

## Enhancements in the lifetimes of NO Rydberg states in dc electric fields: Implications for zero-electron-kinetic-energy photoelectron spectroscopy experiments

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Lifetimes of NO  $p$ - and  $f$ -orbital Rydberg states ( $n=40-122$ ) have been measured under near field-free conditions as well as in the presence of small dc electric fields. The field causes an increase in the observed lifetimes, which is attributed to Stark mixing of the predissociative  $p$  and  $f$  orbitals with high- $l$  orbital angular momentum states. The results indicate that under the conditions existing in high-resolution zero-electron-kinetic-energy (ZEKE) photoelectron spectroscopy experiments, the ZEKE Rydberg states are  $l$  mixed.

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The technique of zero-electron-kinetic-energy photoelectron spectroscopy (ZEKE-PES) has in recent years become a powerful tool for studying the spectroscopy of molecular ions [1]. In this technique, neutral molecules are excited to high principle-quantum-number Rydberg states (typically  $n \approx 200$ ), and the electrons are collected that are created as a result of the application of a small pulsed electric field (typically 1 V/cm), which is turned on some time after the Rydberg excitation (typically 1  $\mu$ sec). With the ZEKE technique spectra at near laser-limited resolution can be obtained.

The success of the ZEKE technique is remarkable, considering that, for many systems where the technique has successfully been applied, the Rydberg states involved were expected to be short-lived. For example, in the ZEKE experiments on NO by Reiser *et al.* [2], the lifetimes of the  $n \approx 200$   $p$ -orbital Rydberg states were expected to be approximately 100 nsec, whereas experimentally no significant loss in ZEKE signal was observed when the pulsed field ionization was delayed by 1.2  $\mu$ sec.

In a recent paper [3] Chupka proposed that the enhanced lifetimes might be due to  $l$  mixing by the small residual dc electric fields that exist in most experiments, or by  $l$ - and  $m$ -changing collisions, most likely with surrounding ions. In the case of NO, the lifetime of the Rydberg states is limited by the predissociation rate, which strongly depends on the orbital angular momentum of the Rydberg electron. The predissociation rate is particularly fast for  $l=1$ ; is significantly slower for  $l=0, 2$ , and 3; and can be virtually ignored for higher-angular-momentum states.

The presence of laboratory 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 [4]. The  $|nkm\rangle$  Stark states can be expressed as superpositions of  $|nlm\rangle$  states.

The decay dynamics of Rydberg states are determined by collision processes of the Rydberg electron with the ionic

core. Near the ionic core, the potential experienced by the electron is dominated by the Coulomb attraction of the ionic core, and in this region the orbital angular momentum is defined. The real-time decay dynamics of Rydberg states in electric fields thus follows from the  $l$  distribution in the Stark levels.

An elegant experiment illustrating this feature was performed by ten Wolde *et al.* [5]. In a picosecond pump-probe experiment, rubidium Rydberg states were excited in the presence of dc electric fields, and the ionization yield was measured as a function of the delay of the ionization laser. The results show quantum beats, illustrating that, following the creation of an electron wave packet with initial condition  $l=2$ , the orbital angular momentum distribution undergoes regular oscillations, spreading out to higher  $l$  and returning to the initial low- $l$  condition at regular intervals. Chupka proposed that in the ZEKE of NO the predissociative  $l=1$  contribution to the Rydberg state could be diluted through similar electric-field-induced  $l$  mixing [3], or through  $l$ - and  $m$ -changing collisions.

A number of authors have attempted to address the relative importance of the two mechanisms proposed by Chupka, through measurements of ZEKE spectra, in the presence of or without an additional dc electric field. Pratt studied pulsed field ionization of NO [6], and observed a significant reduction of the ZEKE signal upon application of a  $\sim 3$ -V/cm dc electric field. He concluded that both  $l$  and  $m$  mixing needed to be invoked to explain the long lifetimes under field-free conditions, lending support to Chupka's collision mechanism. A similar conclusion was reached by Merkt for pulsed field ionization of Ar [7].

