Long Time Stability of Very High Rydberg States of Vibrationally Excited Molecules

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Experimental results which strongly indicate an extreme decoupling of the electronic from nuclear motions in very high Rydberg states of molecules are reported. The states detected for times as long as tens of μs after excitation are neutral even when there is enough energy to both ionize and fragment the molecule. The Born-Oppenheimer separation would lead one to expect strong coupling, at least when the electron is in the core region. The present results are discussed in light of other recent experiments on high Rydberg states and in terms of observation on electron-ion scattering.

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There are several reasons for the current interest [1-6] in the time evolution of very high Rydberg states of large molecules: Such studies provide a direct test of our understanding of delayed ionization [7] and, in general, of the theoretical machinery as now available to discuss the coupling of electronic and nuclear degrees of freedom [8-11] in systems of very high density of states. Furthermore, such studies are necessary for the full understanding of the nature of the measurement in so-called zero electron kinetic energy (ZEKE) spectroscopy [11-13]. Finally, such studies extend the earlier understanding of low and intermediate molecular Rydberg states [8,11,14] to the high end of the spectrum. Such an extension is particularly warranted by the recent direct demonstration [4] that it is not a matter of simple extrapolation.

In the experiment to be discussed below, following the laser (two photon resonance) excitation Rydberg states are detected by the delayed application of a weak dc electrical field. Electrons can also be produced by direct [11] and by prompt [15] ionization and these need to be discriminated against to ensure that the detected signal is due to long living neutral states. In the present setup, a small dc "spoiling field" is applied in the region of excitation; see Fig. 1. This field also causes ionization of the very highest Rydberg states and hence needs to be kept as small as possible. The neutral molecules drift down a region which is maintained as field free as possible by the parallel large plates design shown in Fig. 1. By varying the drift length, the application of the ionizing field can be delayed by as much as 120 μs. For such long times one cannot, however, be sure that the detected molecules are unperturbed by collisions. For the detailed results on benzene as reported below, detection was after 11 μs which we estimate as 10^{-2} of the mean time between collisions. The ions are detected by a mass spectrometer. Experiments on C_6H_6/C_6D_6 mixtures verify that the Rydberg excitation is not transferred from one isotopic species to another.

Rydberg states with a total energy above the lowest ionization potential of the molecule can, in principle, ionize. The question of whether this ionization is prompt [15] or can also be much delayed has been a subject of current discussion. If it is the case that ionization is delayed one can envisage further up-pumping to even higher energy states which again may or may not ionize promptly. An unexpected result of this experiment is that the states remain neutral even after such further laser up-pumping that the total energy is sufficient for both an ejection of an electron and fragmentation of the ionic core.

The excitation scheme uses a first laser to resonantly access the $S_1 6^1$ intermediate state of benzene. A second, variable frequency laser scans the frequency range from below the lowest ionization potential (IP) to above the

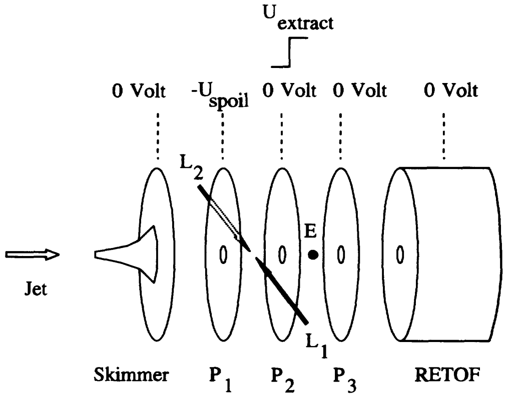

FIG. 1. Schematic of the experimental setup. See text for details. P_1, P_2, and P_3 are plates which have large diameters so as to exclude stray fields. The spoiling field is applied between P_1 and P_2 and the ionization/extraction pulse is applied (with a variable time delay) between P_2 and P_3. L_1 and L_2 are the two lasers. The extraction of ions into the reflectron time of flight (RETOF) mass spectrometer occurs at E.

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threshold for formation of the first excited $\nu_6{}^+$ vibration of the benzene ion. We specifically draw attention to three different regions of the total energy that can be reached in this way: just below and above the lowest IP, above the lowest IP but just below and above the IP to the 6^1 state of the ion, and higher energies due to the absorption of two (or more) photons of the second laser. For all three regions we detect neutral states even for a delay of 11 μs. This is observed not only for the states which are below the higher ionization potential but also for the states which are much higher up in energy.

