Fractional Stark State Selective Electric Field Ionization of Very High-n Rydberg States of Molecules

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For the first time *fractional Stark state selective electric field ionization* of very high-n ($n > 250$) molecular Rydberg states is observed. An "offset" electric pulse selectively ionizes the more fragile "red" (downshifted in energy) Stark states. The more resilient "bluer," or upshifted, ones survive and are shifted down in energy upon application of a second ("probe") pulse of opposite direction (diabatic Stark states' inversion). Hence, even for smaller probe than offset fields ionization is observed. The offset/probe ratio allows one to control spectral peak shapes in zero-kinetic-energy photoelectron spectroscopy. [S0031-9007(96)00130-5]

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Zero-kinetic-energy photoelectron (ZEKE) spectroscopy, introduced in 1984 [1], provides an efficient tool for high resolution studies of molecular and cluster ions [2–6]. The experimental ZEKE technique most commonly employed, either in electron or ion detection (mass analyzed threshold ionization [7–9]), is based on the delayed pulsed field ionization (PFI) of long-lived Rydberg states [10] (*ZEKE Rydberg states*) excited a few wave numbers below each (rovibronic) ionization threshold. For atoms, the selectivity of PFI with respect to the n, l-quantum numbers has been widely exploited in atomic Rydberg states' studies [11,12]. For molecules, the selectivity of PFI was employed recently to optimize the spectral resolution in ZEKE spectroscopy. A staircase slope PFI pulse [5] served to filter narrow (nonoverlapping) n bands of high Rydberg states converging to distinct (rovibronic) ionization thresholds of the molecular cation.

This Letter reports on new experimental results of PFI of very high-n ($n > 250$) molecular ZEKE Rydberg states. Earlier, Chupka [13] pointed out that there exists an inherent limitation of the n selectivity due to the distributed character of the diabatic threshold for PFI [12–15], a conclusion which applies to the stepped ionization [5] as well. In the present work, a new kind of selectivity with respect to the "red" and "blue" Stark states is found, which can be used for a further improvement of the spectral ZEKE resolution. The benzene molecule was chosen as an example, since the achievement of fully rotationally resolved spectra of the benzene cation presents a real challenge considering its small rotational constants ($B \approx 0.2$ cm^{-1}, $C \approx 0.1$ cm^{-1}).

The experimental setup, described in Refs. [16,17], consists of a mutually perpendicular arrangement of a pulsed skimmed supersonic jet of benzene (seeded in 4 bar argon), two counterpropagating frequency-doubled dye laser beams, and two extraction plates in a mumetal shield. The ZEKE-PFI signals are obtained from two-photon, two-color ($1 + 1'$) photoexcitation by using double electric pulses [18], applied with a delay after the light pulse to field ionize the ZEKE Rydberg states. Both electron time-of-flight (TOF) spectra and ZEKE spectra are recorded by a transient digitizer. Calibration of the laser frequencies is obtained from simultaneously measured iodine spectra [19]. Inhomogeneous fields from ions are negligible since less than 100 ions per laser shot are produced in the ionization volume of ~4 mm^3. The diameter/distance ratio (3:1) of the extraction plates leads to minimization of perpendicular components of the residual electric field, which was compensated to less than 10 mV/cm in the z direction [5]. All observations agree with a total residual field (vector sum of stray fields and programmed field) of less than 10 mV/cm well collinear to the z axis. The $D_0\,{}^{ev}E_{1g}(N^+, K^+) \leftarrow S_1 6^1\,{}^{ev}E_{1u}$ ($J' = 4, K' = 4, +l$) transition of benzene is employed with assignments given in Fig. 4. N^+ is the total angular momentum quantum number excluding electronic spin, K^+ its projection onto the D_{6h} highest symmetry axis.

