In recent years, the technique of Zero-Electron-Kinetic-Energy PhotoElectron Spectroscopy (ZEKE-PES), sometimes also referred to as Zero-Electron-Kinetic-Energy Pulsed Field Ionization (ZEKE-PFI), has become a powerful and widely used technique for studying the spectroscopy of molecular ions. In this technique, which was pioneered by Müller-Dethlefs and Schlag1-2, neutral molecules are excited to high principle quantum number Rydberg states (typ. n=200) using a tunable photon source, and the signal consists of the electrons and/or ions which are created as a result of the application of a pulsed electric field (typ. 1 V/cm in ZEKE-PES), which is switched on some time after the Rydberg excitation (typ. 1 μsec). The great strength of the ZEKE technique is that it allows studies of the energy levels of the molecular ions at near-laser resolution, as opposed to conventional PhotoElectron Spectroscopy (PES), where the energy resolution that can be achieved is about 80 cm\(^{-1}\), and the technique of Threshold PhotoElectron Spectroscopy (TPES), where, by measuring the near-zero kinetic energy photoelectrons which are formed at an ionization threshold, a resolution of about 25 cm\(^{-1}\) is possible.

The success of the ZEKE technique is striking in light of the fact that, for many systems where the technique has successfully been applied, the high-n Rydberg states involved in the experiment were expected to be short-lived. For example, in the ZEKE-experiments on NO by Reiser et.al.3, the lifetime towards predissociation of the n=200 p-orbital Rydberg states would be expected to be approximately 100 nsec, based on extrapolation of lifetimes for lower principal quantum number states, whereas experimentally no significant loss in signal was observed when the pulsed field ionization was delayed by 1.2 μsec.

The experimental evidence for enhanced lifetimes for Rydberg states close to ionization thresholds has attracted considerable interest and a number of models have been proposed to account for the observations. Chupka proposed two mechanisms which might be responsible for the enhanced lifetimes encountered in ZEKE-experiments4. The first mechanism is mixing of
orbital angular momentum states by the small residual electric fields of typ. 20-50 mV/cm, which exist in most experiments. Turning our attention once more to the example of the NO molecule, one realizes that the lifetimes of the Rydberg states of NO are determined by the predissociation rates, which strongly depend on the orbital angular momentum of the Rydberg electron. The predissociation rate is particularly fast for $l=1$, due to the fact that an $l=1$ Rydberg electron interacts strongly with the anti-bonding $2p\sigma_u^*$ electron in the repulsive $A'^2\Sigma_u^+$ state. The predissociation rate is significantly slower for $l=0,2,3$, and can be virtually ignored for higher angular momentum states. A mechanism which impacts on the angular momentum can thus be expected to significantly alter the lifetimes the Rydberg states.

The presence of external electric fields breaks the spherical symmetry in the Hamiltonian in near-hydrogenic systems, and as a result the orbital angular momentum $l$ is no longer a good quantum number. For the hydrogen atom, the Stark Hamiltonian is separable in parabolic coordinates $(\xi=r+z, \eta=r-z, \nu)$, and the Stark states are specified by the quantum numbers $n, k,$ and $m$, where $k = n_1-n_2$ and $n_1$ and $n_2$ are the parabolic quantum numbers. Referring back to the field-free eigenstates, we note that the $|n km\rangle$ Stark states can be expressed as superpositions of $|n lm\rangle$ states.

The decay dynamics of Rydberg states, whether the decay process be fluorescence, predissociation or autoionization, are determined by collision processes of the Rydberg electron with the ionic core. Near the ionic core, the potential experienced by the electron, which in atomic units is given by

$$V(\vec{r}) = -\frac{1}{r} + F_z$$

is dominated by the Coulomb attraction (1 a.u. = 5.14 $10^6$ kV/cm), and the orbital angular momentum is defined in this region. Consequently, the real-time decay dynamics of Rydberg states in electric fields, where the orbital angular momentum states are mixed, follow from the $l$-composition of the Stark levels.
Chupka proposed that in ZEKE experiments on NO small DC electric fields mix the orbital angular momentum states, thereby effectively reducing the predissociative $l=1$ contribution to the Rydberg state, and lengthening the lifetime of the state. In the experiment of Reiser et al. the Rydberg states were optically excited from the $A^2\Sigma^+ 3\sigma$ state, which has about 94% s-character, and 5% d-character. Assuming that the dominant photon absorption was to $l=1$ np$\sigma$ and np$\pi$ Rydberg series, Chupka predicted that the lifetime of the Rydberg states under ZEKE conditions might be increased from their field-free values by a factor $n$, since the contributions of all $l$-components $l=0...n-1$ to the Stark state should be equal. Thus the lifetime of the $n=200$ p-orbital Rydberg states of NO might go up to approximately 20 µseconds, in agreement with the experiments by Reiser et al. Under the influence of the electric field, the lifetime is expected to display an $n^4$ dependence on the principle quantum number.

A second mechanism proposed by Chupka involves collisions of the Rydberg molecules with molecules and ions. Owing to the large size of the Rydberg orbital, cross sections for $l$- and $m$-changing collisions are extremely large. Similar to the argument which was given for the lifetime enhancement by $l$-mixing in electric fields, a randomization of $l$ and $m$ over all possible angular momentum states could produce a lifetime enhancement of about a factor $1/2*n^2$, or an $n^5$ dependence of the lifetime on the principle quantum number.

An alternative explanation for the enhanced lifetimes of Rydberg states close to the ionization threshold was put forward by Levine and co-workers, who studied the lifetimes of Rydberg states of phenanthrene. These authors reported that near $n=100$ the lifetimes of the Rydberg states could be fit with an $n^6$ dependence. They attributed this $n$-dependence to the reduction with principal quantum number of the dissipation of the electronic energy of the Rydberg electron into the ro-vibrational modes of the ionic core. A similar interpretation was used in a study of tetracene. This model was subsequently questioned by Chupka, who argued that the $n^6$ lifetime dependence arose from the fact that the $n^3$ dependence from the classical Bohr electron-core collision frequency was taken into account twice. Recently, Levine et al. have reported classical trajectory calculations on the time evolution of high molecular Rydberg states in the presence of small dc electric fields. These results show that at high principal quantum
numbers the weak dc field reduces the frequency of close encounters of the electron with the core by a factor inversely proportional to the principal quantum number, in agreement with the model suggested by Chupka\textsuperscript{4}. In addition to studying the motion of the electron in the presence of a Coulomb and an external field, Levine et al. studied the influence of non-Coulombic parts of the electron-core interaction potential. They concluded that, for $l$-mixing to occur, there exists a lower limit on the external electric field, such that the rate of change in $l$ due to the external electric field is faster than the precession of the orbit due to the non-Coulombic part of the potential.

Several authors have attempted to address the lifetimes of Rydberg states near the ionization threshold experimentally. Merkt studied collisional and electric field effects in delayed pulsed field ionization of Ar for Rydberg series converging on both the $^2\text{P}_{3/2}$ ground ionic state and the $^2\text{P}_{1/2}$ spin-orbit excited state of Ar\textsuperscript{+}\textsuperscript{12}. He observed that in his experiment the lifetime of the $n=85$s' Rydberg state exceeded 200 nsec, while field-free lifetimes for these states are expected to be about 5.8 nsec, based on linewidth measurements for lower members of the autoionizing s' Rydberg series. Merkt concluded that $l$ mixing alone could not explain the increased lifetime of the Ar Rydberg states, but rather, that the results were compatible with Chupka's model involving collisional $l$- and $m$-mixing. Merkt also studied the Ar pulsed-field ionization spectrum in the presence of a DC electric field. Upon application of DC fields of a few V/cm he observed a drastic reduction in the pulsed field ionization signal and he concluded that $l$-mixing by an electric field did not prolong the lifetimes of the Ar Rydberg states, but rather, inhibited the formation of the long-lived ZEKE states.

