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Lifetimes of Rydberg States in ZEKE Experiments II: Electric Field Induced and Collisional Enhancement of Xe Autoionization Lifetimes

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Abstract

Lifetime measurements are reported for high principal quantum number (n=43-87) autoionizing Rydberg states of the Xe atom, prepared individually using state-selective excitation with a narrow bandwidth laser. It is demonstrated that the lifetimes can be increased by *l*-mixing in DC electric fields, as well as by *l*,m-mixing through the presence of surrounding Xe^+ ions. The influence of *l*,m-mixing interactions on the peak intensities in Zero Electron Kinetic Energy (ZEKE) Photoelectron spectroscopy experiments is discussed, and a possible method for increasing the applicability of ZEKE experiments is suggested. In addition, experimental evidence is given for spin-orbit state changing $Xe^*(n)$-Xe collisions.

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Introduction

The success of Zero-Electron Kinetic Energy PhotoElectron Spectroscopy (ZEKE-PES) has been surprising in light of the fact that the lifetimes of the high principle quantum number Rydberg states, which are involved in these experiments, often would be expected to be quite short. In ZEKE experiments, the electrons are collected which originate from pulsed field ionization of high principal quantum Rydberg states ($n \cong 200$) at a timedelay of typically 100 nanoseconds to a few microseconds after their preparation[1]. Experimental observations abound, where these ZEKE signals are observed long after predissociation or autoionization would have been expected to eliminate the population of these Rydberg states. In a companion paper to the current report[2], we demonstrated how, in agreement with ideas first put forward by Chupka[3], the lifetimes towards predissociation of the NO molecule can be enhanced through l-mixing in a DC electric field, as well as through the occurrence of ion-molecule collisions.

In the experiments on NO mentioned before, the predissociation rate was slowed down by reducing the contribution of low-l angular momentum states to the electronic wavefunction. Electrons in low-l orbitals interact strongly with the molecular ion core, in contrast to electrons in non-penetrating high-l orbitals, which therefore have significantly longer lifetimes. In a DC electric field the orbital angular momentum l is no longer a good quantum number, but rather, the optical excitation is to a Stark state characterized by quantum numbers n, k and m. These Stark states can be expressed as a superposition of the original field-free $[n,l,m>$ basis states and it follows that in the Stark state the time-averaged contribution from the low-l components is reduced in comparison to the field-free situation, where a pure, low-l state is excited. In the case of NO, DC electric field induced lifetime enhancements of as much as two orders of magnitude were observed[2].

A similar argument pertains to potential lifetime enhancements which might be induced by ion-molecule collisions[3,4]. If the Rydberg atom or molecule experiences not only a DC electric field but, in addition, the electric field of surrounding ions as well, then the cylindrical symmetry of the electric field is broken and both the orbital angular momentum l and the magnetic quantum number

m are no longer good quantum numbers. As before, the Rydberg state can be expressed as a superposition of field-free [n,*l*,m> states, but in this case it is anticipated that the contribution from the low-*l* states is reduced even further owing to the fact that the higher *l*-states have a (2m+1)-fold degeneracy. As pointed out by Chupka[3], the presence of even a few ions in a ZEKE experiment could in principle lead to a rapid randomization of *l* and m, since the cross-sections for *l*,m-changing ion-molecule collisions are extremely large.

Cross sections for angular momentum-changing Rydberg-ion collisions were studied extensively by MacAdam and co-workers. In collisions of Na Rydberg states with rare gas ions, they determined *l*-changing cross sections by using diabatic selective field-ionization (DSFI)[5]. For collisions of Na(28d) Rydberg states with 1 keV Ne^+ ions the *l*-changing cross sections were found to be about $5*10^{-8}$ cm^2, which exceeds the geometric cross section $n^4\pi a_0^2$ of the Rydberg atom by about three orders of magnitude. The dependence of the *l*-changing cross sections on the principal quantum number of the Rydberg state was also studied in the same work, and was found to be about n^5, which would translate into an *l*-changing cross section of about 10^{-3} cm^2 for an n=200 Rydberg state in a ZEKE experiment, or a collision radius of about 30 μm. Recently Sun and MacAdam studied selective-field ionization of the products of collisions of Na(28d) with slow Na^+ ions (7.3 - 684 eV), and found that the final-state distributions were dominated by dipole-forbidden transitions to very high angular momentum states[6]. MacAdam and co-workers argued that in the ion-Rydberg collision the final orientation of the angular momentum should be near-uniform, distributing the Rydberg population over a wide range of m_l -states[7].

In the argument presented previously to explain the observed lifetimes of Rydberg states of the NO molecule[2], the lifetime of the Rydberg state directly follows from its orbital composition in terms of the *field-free* orbital angular momentum states. This is due to the fact that in the range of the electron-core interaction where the dynamics takes place, namely, when the electron comes close to the core, the internal electron-core interaction momentarily exceeds the external perturbation of the electric field imposed on the Rydberg state. This situation is the basis for quantum defect theory, where a distinction is made between the inner region where the Rydberg

electron is described in molecule-fixed coordinates, as opposed to the outer region, where the Rydberg electron is described in a space fixed coordinate system[8,9]. Consequently the orbital angular momentum is defined in the inner region where the dynamics takes place, and for NO it was observed that the observed lifetimes could be understood in terms of the decay of just a few low-l orbital angular momentum states. One would anticipate that these arguments are not specific to the case of NO, and should be applicable in general to high principal quantum number atomic and molecular Rydberg states. Furthermore, one would anticipate that, in general, for an understanding of the lifetimes of these Rydberg states, a knowledge of the decay behaviour of a few low-l components would suffice, whereas the actual decay mechanism of these components would not really be important. For example, the model should be equally successful at explaining the lifetimes of Rydberg states which decay by predissociation or autoionization. In order to test these ideas, we report here on experiments where electric field effects and collisional effects in lifetimes of autoionizing Rydberg states of the Xe atom were studied. If the ideas presented above are true, then one would anticipate that, in the same way that the transfer of an electron to a high-l state leads to a reduction in the predissociation rate of NO, it can lead to a reduction in the autoionization rate of Xe.

Lifetime effects in the autoionization of rare gas atoms were studied recently by Merkt, who measured pulsed field ionization spectra of Ar, obtained following excitation of the Ar atom to Rydberg states converging on both the ground state and the spin-orbit excited state of the Ar^+ ion[10]. Merkt concluded that the lifetimes of the autoionizing Rydberg states converging on $Ar^+(^2P_{1/2})$ were significantly longer than what would be expected based on linewidth measurements for low-n members of the relevant Rydberg series, and concluded that the lifetimes of the Rydberg states had been enhanced by (l,m) changing collisions. He also studied the effects of the application of a DC electric field on the ZEKE spectrum, and concluded that in his experiments DC electric fields inhibited the formation of the long-lived ZEKE states.

In addition to the work by Merkt on the autoionization of Ar, the possible influences of collisional interactions in ZEKE spectroscopy have been raised by a number of other authors. As

already discussed in our companion paper on the pulsed field ionization of the NO molecule, Pratt interpreted the lifetimes of the NO Rydberg states in his experiment in terms of collisional *l*,m-mixing[11], and indeed, in our own work, collisional stabilization could be observed as well[2]. Zhang et.al. studied the dynamics of molecular Rydberg states of styrene, phenol, phenanthrene and iron[12], and observed that the lifetimes were not only very similar in all four systems but also decreased, rather than increased, for the highest values of the principal quantum number. From this observation they concluded that the observed lifetimes were most likely not determined by intrinsic molecular properties, but rather, were due to an external factor. From the reduction in the observed lifetimes for the highest-n Rydberg states with laser power, they concluded that the lifetimes of these Rydberg states were primarily determined by long range ion-Rydberg or Rydberg-Rydberg interactions, presumably resulting in ionization of the Rydberg states and thus a loss of the observed signal. They reported that the observed lifetimes were not affected by changes in the beam pressure of a factor of 2. A non-monotonic dependence of the lifetime on the principal quantum number was likewise reported for phenanthrene by Bahatt et.al.[13] who however, partly based on the fact that the lifetimes did not change when the stagnation pressure was changed over an order of magnitude or when the seed gas was changed, concluded that the lifetime dependence was caused by a competition between intramolecular relaxation and excess internal energy assisted ionization of the Rydberg state, a conclusion which has since been disputed by Chupka[14].

In this paper we report on pulsed field ionization experiments on the Xe atom, where the lifetimes of autoionizing Rydberg states converging on the $Xe^+(^2P_{1/2})$ state were studied. Our study agrees with Merkt's conclusion concerning the importance of collisions in the stabilization of the Rydberg states, although we arrive at this conclusion for a different reason, and, similar to the case of NO, we find that the application of DC electric fields leads to an increase, rather than a decrease, in the lifetimes of the Rydberg states. It is only when the electric field becomes too strong that this electric field induced lifetime enhancement is negated.

