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Lifetimes of Rydberg states in PFI–ZEKE experiments

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A brief discussion is presented on the alteration of lifetimes of high- n Rydberg states due to external perturbations by DC electric fields and surrounding ions and (short-range) intramolecular couplings. It is emphasized that the lifetime dynamics of molecular Rydberg states can be rationalized in terms of a finite number of universal physical principles, which may, however, lead to different behaviour depending on the molecule under consideration.

In light of the discussion which has developed in this volume concerning the lifetimes of high- n Rydberg states in ZEKE experiments, I would like to present a few results of experiments which we performed in the group of Yuan Lee at UC Berkeley, concerning the effect of DC electric fields and ion densities on the lifetimes of high- n Rydberg states of the NO molecule and the Xe atom (Vrakking & Lee 1995*a, b, c*), as well as state my general view regarding the issue of Rydberg lifetimes in ZEKE experiments. In the experiments in Berkeley we excited *individual* high- n Rydberg states using two-colour double resonance excitation by a near transform-limited ($\Delta\omega = 0.003 \text{ cm}^{-1}$) pulsed dye laser. Lifetimes of the Rydberg states were determined by measuring the NO^+ pulsed-field ionization (PFI) signal, or, in the case of Xe, the PFI electron signal, as a function of the pulsed-field time delay. With this technique, lifetimes of NO Rydberg states greater than or equal to 3 ns and lifetimes of Xe Rydberg states greater than or equal to 10 ns could be determined.

In figure 1 results of the lifetime measurements of predissociating Rydberg states of the NO molecule are shown. When no external electric fields were applied (open circles), i.e. under a condition of stray fields only (characterized to be approximately 25 mV cm^{-1}), f-orbital Rydberg series converging on $N^+ = 2$ showed an eight-fold lifetime enhancement near $n = 65$, whereas p-orbital Rydberg series converging on $N^+ = 0$ showed an extremely sharp lifetime enhancement of nearly two orders of magnitude near $n = 115$. Thus a discontinuity in the lifetime was observed, similar to the results of Professor Even (this volume) in his experiments on DABCO and BBC. Our experiments in Berkeley were motivated by the ideas of Chupka, who had suggested that l -mixing by DC electric fields and l, m -mixing through the presence of ions might be responsible for the observed lifetime enhancements in ZEKE (Chupka 1993). Indeed, in the NO experiments shown in figure 1, the lifetime enhancement is due to a DC electric field effect. For the f-series below $n = 65$, and the p-series

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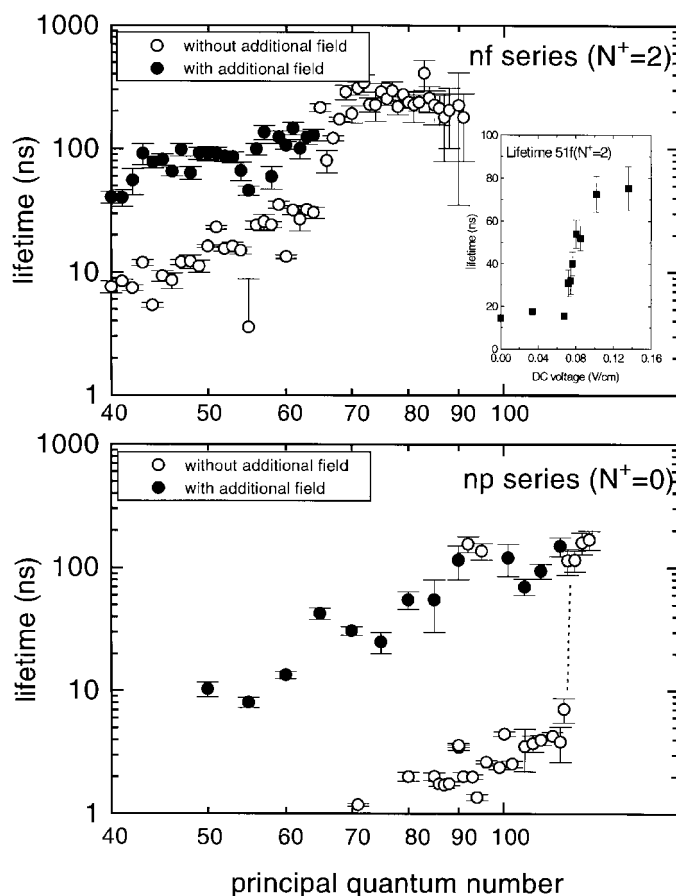