A similar conclusion was reached by Pratt in pulsed field ionization of NO\textsuperscript{13}. Upon application of a $\sim$3 V/cm DC electric field he observed a significant reduction of the NO pulsed field electron signal as well as the total NO$^+$ signal, and concluded that the NO Rydberg states decayed by field-induced predissociation. Pratt observed that the lifetimes of the NO Rydberg states under field-free conditions were at least several hundred nanoseconds, and, considering an estimated field-free lifetime of a 75p Rydberg orbital of about 0.2 nsec, concluded that both $l$- and $m$-mixing needed to be invoked to explain the observed lifetimes, lending support to
Chupka's collision mechanism. Thus he concluded that in the NO molecule predissociation competes with \( l \)-mixing and \( l \) and \( m \)-changing collisions to determine the range of high-\( n \) Rydberg states accessible in ZEKE and delayed pulsed field ionization studies, and that small DC electric fields lead to a depopulation of the high Rydberg states responsible for the ZEKE signal, through mixing of these states with lower-\( n \) Rydberg states converging on higher rotational states. It should be noted that, while Merkt\textsuperscript{12} and Pratt\textsuperscript{13} have both presented data in apparent agreement with the \( l \) and \( m \)-mixing collision mechanism proposed by Chupka, the dependence of the pulsed field ionization spectra on the \( \text{Ar/Ar}^+ \) resp. \( \text{NO/NO}^+ \) densities was not reported in these experiments, precluding a direct confirmation of the validity of this mechanism.

In the experiments of Merkt\textsuperscript{12} and Pratt\textsuperscript{13}, information on the lifetimes of the high-\( n \) Rydberg states and the dependence of the lifetime on external electric fields was extracted from PFI-ZEKE spectra obtained at different pulsed field time delays, with or without the additional application of DC electric fields. In these measurements the Rydberg states that were optically excited could not be spectrally resolved, and the lifetimes of the Rydberg states were inferred from the appearance or disappearance of intensity in particular wavelength regions of the spectrum.

In this series of papers we present a study in which we have performed lifetime measurements on individual high-\( n \) Rydberg states of NO and Xe. The organization of these papers is as follows. In the current report our emphasis is on DC electric field effects in lifetimes of Rydberg states of the NO molecule and we discuss experiments where lifetimes of individual \( np \) and \( nf \) NO Rydberg states, populated by excitation from the \( A^2 \Sigma^+ \) state with a near-transform limited laser, were determined under 'field-free' conditions, as well as in the presence of small additional DC electric fields. As has been discussed in a preliminary report elsewhere\textsuperscript{14}, our results show pronounced lifetime enhancements in the presence of small DC electric fields, in agreement with the \( l \)-mixing lifetime-enhancement mechanism proposed by Chupka, and lead to a reinterpretation of the experiment on NO by Pratt\textsuperscript{13}. A series of experiments was also carried out aimed at investigating the influence of collisional interactions on the lifetimes of the NO Rydberg states, and these experiments are reported here as well. Collisional stabilization of
Rydberg states is further emphasized in our companion paper on the lifetimes of autoionizing Rydberg states of the Xe atom\(^{15}\).

At the end of this introduction, it should be pointed out that prior to the work motivated by Chupka's paper, a number of experiments had been carried out in which electric field-induced lifetime effects were observed. In atomic systems electric field effects on Rydberg states have been studied extensively and Stebbings reported that the fluorescence lifetime of the Xe 25f Rydberg state increased from 8 to 24 \(\mu\text{sec}\) when the excitation was performed in a 25 V/cm DC electric field\(^{16}\). For the molecular systems which have been studied, the result of applying electric fields has most often been a reduction in the lifetime. Forced autoionization has been reported for a large number of diatomic molecules\(^{17-21}\), an interesting exception being the case of Na\(_2\), in which Bordas et.al. observed an increase in the lifetime of vibrationally autoionizing nd Rydberg series in the presence of small electric fields\(^{22}\). For the H\(_2\) molecule, field-induced predissociation of the np Rydberg series converging on N\(^+\)=1 was observed\(^{23-24}\), and similarly, for the H\(_3\) molecule, electric field-induced predissociation of nd Rydberg series through coupling to predissociative p-states was reported\(^{25}\).
Experimental

The experiments on electric field induced lifetime enhancements of NO Rydberg states were carried out on an apparatus where NO\textsuperscript{+} ions, formed by pulsed field ionization, were detected. In this section a detailed description is given of this apparatus as well as the experimental procedures used. On the other hand, the experiments on collisional stabilization of NO Rydberg states discussed in this paper were performed by selectively detecting the electrons formed by pulsed field ionization on a second apparatus, employing a position-sensitive microchannel plate detector to distinguish the zero initial kinetic energy electrons from electrons formed by (resonance-enhanced) multi-photon ionization (RE)MPI. The reader is referred to our companion paper on the lifetimes of autoionizing Rydberg states of the Xe atom for a detailed description of this apparatus\textsuperscript{15}.

The NO Rydberg states were populated using two-color laser excitation, employing the \textit{A}^2\Sigma\textsuperscript{+} state as resonant intermediate. To obtain the 226 nm light required to pump selected A-X (0,0) \textit{P}\textsubscript{1}-transitions\textsuperscript{26}, the continuous output of a Coherent 699-29 ringlaser, operated around 621 nm, was pulse-amplified at 10 Hz in three stages. The visible output of this laser, which has been described in detail before\textsuperscript{27}, was doubled and mixed in KDP and BBO, yielding up to 7.5 mJ/pulse at 207 nm. Given the very modest power requirements in this experiment, the 532 nm output of the Continuum Model YG-592 Nd:YAG laser, which pumps the dye amplifiers, was lowered to a level where the 207 nm light was approximately 3 mJ/pulse. The 207 nm light was focussed into a Raman cell containing \textit{H}_2 at a pressure of 7 atmospheres, using a 300 mm focal length lens, giving approximately 150 \mu J/pulse of the first Stokes line at 226 nm. The bandwidth of the 226 nm light was experimentally determined to be 0.06 cm\textsuperscript{-1}, in contrast to the near-transform limited 0.005 cm\textsuperscript{-1} bandwidth of the 207 nm light. In this experiment, the spectral broadening introduced by the Raman-shifting process was convenient, since it made it very easy to keep the laser tuned to a selected rotational transition to the \textit{A}^1\Sigma\textsuperscript{+} state for many hours, independent of small drifts of the seed laser.
The 226 nm light was recollimated using a 300 mm lens and attenuated to a power level of just a few μJ/pulse by the beam-combining optics and additional neutral density filters, before being focussed to a spot of about 2 mm. This provided a condition where only a negligible fraction of the NO molecules excited to the A-state were ionized by the absorption of an additional 226 nm photon, and where the density of the NO Rydberg molecules and the NO+ ions were anticipated to be low enough that Rydberg-Rydberg or Rydberg-ion collisions would not play a significant role.

Similar to the first laser, the second laser, used to excite the NO molecule from the A-state to the Rydberg states, also was a pulse-amplified Coherent 699-29 ring laser, which in this case was operated near 656 nm. The output after two stages of amplification (typ. 3 mJ/pulse) was frequency-doubled in KDP, and the 328 nm light thus generated was sent into the chamber co-propagating with the 226 nm light, without any focussing. A 50 nsec timedelay was maintained between the 226 nm laser and the 328 nm laser. Neutral density filters were used to attenuate the 328 nm beam, in order to limit the ionization of the Rydberg states by absorption of an additional 328 nm photon.

The two lasers crossed a pulsed molecular beam of NO at the center of a Wiley-McLaren time-of-flight mass spectrometer. The pulsed beam of NO was generated by operating a pulsed valve in a differentially pumped source chamber. The pulsed valve was built according to the design of Proch and Trickf and was operated with a backing pressure of 1.5 atmospheres. In our experiments to measure the lifetimes of NO Rydberg states, lifetimes of up to 400 nsec were observed. A measurement of the lifetime of an 85f Rydberg state converging on N* = 1 (a state for which the Rydberg orbital extends over a distance of approximately \((a_0/2Z)^2 [3n^2 - l(l+1)] = 0.57 \mu m\)), in which the NO backing pressure was reduced to 0.03 atmospheres, did not show any dependence of the measured lifetime on the NO backing pressure, so relaxation of the Rydberg molecules by collisions with neutral NO or NO+ ions is not expected to play a role in the interpretation of the experiment.

