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## COMMUNICATIONS

## Dynamics of very high Rydberg states of aromatic molecules

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A nonmonotonic dependence of the lifetime of very high Rydberg states on the photon energy has been observed in a number of large, ultra cold, aromatic molecules. We report on the essential details of the experiment and propose an interpretation based on a competition between intramolecular relaxation and excess internal energy assisted ionization of the Rydberg state. According to this mechanism, this competition is possible only just below the threshold for ionization. At lower excitation energies, the coupling of the Rydberg electron to the vibrational modes of the molecule is too strong, leading to a very fast intramolecular relaxation.

Lifetimes of Rydberg states have been measured (e.g., in Ref. 1, Benzene) for lower lying states where they are quite short. The limited available evidence (e.g., in Ref. 2 NO) is that for the  $20\text{ cm}^{-1}$  or so, below the thresholds for ionization, the lifetimes become much longer. In our interpretation, this increase is a very steep function of the energy of the Rydberg state measured with respect to the threshold for ionization. The other decay channel, that of rovibrationally assisted ionization, has been very recently discussed<sup>3</sup> in connection with the above-threshold ionization of clusters,<sup>4-8</sup> negative ion<sup>9,10</sup> and large molecules.<sup>3</sup> Our interpretation follows the discussion in Ref. 3. We wish, however, to reiterate that in the present study the molecule is photoexcited to a below threshold Rydberg state.

The experiment uses ZEKE spectroscopy<sup>11,12</sup> with a controllable delay between the photo ionization pulse and the application of an electric extraction pulse. The electrons are guided to the detector by a magnetic bottle design.<sup>13</sup> The delayed ionization is used to determine the lifetime of the Rydberg states that survived. Figure 1 shows the results for phenanthrene and deuterated phenanthrene. The details are as follows. A molecular beam is generated in a three chamber differentially pumped vacuum system by a fast pulsed valve.<sup>14</sup> The expansion mixture contained the carrier gas (30% He in Ne) and 0.1–1 Torr of phenanthrene, deuterated phenanthrene or other aromatic molecules (obtained by heating the nozzle to  $100^\circ\text{C}$ ). The beam was skimmed and passed to a chamber containing a magnetic-bottle electron energy spectrometer. The pressure at the electron spectrometer was maintained at less than  $10^{-6}$  Torr.

The molecular beam was probed by resonant two-color two-photon excitation. One (visible) photon was tuned to the  $S_0 \rightarrow S_1$  transition ( $3408.5\text{ \AA}$  for phenanthrene and  $3397.52\text{ \AA}$  for deuterated phenanthrene) and the other (UV) was scanned near the ionization threshold of the molecule. The two slightly focused (2 mm beam waist) laser beams, overlapping in the excitation region of the spectrometer, were aligned for counter propagation with the molecular beam. The long excitation region minimized the degradation of resolution by space charges generated by  $10^3$  excited molecules. The lasers peak power was carefully adjusted, so that saturation effect and R2P1 were negligible.

A new type of ZEKE spectrometer, Fig. 2, was developed for improved detection efficiency and energy resolution and will be described in detail elsewhere.<sup>15</sup> The excited molecules are field ionized by a delayed, short (15 nsec) 5 Volt/cm pulse. The lifetimes of the excited states were obtained by measuring the ZEKE electrons signal as a function of the delay (200 ns–10  $\mu\text{s}$ ) between the excitation and ionization pulses. Lifetimes at different energies were measured along the line profile. The electrons were detected by fast two-stage micro-channel plates. The signal was collected by a computer-controlled 500 MHz transient recorder.

The separation of ZEKE electrons from prompt energetic electrons is based on the difference in their time-of-flight from the excitation region to the electron detector. If the duration of the extraction pulse is shorter than the flight time of the electrons between the plates, all the electrons will acquire the same momentum. In this case the time resolution of the spectrometer is given by  $L/\delta L$  ( $\delta L$  is the laser beam width;  $L$ , the length of the flight tube) which is 150 even for our short flight tube (300 mm).

The magnetic bottle collection efficiency (above 90%) improves our signal levels. The magnetic guiding of the electrons away from surfaces with stray charges improves the energy resolution. A typical resolution of  $1\text{ cm}^{-1}$  (125  $\mu\text{eV}$ ) was easily achieved at signal levels of  $10^3$  electrons/pulse.

The Rydberg states of interest to us lie but a few wave numbers below the ionization continuum. Using  $I$  to designate the ionization potential and the Bohr result<sup>16</sup>  $E=I/n^2$ , it follows that since  $I$  is of the order of  $6 \times 10^4\text{ cm}^{-1}$ , the

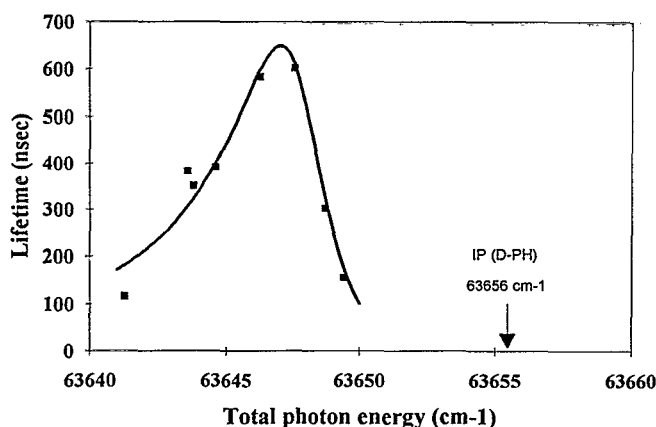
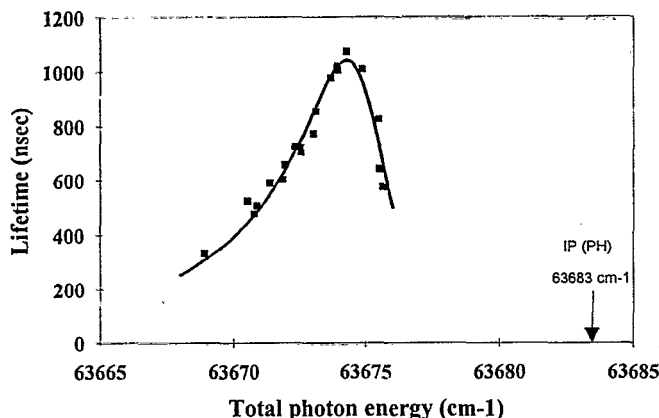