Figure 1. Lifetime of NO $f(N^+ = 2)$ and $p(N^+ = 0)$ Rydberg states as a function of principal quantum number under conditions of stray fields only (open circles) and with the application of appropriate electric fields to induce lifetime enhancement (closed circles). Inset: lifetime of the NO 51f ($N^+ = 2$) Rydberg state as a function of the applied DC electric field at the time of excitation. See text and Vrakking & Lee (1995a, b) for details.

below $n = 115$, the lifetimes of the Rydberg states could be enhanced by applying an appropriate additional electric field (solid circles in figure 1). A detailed example is shown in the inset of figure 1, where the lifetime of the NO 51f ($N^+ = 2$) Rydberg state is shown as a function of the externally applied DC field.

One of the remarkable features of the lifetime enhancements observed for NO was the sharpness in the transition from 'short' to 'long' lifetimes: in figure 1 the p ($N^+ = 0$) series undergoes a twenty-fold lifetime increase when going from $n = 115$ to $n = 116$. In Vrakking (1997) I develop a theory to explain the lifetime enhancement of the NO Rydberg states. This theory is based on a translation of MQDT results by Jungen and Gauyacq (and their co-workers) into matrix form, using a Hund's case (d) basis set, and subsequent introduction of Stark matrix elements. Our calculations, which emphasize the importance of short range interactions, complement recent work by Bixon and Jortner, who used an effective Hamiltonian approach, and considered Stark and long range interactions, concluding that the latter interactions were negligible. They quantitatively reproduced the lifetime enhancements of the f-series, while obtaining qualitative agreements for the p-series. In our new work we

successfully reproduce the sharp onset for the p-series, by considering, in particular, the multi-exponential nature of the decay of the Rydberg states excited in the experiments.

In Berkeley we also carried out experiments which demonstrated the possibility of lifetime alterations due to the presence of ions. In figure 2 a PFI signal is shown which was obtained by exciting Xe atoms to high- n autoionizing Rydberg states converging on the upper spin-orbit state of the ion, similar to the Ar experiments which Even discusses in his paper. Using a measurement procedure where autoionization and pulsed field ionization could be separated (by means of position-sensitive detection), results were obtained which show that while the autoionization signal is linear in the Xe pressure (as expected), the PFI signal has a near-quadratic dependence on the Xe pressure. Further experiments supported the conclusion that the quadratic pressure dependence is due to the fact that the Xe Rydberg states undergo a lifetime enhancement by interactions with surrounding ions. In fact, we were unable to detect *any* PFI signal that did not have the signature of a quadratic pressure dependence. Similar ion-induced lifetime enhancements have now been reported by several other researchers, including Merkt, Hepburn and Schlag.

Much has been said in the previous papers about whether DC electric fields and surrounding ions are: (i) of importance for the very high- n ($n \approx 200$) Rydberg states which are detected in ZEKE; and (ii) whether these effects make the lifetime go up or down. The Xe experiments discussed above illustrate that the observed lifetime behaviour of a Rydberg state is determined by an *interplay* between: (i) the properties of the atom/molecule; and (ii) the possible presence of DC fields and/or surrounding ions. In the inset of figure 2 the Xe PFI signal (for $n^* = 60$) is shown as a function of the applied DC field. For the s' -series ($\mu_{\text{reduced}} \approx 0.01$) it is observed that application of a DC electric field initially increases the signal. Here, mediated by $ns'[\frac{1}{2}]_1/nd'[\frac{1}{2}]_1$ core mixing, the s' -series is Stark-mixed with the nearby high- l manifold (Vracking 1997). However, when the field is further increased the lifetime is reduced again, since a rapidly decaying d' -orbital Rydberg series is mixed in. So depending on the experiment which we do, the application of an electric field can lead to a reduction or an increase in the Rydberg lifetime. Importantly though, the underlying physics is the same in both cases.