The operation of the mass spectrometer was modified for these experiments in the following way. At a variable time delay with respect to the firing of the two lasers, a +1.7 kV
pulse with a 5 nsec risetime and a 200 nsec falltime (Velonex Model V-3571) entered the chamber through a chain of 30 IN914B signal diodes, equalized by 1.2 MΩ resistors, reaching the ion optics without any observable increase in the risetime. The voltage distribution between the repeller and the two accelerators was achieved by the use of Zener diodes, with all additional ion optics components in the apparatus being held at ground. Using this set-up, the falltime of the high voltage pulse was stretched to 25 µseconds. In the experiments to study the influence of electric fields on the lifetimes of the Rydberg states, a DC voltage was superimposed on the high voltage pulse.

The high voltage pulse was used to ionize the NO Rydberg molecules as well as accelerate the NO⁺ towards an approximately 30 cm time-of-flight tube, leading to a Daly-type scintillation detector. The lifetimes of the Rydberg states were determined by measuring the total NO⁺ signal as a function of the time delay between the trigger of the high voltage pulse generator and the firing of the two lasers. Under typical experimental conditions, the NO⁺ signal from pulsed field ionization of NO Rydberg states was about two orders of magnitude larger than the NO⁺ signal from the (1+1) REMPI by the 226 nm laser, and about one order of magnitude larger than the NO⁺ signal corresponding to two-photon (RE)MPI of NO molecules in the A-state by the 328 nm laser. All time delay scans were measured by stepping the time delay for the high voltage pulse generator in random order. At each time delay three measurements were taken. The gated boxcar integrator (Stanford Research Systems SR 250) was used with a 1 sec time-constant, and the signal was integrated for 3 seconds before a datapoint was taken.

A typical example of a time delay scan is shown in Figure 1. The curve contains three distinguishable contributions, namely, (i) a constant (spectrally broad) pulsed field ionization contribution at negative time delays, where the high voltage pulse comes on before the firing of the second laser, followed by (ii) an exponentially decaying pulsed field ionization curve, which reflects the rate of predissociation following the field-free laser excitation, and which sits on top of (iii) a near-constant REMPI contribution. From the experimental decay of the latter REMPI signal, it follows that in the geometry of our experiment, NO⁺ could be detected without serious
loss in the detection efficiency as long as the extraction occurred within 2 μseconds after the laser excitation.

The apparatus described above, while very suitable for studying the effects of the application of an electric field on the lifetimes of the NO Rydberg states, was unsuitable for studying collisional effects for a number of reasons. Experimentally, the number of Rydberg-Rydberg or Rydberg-charged particle collisions can be modified by increasing the NO pressure as well as the power density of the two lasers. Whereas in the current experiment the NO pressure could not be significantly increased any further, an increase in the power of the lasers, carried out along with a reduction in the size of the focal volume of the lasers, led to a deterioration of the ratio between the NO$^+$ ion signal formed by pulsed field ionization and the NO$^+$ ion signal formed by (RE)MPI. Also, the linearity of the detection system was compromised. Therefore, experiments on the collisional stabilization of NO Rydberg states through collisions with NO$^+$ ions, electrons, or other NO Rydberg states, were carried out on the instrument described in the introduction to this section$^{15}$. 
Results

a) DC Electric field effects in pulsed-field ionization starting from $A^1\Sigma^+(N_A=0,J_A=1/2)$

Precise wavelength scans for NO pulsed field ionization starting from the $A^1\Sigma^+(N_A=0,J_A=1/2)$ intermediate state were performed in the frequency range of 30480-30530 cm$^{-1}$. The spectrum was recorded at a time delay of approximately 10 nsec between the laser excitation and the pulsed field ionization and extraction, and shows two dominant Rydberg progressions, namely a series with a quantum defect of 0.7286 converging on $N^+=0$ ($E_0=30522.443$ cm$^{-1}$), assigned as a p-series, and a series with a quantum defect of 0.0101 converging on $N^+=2$ ($E_0=30534.349$ cm$^{-1}$), assigned as an f-series.$^{31}$

A portion of the spectrum is shown in Figure 2. This spectrum was recorded under a condition of minimal residual DC electric field. Experimentally it was observed that simply attaching the ground of the output of the high voltage pulser to the ground of the apparatus did not give the smallest possible residual DC electric field. Rather, a minimum was obtained when a DC bias of about -235 mV/cm was applied to the ion optics. To determine this voltage, we used the fact that, as will be shown shortly, the lifetimes of the p- and f-orbital Rydberg series can be enhanced by the application of a small DC electric field. As shown in Figure 3, the pulsed field ionization signal following excitation to the 50f orbital was measured as a function of the applied DC electric field, at a constant pulsed field time delay of 50 nsec. The voltage that needs to be applied to obtain the smallest residual DC electric field corresponds to the minimum of this curve, which reflects a minimum in the lifetime of the 50f state. As will be demonstrated later, the existing residual DC electric field in the experiment is determined to be about 25 mV/cm under these conditions.

Lifetimes for the high-n Rydberg states excited from the $A^1\Sigma^+(N_A=0,J_A=1/2)$ intermediate state, were determined by carrying out delayed pulsed field ionization scans, as described in the experimental section. Lifetimes for the p-series were determined for $n=50-122$, while lifetimes for the f-series were determined for $n=40-91$. For $n>91$ a sudden increase was observed in the
time constants measured in the pulsed field time delay scans of the f-series, and the decays could no longer be fit by a single exponential. For these states all NO$^+$ ions were formed promptly after the laser excitation, due to the fact that for these states the rate for rotational autoionization to $N^+=0$ exceeded the predissociation rate. Therefore, these time delay scans merely reflect the efficiency for detection of NO$^+$ ions as a function of the delay between the formation of the ions and the pulsed extraction. The onset of the rotational autoionization above $n=91$ allows us to put an upper limit on the residual DC electric field in the experiment. The 91f state of the Rydberg series converging onto $N^+=2$, lies 1.35 cm$^{-1}$ below the experimental field-free $N^+=0$ ionization threshold, obtained from extrapolation of the p-series. The adiabatic lowering of the ionization threshold by a DC electric field is given by

$$\Delta \text{IP} \,(\text{cm}^{-1}) = 6.1 \sqrt{F(V/cm)}$$  \hspace{1cm} (2)$$

and therefore an upper limit of 49 mV/cm is determined for the residual DC electric field at the minimum field condition.

The lifetimes shown in Figure 4 show two sets of data, namely lifetimes determined under the minimum field condition (open circles) and lifetimes which were determined when additional DC electric fields were applied (filled circles). In the minimum DC field measurements, both the p-series and the f-series show sudden increases in the lifetime, starting at $n=116$ for the p-series and at $n=65$ for the f-series. When appropriate DC electric fields are present at the time of the laser excitation, the lifetimes of those p- and f- Rydberg states which remain on the lower curve at the minimum DC field condition, can readily be enhanced. The observed lifetime increases, when no additional DC electric field is applied, are therefore attributed to the influence of the residual DC electric field. As will be discussed in more detail later, the electric fields which are required to induce $l$-mixing scale as

$$F \propto \mu n^{-5}$$  \hspace{1cm} (3)
where $\mu$ is the quantum defect of the Rydberg orbital in question. The fact that, under the minimum DC field condition, the lifetime increases for the f-orbital and the p-orbital occur at $n=65$ and $n=116$, respectively, is consistent with the quantum defects for the f- and p-series.

We mentioned that the lifetimes of p- and f-series Rydberg states which are not yet mixed by the residual DC electric field, can readily be increased by the application of a small additional DC electric field. The magnitudes of the electric fields required to induce the lifetime enhancement were determined by monitoring the amount of NO$^+$ signal that was detected at a time delay of 50 nsec between the laser excitation and the onset of the high voltage pulse. For each state a sudden increase in the signal and, by extension, the lifetime was observed when the electric field was raised above a critical value. The lifetimes shown in Figure 4 were measured at electric fields which typically were about 20% above this critical value.