The Xe Rydberg states in the current experiments were excited using a double-resonance two-color excitation scheme, consisting of a two-photon transition to the $5p^5(^2P_{1/2})6p'[1/2]_0$ state,

followed by a one-photon transition to the high principle quantum number Rydberg levels converging on $Xe^+(^2P_{1/2})$. A representative portion of the Rydberg excitation spectrum, obtained by measuring the total Xe^+ signal as a function of the frequency of the second laser on the apparatus described in the previous paper[2], is shown in Figure 1, and contains transitions to two Rydberg-series, a broad series corresponding to excitation to nd'$[3/2]_1$, with a quantum defect of approximately 2.32[15] and a narrow series, for which hyperfine splittings can be resolved, corresponding to excitation to ns'$[1/2]_1$, with a quantum defect of 4.0106. These autoionizing Rydberg series were studied before by Wang and Knight[15] who measured line positions and linewidths for the ns'$[1/2]_1$ series up to n=40, and for the nd'$[3/2]_1$ series up to n=30. The linewidths which they reported were $1300/n^{*3}$ cm^{-1} for the ns'$[1/2]_1$ series and $35000/n^{*3}$ cm^{-1} for the nd'$[3/2]_1$ series, which translates into autoionization lifetimes of $4.1\ 10^{-3}\ n^{*3}$ psec and $1.5\ 10^{-4}\ n^{*3}$ psec, respectively. In our experiments the Rydberg series could be resolved up to about n=90, where the lifetimes of the ns'$[1/2]_1$ and nd'$[3/2]_1$ state are calculated to be about 3 nsec and 110 psec, respectively. Our experimental resolution did not allow us to measure lifetimes below approximately 5 nsec, and it follows that in our experiments it was not possible to measure lifetimes without first having induced a lifetime enhancement. This however in no way stands in the way of obtaining an understanding of the formation dynamics of the long-lived ZEKE states.

The effect of DC electric fields on the autoionization spectrum of Xe was studied by Ernst et.al.[16], using single-photon xuv-excitation. At low electric fields they observed progressions of the ns' and nd' Rydberg series, while at higher electric fields (appr. 1 kV/cm near n=20) the spectrum showed the appearance of hydrogen-like Stark manifolds. As was already pointed out by Chupka[3], the linewidths of the peaks in these Stark manifolds were significantly narrower than the homogeneous linewidth of the rapidly autoionizing nd' series in the field-free spectra of Ernst et.al., indicating a lengthening of the lifetime of these autoionizing Rydberg states.

Experimental

For the two-photon excitation to the $5p^5(^2P_{1/2})6p'[1/2]_0$ intermediate state, a Coherent 699-29 dye laser was pulse-amplified at 669 nm and the near-transform limited output of this system was upconverted to 223 nm, using doubling and mixing in KDP and BBO crystals. The subsequent excitation to the high Rydberg levels was carried out with the visible output of a similar near-transform limited pulse-amplified system, operated around 540 nm. For a more detailed description of these laser systems the reader is referred elsewhere[17]. Under the conditions used in most experiments the power of the 223 nm laser beam pumping the two-photon transition was attenuated to about 50 μJ/pulse. The spotsize of this laser inside the detector region was about 0.5 mm. The power of the 540 nm laser was typically a few mJ/pulse, with a spotsize of approximately 2 mm.

Xe gas was introduced into the apparatus by operating a pulsed free jet mounted in the vicinity of the extraction region. Xe pressures in the detector region were calibrated by comparing the signals obtained using the pulsed valve with signals obtained when the Xe was introduced through a metering valve. The absolute Xe pressures quoted in this paper correspond to the read-outs of a Bayart-Alpert type ionization gauge.

In order to distinguish pulsed field ionization events from autoionization events, all subsequent experiments were carried out on a second machine, which contained a position-sensitive microchannel plate detector, developed in cooperation with Hamamatsu corporation. Autoionization of Rydberg states close to the $Xe^+(^2P_{1/2})$ series limit leads to the formation of electrons with about 1.3 eV of kinetic energy. This corresponds to a velocity of 0.68 mm/nsec, and in an imaging experiment these electrons can readily be distinguished from the electrons formed by pulsed field ionization, which are accelerated with zero initial kinetic energy. Electrons formed by resonance-enhanced multi-photon ionization (REMPI) can be distinghuished from the pulsed field ionization electrons in a similar way.

In the imaging detector used in these experiments the electrons were accelerated in a 27 mm diameter extraction region, consisting of a solid repeller plate and a fine wire mesh, separated by 2

cm. Between the repeller and the mesh 6 additional electrodes were set up at intermediate voltages, in order to obtain a very homogeneous extraction field. Counterpropagating beams of the 223 nm and 540 nm radiation passed through the center of the extraction region and electrons were extracted at a variable delay with respect to the laser excitation, by distributing a negative 3 kV pulse, with a 10 nsec risetime, obtained from a Spectraphysics Marx bank, between the repeller and the intermediate electrodes. The fine wire mesh was held at ground potential throughout. After passing through the fine wire mesh the electrons entered a 14 cm long flighttube, which was also held at ground potential, leading onto a 32 mm diameter two-stage microchannel plate detector followed by a phosphorscreen. The microchannel plates were operated by applying a 50 nsec long, 1.8 kV pulse to the anode, synchronized to the HV electron extraction pulse. A video camera, connected to an image processor, was set up behind the detector, in order to record the spatial distribution of the electron signal. An example of an electron image, containing contributions from both pulsed field ionization and autoionization, is shown in Figure 2. The pulsed field ionization signal can readily be recognized as the line, corresponding to the laser axis, which traverses the image. Pulsed field ionization decay curves were measured in a similar way as in the preceding paper, namely, the pulsed field ionization signal was measured as a function of the time delay between the laser preparation of the Rydberg state and the onset of the high voltage pulse. Time constants for the decay curves were determined using non-linear least squares fitting. All data could be fit satisfactorily as a combination of a single-exponential decay curves and a DC offset.

The residual DC electric field in the apparatus was determined by measuring the onset for lifetime enhancement for NO f-orbital Rydberg states[2], and was found to be appr. 200 mV/cm

Results

The effect of the application of a DC electric field on the pulsed field ionization signal was measured for a number of states in the s' and d' series. At a constant time delay of 80 nsec between the optical excitation and the onset of the high voltage pulse, the variation of the pulsed field ionization signal as a function of the applied DC electric field was measured, giving the results shown in Figure 3. It was observed that, while the absolute magnitude of the pulsed field ionization signal depended on this particular choice of the delay between the laser pulse and the high voltage pulse, the basic appearance of the curves which are shown in Figure 3 was independent of the time delay.

The curves in Figure 3 illustrate that the autoionizing Rydberg states of Xe undergo electric field induced lifetime enhancements similar to the case of NO in the preceding paper. It is observed that for the s'-series, which has a reduced quantum defect of 0.0106 the application of a DC electric field rapidly leads to an increase in the pulsed field ionization signal, which is understood in terms of mixing of the s' state with the long lifetime high-l zero quantum defect states. The d'-series has a larger reduced quantum defect of 0.32 and therefore requires a significantly larger DC electric field to induce the lifetime enhancement. It is readily apparent that the onset of the d'-series enhancement coincides with a reduction in the signal for the s'-series. This is to be expected, since the lifetime enhancement for the d'-series coincides with the introduction of the rapidly autoionizing l=2 component to the s'-series Stark complex. The slight decrease in pulsed field ionization signal for the d'-series at higher DC voltage is due to the increase in the width of the Stark manifold at higher field, and thus, the reduction in the number of Stark components which have significant overlap with the narrow excitation laser bandwidth at these fields. A similar effect also contributes to a further reduction of the signal for the s'-series at high field.

An alternative way to look at the electric field effects is shown in Figure 4, which shows measurements of the pulsed field ionization signal decay times for two members of the s'-series, as a function of the applied DC electric field. Similar to the curves in Figure 3, the decay time

measurements in Figure 4 reflect the way in which the Rydberg states undergo a lifetime enhancement at low field, owing to *l*-mixing with the high-*l* zero quantum defect states, followed by a reduction at larger field, due to mixing of the former states with the rapidly autoionizing *l*=2 component.

Measurements of the decaytimes of the pulsed field ionization signals, including the electric field induced lifetime enhancement of the Rydberg states, were carried out for members of the s'-series in the range n=43-87. As mentioned in the introduction, the field-free lifetimes of the autoionizing Xe Rydberg states are too short to allow a direct determination of the lifetimes of these states. Throughout these measurements therefore, the values of the DC electric field were chosen by interpolating the voltages at which the s'-curves in Figure 3 show a maximum. It was anticipated that this would correspond to measuring the lifetimes of Rydberg states which would be a superposition of the s' state and the available high angular momentum zero quantum defect states, without admixture of the *l*=2 component. The results of these measurements are shown in Figure 5, where it is observed that the measured decaytimes are nearly independent of the principal quantum number. This is surprising, since the dependence of the electric field enhanced lifetimes on the principal quantum number is anticipated to be n^3 - n^4, depending on the precise lifetime alteration by the electric field. For the d-orbital, by analogy with the predissociative p-orbital series in the pulsed field ionization of NO[11], an n^4 lifetime dependence would be anticipated, whereas for the s-series, by analogy with the predissociative f-orbital series in the pulsed field ionization of NO, a lifetime dependence of no less than the 'normal' n^3 dependence is expected. Therefore these results suggest that the states which are pulsed field ionized *are not* the optically prepared states, but rather, are the result of the optically prepared state having undergone a secondary interaction which has altered its quantum numbers.