The key to the present experiment is the use of double electric field pulses, either both of negative z direction or one of positive and one of negative z direction as outlined in Fig. 1 (left). Throughout this article, *negative* and *positive* z direction are used to indicate a field accelerating the electrons *onto* or *opposite to* the microchannel plate (MCP) detector, respectively. Hence, only the electrons liberated by a negative pulse can be detected and correlated with a signal peak in the corresponding TOF spectrum. The pulses which produce the detected TOF signal (Fig. 1, right) are gray shaded. The TOF spectra reproduced in Fig. 1 are obtained

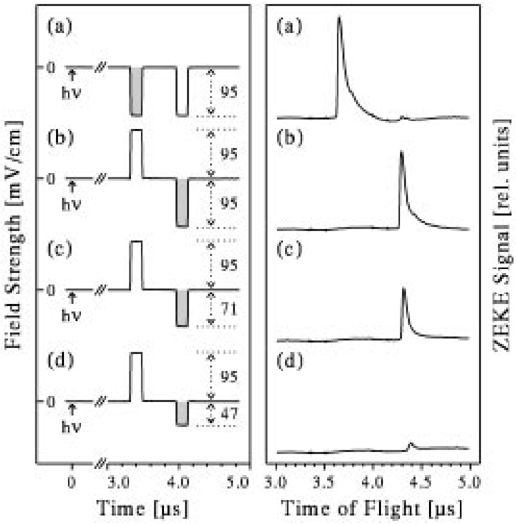

FIG. 1. Left: Double field ionization pulses consisting of (a) two negative pulses (95 mV/cm each) and (b)–(d) a positive offset (95 mV/cm) and a negative probe pulse [(b) 95, (c) 71, and (d) 47 mV/cm]. The first pulse (duration 160 ns) is applied 3.32 μm after photoexcitation, the second one with the same duration 640 ns later. Right: Electron TOF spectra corresponding to a single frequency point ($E = 74\,556.1$ cm^{-1}) of the $D_0\,{}^{ev}E_{1g}(N^+, K^+) \leftarrow S_1 6^1\,{}^{ev}E_{1u}$ $(J' = 4, K' = 4, +l)$ transition of benzene.

for excitation into the long-lived high-n Rydberg state manifold below the corresponding ionization thresholds, the N^+, K^+ rovibronic states of $C_6H_6{}^+$; see also Fig. 3. Two kinds of TOF peaks were monitored, the earlier and later ones, correlated either with the first or second pulse.

In the TOF spectrum (a) (Fig. 1, right) with the two pulses of the same direction signal arises only from the first negative ("offset") pulse F_1 and virtually no signal is produced by the second negative ("probe") pulse of the same magnitude $F_2 = F_1$. In contrast, as depicted in Figs. 1(b)–1(d), applying two pulses of opposite direction with a positive offset pulse $F_1 > 0$ and a negative probe pulse $F_2 < 0$ even of lower magnitude $|F_2| \le |F_1|$ distinct signal can be attributed to the second one. This signal is "forbidden" within the simple model of PFI in which the field-lowered threshold is expected to have a sharp boundary; i.e., all ZEKE Rydberg states with an energy above threshold will ionize while all states below threshold remain bound. The observation of quite a strong forbidden signal means that at the given conditions the offset pulse causes incomplete *fractional ionization.* The survived fraction of the initial population "remembers" the direction of the offset field and has lower stability towards the ionizing field of opposite direction.

These results are consistent with the model of predominantly diabatic ionization. Optical excitation in the presence of a stray field above the Inglis-Teller limit ($F_{\mathrm{IT}} \le 1.8$ mV/cm at $n \ge 250$) creates a narrow-n distribution of ZEKE Rydberg Stark states. On a time scale of ~ 3 μs to some extent there may occur m_l randomization [13,20], though the contribution of the ions to this process is likely to be negligible considering their low density of less than $\sim 20-30$/mm^3, which results in inhomogeneous, nonstationary fields of less than 0.1 mV/cm. At the high n's of interest, $n \ge 250$, the critical slew rate of the field for diabatic ionization, $(dF/dt)_{\mathrm{cr}} \le 6 \times 10^{-5}$ mV/(cm ns) [Eq. (12) of Ref. [13]], is much lower than the experimental one, 100 mV/(cm 10 ns). The ensemble of parabolic Stark states $|n_1, n_2, m\rangle$ $(n = n_1 + n_2 + |m| + 1)$ diabatically passes to ionization through the above Inglis-Teller field region (Fig. 2). Based on the experimentally determined field shift of the ionization onset, $\Delta E = 3.9F^{1/2}$ cm^{-1} (F in V/cm) [5], as expected for diabatic ionization, autoionization of the "blue" Stark states into the "red" continua [12] can be ruled out. This conclusion agrees with the general trend in stabilized ZEKE Rydberg states [13,20] towards immunity against all kinds of core-induced perturbations. Hence, the states of a given n ionize at distinct hydrogenic threshold fields $F_{\mathrm{thr}}(n_1, n_2, m)$, with the blue, or upshifted, Stark states higher in energy (orbital dipole antiparallel to the field) being more resilient to ionization than the red, or downshifted, ones (parallel alignment). At a given field F_1, there exists an interval of excitation energies (specified, in terms of n, by the equation $0.130 = \Phi_{\min} < F_1 n^4 < \Phi_{\max} = 0.383$, in atomic units) [15], where the ionization yield changes from 0 to 1 and the ensembles of Stark states undergo a *fractional* Stark state *selective* ionization. The "redder" states ionize, the "bluer" ones survive (Fig. 2, right).