I think it is important that we realize that with the same underlying physics, different atoms and molecules may respond differently, and that for a single atom/molecule it is possible that angular momentum mixing induced by the presence of DC fields and/or ions may increase or decrease the lifetime of the Rydberg states, depending on the strength of the field or the ion density. However, if enough information is available about both the perturbation-free spectroscopy and decay dynamics of the Rydberg states and the experimental conditions, the lifetime enhancements/decreases can be rationalized in terms of a finite number of physical principles. This implies that we need to take a practical attitude towards the question of the necessity of angular momentum mixing in ZEKE experiments. If the lifetime of an $n \approx 200$ Rydberg state is intrinsically in the μs range, as discussed by Müller-Dethlefs in relation to a number of his experiments, then DC fields and/or surrounding ions may not be necessary. In fact, as illustrated by Merkt, they may be detrimental to the resolution of a ZEKE experiment. On the other hand, if the lifetime of the $n \approx 200$ Rydberg states is in the low ns range (as in the case of Xe autoionization) then we may be able to use DC fields and/or surrounding ions to our advantage. To illustrate this, I would like to mention vibrational wavepacket experiments on the I_2 molecule which

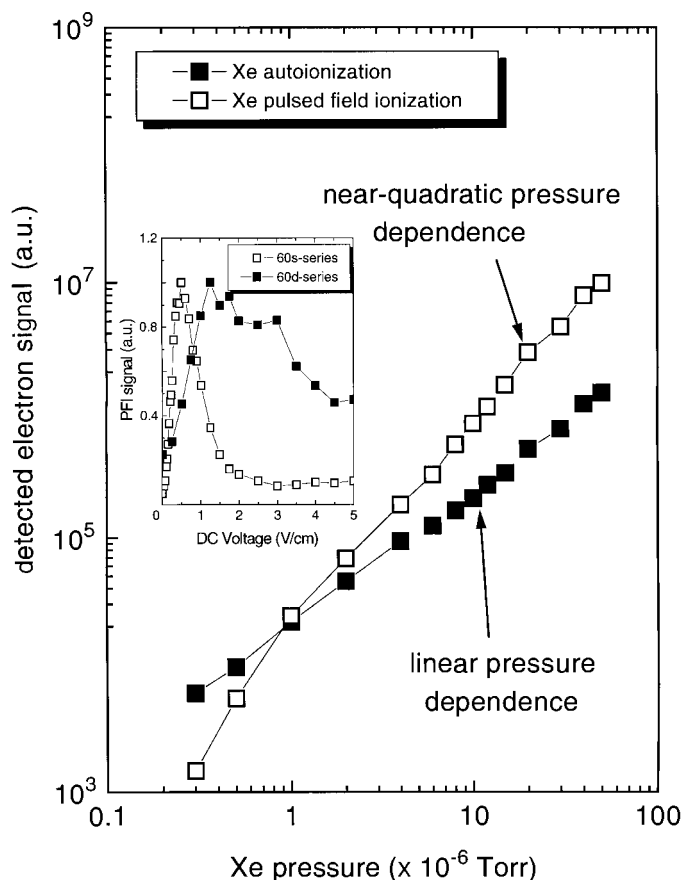


Figure 2. Dependence of Xe autoionization signal (closed blocks) and Xe PFI signal (open blocks) on the Xe pressure. Inset: dependence of the PFI signal via excitation to the $60s'$ orbital (open blocks) and the $60d'$ orbital (closed blocks), on the applied DC electric field at the time of excitation (measured at a delay of 80 ns). See text and Vrakking & Lee (1995c) for details.

we carried out using ZEKE detection at the National Research Council in Ottawa (Vrakking *et al.* 1995). By means of introduction of ions prior to the femtosecond pump-probe experiment (produced by non-resonant multi-photon ionization with a picosecond Nd:YAG laser), we were able to 'amplify' our pump-probe ZEKE signals about six-fold.

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