In order to test the idea that the pulsed field ionization signal which is detected might not come directly from the Rydberg states which are optically excited in the experiment, a pressure dependence study was undertaken. Electron images were measured as a function of the Xe-pressure, and used to measure, separately, the pressure dependence of the autoionization/REMPI

signal and the pulsed field ionization signal. As discussed before, electrons due to autoionization/REMPI and ZEKE electrons can readily be distinghuished on the position-sensitive detector. The results of these measurements are shown in Figure 6. As expected, the autoionization/REMPI signal simply follows a linear pressure dependence, however, the pulsed field ionization signal can be fit by a curve of the form $I \infty p^{1.73}$, suggesting that the detected Rydberg states are the result of a secondary interaction of the optically prepared Rydberg state with a Xe atom or ion. To summarize, our interpretation of the results in Figures 3-6 then is, firstly, that the DC electric field induces *l*-mixing in the optically excited Rydberg state. Secondly, an additional - collisional - stabilization is necessary for detection of the Rydberg states. The DC electric field aids in this stabilization to the effect that electric field induced *l*-mixing influences the amount of time that the optically prepared Rydberg state has available for the collisional stabilization. And thirdly, as demonstrated by the measurements in Figure 4, after the secondary interaction has changed some of the quantum numbers of the Rydberg electron, the DC electric field influences the extent of *l*-mixing in the resultant Rydberg states, and thus the actual lifetimes of these Rydberg states. It is due to the complexity of this mechanism that we have refrained from calling the measured decay times in Figure 4 'lifetimes', since the decay times are more appropriately interpreted to reflect the *distribution of lifetimes* of the Rydberg states formed in these collisional interactions. The fact that the measured decaytimes do not show any strong dependence on the principal quantum number of the optically prepared Rydberg state indicates that alterations in the quantum number of the electrons in the collisional processes are sufficiently extensive that in the signal that can subsequently be detected all memory about the original state is lost. In this regard it should also be realized that in the measurements reported above we are only sensitive to collision products with a lifetime ≥ 5 nsec, and that these experiments do no give direct information about the distribution of the collision products over the available final Rydberg states. Attempts were made to find evidence for pulsed field ionization from the initially prepared *l*-mixed Rydberg states (which do not undergo any collisional stabilization). The lifetimes of these states were too short to be measured, however, since, at the required short time delays between the laser excitation

and the pulsed field ionization, it was not possible to experimentally distinguish the electrons corresponding to pulsed field ionization events from the electrons formed at almost the same time by autoionization and REMPI.

In the experimental arrangement used in the experiment it was difficult to record dependence of the pulsed field ionization signal on the power levels of the two excitation lasers. It was clearly observed however, that the ratio of the pulsed field ionization signal to the autoionization/REMPI signal increased with increasing laser powers. This suggests that the Xe atom which is involved in the lifetime enhancement of the optically excited Rydberg states, has been excited in the same way as the Rydberg atom, suggesting that the stabilizing interaction is either with a Rydberg atom or a Xe^+ ion. Electrons formed in conjunction with the Xe^+ ions are anticipated to leave the interaction region too fast to have a lasting effect on the l,m composition of the Rydberg state. Furthermore, the fact that the measured pressure dependence does not deviate significantly from a p^2 dependence on the Xe pressure, indicates that under the conditions in the experiment the majority of the Rydberg atoms which are prepared autoionize within the first 100 nanoseconds. In other words, the experiments were carried out under a condition where only a small percentage of the Xe Rydberg states was stabilized through a collisional interaction, and most of the Xe Rydberg states underwent autoionization, forming a Xe^+ ion. Assuming that the stabilizing interaction from a Xe^+ ion and a second high principal quantum number Xe Rydberg state might be very similar, this suggests that the stabilization is predominantly by Xe^+ ions.

In the pulsed field ionization decay curve measurements reported above, it was observed that following a rapid decay according to the time constants given in Figure 4, a residual Xe high-Rydberg population remained, which could be detected without noticable drop-off in the signal intensity for many microseconds. On the imaging detector the position of a ZEKE electron reflects the location of the Rydberg atom in the extraction region prior to the pulsed field ionization and extraction. From this it follows that the electron image broadens as a function of the time delay between the laser excitation and the pulsed field ionization, in accordance with the velocity distribution of the Xe Rydberg atoms. A striking feature of this second Xe pulsed field ionization

signal was the fact that the kinetic energy of these Xe Rydberg atoms was more than one order of magnitude higher than the anticipated, near-thermal kinetic energy of the Xe atoms prior to the laser excitation. Given then that these Xe Rydberg states show the same collisional dependence as the signal discussed before, we interpret this signal as being due to the collisional formation of Rydberg states converging on the lower spin-orbit state $Xe^+(^2P_{3/2})$ according to

$$[Xe^+(^2P_{1/2})]ns'/nd' + Xe \text{ --> } [Xe^+(^2P_{3/2})]nl + Xe \qquad (1)$$

In this collision 1.3 eV of Xe spin-orbit energy is converted into kinetic energy shared between the two Xe atoms involved, accounting for the large velocities observed. The fact that the Rydberg states formed in this proces now converges on the lower spin-orbit state, $Xe^+(^2P_{3/2})$, where autoionization is no longer an available decay mechanism, explains the extremely long lifetimes observed for these Rydberg states.

In order to determine the Xe velocity distribution electron images were measured as a function of the time delay between the laser excitation and the onset of the high voltage pulse. Assuming an isotropic angular distribution for the recoiling Xe Rydberg states, profiles of the ZEKE images perpendicular to the laser axis were fit to the following form:

$$I(y,\tau) = \int P(v) \int P(v_x)\ 1/\sqrt{[1-(y/\tau)^2/(v^2-v_x^2)]}\ dv\ dv_x \qquad (2)$$

The results of a non-linear least squares fit are shown in Figures 7 and 8. The measured electron images are well represented by the isotropic recoil distribution represented by Equation 2, and it is observed that the recoil energies are in very reasonable agreement with the assumption that the energy release is according to the reaction mechanism given in Equation 1, as shown by the arrow in Figure 8, which indicates the kinetic energy which each of the two colliding Xe atoms will pick up when the spin-orbit energy is made available.

It should be noted that, in further support of this interpretation of the formation of the 'fast' Xe Rydberg states, the pressure dependence of the profiles shown in Figure 7 was studied, and no evidence was seen indicating any influence of space charge effects in these measurements, as the profiles stayed essentially the same down to countrates as low as a single pulsed field ionization event per lasershot.

Discussion

In this paper lifetime measurements have been reported for high principal quantum number (n=43-87) Rydberg states of the Xe atom, converging on the upper spin orbit excited state of the Xe^+ ion. Based on reported measurements of the linewidths of lower members of these Rydberg series, one would expect these Rydberg to autoionize on a timescale of no more than a few nanoseconds, however, by manipulating the angular momentum of the Rydberg orbital, the lifetime of the autoionizing Rydberg states could be stretched to about 50 nsec. The scenario for lifetime enhancement of the Rydberg states has been shown to consist of two stages. First, the presence of a small homogeneous DC electric field causes l-mixing in the optically excited state, since in the field the orbital angular momentum l is no longer a good quantum number, and rather, the excited state is a Stark state, where the orbital angular momentum quantum numbers are replaced by parabolic quantum numbers, which describe the quantization in the external field. Secondly, the lifetime is enhanced through the presence of Xe^+ ions in the vicinity of the Rydberg atom. The presence of these ions breaks the cylindrical symmetry of the electric field, and causes a scrambling of the magnetic quantum number m. The pulsed field ionization signal is thus believed to be due to Rydberg states of Xe which are coherent superpositions of $[n,l,m>$ states, in which the contribution of the rapidly autoionizing low-l states is greatly diluted. Our experiments thus strongly support the mechanisms first suggested by Chupka[3].

In our companion paper on the lifetimes of predissociating high principal quantum number Rydberg states of NO[2], the lifetime enhancements introduced by the presence of small DC electric fields were already discussed in detail. In what follows we will therefore limit our discussion to the collisional interactions which were observed in the current experiments.

In a recent paper, Merkt and Zare presented calculations on the influence of the presence of ions in ZEKE experiments[4]. Merkt and Zare calculated l- and m_l-mixing in the presence of a non-cylindrically symmetric electric field consisting of a small homogeneous dc field and the Coulomb fields (on the ionic core and the Rydberg electron) caused by the presence of a singly-charged ion at

some distance from the ionic core of the Rydberg atom or molecule. They calculated that for a typical high principal quantum number Rydberg state (n=100, l=30) in a DC field of 100 mV/cm, m-mixing should become nearly complete on a time-scale of about 100 nanoseconds if an ion is present within 50 μm. Though a precise comparison of these numbers with our experiments is difficult, it is interesting to attempt to estimate the average (Rydberg-ion) spacing in our experiments. Provided that the microchannel plate detector remains approximately linear under these conditions, we would estimate that in our experiment, at a pressure of 10^{-5} Torr, the production of Xe^+ through both autoionization and REMPI would be about 10^4 ions/lasershot. Given that our detection volume was about 5 mm^3, this would correspond to an ionization efficiency of about 10^{-3}, which seems reasonable at the power levels used. Thus we would estimate that in our experiments stabilization became appreciable when the density of the Xe^+ ions was about $2*10^6$/cc. Since the total number of ions and the effective detection volume are both difficult to determine, this number is subject to considerable uncertainty, however a fairly conservative estimate would be that the experimental Xe^+ density should not differ from this value by more than one order of magnitude. A Xe^+ ion density of $2*10^6$/cc would correspond to an average (Rydberg-ion) spacing of 80 μm, which is certainly of the same order of magnitude as the calculations by Merkt and Zare.