In the diabatic picture, both the dipole orientation and the parabolic quantum numbers are preserved (memory effect), at least approximately, during the fast fall (10

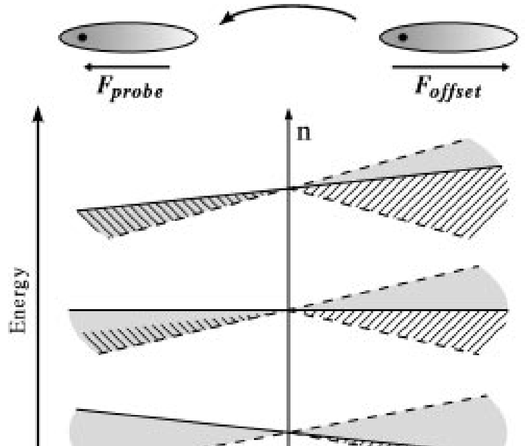

FIG. 2. Mechanism of FSSFI and increased resolution. The offset pulse (right) selectively ionizes the more fragile red Stark states (dashed region); the more resilient bluer ones (gray-shaded region) remain untouched. By employing a probe pulse of opposite direction (left) the survived states turn red and ionize (gray-shaded/dashed region). The orientation of the electric dipole moment is preserved.

ns) of the first field, the subsequent period with the residual field and the rise of the second field in the same or opposite direction. Hence, the field inversion implies Stark states' inversion (SSI). The survived bluer states become less resilient red ones with respect to the second field and can be ionized even with reduced magnitude of the probe pulse $|F_2| \le |F_1|$, yielding the so-called *forbidden* ionization signal (Fig. 2, left). Without inversion, the probe field has to be increased, $F_2 = F_1 + \delta F$, in order to cause ionization. In this case, even the ultimate reduction of the field increment, $\delta F \to 0$, cannot reduce the spectral width of the ionization below an inherent limit, theoretically determined as FWHM = $0.8F^{1/2}$ cm^{-1}(V/cm)$^{-1/2}$ [21]. At all excitation energies within the interval of fractional ionization the probe pulse will harvest a signal due to the survived states. With the inversion ("positive offset" scheme), the probe field can be reduced in order to selectively ionize only the most fragile red states of the highest survived n's (Fig. 2, left) and, thereby, confine ionization to a small subinterval of the full interval of the inherent width.

