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**Enhancements in the Lifetimes of NO Rydberg States in
DC Electric Fields: Implications for ZEKE-experiments**

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Abstract

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 PhotoElectron Spectroscopy (ZEKE-PES) 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 ions¹⁾. In this technique, neutral molecules are excited to high principle quantum number Rydberg states (typ. $n \approx 200$), and the electrons are collected which are created as a result of the application of a small pulsed electric field (typ. 1 V/cm), which is turned on some time after the Rydberg excitation (typ. 1 μ 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 μ sec.

In a recent paper³⁾ Chupka proposed that the enhanced lifetimes might be due to l -mixing by the small residual DC electric fields which 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 ($\xi=r+z$, $\eta=r-z$, ν), 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 numbers⁴⁾. The $|nkm\rangle$ Stark states can be expressed as superpositions of $|nlm\rangle$ states in which the populations of individual l -components are time-dependent.

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 time-dependence of 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 -mixing³⁾, 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 NO⁶⁾, and observed a significant reduction of the ZEKE signal upon application of a ~ 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 Ar⁷.

In this letter 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 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 Pratt⁶. To our knowledge, this is the first direct determination of an electric field-induced lifetime-enhancement through the suppression of predissociation.

The NO Rydberg states were populated using two-color laser excitation, employing the A¹Σ⁺ state as resonant intermediate. The 226 nm light required to pump selected A-X (0,0) P₁-transitions was obtained by Raman-shifting the third harmonic of a pulsed amplified Coherent 699-29 ringlaser⁸), 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 pulse-amplified Coherent 699-29 ringlaser, operated near 656 nm. The bandwidths of the 226 nm and 328 nm lasers were 0.06 cm⁻¹ and 0.007 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 focussed to a 2 mm spot. At a variable time delay, a +1.7 kV pulse with a

5 nsec risetime was applied to the ion optics. This pulse was used to ionize the NO Rydberg molecules as well as accelerate the 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 A¹Σ⁺(N_A=0, j_A=1/2) intermediate state show two dominant Rydberg progressions, namely a series with a quantum defect of 0.7286 converging on N⁺=0 (E_o=30522.443 cm⁻¹), assigned as a p-series, and a series with a quantum defect of 0.0101 converging on N⁺=2 (E_o=30534.349 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 Figure 1. Two sets of data are shown, namely lifetimes determined with the minimum residual DC electric field achievable in our set-up (open circles) and lifetimes which 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 which 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 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 Figure 1 were measured at electric fields which were about 20 % above this critical value.

The lifetime enhancement around the critical electric field strength is shown in more detail in Figure 2 for excitation to the 51f orbital. This figure shows that the lifetime of the 51f orbital is constant at its near field-free value until the DC electric field is 70 mV/cm, at which point a sudden five-fold 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 Figure 3. The data is well represented by a fit to a $F \propto n^{-5}$ dependence, which is also shown in Figure 3.

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

$$\Delta E_{stark} = 3Fn^2 \quad (1)$$

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

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

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 Figure 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 criterium to the p -series and f -series converging on $N^+=0$ and $N^+=2$, as well as similar measurements using different A-state intermediates⁹⁾, yields a determination of the residual DC field in our apparatus of 25.1 ± 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 $n=62$, 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 f -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 a $n^{4.17 \pm 0.25}$ 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-orbital⁹).

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 criterium 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 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 letter, no collisional

effects were observed. In subsequent experiments, to be reported in detail later⁹⁾, 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.

Acknowledgements

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Figure captions

Figure 1 Lifetimes of NO Rydberg series excited from the $A^1\Sigma^+(N_A=0, J_A=1/2)$ 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 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 lifetime (see text for details). The enhanced field-free 92p and 95p lifetimes are due to mixing with high- l angular momentum states converging on $N^+=1$ ⁹.