In addition to changes in the lifetime, the data in Figure 4 also shows changes in the dependence of the lifetime on the principal quantum number $n$. Under field-free conditions the predissociation lifetimes of NO are expected to show an $n^3$ dependence on the value of the principal quantum number, following from the fact that the Bohr frequency, which describes the rate of the collisions of the Rydberg electron with the ionic core, scales as $n^{-3}$. For principal quantum numbers $n<65$, where the residual DC electric field is too weak to induce the $l$-mixing, the coefficient for the $n$-dependence of the lifetimes of the f-series was determined to be $3.00 \pm 0.13$, in excellent agreement with the expected value. The lifetimes of the p-series are too short to be measured very accurately in our experiment. The coefficient for the $n$-dependence was fit as $2.47 \pm 2.49$, which does not allow a comparison with theory. By contrast, the lifetimes of the p-series after the electric field induced $l$-mixing were fit to a slope of $4.17 \pm 0.25$, which confirms Chupka's contention, that, upon $l$-mixing, the lifetime of the p-orbital, which dominates the predissociation rate, might go up by a factor $n$. The lifetimes of the f-series after the electric field induced $l$-mixing cannot be reproduced well in a fit with a single coefficient for the $n$-dependence. The measured lifetimes reach a maximum of approximately 400 nsec near $n=80$, and slowly decrease thereafter. The observed saturation of the lifetimes of the $l$-mixed f-orbitals
is likely to be due to varying amounts of admixture of other low-\(l\) angular momentum components. This is clearest for \(n \geq 116\), when the lifetime enhancement of the p-series indicates mixing of the p-orbital with the \(l \geq 3\) orbital angular momentum states responsible for the lifetime enhancement of the f-series, and therefore obviously with the f-series itself as well. Between \(n = 80\) and \(n = 116\) the saturation of the f-orbital lifetime may be due in part to mixing with s- and d-orbitals. It is not believed to be due to quenching of the Rydberg states by collisions. As described in the experimental section, no dependence of the observed lifetimes on the NO pressure was observed.

In Figure 5 the lifetime enhancement around the critical electric field strength is shown in more detail for excitation to the 51f orbital. This state was chosen because its lifetimes with and without the electric field induced lifetime enhancement are on a timescale where they both can be measured accurately. Figure 5 shows that the lifetime of the 51f orbital is constant at its near field-free value until the DC electric field exceeds approximately 70 mV/cm, at which point a sudden five-fold increase is observed over a range of approximately 25 mV/cm. A modest subsequent increase of the voltage does not lead to a further increase in the lifetime.

In order to determine the magnitude of the electric field required to induce the lifetime enhancement as a function of the principal quantum number, the electric field strengths for inducing the lifetime enhancement were measured for selected members of the p-series. In this instance the p-series was chosen because the p-orbital quantum defect is larger than the quantum defect for the f-series, and thus the applied electric fields to induce the mixing are larger. Furthermore, the lifetimes of the p-orbitals without mixing are virtually negligible, so the onset of the lifetime enhancement can be determined more accurately. As in the measurements described above, the DC electric field was determined where the pulsed field ionization signal, measured at a fixed time delay of 50 nsec between the laser excitation and the onset of the high voltage pulse, showed a sudden increase. The results are shown in Figure 6 along with the results of a fit to an \( F \sim n^5 \) dependence. While the deviations of the fit from the experimental data points exceed the statistical uncertainties in the measured field strengths, the data is well represented by
a $n^5$ dependence. The implications of the absolute magnitude of the determined critical field strengths will be discussed further below.

Finally, wavelength scans were performed to investigate spectral changes as a function of the applied electric field. Figure 7 shows pulsed field ionization spectra for excitation to the 51f orbital in the presence of a variable electric field. The spectra show the mixing of the 51f orbital with the zero quantum defect states, which appear at a frequency which is .5 GHz higher than the 51f orbital. The onset of this mixing can even be seen at the minimum field condition. The third measurement (Figure 3c) corresponds to the electric field strength where a sudden enhancement of the lifetime is observed. Figure 7 also shows evidence for the afore-mentioned mixing with additional low-$l$ angular momentum components, since a narrow d-orbital contribution is observed growing in about 4 GHz to the blue of the peak corresponding to the 51f orbital.

Wavelength scans monitoring the spectral changes occurring for the p-series look considerably more complicated, since the mixing of the p-series happens at field strengths significantly larger than the critical field strength for mixing of orbitals of the f-series. Frequency scans around the threshold for mixing of the 71p state, recorded at a time delay of 10 nsec between the laser excitation and the onset of the pulsed electric field, are shown in Figure 8. The spectrum shown in Figure 8a was obtained at the minimum field condition, and shows pulsed field ionization of 57f and 58f orbitals converging on $N^+=2$. The p-series converging on $N^+=0$ is absent from this spectrum, owing to the rapid predissociation of the p-orbitals. As the electric field is increased the f-lines couple to the $l\geq3$ orbital angular momentum states and show considerable broadening (Figure 8b). Eventually the electric field is strong enough to couple the p-orbitals to the higher angular momentum states as well. This happens in Figure 8c for the 73p orbital, and in Figure 8d for the 71p orbital. Upon further increase of the electric field the spectrum becomes increasingly complex, and individual quantum states cannot be resolved anymore. For lower values of the principal quantum number, it was observed that eventually a Stark manifold very similar to those seen in rare gas and alkali atoms is obtained$^{32}$.

For a few states for which lifetime measurements were done anomalous behaviour was observed. In the f-series, the 55f orbital had a lifetime of only 3.4 nsec, while a fit of the
neighbouring \( f \)-states below the threshold for \( l \)-mixing would predict a lifetime of approximately 25 nsec for this state. After electric field-induced \( l \)-mixing the lifetime went up to 46 nsec, whereas a lifetime of about 100 nsec would be anticipated. We have as yet not been able to determine a most likely candidate that might be perturbing the 55f level.

In the p-series, examples of the opposite behaviour are observed. As discussed, the onset for DC electric field induced lifetime enhancement at the minimum field condition occurs at \( n=116 \). The 92p and 95p states, however, already display lifetime enhancement under the minimum field condition. These lifetime enhancements can be interpreted in terms of mixing between the p-series converging onto \( N^+=0 \) and the zero quantum defect states converging onto \( N^+=1 \). From the difference between the convergence limits for the p-series and the f-series under consideration here, the rotational constant of \( \text{NO}^+(v=0) \) can be determined to be 1.9842 cm\(^{-1}\).

Inspection of the energies at which zero-quantum defect Rydberg states converging onto successive rotational levels of \( \text{NO}^+ \) are expected to appear, shows that the 92p state converging onto \( N^+=0 \), lies within approximately 0.005 cm\(^{-1}\) from the \( n=80 \) zero quantum defect states converging onto \( N^+=1 \), whereas the 95p state converging onto \( N^+=0 \) is calculated to differ from the \( n=82 \) zero quantum defect states converging onto \( N^+=1 \) by merely 0.004 cm\(^{-1}\). To put these numbers in perspective, the 65f and 116p states converging onto \( N^+=0 \), which, as demonstrated above, are \( l \)-mixed by the residual DC electric field, differ from the closest zero quantum defect states by 0.008 cm\(^{-1}\) and 0.04 cm\(^{-1}\) respectively. Among the p-states converging onto \( N^+=0 \) that were studied, the 92p and 95p states are the only ones for which a lifetime enhancement might be anticipated due to the close proximity of zero quantum defect states converging onto \( N^+=1 \). The observation of this mixing has implications for the rotational branching ratios that are observed in ZEKE-experiments, since these accidental degeneracies are expected to become increasingly likely for higher principal quantum numbers. For a review of effects determining rotational line intensities in ZEKE-experiments, the reader is referred to the recent article by Merkt and Softley.\(^{33}\)

b) DC electric field effects in pulsed-field ionization starting from \( A^1\Sigma^+(N_A=1, J_A=3/2) \)
In the NO pulsed field ionization spectrum starting from the $A^1\Sigma^+(N_A=1, J_A=3/2)$ intermediate state, three Rydberg progressions were observed. The spectrum showed two Rydberg series converging on $N^+=1$ ($E_0=30522.439$), with quantum defects of 0.0168 and 0.7038, respectively, which were assigned as an f- and a p-series. In addition, a very strong Rydberg series with a quantum defect of 0.021 was observed, converging on $N^+=3$ ($E_0=30542.326$), which also was assigned as an f-series. Lifetime measurements were performed for the f- and p-series converging on $N^+=1$.