In the experiment benzene at 0 °C seeded in He at 4 bars is expanded through a pulsed nozzle with a 200 μm orifice into the vacuum (Fig. 1). This supersonic jet is skimmed 5 cm downstream and the center part then enters the ion optics through a first plate $P1$ and interacts with two counterpropagating pulsed lasers. Here the first laser is tuned to excite to the resonant 6^1 intermediate state. From there the second laser 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 $P1$ which generates an electric field between the plates $P1$ and $P2$, 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 typically 1 V/cm was used and all ions in this case will be decelerated and cannot penetrate through the hole in plate $P2$, whereas the neutrals will arrive after a drift time of 11 μs at a fixed point between the plates $P2$ and $P3$. At that time a fast rising positive extraction pulse is applied to plate $P2$ leading to an 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 [16,17]. In this case the ions also drift into the region between plates $P2$ and $P3$ and can be extracted into the RETOF leading to a conventional resonance enhanced multiphoton ionization (REMPI) excitation spectrum as a result of scanning the second laser. At a spoiling field between 0 and 0.5 V/cm, ion signals from both 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.

Using a low intensity of the second laser leads to soft ionization for the REMPI spectrum with only the molecular benzene ion peak being present in the spectrum. This is also found for the delayed PFI spectrum at that low intensity [Fig. 2(a)]. Here the spectrum arises from the Rydberg states just below the IP and the Rydberg series converging to the $\nu_6{}^+(\pm 3/2)$ states in the ion [18], and demonstrates the long lifetime of the ZEKE states 350 cm^{-1} above the IP of the molecule.

If one now increases the intensity of the second laser, further absorption from the Rydberg states will occur. Here already the absorption of one more photon deposits an excess energy of more than 4.4 eV above the IP in the molecule. This large excess energy leads to fragmentation in the direct ionization and $C_4H_n{}^+$ ions are observed in the mass spectrum. When one positions the detection gate in the TOF signal to this mass peak, the REMPI excitation is similar to the spectrum with probing at the mass of the bare benzene molecule. A very surprising result is now obtained by also performing the delayed PFI experiment with detection at the mass of the $C_4H_n{}^+$ ions (Fig. 2). Here the signature of the Rydberg states just below the IP and the $\nu_6{}^+(\pm 3/2)$ states is also seen which clearly indicates that the absorption of a further photon from these Rydberg states did take place. Moreover, these states which contain over 4.4 eV above the

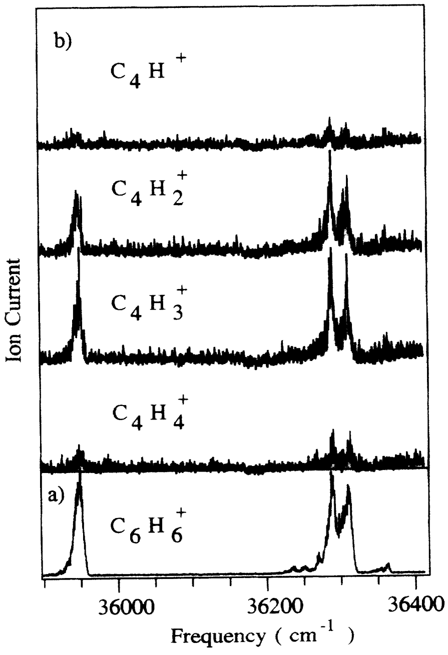

FIG. 2. Delayed pulsed field ionization spectra of benzene with two color laser excitation. A first laser performs the resonant excitation of the S_16^1 intermediate state. The second laser then scans the region from below the IP to the $6^{1+}(\pm 3/2)$ state in the ion. The ion current after delayed PFI is recorded with a RETOF mass spectrometer. Shown is the ion current vs the frequency of the second laser. (a) The detection window set to the mass of the benzene molecule. (b) The detection window set to the mass of $C_4H_n{}^+$ fragments.

ionization threshold did survive as neutrals for 11 μs prior to the ionization.

The problem of the extreme stability of the neutral states is actually twofold. On the one hand, even though there are many open channels these states do not ionize. On the other hand, there are even more channels [15] for the intramolecular quenching of the excess electronic energy. Such radiationless transitions are well known [8,14,19] for low lying Rydberg states of aromatic molecules and there is both indirect and direct evidence that the electronic energy transfer is to the vibrational modes [20]. Equally, there is evidence that vibrational excitation can be made available for the ionization of low lying Rydberg states of aromatic molecules [14,21]. Vibrational autoionization is, of course, well documented for lower Rydberg states of diatomic molecules [11]. The present results as well as the recent [4] measurements on resonant pumping via a vibrationally excited (by ca. 1000 cm^{-1}) intermediate state suggest that the coupling of the electronic motion to the vibrational modes is very ineffective. This is in contrast to coupling to the van der Waals mode in benzene-Ar [18] or to the situation in metallic clusters [7,22], where the mean free path of an electron is very low. It appears to be a matter of time scales: The slow moving high Rydberg electron is not resonant with the far faster typical molecular vibration. Support for this point of view is provided by the known [23] inefficiency of vibrational excitation of molecules by collisions with slow electrons. This is typically interpreted in terms of momentum transfer but the two points of view are clearly related. On the other hand, rotational excitation of molecules and particularly so of ions by electron impact is very efficient and provides, we believe, the required physics for the understanding of both aspects of the extreme stability of the very high Rydberg states.