The fact that both theory and experiment indicate that there can be a role for collisional stabilization in ZEKE experiments has a number of important consequences. The first of these is the fact that collisional stabilization may have a considerably effect on peak intensitities in ZEKE spectra. In ZEKE experiments, at the time of the laser excitation two categories of ions are produced in addition to the Rydberg atoms or molecules. The first category consists of ions which are produced through further laser excitation or decay of the Rydberg states. The number of ions produced via this route will scale with the number of Rydberg states populated. The second category of ions consists of all other ions which are produced in the detection volume, namely ions which are produced by alternative REMPI processes or ions which might even result from ionization of background gasses in the vacuum chamber. The current experiment on Xe provides an

illustrative example, in that ions are produced both through autoionization or REMPI of Rydberg states (which scales with the prepared population of the Rydberg state) as well as through (2+1) two-photon resonant one-color REMPI (which is independent of the population of the Rydberg state).

The magnitude of the ZEKE signal is given as the initial Rydberg excitation to the high-n states which can be field-ionized, multiplied by the survival probability of the Rydberg state until the moment when the ionization field is switched on, or

$$I_{ZEKE}(\tau) \propto N_{rydberg} * P_{survival}(\tau) \tag{3}$$

If collisional stabilization is important and the number of ions is still small enough that collisional ionization can be ignored, then our experiments suggest that

$$P_{survival}(\tau) \propto N_{ions} = N^{+}_{\text{'Rydberg'}} + N^{+}_{\text{non-Rydberg+other}} \tag{4}$$

If the total number of ions is dominated by the ions whose excitation process does not require resonance of the laser with the Rydberg states ($N^{+}_{\text{Rydberg + other}}$), then the detection probablity of the Rydberg states is independent of the number of Rydberg states (and associated ions) produced, and, if there are no other state-dependent effects which affect lifetimes of the Rydberg states, the intensities in the ZEKE spectrum will reflect the population of the initially prepared Rydberg states. A quite different situation may arise however, if the number of ions that are produced scales with the number of Rydberg states which are excited. In this case, if collisional stabilization is required for detection of the Rydberg state, the survival probability of the Rydberg states will depend on the number of Rydberg states, or, if the number of non-Rydberg related and background ions is neglegibly small,

$$I_{ZEKE} \propto N_{rydberg}^{2} \quad (5)$$

Thus, in this situation, the intensities in the ZEKE spectrum will be proportional to the square of the initially prepared Rydberg population. Collisional stabilization therefore can greatly influence relative intensities in a ZEKE spectrum.

In this respect it is interesting to mention an experiment which was carried out recently by Stolow and co-workers at the National Research Council in Ottawa, Canada[18]. In this experiment, in which one of us participated, iodine B-state wavepacket dynamics was studied using a femtosecond pump-probe technique, applying detection of either ZEKE electrons or I_2^+/I^+ ions. Similar to the fluorescence detection experiments reported by Zewail and co-workers[19], quantum beats were observed which reflect the time-dependence of the Franck-Condon overlap between the B-state wavepacket and the ionic state. It was observed that in the quantum beat spectra the peak-to-valley ratios, when measuring ZEKE signals, were considerably larger than the peak-to-valley ratios, when measuring the ion signals. The results obtained in our Xe autoionization experiment suggested that this might be due to the fact that peaks in the quantum beat spectra correspond to a situation where a large number of both Rydberg states and ions are formed, whereas valleys in the quantum beat spectra correspond to a situation where smaller numbers of Rydberg states and ions are formed. In other words, peaks in the quantum beat spectra correspond to a situation where the survival probability of the Rydberg states is relatively large, whereas in valleys the survival probability of the Rydberg states is relatively smaller. Convincing evidence for this conclusion was obtained by introducing an alternative method of producing the ions which are required for the stabilization. The 4th harmonic of a 100 psec Nd:YAG laser was used in order to non-resonantly prepare a larger concentration of ions, which exceeded the ion density without this laser by about one order of magnitude. Not only was it clearly observed how the introduction of this laser greatly enhanced the pump-probe ZEKE signal, but furthermore it was observed that in this case, where the total number of ions *did not* depend on the number of Rydberg states populated, the peak-to-valley ratios in the ZEKE signal were more similar to those in the ion quantum beat spectra.

The discussion above brings us to the second important implication to be discussed here. If ZEKE is performed using Rydberg states which have a lifetime which is relatively short, such that a large part of the Rydberg population decays prior to the pulsed field ionization and extraction, then the purposeful production of background ions through an unrelated ionization process may be viable method for enhancing the intensity of a ZEKE spectrum. Clearly, both in the experiments reported in this paper, where no pulsed field ionization could be detected other than the signal which depended quadratically on the Xe pressure, as well as in the Ottawa experiment, where the introduction of 266 nm radiation led to a significant increase in the pump-probe ZEKE signal, the surrounding ions can act as an 'amplifier' of the ZEKE signal. Indeed, although it is a provocative notion, one cannot help but wonder how many ZEKE-experiments have already been carried out, where background ions, which may inadvertently have been present during the experiment, were responsible for its success.

With respect to the application of this amplification technique in a ZEKE experiment, the options which are available are either the introduction of an additional chemical species, which can readily be ionized by the existing lasers in the experiment, or the introduction of an additional laser, which non-resonantly ionizes the atom or molecule which is studied. In either case, one could imagine tuning the concentration of the additional chemical species or the power in the additional laser, in order to optimize the ZEKE signal of interest. Some reservations are in order since the technique is likely to enhance shot-to-shot fluctuations in the experiment, and therefore, if ZEKE spectra can be collected without introducing collisional interactions, this is certainly preferable. The density of the ions, which are to stabilize the Rydberg states, needs to be carefully controlled. If the density of the surrounding ions is too high, the Rydberg states may be ionized by the electric field of the ions[12], and at large ion densities non-zero kinetic energy electrons may become trapped in the attractive well which is established once fast electrons start to leave the interaction region[20]. In addition, at high ion densities, reactive processes like the spin-orbit exchange mechanism encountered in this work will become increasingly likely. Under unfavourable conditions this may lead to a significant loss in spectral resolution. An interesting example of a charge transfer mechanism was recently reported by Pratt in the ZEKE of HI[21]. He reported that in his experiments

the lifetime of the ZEKE Rydberg states of HI was inversely proportional to the density of HI, due to the fact that Rydberg states are lost when the Rydberg electron dissociatively attaches itself to a surrounding HI molecule.

In conclusion, we believe that in this paper, and in its companion paper on the pulsed field ionization of the NO molecule[2)] we have demonstrated how under typical ZEKE conditions, the lifetimes of the high principal quantum number Rydberg states can be affected by electric field effects from existing DC fields and surrounding ions. We have shown how in the presence of a DC electric field the Rydberg excitation leads to the formation of a Stark state, where the contribution of low-l angular momentum components to the electron wavefunction is reduced, and we have shown how this can lead to a major enhancement in the lifetime of the Rydberg state. And furthermore we have demonstrated how the interaction of the Rydberg atom or molecule with surrounding ions can lead to a further enhancement in the lifetime, associated with changes in the magnetic quantum number.

Acknowledgements

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Figure Captions

Figure 1: Portion of the Xe autoionization spectrum, showing ns' and nd' Rydberg states converging on $Xe^+(^2P_{1/2})$ (convergence limit at 18510.68 cm^{-1}). The spectrum was obtained by measuring the total Xe^+ ion yield as a function of the frequency of the visible laser which excites the Xe atom from the $6p'(^2P_{1/2})$ level.

Figure 2: Typical electron images recorded using the position-sensitive microchannel plate detector. These images were recorded after excitation of the 52s' Rydberg state, in the absence of an externally applied DC electric field (a) and in the presence of a 2 V/cm DC electric field (b). In the absence of the DC electric field, the recoil of the non-zero kinetic energy electrons due to Xe autoionization and REMPI leads to a near-homogeneous illumination of the detector (the transverse asymmetry in the image is due to the existence of finite magnetic fields in the experiments). In the presence of the DC electric field (b), pulsed field ionization signal is detected as a line across the detector, which corresponds to the laser axis, and which reflects the zero recoil velocity of the Rydberg electrons.

Figure 3: Dependence of the Xe pulsed field ionization signal obtained at a fixed time delay of 80 nsec between the laser excitation and the pulsed field ionization and extraction, on the ambient DC electric field. Curves were obtained for excitation to a) $n^*=80$, b) $n^*=70$, c) $n^*=60$, d) $n^*=52$ and e) $n^*=43$. Squares represent excitation to an ns' level, whereas triangles represent excitation of an nd' level.

Figure 4: Dependence of the decay time of the Xe pulsed field ionization signal, on the selected ns' Rydberg state and the DC electric field. The decaytimes were determined using a non-lineast squares fit of experimental pulsed field ionization

time delay scans. Squares represent excitation of the $n^*=70$ orbital, whereas triangles represent excitation of the $n^*=52$ orbital.