Lifetimes at the minimum field condition described in the previous paragraph were measured for $n=40$-127 for the f-series, and for $n=72$-125 for the p-series, and are shown in Figure 9. Qualitatively the lifetime measurements for $N_A=1$ are seen to be very similar to the lifetime measurements for $N_A=0$. There is a DC electric field induced lifetime enhancement, which comes at $n=69$ for the f-series, and at $n=118$ for the p-series. Furthermore, similar to the results in the previous paragraph, the lifetimes of the un-mixed p- and f-series Rydberg states excited from $N_A=1$ can readily be enhanced by the application of an appropriate electric field.

The simultaneous observation of a p-series and an f-series converging onto the same ionization threshold, allows us to assess the relative importance of these orbitals in a ZEKE experiment. In Figure 10 the pulsed field ionization spectrum is shown in the frequency range corresponding to excitation to $n=106$-128, obtained at two time delays between the laser excitation and the onset of the high voltage pulse. In the upper panel (Figure 10a) the high voltage is turned on during the laser pulse, and the p-series can be observed as a progression of sharp peaks until approximately $n=120$. In the lower panel (Figure 10b) the onset of the high voltage pulse comes approximately 10 nsec after the laser pulse, and the intensity of the rapidly predissociating p-series for is greatly diminished for $n<118$. By contrast, for $n\geq118$, where the p-series displays lifetime enhancement, the peaks associated with the p-orbital absorption are relatively much stronger and dominate the spectrum. Both in the upper and lower part of Figure 10, the contribution from absorption to the f-orbital appears as a small, broad feature, which is centered at a slightly lower transition frequency than the p-series, and which does not change.
significantly over this range of principal quantum numbers. This of course is due to the fact for 
\( n \geq 68 \) the f-orbital Rydberg series is mixed with the \( l > 3 \) angular momentum states.

It should be noted that in the regime where the p-orbitals undergo a lifetime enhancement 
through \( l \)-mixing with the near zero quantum defect states, it becomes increasingly inappropriate 
to talk about the Rydberg excitation in terms of excitation to a p-orbital or an f-orbital, since this 
represents a regime where the \( l \)-mixing is strong enough that the orbital angular momenta 
become very poorly defined quantities. Still, as shown in Figures 7 and 8, it is possible to identify 
contributions to the Rydberg excitation centered on peak positions that conform to the quantum 
defects of either the p-orbital or the f-orbital. While it is not possible to separate the individual 
contributions, the results shown in Figure 10 suggest that for \( n \geq 118 \), and therefore also for the 
\( n=200 \) Rydberg states which constitute the ZEKE signal, the oscillator strength is carried by 
excitation to what is nominally a p-orbital. This agrees with measured NO absorption spectra, 
which show that the oscillator strength is largest for excitation to p-orbitals\(^{34}\). Thus our 
experiments provide considerable support for the explanation of the success of ZEKE of NO 
proposed by Chupka, namely that the lifetime of the ZEKE Rydberg states is enhanced by 
approximately a factor \( n \), since the p-orbital Rydberg states, which dominate both the absorption 
and the predissociation, are mixed with higher angular momentum states.

c) **Collisional effects in pulsed-field ionization starting from \( \Lambda^1\Sigma^+ (N_A=0,J_A=3/2) \)**

Using the experimental approach outlined in the experimental section of our companion paper on 
the lifetimes of autoionizing Rydberg states of Xe\(^{15}\), the influence of collisions on the lifetimes 
of NO Rydberg states were studied. Briefly, electrons resulting from pulsed field ionization of 
NO Rydberg states were detected on a position-sensitive microchannel plate detector, using the 
fact that ZEKE electrons can be distinguished from (RE)MPI electrons through the fact that 
ZEKE electrons have zero recoil velocity, and are detected at a position which is solely 
determined by the acceleration field.
In Figures 11 and 12 a series of time delay scans are shown, obtained for excitation to a 42f orbital converging on N\(^+\)=3. In each Figure decay curves are shown, which were obtained at NO pressures of \(2 \times 10^{-6}\) Torr and \(4 \times 10^{-5}\) Torr, respectively, and the signals at the former pressure were multiplied by a factor 20, such that the two curves will look similar in the absence of collisional effects. The measurements in Figure 11 were obtained without DC electric field induced lifetime enhancement, and were performed at the low laser powers which were used in the experiments described in the previous sections. Under these conditions the pressure dependence of the pulsed field ionization signal is purely linear. On the other hand, in the measurements shown in Figure 12, the lifetime of the 42f orbital was enhanced from 5 nsec to 48 nsec by applying a DC field of 250 mV/cm, and the power of the two excitation lasers was raised substantially. Under these conditions it is observed that an increase in the NO pressure leads to an increase in the pulsed field ionization signal which is more than proportional to the NO pressure. A measurement of the pressure dependence of the pulsed field ionization signal under these conditions reveals a clear transition from a linear to a (linear+quadratic) pressure dependence.

Decaytime measurements for NO Rydberg states formed in the quadratic pressure dependence regime were carried out for the f-series Rydberg states converging on N\(^+\)=1, for principal quantum numbers \(n=42-66\). The decaytimes which are shown in Figure 13 were determined by fitting pulsed field ionization time delay measurements which started 250 nsec after the Rydberg excitation, a time at which the residual signal from NO molecules which do not undergo a collision is negligible. The results in Figure 13 show the presence of Rydberg states with a lifetime of about 500 nsec, which is about one order of magnitude longer than the DC electric field enhanced lifetimes of NO Rydberg states in this principal quantum number range, without collisional interactions. The decaytimes shown in Figure 13 do not show a clear dependence on the principal quantum number. While this observation may seem surprising at first sight, we believe that this reflects the fact that in the collisional interactions which are in evidence in these experiments, Rydberg states with a wide range of \((n,l,m)\) quantum numbers are formed, such that our measurement is relatively insensitive to the identity of the optically
prepared Rydberg state. This statement is supported by closer inspection of Figure 12, which shows that the introduction of collisions not only leads to the enhanced formation of Rydberg states with very long lifetimes, but also leads to a substantial enhancement of the pulsed field ionization signal at shorter time delays. The decay times shown in Figure 13, therefore, reflect the decay of only a portion of the Rydberg states that are formed in the collisions that the NO Rydberg molecules undergo, and do not directly address the question as to which fraction of the molecules are formed in these states. The importance of the measurements shown in Figure 13 is that they show that, through collisional interactions, it is possible to further stabilize a Rydberg molecule, obtaining a lifetime which is beyond the values that can be obtained by $l$-mixing in a DC electric field alone.

Our interpretation of the observations given above is that interactions of the Rydberg molecule with surrounding ions lead to changes in the angular momentum projection quantum number $m_l$ and subsequent trapping of the electron in a superposition of orbital angular momentum states $l \geq m_l$. These states are unlikely to decay unless $m_l$ is equal to or returns to a value smaller or equal than 3. If the value of $m_l$ becomes completely randomized, while the principal quantum number stays constant, an $n$-fold increase in the lifetime would be anticipated. A more detailed discussion of the mechanism of collisional lifetime enhancement will be developed in our companion paper on the lifetimes of autoionizing Rydberg states of Xe.
Discussion

a) A model for the lifetimes of NO Rydberg states in DC electric fields and a calculation of the measured ZEKE spectrum

In recent experiments on the effects of the applications of a DC electric field on the pulsed field ionization of NO by Pratt, a conclusion was reached which seemingly contradicts our experiments on the lifetime enhancement of the NO Rydberg states in the presence of electric fields\textsuperscript{13}. Pratt observed that the application of a \( \sim 3 \) V/cm DC electric field led to a large decrease in the pulsed field ionization signal measured at a pulsed field time delay of 800 nsec, and concluded that the electric field, rather than increasing the lifetime by \( l \)-mixing, decreased the lifetime by a field-induced predissociation mechanism, which couples the high-\( n \) p-orbital ZEKE Rydberg states, to lower-\( n \) Rydberg states converging on rotationally excited states of the ion.