In this Rapid Communication the first results of a study are presented in which lifetime measurements have been performed for individual spectrally resolved high- $n$  Rydberg states of NO. The Rydberg states were populated by excitation with a near-transform-limited pulsed laser, and lifetimes under "field-free" conditions, as well as in the presence of small additional dc electric fields, were determined by measuring the  $\text{NO}^+$  obtained from pulsed field ionization, as a function of the time delay between the switching of the pulsed electric field and the laser excitation. Our results

show pronounced lifetime enhancements in the presence of small dc electric fields, in agreement with the electric-field-induced  $l$ -mixing mechanism proposed by Chupka, and lead to a reinterpretation of the experiment by Pratt [6].

The NO Rydberg states were populated using two-color laser excitation, employing the  $A^1\Sigma^+$  state as resonant intermediate. The 226-nm light required to pump selected  $A-X(0,0)P_1-$  transitions was obtained by Raman shifting the third harmonic of a pulsed amplified Coherent 699-29 ring laser [8], operated around 621 nm. The laser used to excite the NO from the  $A$  state to the Rydberg states, was the doubled output of a pulsed-amplified Coherent 699-29 ring laser, operated near 656 nm. The bandwidths of the 226- and 328-nm lasers were 0.06 and 0.007  $\text{cm}^{-1}$ , respectively. Both lasers were attenuated using appropriate neutral density filters.

The two lasers crossed a pulsed molecular beam of NO at the center of a Wiley-McLaren time-of-flight mass spectrometer. The size of the interaction region was determined by the 226-nm laser, which was focused to a 2-mm spot. At a variable time delay, a +1.7-kV pulse with a 5-nsec rise time was applied to the ion optics. This pulse was used to ionize the NO Rydberg molecules as well as accelerate the  $\text{NO}^+$  into an approximately 30-cm-long time-of-flight tube, leading to a Daly-type scintillation detector.

The NO pulsed field ionization spectra using the  $A^1\Sigma^+(N_A=0, j_A=\frac{1}{2})$  intermediate state show two dominant Rydberg progressions, namely a series with a quantum defect of 0.7286 converging on  $N^+=0$  ( $E_0=30\,522.443\text{ cm}^{-1}$ ), assigned as a  $p$  series, and a series with a quantum defect of 0.0101 converging on  $N^+=2$  ( $E_0=30\,534.349\text{ cm}^{-1}$ ), assigned as an  $f$  series. Lifetimes for the  $p$  series were determined for  $n=50$ –122, while lifetimes for the  $f$  series were determined for  $n=40$ –91. The results of these measurements are shown in Fig. 1. Two sets of data are shown, namely lifetimes determined with the minimum residual dc electric field achievable in our setup (open circles) and lifetimes that were determined when additional dc electric fields were applied (filled circles). In the minimum field measurements, both the  $p$  series and the  $f$  series show a sudden increase in the lifetime, starting at  $n=116$  for the  $p$  series and at  $n=65$  for the  $f$  series. This lifetime increase is attributed to  $l$  mixing by the residual dc electric field in our experiment. For the  $f$  series the lifetime enhancement is modest, owing to the fact that the  $l=3$  predissociation rate is relatively slow already, whereas for the  $p$  series an approximately  $n$ -fold increase is observed.

The lifetimes of  $p$ - and  $f$ -series Rydberg states that are not yet mixed by the residual dc electric field can readily be increased by the application of a small additional field. The magnitude of the electric fields required to induce the lifetime enhancement was determined by monitoring the amount of  $\text{NO}^+$  signal detected at a fixed 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 enhanced lifetimes shown in Fig. 1 were measured at electric fields that were about 20% above this critical value.