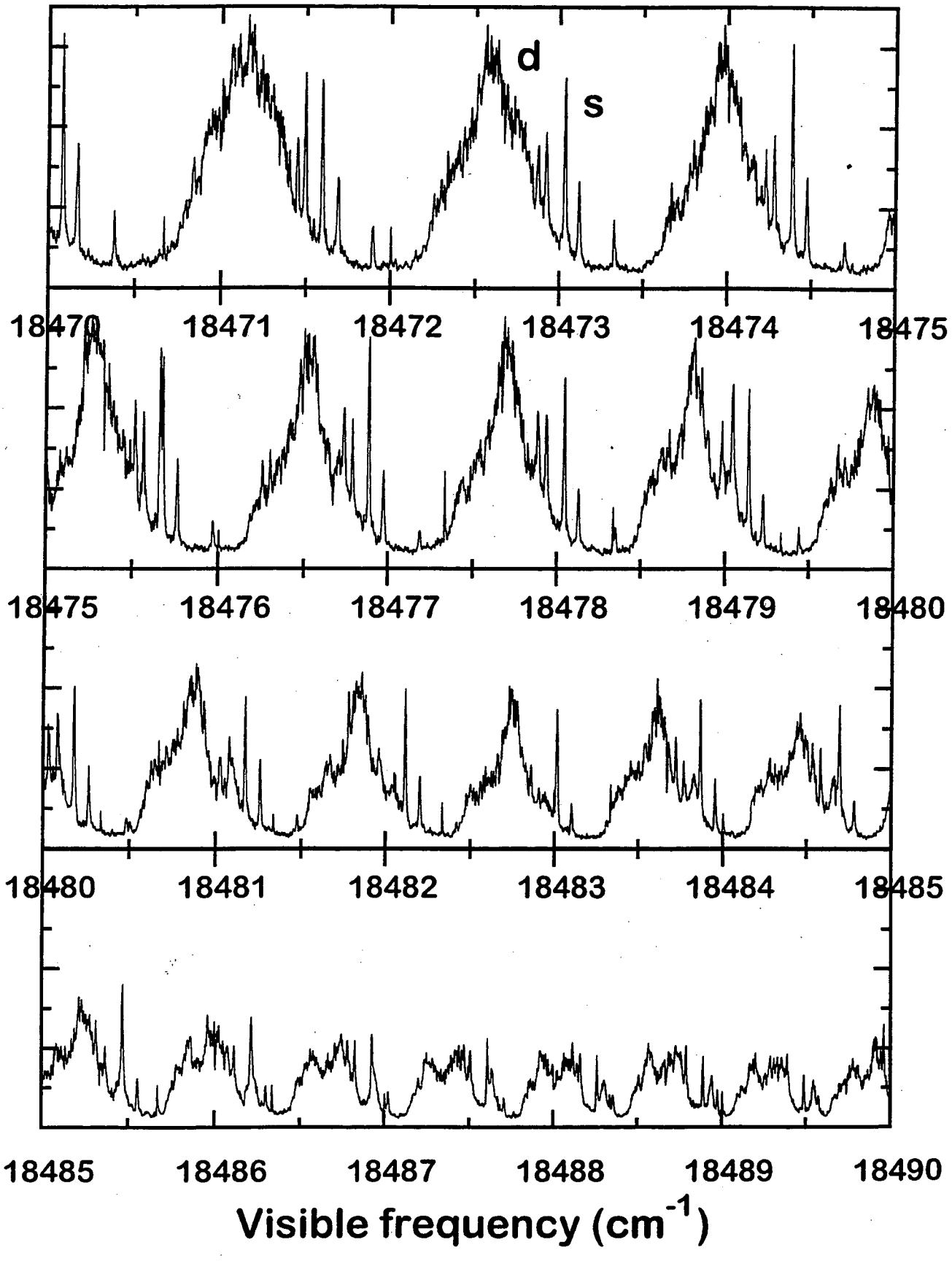
Figure 5: Decaytimes of Xe pulsed field ionization signals as a function of the principal quantum number, following excitation of members of the ns' Rydberg series. The decaytimes were determined using a non-lineast squares fit of the experimental data. The ambient DC voltage was chosen through extrapolation of the maxima for the ns' series in Figure 3.

Figure 6: Pressure dependence of the Xe autoionization/REMPI (triangles) and pulsed field ionization (squares) signals, measured by separating the contributions of zero and non-zero kinetic energy electrons in the electron images collected with the position-sensitive microchannel plate detector. The autoionization/REMPI signal exhibits a linear dependence on the Xe pressure, whereas the pulsed field ionization signal increases as $I \propto p^{1.73}$.

Figure 7: Time dependence of the spatial projection perpendicular to the laser axis of the Xe pulsed field ionization signal, obtained at long time delays between the laser excitation and the pulsed field ionization and extraction. The experimental results were obtained by integrating electron images in the dimension corresponding to the laser axis, for segments near the center of the position-sensitive detector. The time delays between the laser excitation and the pulsed field ionization were a) 2.2 μsec, b) 3.2 μsec, c) 4.2 μsec, d) 5.2 μsec, e) 6.2 μsec, and f) 7.2 μsec. The dotted line represents the experimental data, whereas the solid line represents the result of a non-linear least squares fit, according to Equation (2), resulting in the Xe Rydberg velocity distribution shown in Figure 8.

Figure 8: Velocity distribution of Xe Rydberg atoms detected at a delay of 2.2 - 7.2 μsec between the excitation laser and the pulsed field ionization and extraction, obtained by a non-linear least squares fit of the experimental results shown in Figure 7. The arrow indicating $E_{spin\text{-}orbit}$ corresponds to the velocity of a Xe atom with a kinetic energy which is half the spin-orbit splitting between $Xe^+(^2P_{3/2})$ and $Xe^+(^2P_{1/2})$.

Figure 1


d
s
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18486
18487
18488
18489
18490
Visible frequency (cm^{-1})