As will be demonstrated below, our experiments can be described according to a very simple model, which qualitatively reproduces all the main results of not only our experiment, but the experiments by Pratt as well. This model leads to a reinterpretation of the experiments by Pratt, with two main ingredients. First of all, we conclude that the pulsed field ionization signal in Pratt’s experiment, which can be observed when no external DC electric field is applied from approximately 20 cm\(^{-1}\) below the ionization threshold, contains large contributions from absorption to an f-orbital, rather than a p-orbital, as assumed by Pratt. And secondly, our model indicates that under the 'field-free' conditions in which Pratt observed very long lifetimes of the NO Rydberg states, these f-states are in fact \( l \)-mixed with the near-degenerate higher angular momentum states\textsuperscript{35).} The decrease in the lifetime of the Rydberg states upon introduction of a \( \sim 3 \) V/cm DC field, which Pratt observed, is predicted by our model in terms of mixing of the strongly predissociative p-orbital with the high-\( l \) orbital angular momentum states mentioned above.
In his experiment, Pratt noted that there was a discrepancy between the observed long lifetimes without application of external DC electric fields, and the very short lifetimes which he anticipated based on linewidth measurements for low-n p-orbital Rydberg states. He concluded that this discrepancy could only be explained in terms of a lifetime enhancement mechanism invoking randomization of both $l$ and $m$. Consequently he concluded that the large lifetime of NO in ZEKE experiments must be due to collisions of the optically prepared low angular momentum Rydberg molecules, most likely with ions. In our model the lifetimes without application of additional external fields can be explained in terms of $l$-mixing of the f-orbital with higher angular momentum states. Though collisional stabilization may well have played a role in the experiments, the observations reported by Pratt do not require explanation through an $l$- and $m$-mixing collision mechanism.

The basis of our model is that the optical excitation leads to the formation of a Stark state which can be written as a superposition of angular momentum states. Depending on the principal quantum number, the electric field, and the quantum defects, this superposition is confined to those angular momenta whose unperturbed energy levels lie within the range of the Stark manifold. This conjecture follows directly from our experimental determination of the electric field strengths which are required to give specific principal quantum states of the nf and np series a lifetime-enhancement. The width of the Stark manifold is equal to

$$\Delta E_{\text{Stark}} = 3Fn^2$$  \hspace{1cm} (4)$$

while the energy difference between a state with a non-zero quantum defect and the $l>3$ states with quantum defect equal to zero is given by

$$\Delta E_{\text{quantum defect}} = \frac{2\mu_{\text{reduced}}}{n^3}$$  \hspace{1cm} (5)$$
where -0.5 < \mu_{\text{reduced}} \leq 0.5. Our measurements of the threshold electric field for l-mixing of the np series converging onto N^+ = 0 (\mu = 0.729), shown in Figure 6, indicate that the l-mixing lifetime enhancement mechanism sets in as soon as

$$\Delta E_{\text{Stark}} = 0.66 \times \Delta E_{\text{quantum defect}}$$

(6)

Applying this empirical criterion to the p-series and f-series converging on N^+ = 0 and N^+ = 1, yields a determination of the residual DC field of 25.1 ± 2.6 mV/cm. As shown in Table I, Equation 6 allows us to predict the principal quantum numbers where the electric field induced lifetime enhancement is expected to start under our experimental conditions. Reasonable agreement is observed between all calculated and experimental values (see Figures 4 and 10).

It is interesting to compare the criterion given in equation 6 to recent results obtained by Levine et.al. who carried out classical trajectory calculations for high molecular Rydberg states in weak DC electric fields. Levine et.al. concluded that a weak DC field leads to a reduction of the frequency of close encounters of the electron with the core (a 'stretching of the time axis') in agreement with Chupka's l-mixing mechanism, provided the changes in l due to the electric field are faster than the precession of the electron orbit, due to the non-Coulombic part of the electron-core interaction potential, or

$$3n^5 F > \mu_{\text{reduced}} l_0$$

(7)

where \(l_0\) is the largest value of the orbital angular momentum for which the electrons interact efficiently with the ionic core. For a choice of \(l_0 = 2\), equation 7, based on classical arguments related to the Keplerian motion of the electron, reduces to the criterion given in equation 6, based on our experimental results.
Once the composition of the Stark state has been determined using the criterium given in equation 6, our model assigns equal probabilities for the occurrence of any one of the angular momentum states. Near the onset of $l$-mixing the $l$-distribution of the Stark state is expected to be highly non-homogeneous, in violation of this assumption, however, at fields significantly beyond the $l$-mixing threshold this assumption should be reasonable\textsuperscript{4,32,36}. The total decay rate of the Stark state is thus given as the weighted average of the decay rates of the individual angular momentum components. The decay rates for the $p$- and $f$-components were determined from the low-$n$ portions of our lifetime measurements, in which these orbitals were not yet $l$-mixed, and fit according to

$$R_l(n) = R_0 l n^{-3}$$  \hspace{1cm} (8)

For convenience, for $l>3$ a small $l$-independent uniform decay rate was assumed, which was chosen to match the observed lifetime-enhancement for the $f$-series. The influence of $s$ and $d$ orbitals, which reportedly have low predissociation rates\textsuperscript{41}, was neglected. Likewise intermanifold couplings, which are anticipated for the highest principal quantum numbers, where the residual DC electric field is larger than the Inglis-Teller limit ($3F_\text{m}^5 = 1$), and which are expected to increase or decrease the calculated lifetimes by no more than a factor 2, were neglected.

The range of principal quantum numbers contributing to the pulsed field ionization signal was truncated at high-$n$ according to the adiabatic lowering of the ionization potential given in Equation 2. At low-$n$ the range of principal quantum numbers contributing to the pulsed field ionization signal was truncated according to the diabatic lowering of the ionization potential

$$\Delta \text{IP (cm}^{-1} \text{)} = 4.0 \sqrt{F (V / \text{cm})}$$  \hspace{1cm} (9)
In our calculations, the case was considered of a p- and f-orbital which simultaneously converge on the N\(^{+}=0\) ionic state. For Rydberg series converging on higher ionic rotational states the results should be very similar, except for the increased role of autoionization. In Figure 14 calculated lifetimes of NO p- and f-orbital Rydberg states are shown which contribute to the pulsed field ionization signal in the presence of a 25 mV/cm residual electric field. In agreement with our experimental data (Figures 4 and 9), the calculations show that the lifetime of the f-orbitals is enhanced by about one order of magnitude starting at n=65, due to l-mixing of the f-orbital with the near-degenerate l>3 orbitals. The l-mixing of the p-orbital does not set in until n=116, at which point the lifetime of the p-orbital goes up by nearly two orders of magnitude. Conversely, the lifetime of the f-orbital is reduced at this point by p-orbital mixing.

In Figure 15 calculated lifetimes of NO f-orbital Rydberg states are shown in the presence of a DC electric field of 3 V/cm, as in the experiments of Pratt\(^{13}\), and compared to the near field-free calculations of Figure 14. The lifetimes of the n=65-115 Rydberg states are reduced by about one order of magnitude due to the fact that at these electric field strengths the p-orbital is mixed in over the entire range of states that are pulsed field ionized. Furthermore, due to the lowering of the ionization potential by the DC electric field, all Rydberg states above n=101 are ionized adiabatically by the field, leading to a further limitation on the maximum observable lifetime. In Pratt's experiment the extraction pulse was 46 V/cm, which means that diabatic field-ionization was possible in his experiment down to n=64, at 27 cm\(^{-1}\) below the field-free ionization threshold. The calculation shown in Figure 15 was performed for an extraction pulse of 200 V/cm, meaning that diabatic field-ionization is possible down to n=44, at 56 cm\(^{-1}\) below the field-free ionization threshold. The calculations shown in Figure 15 indicate that for a DC electric field of 3 V/cm the p- and f-states are de-coupled below n=46.

