COMMUNICATIONS

Resonant enhancement of pulsed-field ionization zero-kinetic-energy photoelectron spectra using microwave fields

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In pulsed-field ionization zero-kinetic-energy spectroscopy (PFI-ZEKE), Rydberg states are typically field-ionized approximately 1 μs after photoexcitation. During this waiting period optically accessible Rydberg states in zero field would decay due to autoionization or predissociation, however their lifetimes are lengthened by the electric fields due to ions or macroscopically applied fields. In this work, we experimentally demonstrate that the introduction of an appropriate microwave field can appreciably lengthen the lifetimes of Rydberg states of the NO molecule, which would otherwise decay by predissociation. The microwave field mixes optically accessible states with longer-lived noncore penetrating states. The resulting enhancement in field-ionization signal is seen at energies where the n, $n+1$ spacing matches the microwave frequency. This method of suppressing predissociation introduces sharp, symmetric, resonances in the PFI-ZEKE spectra, at specific energies below the ionization thresholds, thus providing a new technique for the accurate determination of molecular ionization thresholds. © *2000 American Institute of Physics.* [S0021-9606(00)01928-0]

In pulsed-field ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy, an important technique for the determination of ionic energy levels and molecular ionization thresholds is based on the optical excitation of Rydberg states which live for microseconds.[1,2] Other applications of molecular Rydberg states, such as the production of state selected ions for reaction studies,[3,4] and the potential for state-specific probing of molecular photolysis products using ''Rydberg tagging'' [5] have similar requirements.

In 1993, Chupka argued that the optically accessible Rydberg states, thought to be excited in PFI-ZEKE spectroscopy should decay quickly ($\ll$1 μs) under isolated field-free conditions,[6] in apparent contradiction to the experimental results. This discrepancy was resolved by noting the presence of external perturbations due to stray fields and nearby ions lengthen lifetimes by mixing the optically accessible (and rapidly decaying) low-l states with the longer lived noncore penetrating high-l states. The presence of these fields is often unavoidable, and their properties are not controllable except under the most ideal experimental conditions.

Given the serendipity involved in these environmental factors in PFI-ZEKE, it is reasonable to investigate other, more direct, approaches to lifetime control, especially for lower n's than normally used in PFI-ZEKE, where stray fields are often insufficient to lengthen lifetimes to microseconds.[7] In this vein, Held *et al.*[8] have recently demonstrated that one may excite long-lived Rydberg states ($>$10 μs) of NO at quite low n ($n\approx45$) by applying a dc electric field during photoexcitation, and rapidly switching it off afterwards. The idea behind this technique is the Stark effect: a dc electric-field mixes optically accessible low-l states—which normally decay rapidly by predissociation—with high-l states. This field is switched off diabatically shortly after photoexcitation and some population is projected onto the long-lived high-l states, which are now no longer coupled to the rapidly decaying low-l states.

In the present work, we have demonstrated for the first time that the application of an appropriate microwave field can prevent the predissociation of molecular Rydberg states. Suppressing predissociation enhances the normally observed PFI-ZEKE spectra—in a manner significantly different from that observed by Held *et al.*[8] In particular, enhancement is observed over a small, *controllable* range of n's for which the microwave frequency matches the $n\rightarrow n+1$ energy spacing, producing a resonance in the PFI-ZEKE spectrum at a well-defined energy below the ionization limit. The advantages of this will be discussed in the following.

For experimental convenience, and comparison with previous studies, the influence of microwaves on the PFI-ZEKE spectra of NO was studied. A $1+1'$ multiphoton excitation scheme was used to excite supersonically cooled NO molecules to the vicinity of the first ionization threshold. A pulsed nanosecond dye laser was frequency doubled to produce light ($\approx$225 nm) to excite the NO molecules to the $A\ ^2\Sigma^+$, $v=0$, $N=0$ intermediate state. The wavelength of this laser was fixed. A second frequency doubled dye laser ($\approx$327 nm), delayed by a few nanoseconds, further excites the molecules to energies in the region of the first ionization threshold. The photon energy of the second excitation laser was calibrated using etalon fringes and tabulated uranium transitions observed using the optogalvanic effect in a hollow cathode discharge lamp.[9] The uncertainty in the calibra-