Figure 2a

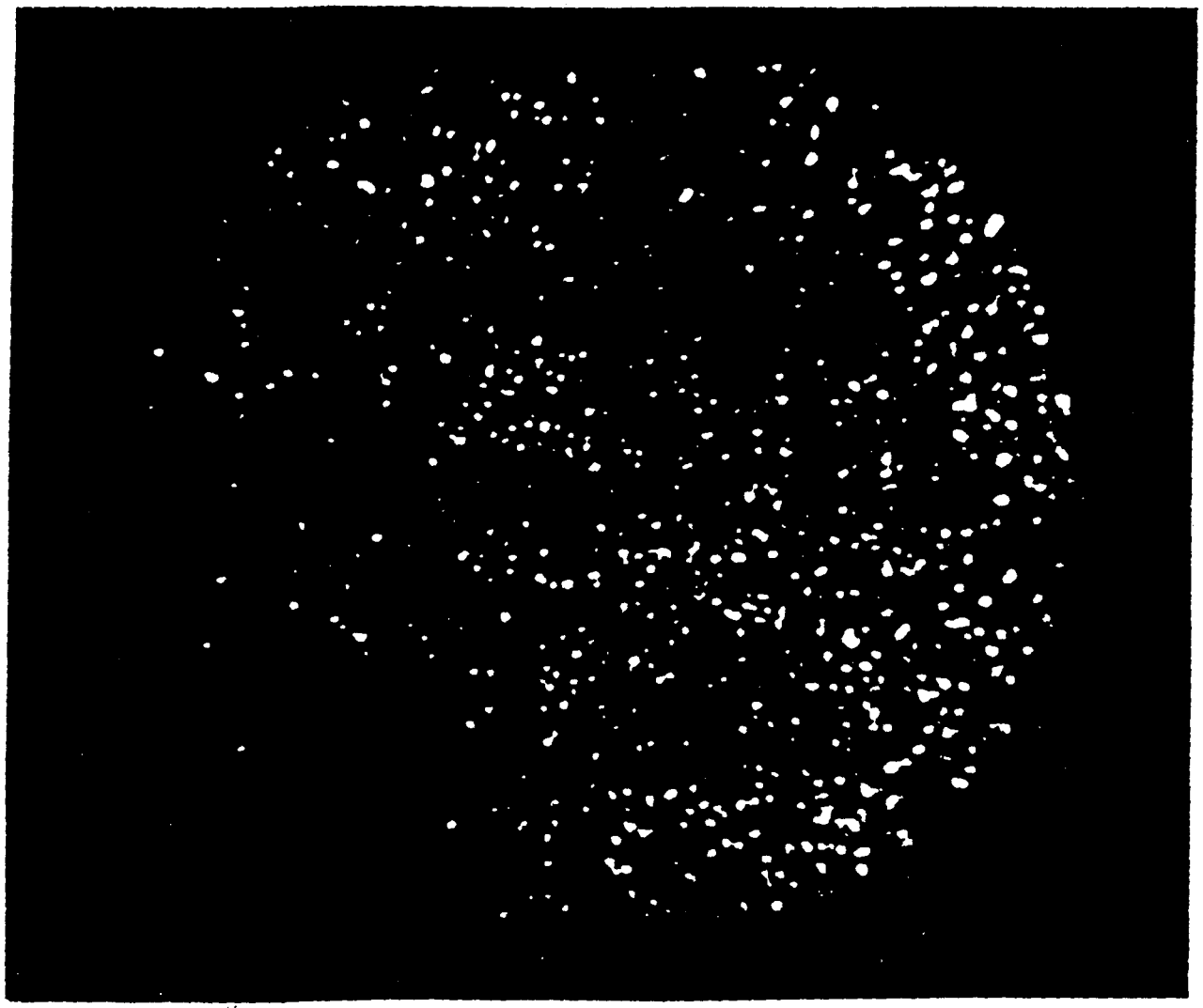


Figure 2b

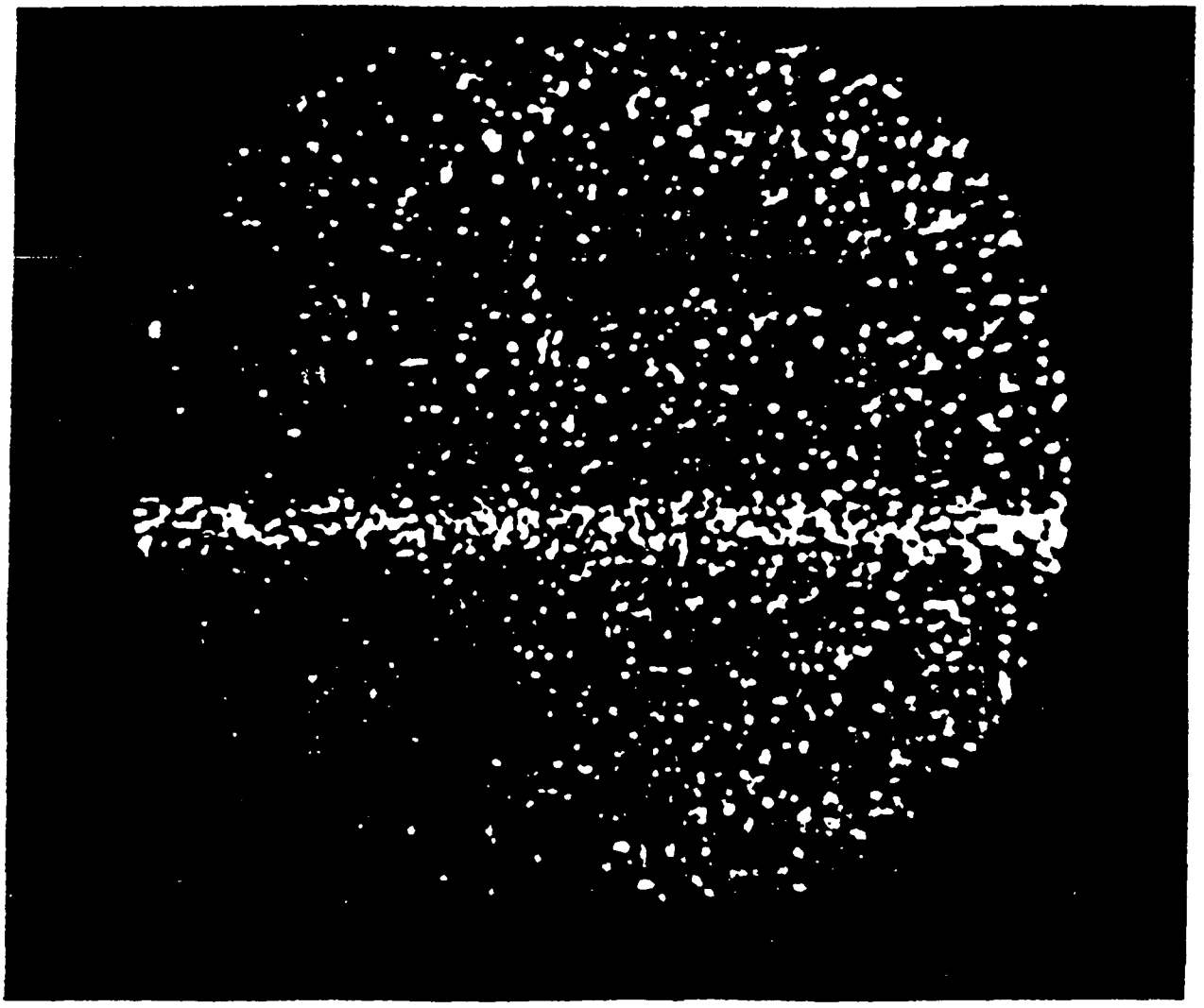


Figure 3

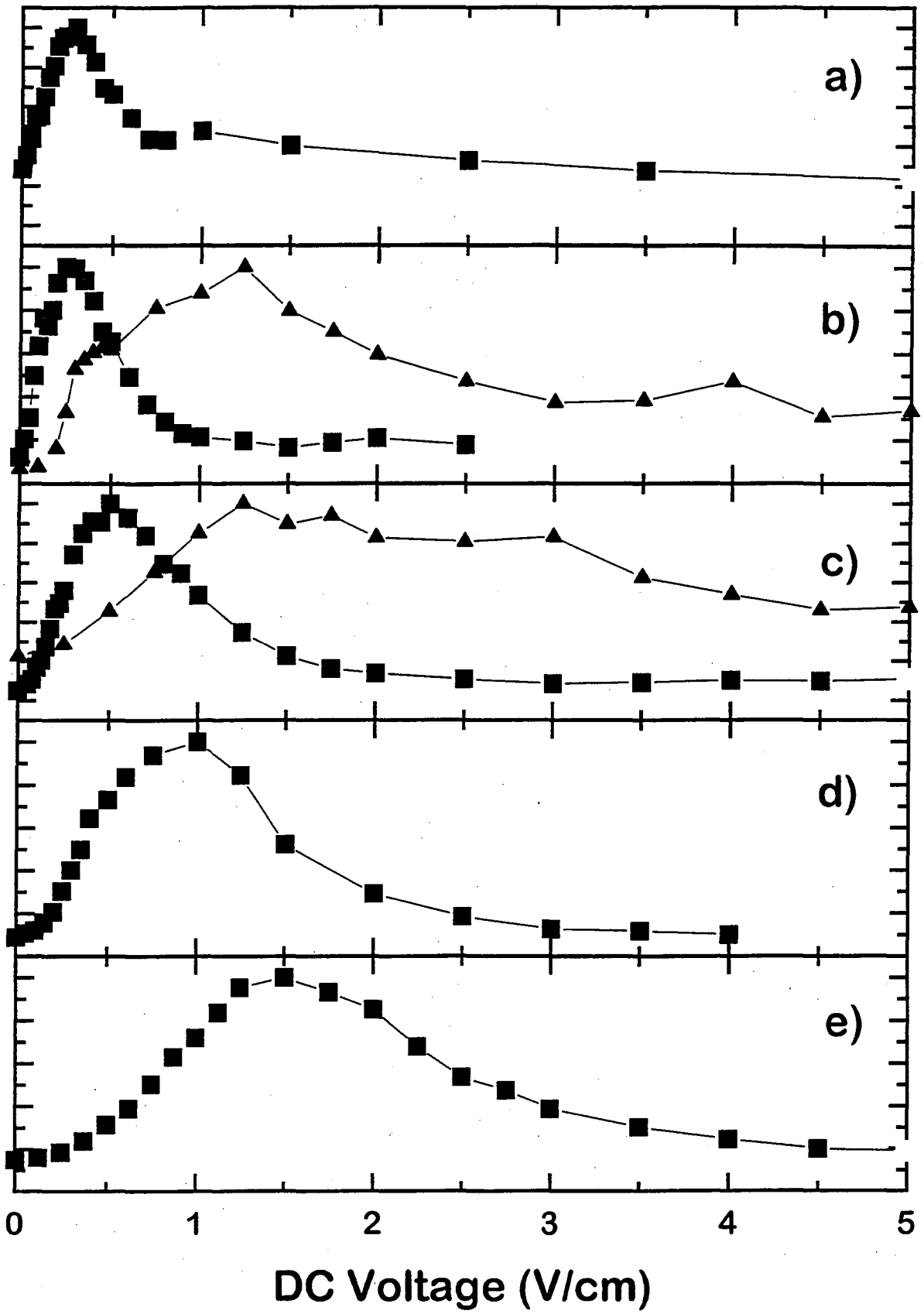


Figure 4

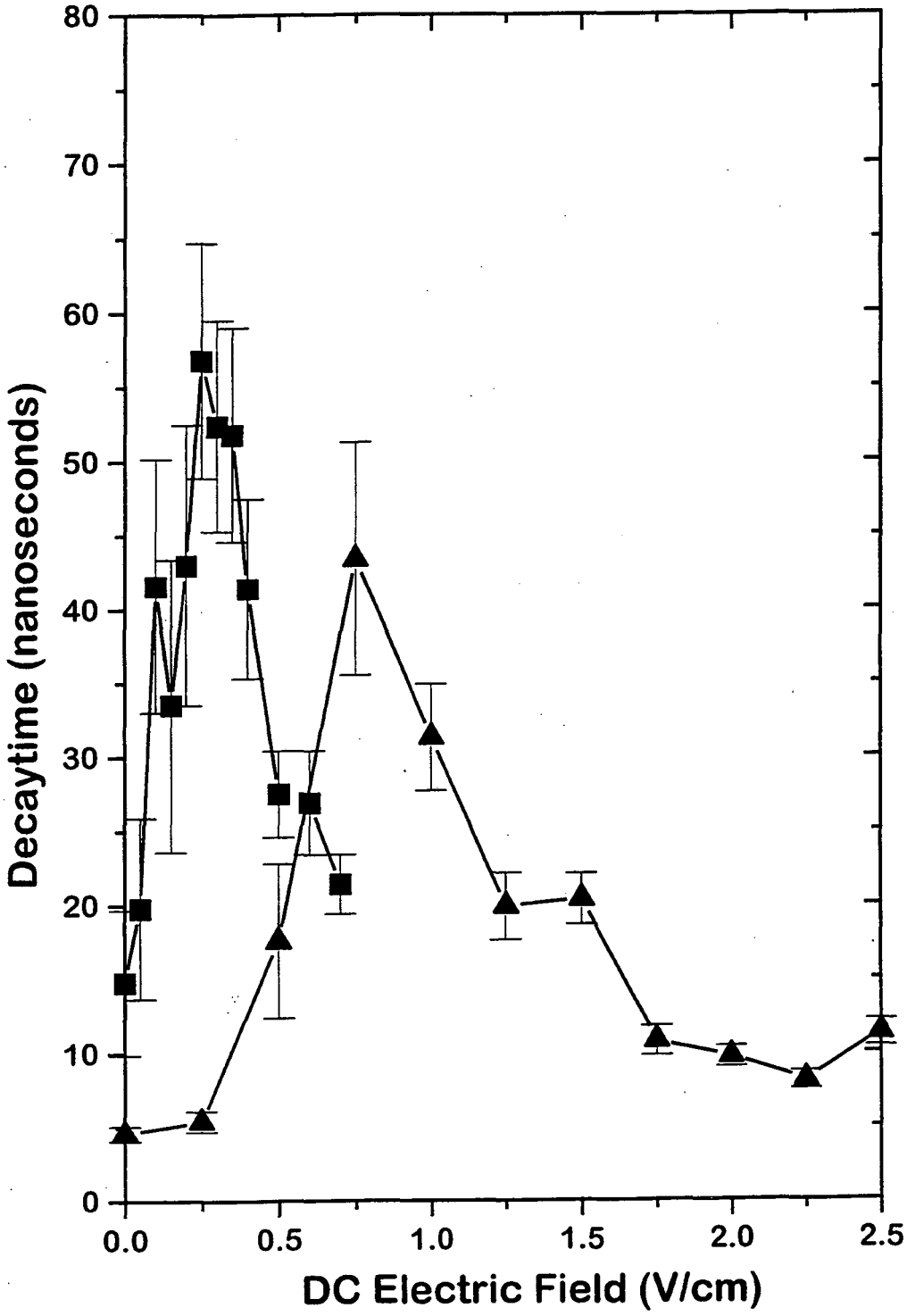

80
70
60
50
40
30
20
10
0
Decaytime (nanoseconds)
0.0
0.5
1.0
1.5
2.0
2.5
DC Electric Field (V/cm)