The lifetime enhancement around the critical electric-field strength is shown in more detail in Fig. 2 for excitation to the

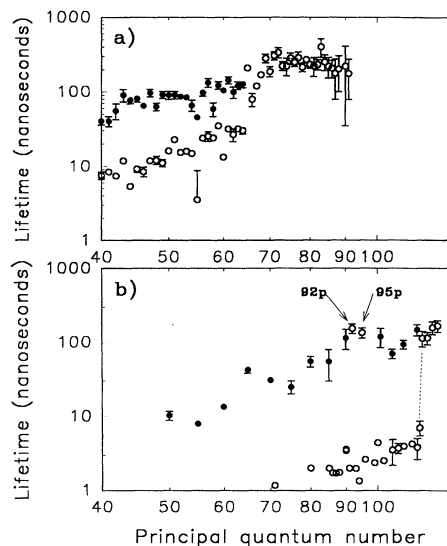


FIG. 1. Lifetimes of NO Rydberg series excited from the  $A^1\Sigma^+(N_A=0, j_A=\frac{1}{2})$  intermediate state, determined using delayed pulsed field ionization. The upper panel shows lifetimes for an  $f$  series converging on  $N^+=2$ , and the lower panel shows lifetimes for a  $p$  series converging on  $N^+=0$ . Open circles represent measurements with 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 lifetimes (see text for details). The enhanced field-free 92 $p$  and 95 $p$  lifetimes are due to mixing with high- $l$  angular momentum states converging on  $N^+=1$  [9].

51 $f$  orbital. This figure shows that the lifetime of the 51 $f$  orbital is constant at its near field-free value until the dc electric field is 70 mV/cm, at which point a sudden fivefold increase is observed. A modest subsequent increase of the voltage does not lead to a further increase in the lifetime.

Precise measurements of the required field strengths for inducing the lifetime enhancement were performed for selected members of the  $p$  series and are shown in Fig. 3. The data are well represented by a fit to an  $F \propto n^{-5}$  dependence, which is also shown in Fig. 3.

The lifetime enhancements shown in Fig. 1 and the measured required electric-field strengths for the  $p$  series shown in Fig. 3 are consistent with a model in which the optical

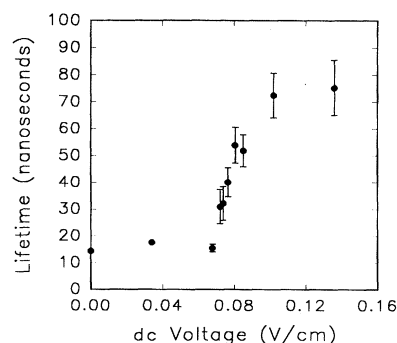


FIG. 2. Measured lifetimes for the 51 $f$  Rydberg state converging on  $N^+=2$ , as a function of the applied dc electric field.

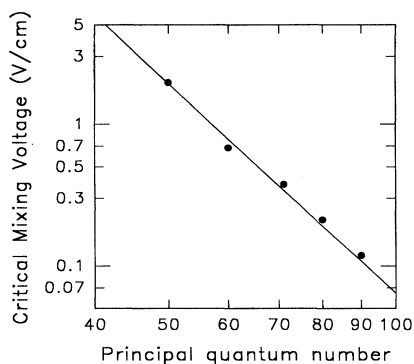


FIG. 3. Critical electric-field strengths for inducing lifetime enhancements for the  $p$  series converging on  $N^+ = 0$ . The line represents the result of a nonlinear least-squares fit  $F$  (V/cm) =  $(6.0 \times 10^8 \pm 3.2 \times 10^7)n^{-5}$ .

excitation leads to the formation of a coherent superposition of  $l$  states, which, depending on the principal quantum number  $n$ , the electric field  $F$ , and the quantum defects  $\mu$ , is confined to those angular momenta whose energy levels lie within the range of the Stark manifold. The width of the Stark manifold is equal to

$$\Delta E_{\text{Stark}} = 3Fn^2, \quad (1)$$

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

$$\Delta E_{\text{quantum defect}} = \frac{2\mu_{\text{reduced}}}{n^3}, \quad (2)$$

where  $-0.5 < \mu_{\text{reduced}} \leq 0.5$ . Our measurements of the threshold for  $l$  mixing of the  $np$  series converging onto  $N^+ = 0$  ( $\mu = 0.7286$ ), shown in Fig. 3, indicate that the  $l$ -mixing mechanism sets in as soon as

$$\Delta E_{\text{Stark}} \geq 0.65 \Delta E_{\text{quantum defect}}. \quad (3)$$

Applying this criterion to the  $p$  series and  $f$  series converging on  $N^+ = 0$  and  $N^+ = 2$ , as well as similar measurements using different  $A$ -state intermediates [9], yields a determination of the residual dc field in our apparatus of  $25.1 \pm 2.6$  mV/cm, and a prediction for the onset of the lifetime enhancement for the  $p$  series and the  $f$  series at  $n = 119$  and 62, respectively, in very reasonable agreement with the experiment.

