Long Lived ZEKE states above the Ionization Threshold

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Experiments on threshold photoionization of benzene are performed which show very long lived neutral molecular states above the ionization threshold. These states are shown to have lifetimes of tens of microseconds and longer in the energy range of vibrational excitation of the molecular core as well as for electronic excitation in the range of 5 eV above the ionization potential (IP).

Key words: Benzene, Ionization, Mass spectroscopy, ZEKE (zero electron kinetic energy), Rydberg states.

Introduction

We here report on extremely stable neutral molecular states in three regions of the spectrum:

(a) just below the ionization energy,
(b) above the ionization energy, but just below the v_6 vibration in the ion, and
(c) high intensity up-pumping from (b) to produce-fragments.

In all three cases ionization only occurs upon application of a D.C. field. For (a) this is expected, but quite surprising for (b) and (c). These states are observed to be stable as neutrals, even after some 100 μs. Clearly these are long lived Rydberg type states of anomalous lifetime, probably due to high l quantum numbers which are formed from the original low l optical Rydberg state.

In the present experiment we probe the excited molecules 11 μs after laser excitation. Due the experimental setup prompt ions which are formed at the laser time are removed at an early stage. From then on the excited molecules first drift in the weak spoiling field and then for a total of 5 μs under field free conditions in the low density jet at which point they are field ionized. From this the observed lifetime is affected only by intramolecular processes, as influences from larger external fields, collisions, or electric fields due to surrounding ions [1] can be neglected. This permits the study of the energy dependence of isolated molecules excited to Rydberg states relative to the ionization potential (IP) even at higher excess energies. Although long lived molecular Rydberg states beyond the IP have been observed [2], we here also see long lived states with an excess energy of many eV above the IP, a fact which bears on the question of l-mixing in highly excited Rydberg states.

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Experimental

In the experiment, benzene at 0 °C seeded in He at 4 bar is expanded in through a pulsed nozzle with a 200 μm orifice into the vacuum (Figure 1). This supersonic jet is skimmed 5 cm downstream and the center part then enters the ion optics through a first plate P_1 and interacts with two counterpropagating pulsed lasers. Here the first laser is tuned to excite the resonant $S_1\ 6^1$ inter-mediated state. From there the second laser then scans the region from below the ionization threshold to the region of the $6^1(\pm 3/2)$ transition in the ion. With this laser, excitation of Rydberg states as well as direct ionization of the benzene molecules is performed. The excited neutrals as well as the ions then continue to move together with the speed of the jet. A small negative voltage U_{spoil} is applied to plate P_1, which generates an electric field between the plates P_1 and P_2, whereas the electric field is kept zero in the rest of the ion optics. The spoiling potential is chosen such that the kinetic energy of the ions in the jet which are formed immediately with the laser is compensated. This gives a lower limit of 0.5 V/cm for the spoiling field in our setup. To remove "fast" ions arising from the velocity distribution of the jet particles, a field of

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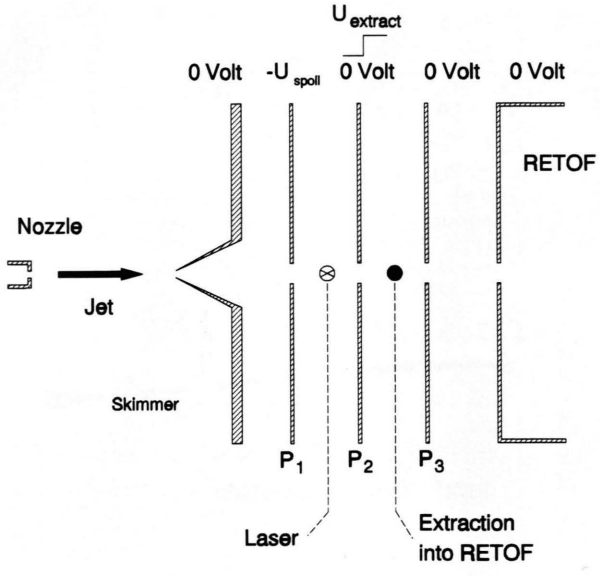

Fig. 1. Experimental setup of the ion optics for the delayed PFI experiment. The molecules in the jet are excited from two perpendicular counterpropagation laser beams between plates P_1 and P_2. Prompt ions are rejected with a small spoiling voltage U_{spoil} applied to plate P_1. The molecules in excited Rydberg states are field ionized after a drift time of 11 μs by applying a fast voltage pulse $U_{extract}$ to plate P_2 and extracted through plate P_3 into the RETOF mass spectrometer.