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

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

Figure 1

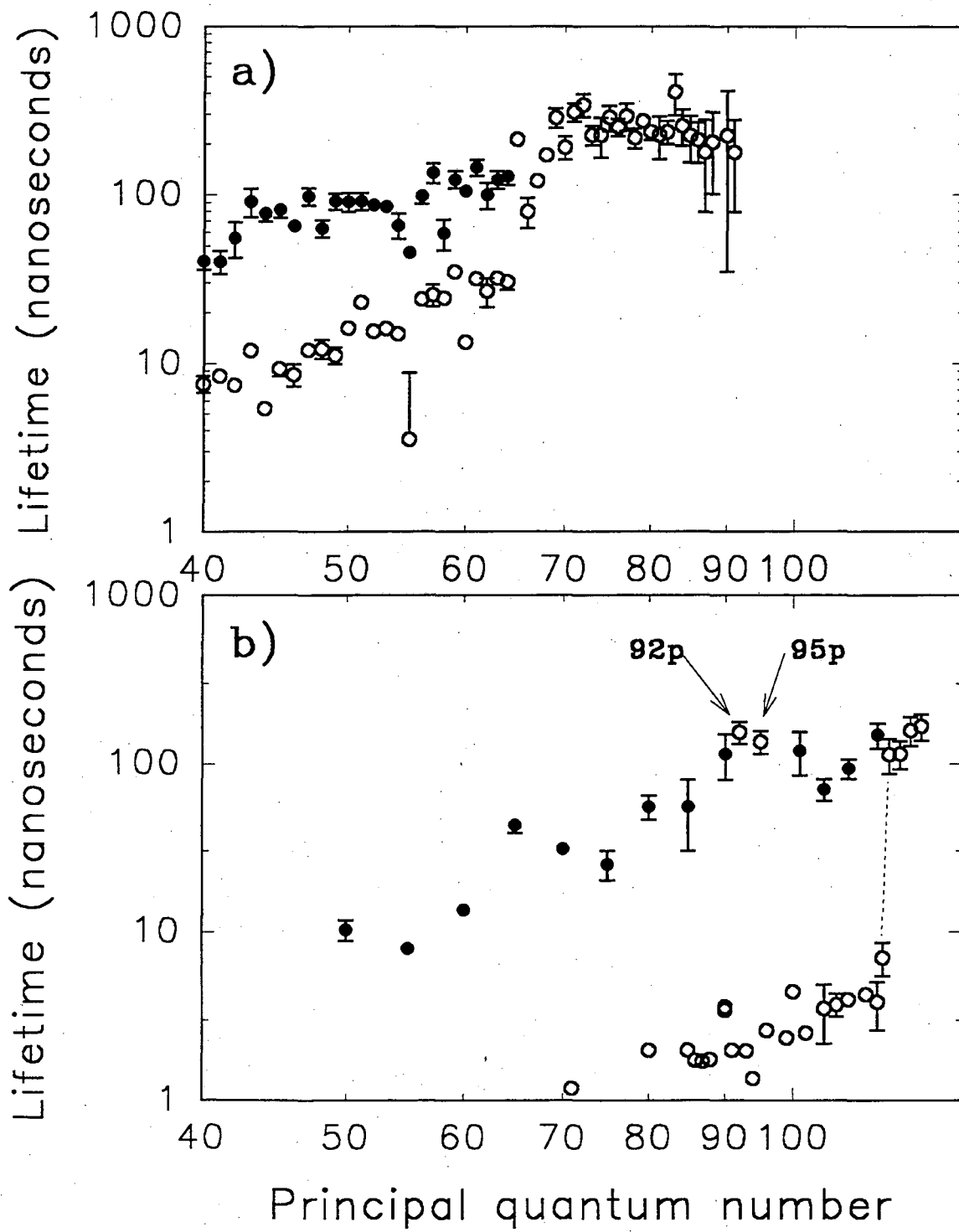