Figure 5

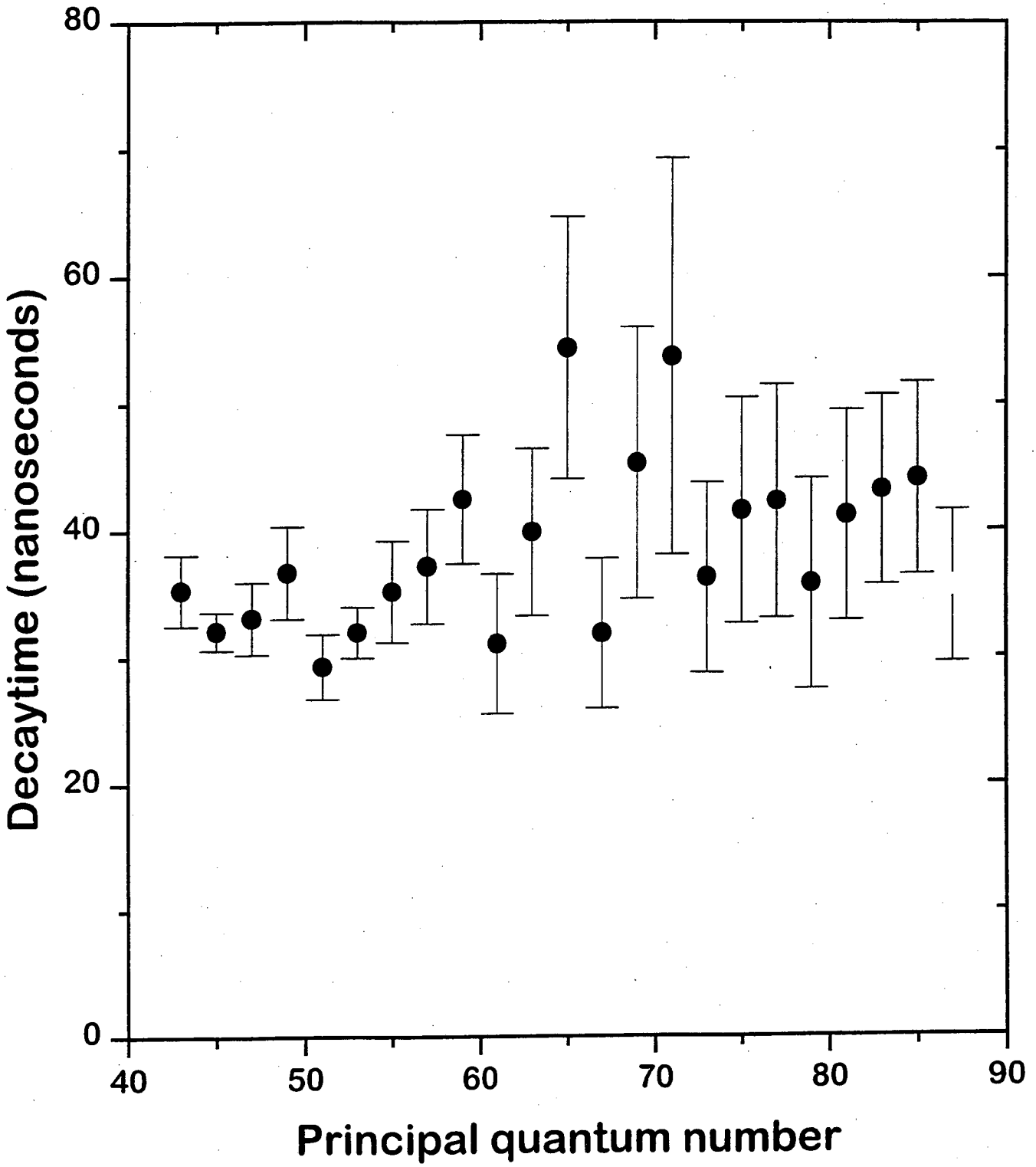

80
60
40
20
0
Decaytime (nanoseconds)
40
50
60
70
80
90
Principal quantum number

Figure 6

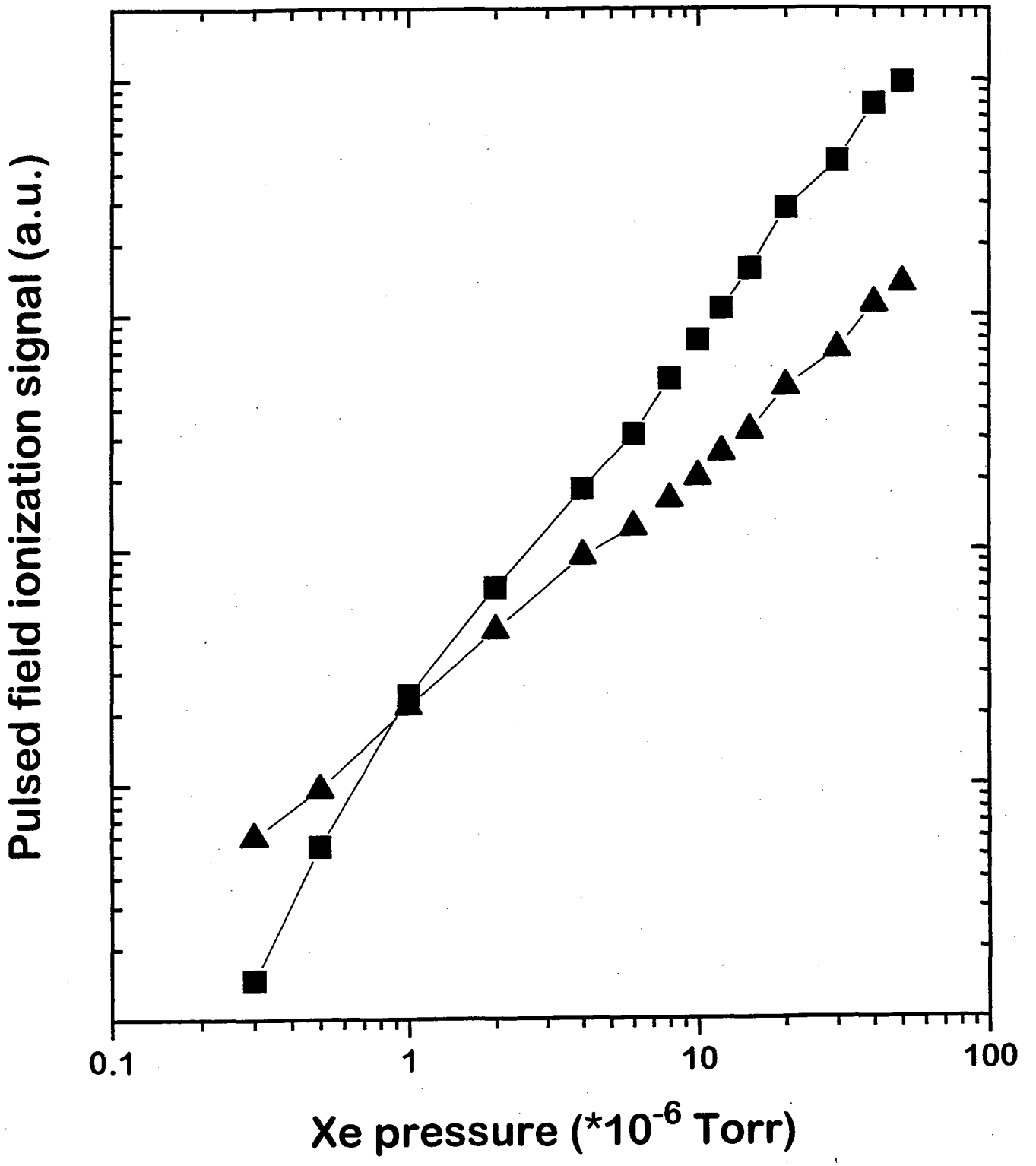

Pulsed field ionization signal (a.u.)
0.1
1
10
100
Xe pressure (*10-6 Torr)

Figure 7

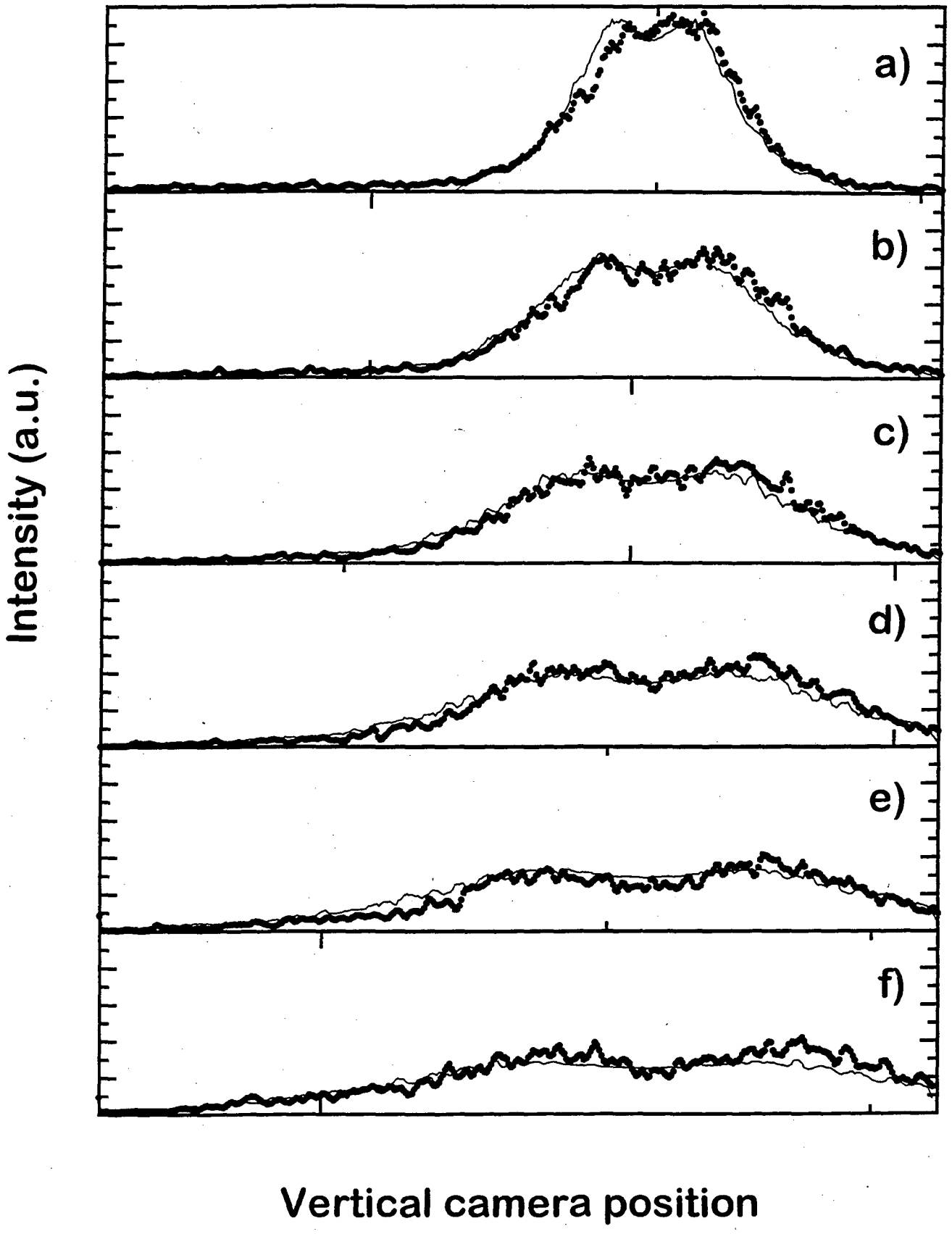