The implications of the lifetime-lowering by the above described p/f mixing for the pulsed field ionization spectrum are profound. In Figure 16 the calculated pulsed field ionization spectrum is shown when the residual field is 25 mV/cm. The extraction pulse was again taken to be 200 V/cm. At an energy of 26 cm\(^{-1}\) below the field-free ionization threshold the first signal is observed, due to the fact that the onset of l-mixing increases the lifetime of the f-orbitals for
n>65. Below the threshold for mixing of the p-orbital with the higher angular momentum states the pulsed field ionization spectrum remains dominated by contributions from the f-orbital, while the p-orbitals predissociate too rapidly to contribute. Above the threshold for p-orbital mixing, the spectrum is dominated by contributions from the p-orbital, which has a larger oscillator strength and, in this regime, the same lifetime as the f-orbital.

As shown in Figure 17, upon application of a 3 V/cm DC electric field, the contribution from the lifetime enhanced f-orbitals is quenched, while the contribution from mixed p/f orbitals is reduced owing to the n⁴ lifetime dependence of the l-mixed Rydberg states, which are limited to principal quantum numbers smaller than n=102. As a consequence, at a time delay of 800 nsec, as in the experiment of Pratt, the pulsed field ionization signal becomes virtually negligible.

Returning to Figure 14, we can understand how the assumption that absorption into a p-orbital was responsible for the observed pulsed field ionization spectrum around n=75 led Pratt to the conclusion that both l- and m-mixing need to be invoked in order to explain the enhanced lifetimes of the ZEKE Rydberg states. Lifetimes on the curve corresponding to the l-mixed f-orbitals (curve II) are about 300 times higher than lifetimes on the curve corresponding to unmixed p-orbitals (curve III). However, as we have argued, the pulsed field ionization signal in this region is not due to excitation to a p-orbital, but to an f-orbital, and the lifetime-enhancement of these states over their field-free counterparts (curve I --> curve II) is only one order of magnitude, which can be explained through a mechanism where only the orbital angular momenta l are mixed.

While the conclusion is thus reached that the observations in Pratt's experiment can be explained without invoking a collision mechanism, mention needs to be made of the fact that under the experimental conditions existing in his experiment, it is very likely that collisions did actually play a role. In Pratt's experiments, the NO was admitted into the vacuum chamber using a pulsed valve with a 0.25 mm diameter nozzle, operated with a stagnation pressure of 500-700 Torr of neat NO, and the lasers were tightly focussed (φ = 10 μm) at a distance 19 mm downstream from the nozzle. While the laser powers used in the experiment are not reported in ref. 13, it seems likely that under these conditions the density of NO Rydberg molecules and ions...
would be at least as high as in the collisional stabilization experiments, reported in part c) of our Results section. Consequently, our interpretation of Pratt's results is that the electric field effects in Pratt's experiment most likely reflect the dependence of the collisional stabilization on the lifetime of the optically prepared Rydberg state. In our own experiments on collisional stabilization of NO Rydberg states, as well as in our studies of autoionization of Xe\textsuperscript{15}, we readily observed the same phenomenon.

b) Implications for other ZEKE experiments

The experiments reported in this paper have important implications for ZEKE experiments, since, as we will argue, ZEKE experiments are typically carried out under conditions where one may anticipate that the Rydberg states that are relevant for the experiment are \(l\)-mixed by the DC electric field which exists at the time of the laser excitation. In a typical ZEKE experiment, this field is about 20-50 mV/cm. Given the fact that \(\mu_{\text{reduced}} \leq 0.5\), the onset for \(l\)-mixing is anticipated starting at \(n=128-154\), using the empirical criterium of Equation 6. In a high-resolution ZEKE-PES experiment the magnitude of the extraction pulse is approximately 1 V/cm, meaning that Rydberg states within 4-6.1 cm\(^{-1}\) of the ionization threshold will contribute to the ZEKE signal, depending on whether the ionization mechanism is diabatic or adiabatic. This energy range corresponds to principal quantum numbers \(n \geq 134-165\). This leads to the conclusion that under typical ZEKE-PES conditions the Rydberg states which are ionized lie beyond the onset for \(l\)-mixing by the residual DC electric field. The Rydberg states which give rise to the ZEKE signal therefore are Stark states, which decay at a rate, which is given as the weighted average of the decay rates of all angular momentum components \(l = 0...n-1\). The validity of this conclusion is expected to be quite general.

The conclusion reached above provides an insight into the requirements that may need to be met in a successful ZEKE experiment. If, for the molecule of interest, sufficient data are available on the decay dynamics and, in particular, decay rates of low-\(l\) Rydberg states, it is possible to estimate the lifetimes of the ZEKE Rydberg states in the presence of the small DC
electric field which exists in the experiment. It will be possible to assess whether the lifetime is long enough for pulsed field ionization detection, or, whether the lifetime needs to be enhanced further by working at relatively high pressures, in which case a further collisional stabilization of the Rydberg molecule can be achieved. It is important to note that our experiment suggests that quite significant n-mixing may occur under these conditions, which may affect the resolution of the experiment. In our work on the pulsed field ionization of Xe (this issue) a situation was encountered where the electric field enhanced lifetimes were still too short to allow for direct detection of the optically excited Rydberg atoms, and where a pulsed field ionization signal could only be observed if the atom was allowed to undergo a collisional stabilization.

It is interesting to consider a number of observations in reported ZEKE-experiments in light of the conclusion reached above about the influence of DC electric fields. As an example we will consider the ZEKE-experiments of Tonkyn and White on the H₂O and H₂S molecules, using one photon vuv-excitation. While the MQDT treatment of Child and Jungen predicted a propensity towards c-type transitions in this experiment, Tonkyn and White saw not only c-type transitions, but a-type transitions as well. Their experiment prompted theoretical work by Child and McKoy, who offered similar explanations for the observed transitions, namely that in a collision of the electron with the ionic core a torque is exerted on the electron orbital, which in this particular case couples the optically allowed d-series to near-degenerate np-orbitals converging on rotational states of the ion conforming to a-type selection rules. Both Child's model and McKoy's model explain the observed transitions in terms of properties which are intrinsic to the isolated H₂O molecule. Our experiments suggest that the experiments were almost certainly carried out, however, in a regime where the existing DC electric field would provide a dipole-coupling mechanism between the d- and p-orbital as well.
Acknowledgements

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Table I: Determination of residual DC electric field

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References

26) See, for example, D.C. Jacobs, R.J. Madix and R.N. Zare, J. Chem. Phys. 85, 5469 (1986).
31) No attempt was made to determine precise excitation energies from the ground electronic state to the Rydberg states. Precise transition frequencies from the A$^1\Sigma^+$ state to the Rydberg states are available from the authors on request.
35) While the residual DC stray electric field are not exactly known, Pratt reports in ref. 13 that the shifts of the ionization thresholds in his experiments are of the same order of magnitude as the shifts observed by Reiser et.al31.
36) Theoretical work is currently under way to model the l-composition of the excited Rydberg states realistically, using methods similar to ref. 32.
Figure captions

Figure 1: Delayed pulsed field ionization measurement for the 50f Rydberg orbital converging on N^+ = 2, excited using the A^1Σ^+(N_A = 0, J_A = 1/2) intermediate state. The solid line is the result of a non-linear least squares fit for all points at pulsed field delay times > 5 nsec.

Figure 2: Portion of the NO pulsed field ionization spectrum from the A^1Σ^+(N_A = 0, J_A = 1/2) intermediate state. The two progressions in the spectrum are a p-series (μ = 0.7286, peaks indicated by dashed lines) converging on N^+ = 0 and an f-series (μ = 0.1010, peaks indicated by solid lines) converging onto N^+ = 2. The field-free N^+ = 0 ionization threshold lies at 30522.443 cm\(^{-1}\). All spectral features are below the adiabatically lowered ionization threshold.