Experimental manifestation of the hydrogenic memory effect in a molecular system is an interesting result. Multilevel anticrossing at zero field (ZFA) is not a limitation to diabatic SSI in the present experiments. Higgs *et al.* [22] and Rolfes, Smith, and MacAdam [23] have observed diabatic passage through ZFA upon sudden field reversal (slew rate of about 2×10^7–10^9 V/cm s) even in low-m_l moderately high-n ($n \approx 30$–40) Rydberg states of helium and sodium. The probability of diabatic passage was found as a steeply rising function $\sim n^{8.3}$ [23] of the principal quantum number n. The theoretical approach of Ref. [24] (see also [11–13]) enables one to estimate the total probability of the nondiabatic transitions at ZFA in the weakly nondiabatic regime in good agreement [21] with the experimental data of Refs. [22,23]. A rough upper bound estimate is $P_{\mathrm{nondiab}} \approx (dF/dt)_{\mathrm{cr}}/(dF/dt)$, where $(dF/dt)_{\mathrm{cr}} \approx (4\pi/3)\,(|\delta_l'| - \delta_l'^2)^2[\ln(n/2) + 0.6]/n^9$ (compare to [25]), δ_l' being the largest fractional ($|\delta_l'| \le 0.5$) quantum defect in a given m_l manifold. In the worst case, $m_l = 0$ and $|\delta_0'| = 0.5$, the critical slew rate $(dF/dt)_{\mathrm{cr}}$ amounts to 8×10^{-2}, 2.5×10^2, and 6×10^3 mV/cm ns at $n = 250$, 100, and 70, respectively. The experimental observation of diabatic SSI can be hindered in the presence of a residual perpendicular field $F_\perp$. Accurate compensation of the collinear stray field *only* during the interval between the pulses would result in the full dephasing of the parabolic states (memory loss) on the time scale of $\tau_d = 2\pi/6nF_\perp$, which is 260 ns at $n = 250, F_\perp = 2$ mV/cm. Based on the large difference in the intensities of the forbidden signal obtained with positive and negative offsets, it is concluded that the residual field is practically collinear to the z axis.

The effect of a variation of the offset/probe field ratio on the peak shapes in ZEKE spectra of benzene is shown in Fig. 3. Individual peaks in the spectra correspond to selectively ionized narrow-n bands of ZEKE Rydberg states excited below each specific rovibronic ionization threshold of the benzene cation. Inspection of the forbidden ionization spectra in Fig. 3 [(b)–(d), top and (a)–(c), bottom] verifies that, in accordance with the foregoing model, the energy position of the high-n edge of each peak is determined entirely by the offset pulse. The low-n onset is determined by the magnitude of the probe pulse (see Fig. 2, left) and corresponds to the experimentally found field shift equation for the diabatic ionization onset: $\Delta E = 3.9F^{1/2}$ cm^{-1} (F in V/cm) [5]. Above the high-n edge, the higher-n ensembles were already completely ionized by the offset field and cannot contribute to the probe signal [compare forbidden spectrum (b) to the "normal" one (a), both in Fig. 3, top]. In the region below the high-n edge the normal peaks overlap with the forbidden ones since both the offset and probe pulses harvest certain fractions of the initial population (compare left and right dashed regions in Fig. 2).

The *fractional Stark state selective electric field ionization* (FSSFI) of molecular ZEKE Rydberg states, as outlined above, can be used to control the states to be ionized in order to optimize the spectral ZEKE resolution. The ZEKE spectrum (a) (Fig. 3, top) exemplifies a normal resolution (FWHM ≈ 1.2 cm^{-1}) corresponding to a single ionizing pulse of 95 mV/cm. The peak width in the forbidden spectra (b)–(d) (Fig. 3, top), obtained with positive offset/negative probe double pulses, is reduced by a factor of 1.3 (b), 1.5 (c), and 1.8 (d). Within the present