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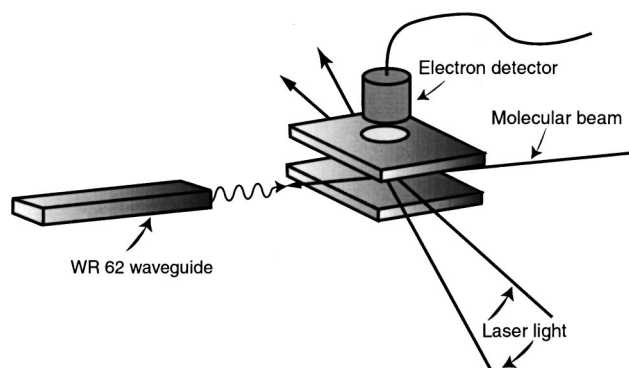[a]Electronic mail: jm5zy@virginia.edu

FIG. 1. Experimental apparatus. The NO molecules are introduced using a supersonically cooled molecular beam from a pulsed valve. With the beam on, the average vacuum chamber pressure is 10^{-5} Torr.

tion of photon energy (after doubling) is roughly the same as the bandwidth (0.5 cm^{-1}). The molecular and two laser beams crossed halfway between two parallel aluminum plates separated by 1.27 cm (see Fig. 1). A field ionization pulse of 315 V/cm was applied using these plates, approximately 750 ns after photoexcitation, and the electrons from field ionization were extracted through a mesh covered hole in the upper plate to a microchannel plate detector. Electrons, due to this field ionization pulse, if any, were selectively detected with a gated integrator so that prompt photoelectrons, and electrons due to autoionization did not contribute to the observed signal. Scanning the photon energy resulted
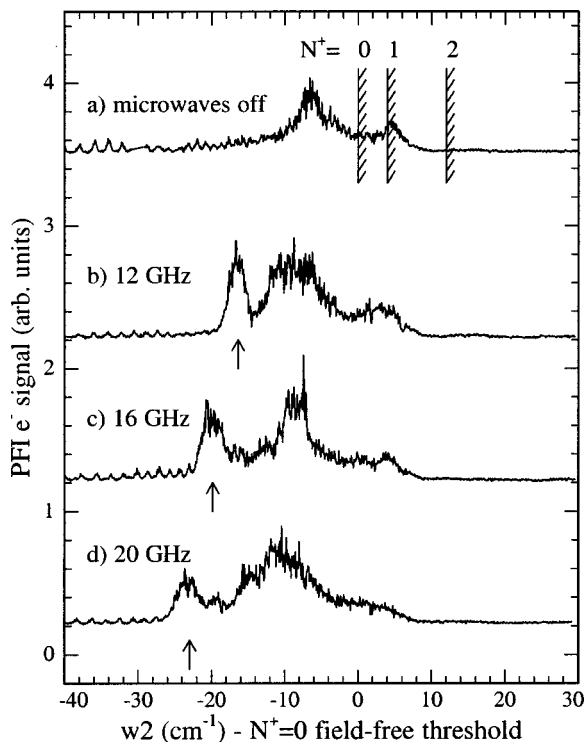

FIG. 2. PFI-ZEKE spectra of NO taken (a) without microwaves, and with microwave fields of (b) 12 GHz, 0.020 mW/cm^2, (c) 16 GHz, 0.036 mW/cm^2, and (d) 20 GHz, 0.082 mW/cm^2. All spectra (a)–(d), are taken in the presence of a 1.2 V/cm dc electric field, parallel to the microwave field polarization. The microwaves are on during photoexcitation, and switched off 100 ns later. The delay between excitation and field ionization is 750 ns. The field ionization pulse is 315 V/cm, with a rise time of roughly 50 ns. The vertical arrows indicate the resonance positions computed using Eq. (4).

in a PFI-ZEKE spectrum of NO similar to those obtained in previous studies.[10] In Fig. 2(a) we show a spectrum obtained with a static electric field of 1.2 V/cm. All spectra in this paper are displayed with energy scales relative to the $N^+ = 0$ ionization threshold. (This is determined by extrapolation of the Rydberg series observed approaching the $N^+ = 2$ threshold, together with the $N^+ = 0$, $N^+ = 2$ rotational spacing of 11.9 cm^{-1}.)

The microwave field was introduced using an open ended piece of WR62 waveguide directed toward the excitation region. The end of the waveguide was located approximately 3.2 cm from the interaction region. The microwave oscillator was a Hewlett–Packard 83620A sweep generator. The power available from this oscillator is ≈ 20 mW over the frequency range of interest: 12–20 GHz. Quoted microwave intensities given throughout this paper are estimated by dividing the total power emitted by the waveguide by 10 cm^2. (This is based on the bounds established by the theoretical centerline intensity within the waveguide and that expected in the far-field radiation pattern.[11]) The resulting estimated intensities are expected to be accurate to within an order of magnitude. To switch the microwaves on and off, the external pulse modulation input of the sweep generator was used. This generates microwave pulses of variable length, having rise and fall times of 50 ns.