Figure 3: Pulsed field ionization signal for the 51f orbital converging on N^+ = 2 at a fixed time delay of 50 nsec between the laser excitation and the pulsed field ionization, as a function of the experimentally applied DC electric field. The minimum in the curve corresponds to a minimum in the DC electric field in the apparatus, with a residual electric field determined at 25.1 ± 2.6 mV/cm.

Figure 4: Lifetimes of Rydberg series excited from the A^1Σ^+(N_A = 0, J_A = 1/2) intermediate state, determined using delayed pulsed field ionization. The upper panel shows lifetimes for an f-series converging on N^+ = 2, and the lower panel shows lifetimes for a p-series converging on N^+ = 0. Open circles represent measurements in the minimum DC electric field condition (25 mV/cm), whereas filled circles represent measurements where appropriate DC electric fields are applied to observe an
enhancement of the lifetime. See text for details. (Reproduced with permission from ref. 14).

Figure 5

Measured lifetimes for the 51f Rydberg state converging on N⁺=2 excited from the A¹Σ⁺(N_A=0,J_A=1/2) intermediate state, as a function of the applied DC electric field (reproduced with permission from ref. 14).

Figure 6

Critical electric field strengths for inducing lifetime enhancement of the p-series converging on N⁺=0, determined as the electric field strength for which the signal, at a time delay of 50 nsec between the laser excitation and the onset of the high voltage pulse, shows a sudden enhancement. Each point is the result of three independent measurements. Experimental standard deviations (~ 3 mV/cm) are smaller than the size of the points. The line represents the results of a non-linear least squares fit F (V/cm) = (6.0 ± 3.2) x 10⁷ V/cm (reproduced with permission from ref. 14).

Figure 7

Pulsed field ionization spectra showing excitation of the 51f orbital converging on N⁺=2, using the A¹Σ⁺(N_A=0,J_A=1/2) intermediate state. The externally applied electric fields strengths in these scans were a) 0.0 V (minimum field condition ~ 25 mV/cm), b) 42 mV/cm, c) 76 mV/cm, d) 110 mV/cm, e) 126 mV/cm and f) 237 mV/cm.

Figure 8

Pulsed field ionization spectra in the vicinity of the 71p-73p orbitals converging on N⁺=0, using the A¹Σ⁺(N_A=0,J_A=1/2) intermediate state. The time delay between the laser excitation and the onset of the pulsed electric field was 10 nsec. The applied electric fields strengths in these scans were a) 0.0 V (minimum field condition ~ 25 mV/cm), b) 136 mV/cm, c) 305 mV/cm, d) 373 mV/cm, e) 577 mV/cm and f) 7 V/cm.
Figure 9  Lifetimes of Rydberg series excited from the $A^1\Sigma^+(N_A=1,J_A=3/2)$ intermediate state, determined using delayed pulsed field ionization. The upper and lower panel show lifetimes for an f-series and a p-series converging on $N^*=1$. Open circles represent measurements in the minimum DC electric field condition (25 mV/cm), whereas filled circles represent measurements where appropriate DC electric fields are applied to observe an enhancement of the lifetime (see text for details).

Figure 10  Portion of the NO pulsed field ionization spectrum from the $A^1\Sigma^+(N_A=1,J_A=3/2)$ intermediate state. The spectrum shows a p-series ($\mu=0.7038$) and an f-series ($\mu=0.0168$) converging onto $N^*=1$, as well as members of an f-series ($\mu=0.021$) converging on $N^*=3$. The field-free $N^*=0$ ionization threshold lies at 30522.443 cm$^{-1}$. All spectral features are below the adiabatically lowered ionization threshold. In a) the high voltage is turned on during the laser pulse, whereas in b) the onset of the high voltage pulse comes approximately 10 nsec after the laser pulse.

Figure 11  Delayed pulsed field ionization measurements for the 42f Rydberg orbital converging on $N^*=3$, excited using the $A^1\Sigma^+(N_A=1,J_A=3/2)$ intermediate state, obtained without DC electric field induced lifetime enhancement, and at low laser powers. The solid dots represent a measurement at an NO pressure of $2*10^{-6}$ Torr, which has been multiplied *20, for comparison with the open circles, which represent a measurement at an NO pressure of $4*10^{-5}$ Torr.

Figure 12  Delayed pulsed field ionization measurements for the 42f Rydberg orbital converging on $N^*=3$, excited using the $A^1\Sigma^+(N_A=1,J_A=3/2)$ intermediate state, obtained with DC electric field induced lifetime enhancement, and at high laser
powers. The solid dots represent a measurement at an NO pressure of $2 \times 10^6$ Torr, which has been multiplied *20, for comparison with the open circles, which represent a measurement at an NO pressure of $4 \times 10^5$ Torr.

**Figure 13** Measured decaytimes for quadratically pressure-dependent NO Rydberg molecules, prepared by excitation to an f-series converging on $N^+=1$, excited using the $A^1\Sigma^+(N_A=0,J_A=1/2)$ intermediate state. The decaytimes were determined by fitting pulsed field ionization time delay measurements starting at a delay of 250 nsec with respect to the laser excitation, under conditions of electric field induced lifetime enhancement.

**Figure 14** Predicted lifetimes for an f-series ($\mu_{\text{reduced}}=0.017$, dotted line) and a p-series ($\mu_{\text{reduced}}=0.271$, dash-dotted line) converging on $N^+=0$, as a function of the principal quantum number, under the minimum field condition (25 mV/cm). Curves I and III correspond to un-mixed f- and p-orbitals, curve II corresponds to mixing of the f-orbital to $l>3$ orbitals, and curve IV corresponds to complete mixing of all orbitals. In order to obtain agreement with the experimental data, the ratio of the predissociation rates for the p-, f- and $l>3$ components were chosen as $1 : 0.024 : 0.0045$.

**Figure 15** Comparison of the predicted lifetimes for an f-series converging on $N^+=0$, as a function of the principal quantum number, for DC electric field strengths of 25 mV/cm (dotted line) and 3 V/cm (dash-dotted line). The Roman numbers follow the same definition as in Figure 14.

**Figure 16** Calculated ZEKE spectrum (dashed line) for an f-series and a p-series converging on $N^+=0$, for a DC electric field strength of 25 mV/cm. The individual contributions due to excitation to an f-orbital and a p-orbital are shown as a dash-
dotted line and a dotted line, respectively. The ratio of the oscillator strengths for p- and f-orbital excitation is taken as 5:1.

Figure 17  Calculated ZEKE spectrum for an f-series and a p-series converging on N* = 0, for a DC electric field strength of a) 25 mV/cm and b) 3 V/cm.
FIGURE 4

(a) Lifetime (nanoseconds) vs. Principal quantum number

(b) Lifetime (nanoseconds) vs. Principal quantum number with annotations '92p' and '95p'
Figure 5

The graph shows the relationship between DC Voltage (V/cm) and Lifetime (nanoseconds). The data points indicate a trend where the Lifetime increases with increasing DC Voltage.
FIGURE 6

Critical Mixing Voltage (V/cm)

Principal quantum number
FIGURE 9

(a) and (b) show plots of lifetime versus principal quantum number. The data points are represented with error bars, indicating the variability in the measurements. The lifetime is measured in nanoseconds, with the y-axis on a logarithmic scale.
FIGURE 11

Intensity (a.u.)

Pulsed field delay (nanoseconds)
FIGURE 14

Principal quantum number vs. Lifetime (nanoseconds)
FIGURE 15

Principal quantum number

Lifetime (nanoseconds)
FIGURE 16

ZEKE Intensity (a.u.)

Rydberg energy (cm$^{-1}$)
Figure 17

ZEKE Intensity (a.u.)

Rydberg energy (cm\(^{-1}\))

-30 -25 -20 -15 -10 0

0.0 0.2 0.4 0.6 0.8 1.0 1.2

a)

(*20)

b)

ZA0