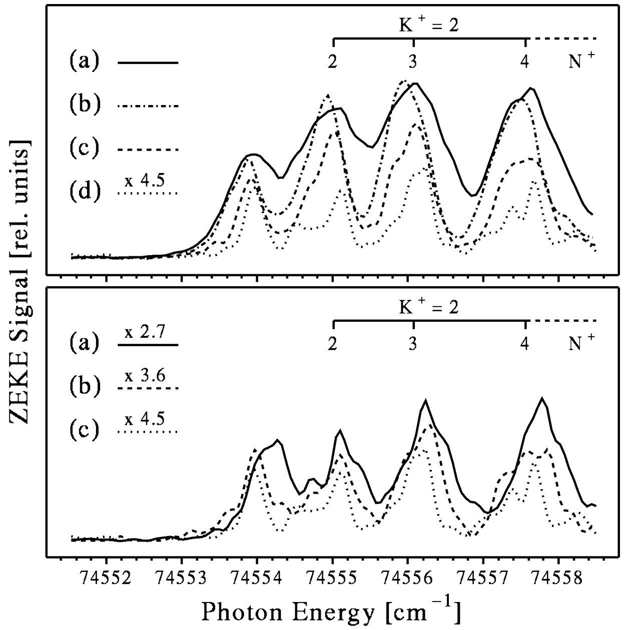

FIG. 3. Top: ZEKE spectra of the $D_0\,{}^{ev}E_{1g}(N^+,K^+) \leftarrow S_1 6^1\,{}^{ev}E_{1u}$ ($J' = 4, K' = 4, +l$) transition of benzene with (a)–(d) corresponding to the double pulses and TOF peaks reproduced in Figs. 1(a)–1(d). Bottom: ZEKE spectra correlated to double pulses consisting of a positive offset [(a) 47, (b) 71, and (c) 95 mV/cm] and a negative probe pulse [(a)–(c), 47 mV/cm]. All other conditions are identical to those of Fig. 1 and the top of this figure.

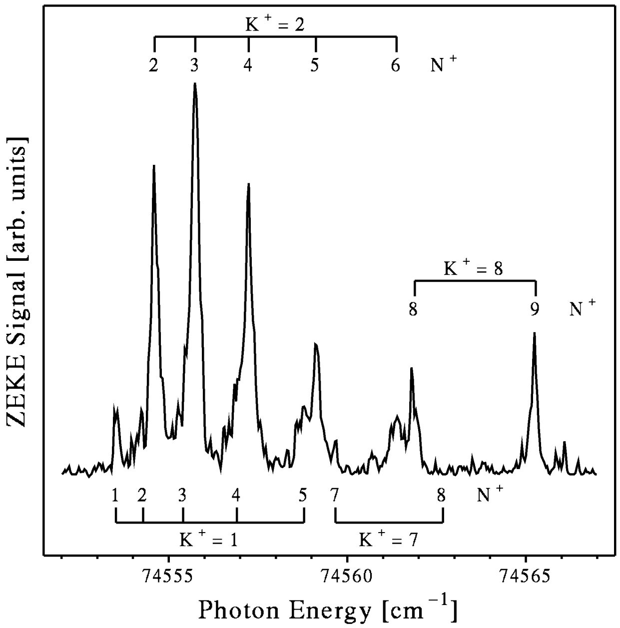

FIG. 4. ZEKE spectrum of the $D_0\,{}^{ev}E_{1g}(N^+, K^+ = 2, 8) \leftarrow S_1 6^1\,{}^{ev}E_{1u}$ $(J' = 4, K' = 4, +l)$ transition (dominant) of benzene obtained in the fifth step (96–120 mV/cm) of a negative stepped probe pulse (24 mV/cm per step) applied 3.32 μm after photoexcitation. The positive offset pulse (magnitude 189 mV/cm, duration 2.5 μs) is applied 660 ns after photoexcitation in the presence of a positive static field of 24 mV/cm.

experimental conditions, spectrum (b) has the same intensity at its maximum as spectrum (a), while a further reduction of the linewidth occurs at the expense of a decrease in intensity by a factor of 1.3 in (c) and 8.4 in (d), in accordance with the fractional yield of ionization. No signal is detected with F_2 as low as 24 mV/cm.

A forthcoming full article [21] will provide a detailed analysis of the new FSSFI technique. To demonstrate the improvement in resolution, the so far best resolved ZEKE spectrum of a molecule (FWHM between 0.15 and 0.25 cm^{-1}) is reproduced in Fig. 4. A substantial part of the total width is due to the second laser (FWHM $= 0.10\ \mathrm{cm}^{-1}$ after frequency doubling) which excites the $D_0 \rightarrow S_1$ transition *from* the intermediate state. The first laser of equal bandwidth precludes a full resolution [26] of the $S_1 \rightarrow S_0$ transition *to* the dominant $S_1 6^1\,{}^{ev}E_{1u}(J' = 4, K' = 4, +l)$ intermediate state. This accounts for an admixture of the $D_0\,{}^{ev}E_{1g}(N^+, K^+ = 1, 7) \leftarrow S_1 6^1\,{}^{ev}E_{1u}(J' = 4, K' = 3, +l)$ transition in the ZEKE spectrum, marked in Fig. 4.

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