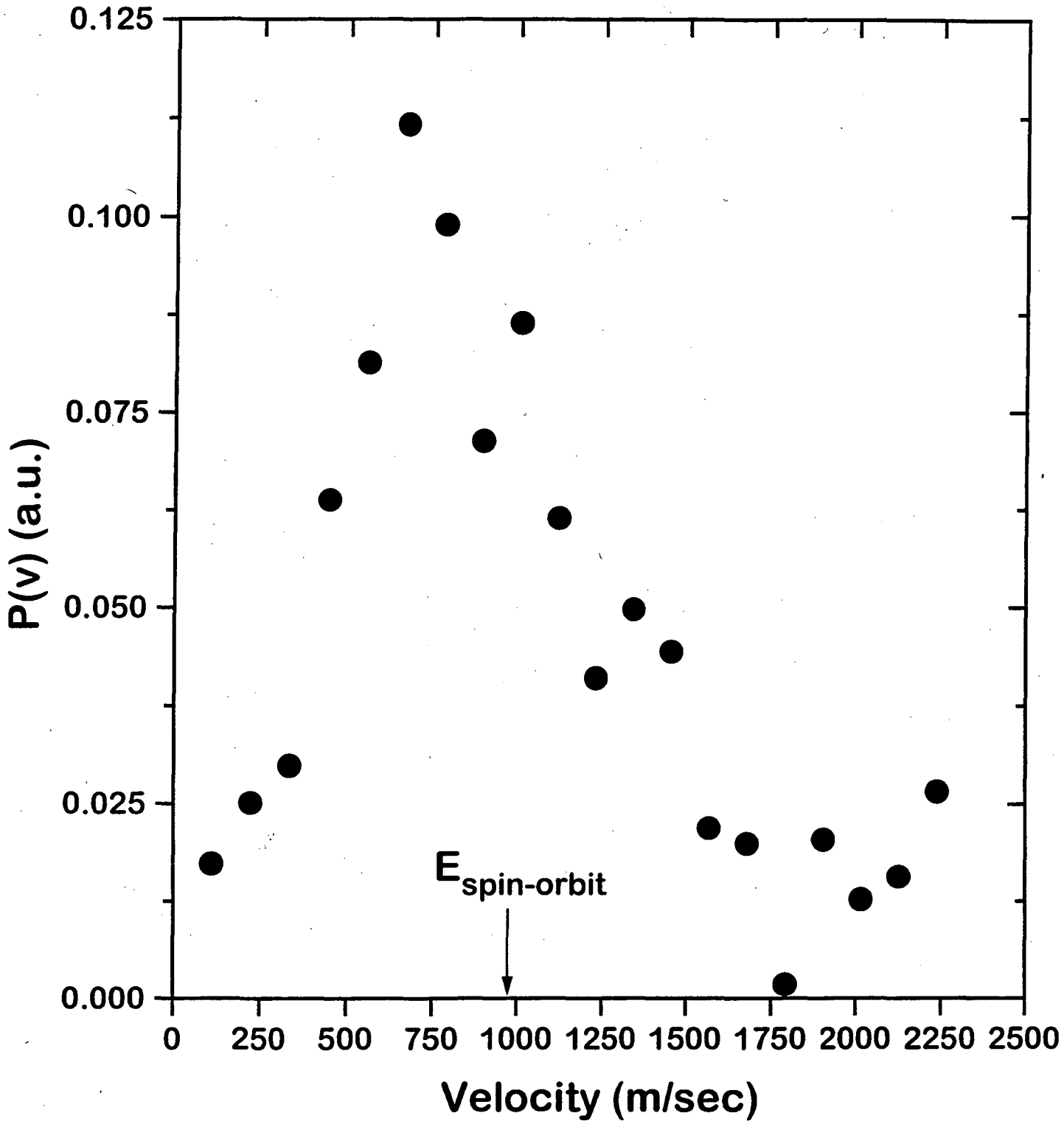


Figure 8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0.050
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P(v) (a.u.)
0
250
500
750
1000
1250
1500
1750
2000
2250
2500
Velocity (m/sec)
E spin-orbit

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