The observed lifetime enhancements for the  $p$  and  $f$  series can be understood assuming an equal probability for the occurrence of any one of the angular momentum states that contribute to the Stark state. The predissociation rate is dominated by the  $l = 1$  component and consequently the lifetimes of the  $p$  orbitals go up by nearly a factor  $n$  upon mixing with the higher-angular-momentum states. For the

orbital the predissociation rate is slower, and consequently the increase is modest. While the lifetimes of the  $l$ -mixed  $p$  series can be fit to an  $n^{4.17+/-0.25}$  dependence, the lifetimes of the  $l$ -mixed  $f$  series show saturation, which is attributed to mixing with  $l = 0-2$ .

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, spectroscopically it is possible to identify peak positions that conform to the quantum defects of either the  $p$  orbital or the  $f$  orbital [9].

Our observations have important implications for ZEKE experiments. In a typical ZEKE experiment, the residual electric field at the time of the laser excitation is about 20–50 mV/cm. Given that  $|\mu_{\text{reduced}}| \leq 0.5$ , the criterion given in Eq. (3) predicts that the Rydberg states can be considered fully  $l$  mixed starting at  $n = 117-141$ . In a high-resolution ZEKE-PES experiment the magnitude of the extraction pulse is approximately 1 V/cm, which means that Rydberg states within  $4-6.1 \text{ cm}^{-1}$  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  $n \geq 134-165$ , and leads to the important conclusion that under typical ZEKE-PES conditions the Rydberg states are Stark states with a decay rate given as the approximately evenly weighted average of the decay rates of all angular momentum components  $l = 0, \dots, n-1$ .

In his experiment, Pratt attributed the long lifetimes of the NO Rydberg states to  $l$ - and  $m$ -changing collisions. This conclusion was based on the fact that near  $n = 75$  the lifetime of the  $p$  orbital, thought to be responsible for the ZEKE signal, appeared to be lengthened from its anticipated field-free value by a factor of 200–400. Our experiments indicate that, under the “field-free” conditions in Pratt’s experiment, the  $f$  states near  $n = 75$  are  $l$  mixed, whereas the rapidly predissociating  $p$  states are not. Therefore the observed field-free ZEKE signal is due to absorption to an  $f$  orbital, and the reduction of the ZEKE signal upon application of a 3-V/cm dc electric field is due to a reduction of the lifetime of these  $l$ -mixed  $f$  complexes, through mixing with the strongly predissociative  $p$  orbital.

Under the conditions existing in the experiments reported in this Rapid Communication, no collisional effects were observed. In subsequent experiments, to be reported in detail later [9], evidence has been observed for a further collisional stabilization of the NO Rydberg molecules. In this case the electric-field-enhanced lifetimes increase the time available for the collisional stabilization process.

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- [1] K. Müller-Dethlefs and E. W. Schlag, *Annu. Rev. Phys. Chem.* **42**, 109 (1991).
- [2] G. Reiser, W. Habenicht, K. Müller-Dethlefs, and E. W. Schlag, *Chem. Phys. Lett.* **152**, 119 (1988).
- [3] W. A. Chupka, *J. Chem. Phys.* **98**, 4520 (1993).
- [4] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957).
- [5] A. ten Wolde, L. D. Noordam, A. Lagendijk, and H. V. van Linden van den Heuvel, *Phys. Rev. A* **40**, 485 (1989).
- [6] S. T. Pratt, *J. Chem. Phys.* **98**, 9241 (1993).
- [7] F. Merkt, *J. Chem. Phys.* **100**, 2623 (1994).
- [8] E. Cromwell, T. Trickl, A. H. Kung, and Y. T. Lee, *Rev. Sci. Instrum.* **60**, 2888 (1989).
- [9] M. J. J. Vrakking and Y. T. Lee (unpublished).