Figure 2(b) shows how a PFI-ZEKE spectrum of NO is modified by applying a microwave field (12 GHz, 0.02 mW/cm^2) during photoexcitation, and switching it off 100 ns later. The obvious difference from Fig. 2(a) is the strong, spectrally sharp enhancement approximately 16 cm^{-1} below the $N^+ = 0$ ionization threshold. As shown by Figs. 2(c) and 2(d), when the microwave frequency is varied from 12 to 20 GHz, the position of this ''resonant'' enhancement shifts to lower energy, whereas the broader enhancement observed at higher energies does not shift significantly.

The strong, spectrally sharp, enhancement of signal in Fig. 2(b) is due to the suppression of predissociation by resonant mixing of the states of adjacent n using the microwave field—more or less the resonant analog of Stark mixing in a dc field. We shall return to the details of how the mixing occurs and first show how the frequency of the applied microwave field is related to the energy at which the resonance is observed in the PFI-ZEKE spectra. In atomic units, the microwave angular frequency ω matches the $n \to n+1$ transition when

$$\omega = \frac{1}{n^3}, \tag{1}$$

and the energy W is given by

$$W = -\frac{1}{2n^2}. \tag{2}$$

Combining these two equations gives the location of the resonance as

$$W = -\frac{\omega^{2/3}}{2}. \tag{3}$$

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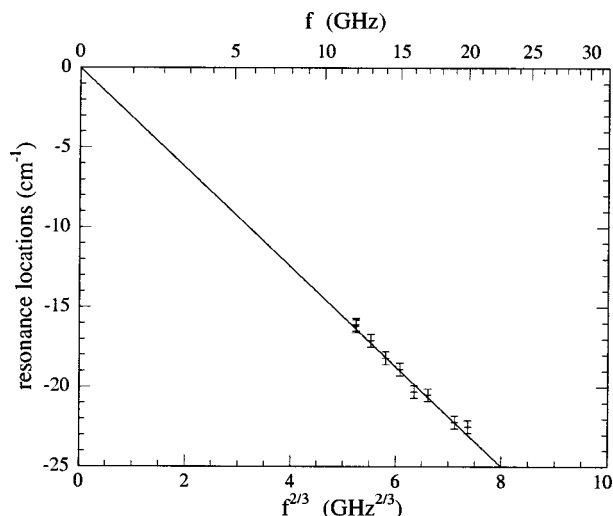Resonant enhancement of photoelectron spectra   1323

FIG. 3. Microwave-induced resonance locations as a function of microwave frequency. Conditions were similar to those for Fig. 2. The solid line refers to the relationship given by Eq. (4).

FIG. 4. PFI-ZEKE spectra in the presence of a 20 GHz, 0.082 mW/cm^2 microwave field, which is switched off 100 ns following photoexcitation, both (a) without, and (b) with the presence of a dc electric field. Relative signal levels are comparable but (a) has been reduced in vertical scale by a factor of 2. All other conditions are identical to those of Fig. 2.

Rewriting in laboratory units [W in cm^{-1}, and $f = \omega/(2\pi)$ in GHz]:

$$W = -(f/0.181)^{2/3} [\text{cm}^{-1} \text{GHz}^{-2/3}]. \quad (4)$$

For example, a frequency of 12 GHz should give a resonance 16 cm^{-1} below the ionization limit. This relationship between the applied microwave frequency and the observed energy of microwave induced resonant enhancement was tested by collecting a series of spectra using microwave frequencies from 12 to 20 GHz. Figure 3 shows the position of the observed resonance in each spectrum plotted as a function of the 2/3 power of the applied microwave frequency. Agreement with Eq. (4) is exact to within the experimental error (which is dominated by the uncertainty in the laser wavelength calibration).

A potentially important application of this microwave enhancement technique is the determination of ionization potentials. By measuring the photon energy at which a resonance appears, and adding the energy given by Eq. (4), the energetic threshold for ionization would be determined. Two spectra, taken with different microwave frequencies would be sufficient to identify the resonances and confirm their expected shifts. Given the sharpness and symmetry of the observed resonances, one should expect less ambiguity than with a traditional extrapolation, using a series of PFI-ZEKE spectra taken with different dc electric field strengths.[10]

In order to observe the microwave enhancement peak discussed previously, we found experimentally that a small dc electric field must be present [i.e., Fig. 2(b) was taken with a field of 1.2 V/cm]. This is explicitly illustrated in Fig. 4, which shows that without a field the resonance does not appear. Above a certain dc field strength, the signal at the center of the resonance does not increase, although the resonance widens spectrally. However the center of the resonance does not shift, still obeying the simple relation given by Eq. (4).