typically 1 V/cm was used and all ions in this case will be decelerated and cannot penetrate through the hole in plate P_2, whereas the neutrals will arrive after a drift time of 11 μs at a certain point between the plates P_2 and P_3. At that time a fast rising positive extraction pulse is applied plate P_2 leading to a electric field of 200 V/cm. From this the neutrals can be ionized and are extracted into the reflectron time of flight (RETOF) mass spectrometer. The observed ion signal then arises solely from field ionized Rydberg states. It is also possible to measure the directly formed ions if the spoiling voltage is set to zero. In this case the ions also drift into the region between the plates P_2 and P_3 and can be extracted into the RETOF leading to a conventional resonance enhanced multiphoton ionization (REMPI) excitation spectrum from scanning the second laser. At a spoiling field between 0 and 0.5 V/cm, both ion signals from delayed pulsed field ionization (PFI) of the Rydberg excited molecules and from REMPI are detected by the RETOF but are observed as separated mass peaks; and by increasing the spoiling field, the REMPI mass peak completely vanishes. Besides obtaining delayed PFI and REMPI spectra at a given mass, one also can position the wavelength of the second laser to the transition of a selected Rydberg state in the PFI case or to a state in the ionization continuum in the REMPI case and measure the corresponding mass spectrum. At a low laser intensity one obtains a soft ionization of the benzene molecule without fragmentation for the REMPI experiment or the excitation of a Rydberg state without further internal vibrational energy.

Results

The specific results reported here are for Benzene excited (via the $S_1\ 6^1$ intermediate at 38 607 cm^{-1}) from below the lowest ionization threshold to above the ionization threshold of the v_6^+ of the ion. This v_6^+ vibration is known [3] to be split into two Jahn-Teller components. The lower v_6^+ (3/2) component in addition shows two peaks from a quadratic Jahn-Teller splitting [4], both of which are observable in the spectrum shown in Figure 2. Note in this figure how these ZEKE states disappear just above the respective thresholds. Shown also in Fig. 2 is the yield of ions produced by the familiar [5] REMPI process [6]. We have verified that the spectrum of ZEKE states, determined as discussed below and shown in Fig. 2, is reproduced in all respects by subtracting the yield of REMPI ions from the total yield of ions. These results (not shown as a figure) indicate that the ZEKE states are produced but not detected (except for the unintentional presence of stray electrical fields), in a standard REMPI experiment.

By increasing the laser intensity in a REMPI experiment one can induce extensive fragmentation into ionic products [7, 5]. Indeed, one can typically span the entire range from soft ionization producing only the parent ion to hard fragmentation. We have observed a similar but not identical process for the giant ZEKE states, using the technique of mass selected ZEKE spectroscopy [4, 8]. The essential difference is that we have demonstrated that upon further up-pumping the ZEKE states survive as neutrals. This has been verified for the states below the v_6^+ threshold of the ions (a case further discussed below), as well as for the ZEKE states below the lowest ionization threshold. From the point of view of REMPI mass spectrometry [9] the up-pumping occurs, for the ZEKE states, along the neutrals ladder. This is not

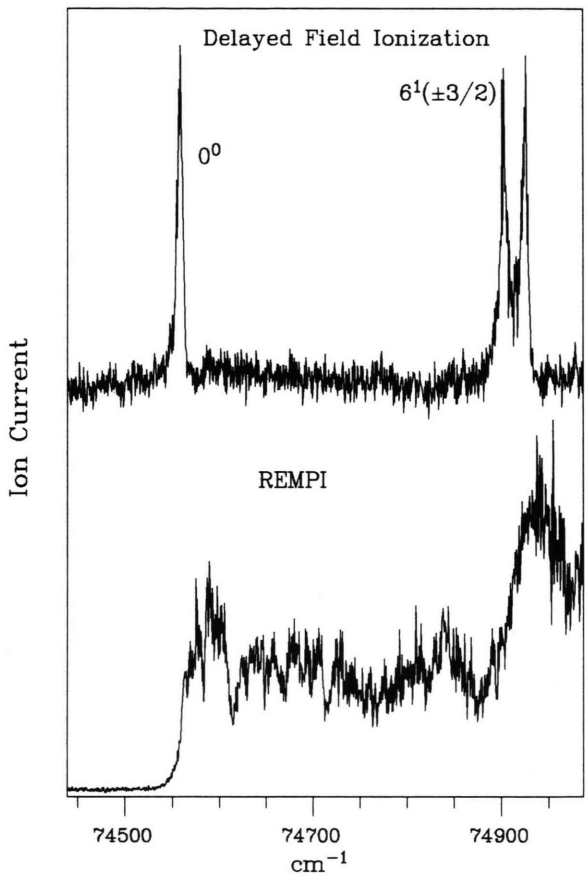

Fig. 2. Excitation spectra of benzene in the region of the ionization threshold. The lower trace shows a two color REMPI excitation spectrum via the $S_1\ 6^1$ state when no spoiling field is applied. The upper spectrum shows the pulsed field ionization spectrum with the spoiling field applied. The ion signal here arises from pulsed field ionization of neutral Rydberg states after 11 μs.