Figure 2

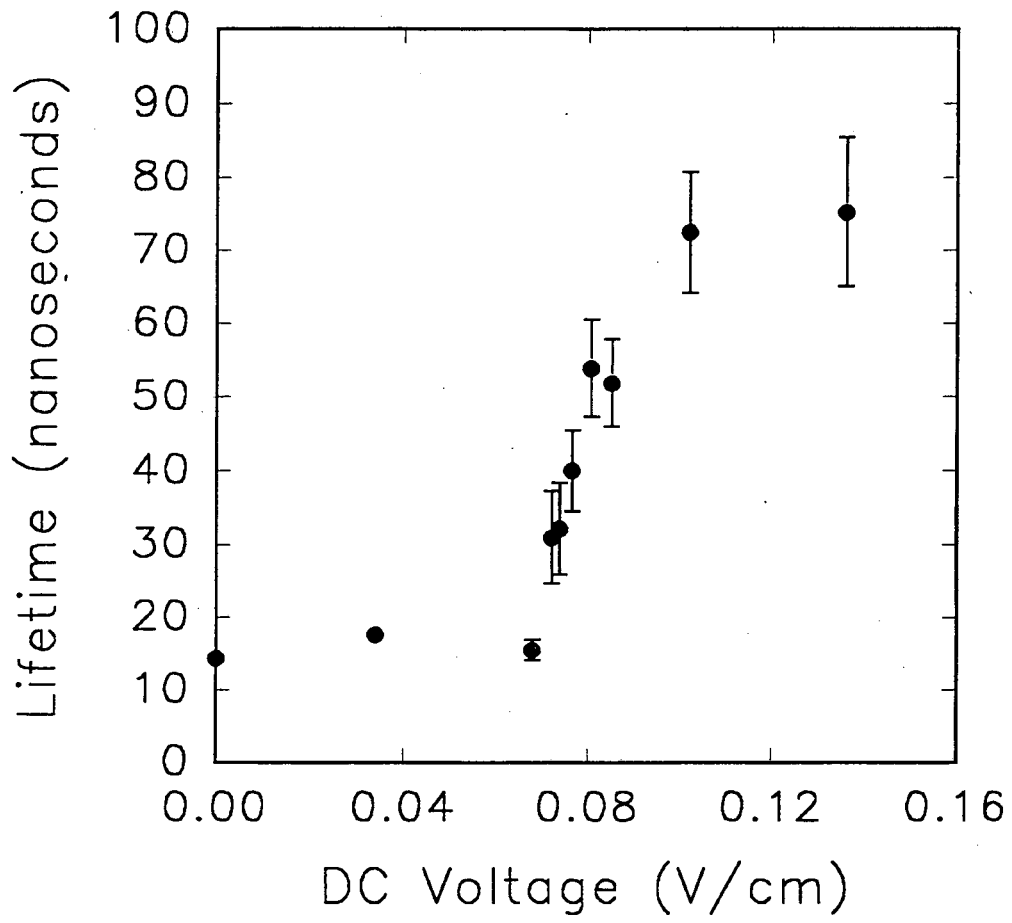
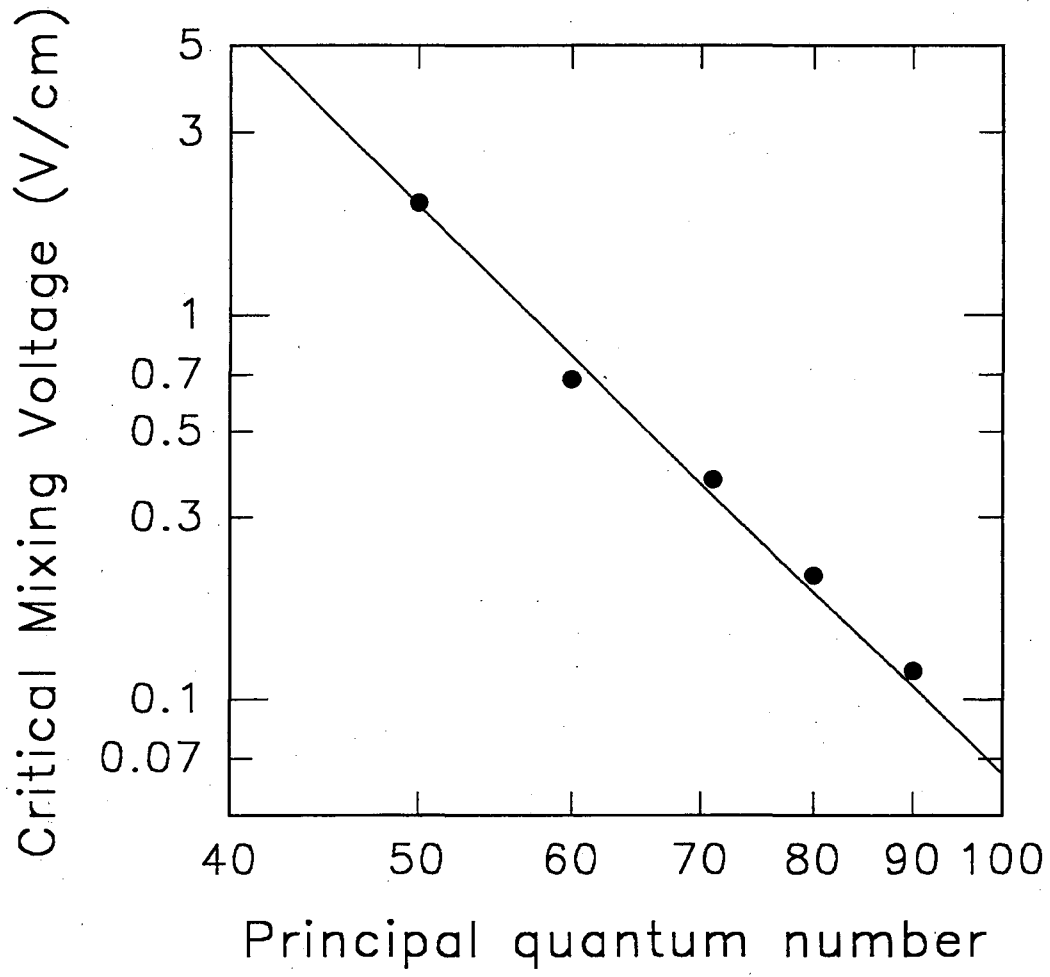


Figure 3





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