The classical Bohr-Sommerfeld orbit of a high n but low l electron is extremely elliptical. Most of the time it is very far from the core. As it gets near it accelerates but its radial velocity and its distance of closest approach are very sensitive to l; for $l < n$, the latter is $l(l+1)/2$ in a.u. (cf. Fig. 3 below). It follows for a typical value of $n=100$ that an electron with $l=10$ does not get near the core. The potential of the ionic core as seen by an electron that is nonpenetrating is not purely Coulombic. There are long range higher multipoles of which the dipole (if present) and the quadrupole are the leading terms. These can induce efficient exchange of angular momentum between the electron and the core. The threshold for ionization into rotationally excited states of the ion will be higher by a small but finite amount as compared to the lowest IP which is the threshold for ionization into the ground state of the ion. Each rotational state of the ion can thus have a whole manifold of high Rydberg states. Most of these will be truly bound. The highest will be quasibound [24]. Their total energy will be above the lowest IP but their ionization requires an angular momentum transfer between the core and the Rydberg electron. Such a transfer requires the electron to be near the core, which occurs once every $1.5 \times 10^{-16} n^3$ s, and the probability of the transfer diminishes, the higher the l value of the electron. Equally, the higher l values orbit precludes the intramolecular quenching of the Rydberg electron.

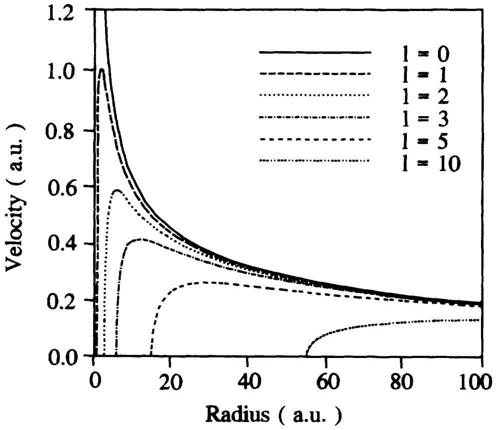

FIG. 3. The radial velocity of an electron in a Coulombic field vs its radius, both in a.u. drawn for $n=100$ and several values of l as indicated. Note the low velocity and higher distance of closest approach for the higher values of l.

The Rydberg electron, promoted by a two photon absorption from the highest occupied molecular orbital of benzene, will already have a small but finite l value. During its first few rounds it will scatter [25] off the core. Many such scatterings will lead to ionization or to the quenching of the Rydberg electron and the resulting decay in the number of detectable Rydberg states has been observed [1,2] and also seen in simulations [26]. Some trajectories will, however, result in an increase in l with or without a concomitant increase in n. These are the long living stable states. In these states the electron has a very low kinetic energy over essentially all of its orbit. Hence we refer to them as ZEKE states. Figure 3, while quite trivial, is meant to emphasize that the label ZEKE is indeed appropriate. It shows the radial velocity of the electron near the core for $n=10$ and several low l values. The acceleration near the core, evident for $l=0,12$ is over by $l=5$, and for $l > 5$ the electron is slow moving over its entire orbit nor does it get very near the core. For very high Rydberg states and for $0 < l(l+1)/n^2 \ll 1$, one can show that the radial velocity scales as l^{-1}. The tangential velocity also declines with increasing l [because of the increase of the point of closest approach as $l(l+1)/2$].

Our proposed mechanism for both the quenching and the long term stability is an intramolecular interaction with the core. It invokes an essentially diffusionlike motion of the electron in action space. We consider that a Brownian-like picture [7] for the high n electron is appropriate because it is the slowest moving particle in the system and it is buffeted by the rotation (and, eventually, by the vibration) of the core. This interpretation of the extreme stability of the ZEKE states is consistent with their being observed also in experiments where the excitation is carried out under as much as possible field free conditions [16]. In the presence of an electrical field l is not a good quantum number so that the diffusion in phase space will be accelerated by a field [6], even for large l. The simulations very much verify [2] the expectation that the ZEKE orbit is only perturbed near the core. The rarity in time of this event (due to the high n value) and the low probability of a change (whenever $l > 0$) suggest that a suitable quantum mechanics basis zeroth order set are the manifolds of (high) Rydberg states, one for each state of the ion. One should, of course, take advantage of the conservation of the total angular momentum but the necessary recoupling coefficients have long been worked out in connection with atom-molecule rotational scattering [27]. This basis set is inverse to the usual Born-Oppenheimer basis which one would use for lower Rydberg states. In the latter, the high Rydberg states are very strongly coupled because the strength of the coupling, expected [28] to scale as $n^{-3/2}$, is comparable to the spacing of the zero-order basis states. The criterion $V\rho > 1$ for strong coupling [19,20], where ρ is the density of states, is thus satisfied in the Born-Oppenheimer basis. Yet, as discussed, the ZEKE states manifest very weak coupling between the electron and the nuclear degrees of freedom.

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