If the dc electric field were not required to see the microwave enhancement, our results might be relatively straightforward to explain: 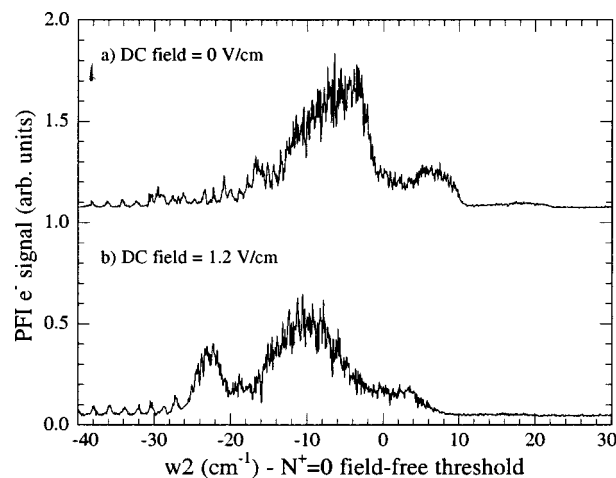the laser excites the molecule to a low-l state, $|n,l\rangle$, which would normally decay quickly. However the presence of the microwave field with $\omega = 1/n^3$ induces the resonant dipole coupling:

$$|n,l\rangle \leftrightarrow |n+1,l+1\rangle \leftrightarrow |n,l+2\rangle \cdots, \quad (5)$$

which causes population transfer to longer-lived high-l states. Once the initial spreading of l has occurred, the low-l states act as a drain, and the microwave field should be turned off. However, in anything other than atomic hydrogen, a modest microwave field at a frequency of $\omega = 1/n^3$ only provides the required $|n,l\rangle \leftrightarrow |n+1,l+1\rangle$ resonant coupling for high-l states, since the optically accessible low-l states have nonzero quantum defects, and their transitions do not occur at $\omega = 1/n^3$. In other words, the resonance condition cannot be simultaneously satisfied for both low and high-l states. Thus the presence of no or little enhancement with zero dc electric field is perhaps not surprising.

Experimentally, we observe that the dc field required to see a microwave effect is approximately the magnitude of the Inglis–Teller field $1/(3n^5)$ (in atomic units[12]) at the n where the resonance is observed, and that this field decreases with increasing n (decreasing f). If the dc field exceeds the Inglis–Teller field, the lower-l states are mixed into the Stark manifold, making the Stark states optically accessible. If the Stark states were all composed of equal parts of high-l and low-l character, they would all be equally easy to excite optically and have the same predissociation rates, and driving transitions between them would have no effect. However, even in hydrogen, only the s states are evenly spread over the Stark states, all other l states are spread nonuniformly.[13] Adding a finite sized ionic core makes the uniformity of the low-l distributions worse,[14] and in a molecular system interseries coupling further complicates the problem.[15] In short, it is reasonable to expect the most optically accessible Stark states to have short lifetimes so that coupling them to other Stark states with a resonant microwave field will lengthen their lifetimes.

We are now led to the question of why there is a resonant microwave coupling of the Stark states. In the case of hydrogen, Stark states of the same n are not dipole coupled. Although there is not a rigorous dipole selection rule for transitions between hydrogenic Stark states of adjacent n, there is a propensity for couplings with $\Delta k = \pm 1$, where k is the Stark quantum number [see Eq. (65.1) of Ref. 16]. Since Stark states differing in n by one, and differing in k by one, will have almost identical Stark shifts, the resonant frequency is still $\omega = 1/n^3$, just as in zero field. Changing only the principal quantum number does not change the lifetime very much, but the changes in k induced by the microwave field will lead to a sampling of all the Stark states, including those with long lifetimes. Turning the microwave field off will leave some molecules in these states. Experimentally, we observe that microwave-stabilized Rydberg states have lifetimes exceeding a microsecond (which we observe by delaying the time of the field ionization pulse).

Although we have presented results for NO, nothing limits this technique to NO alone. Roughly analogous results have been obtained[17] for the dielectronic recombination of Ba[18] in the presence of a microwave field. In the future, it would be useful to examine the effects of higher microwave powers, explore different polarizations of the static and microwave fields, and extend the measurements to higher and perhaps two frequencies. In addition, it is of interest to test the applicability of this technique to other molecular systems. As previously stated, the observation of clean microwave-induced resonances could be useful for the determination of molecular ionization thresholds. This microwave-induced enhancement could also be applied to situations where background ions, and the deliberate application of a homogeneous electric field are insufficient to lengthen lifetimes to the microsecond time scale required for many experiments (see, e.g., Ref. 19).

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