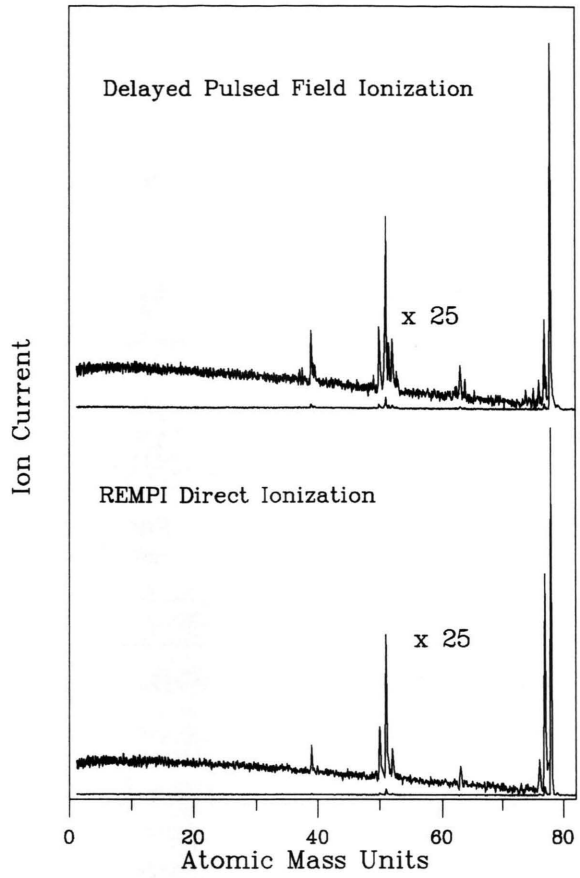

Fig. 3. RETOF mass spectra of benzene. The lower trace shows the REMPI mass spectrum of benzene from photoionization via the $S_1\ 6^1$ state. The ionization laser is set to the higher energy PFI peak of the $6^{1+}(\pm 3/2)$ transition. Fragmentation to $C_4H_x^+$ occurs due to increased intensity of the ionizing laser. The upper trace shows the corresponding mass spectrum from pulsed field ionization with the same laser settings. In this spectrum also $C_4H_x^+$ fragments are observed which arise from up-pumping of Rydberg states belonging to the upper of the $6^{1+}(\pm 3/2)$ states.

necessarily the case for the familiar REMPI scheme where 'ladder switching' [9, 10, 11] can occur so that ionization of the parent precedes the further absorption of photons.

The up-pumped ZEKE states remain as neutrals until a weak DC field is applied, leading to an entire ionic fragments mass spectrum. The extent of fragmentation depends on the laser intensity. The mass spectra obtained upon further up-pumping at a frequency of 36 311 cm^{-1} are shown in Figure 3. This frequency corresponds to the ZEKE states just below the threshold of the upper of the two $6^{1+}(\pm 3/2)$ states of the ion, thus the experiment reproduces the signature of this vibration above the IP. The laser intensity is the same for both mass spectra. However, REMPI [12] is known to result in a finite spread in the kinetic energy of the electrons. In the ZEKE experiment essentially all of the excess energy is retained by the core. There is indeed somewhat more fragmentation evident in the mass spectrum obtained following field ionization of the up-pumped ZEKE states. A similar experiment with similar results was carried out for pumping just above (35 987 cm^{-1}) or just below (35 948 cm^{-1}) the lowest ionization threshold.

Conclusions

In this paper we have demonstrated the extreme stability of the high l ZEKE electron precursor Rydberg states formed from the low l optically prepared states. These ZEKE states were formed in three energy regimes. The lowest is below the first ionization limit where the only competing process is radiationless transitions [13, 14] possibly terminating in dissociation into neutral fragments. In the second regime, just below the v_6^+ threshold, the ZEKE states are isoenergetic with the ionization continuum of the ground state ion. One would expect an autoionizing process on a very short subnanosecond timescale from the interaction of the Rydberg electron which is prepared in a low l state with the vibronically excited ionic core. But rather a long lifetime is observed here. When we increase the laser power of the second laser, a further photon will be absorbed in the molecule, preparing a highly excited Rydberg type state which we found to survive also for this long time off 11 μs and which upon field ionization will yield fragment ions. This is also unexpected for Rydberg states prepared with low l due to the photoexcitation. To explain this one has to conclude that the low l Rydberg electrons have gained high l, that is changed to orbitals which are not penetrating near the core, and this rapidly. In this case the Rydberg electron will no longer be influenced by the nuclear motions of the molecular core which will lead to the observed long lifetimes. This is also confirmed by the fact that in our experiments these long lived Rydberg states are only observed for high n, as observed from the narrow bands in the pulsed field ionization spectra [15].

In conclusion we have shown that long lived Rydberg states can be prepared in three regimes, below the IP, with vibrational excitation above the IP and even with an electronic excess energy of more than 4 eV. In all three regions they remain for many μs as neutrals until a field is applied, even though the energetics would suffice for direct ionization.

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