FIG. 1. Lifetimes (in ns) of the Rydberg state vs. the sum of the photon energies (in  $\text{cm}^{-1}$ ) for (a) phenanthrene and (b) deuterated phenanthrene. The continuous curve is the fit to  $1/(k_1 + k')$  where  $k_1$  and  $k'$  are the decay rates for the intramolecular dissipation and thermally-assisted ionization, respectively. See text for details. The fitted value of the ionization potential is indicated by the arrow.

relevant states have a principal quantum number  $n$  of 100 or more. It is therefore realistic to discuss the initially excited states using the Bohr-Sommerfeld orbits of the old quantum theory.<sup>16</sup> These are ellipses which for low values of the azimuthal quantum number  $k$  are very eccentric. Their major and minor semiaxes have the values  $a = n^2 a_0$  and  $b = n k a_0$ , respectively, where  $a_0$  is the Bohr radius and the Rydberg photo excited electron will have a rather low angular momentum. Furthermore, even the minor semiaxis  $b$  is still large compared to the dimension of the molecule. Due to the high value of  $a/b$ , much of the time the electron is effectively uncoupled to the rovibrational modes of the molecule. It is only when the electron is close in and where it accelerates (recall Kepler's second law), that it can effectively interact with the nuclear degrees of freedom. We expect such couplings to decrease exponentially with the distance of the electron.<sup>17</sup> The expectation value of such a coupling declines rapidly with the quantum number  $n$ . In the fit to the data we use a power law decline with  $n$ . Specifically we use an  $n^{-3}$  decrease. [This is the result of

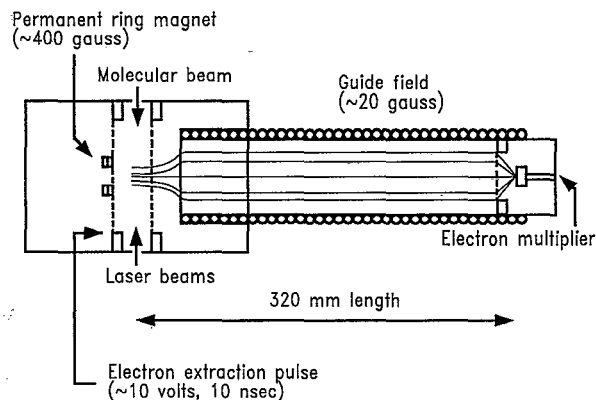


FIG. 2. A schematic representation of the ZEKE spectrometer. The residual electric field between the plates is estimated to be smaller than 100 mV/cm. The magnetic field is about 200 gauss. The carrier gas is a 70/30 mixture of Ne/He.

both a semiclassical and of a numerical evaluation of the expectation value of  $\exp(-r/a_0\sigma)$  in a given Rydberg state.] Here  $\sigma$  is the range parameter of the potential and the  $(\sigma/n)^3$  dependence is valid for any reasonable potential whose range  $a_0\sigma$  is short compared to  $b$ . (This point will be further discussed in the full report on this work.) The rate  $k_1$  of intramolecular dissipation of the Rydberg state is thus expected to decline with  $n$  faster than  $\bar{\nu}$  [ $\bar{\nu} = (me^4/\hbar^3)n^{-3} = 4.13 \times 10^{16} n^{-3} \text{ s}^{-1}$ ], is the number of orbits per unit time or the frequency with which the electron comes close to the core. The motion is not harmonic and contains a wide range of Fourier components. The area swept per unit time is  $\hbar k/2m$ . It follows that the harmonic frequency components due to the motion at the close end are  $n^2$  higher than those at the far end, and as such allow the electron to couple even to the vibrational degrees of freedom of the molecule.

The rate of intramolecular dissipation of the higher Rydberg states scales with the quantum number of the state as

$$k_1 = 4.13 \times 10^{16} n^{-3} (\sigma/n)^3. \quad (1)$$

The energy dependence of  $k_1$  is remarkably steep, Fig. 3, and is quite sensitive to the value of the range parameter  $\sigma$ . What is possibly fortuitous is how well the magnitude of the lifetime predicted by (1) agrees with the experimental results.

Competing against the steep increase in the lifetime of the Rydberg state as the frequency is increased and one approaches the ionization threshold is the decrease in the lifetime due to ionization. This decrease is due to the lower energy that needs to be delivered to the electron by the nuclear degrees of freedom for it to escape. We expect that the main source for the energy (beyond  $h\nu$ ) necessary for the ionization is the internal energy content of the molecule.<sup>3</sup> However, in view of the rather high geometrical cross section ( $\pi ab$ ) of the Rydberg state, one cannot rule out external perturbations (e.g., collisions with the carrier gas, stray electrical fields, black body radiation) as contributing to the rate of ionization. Changing the stagnation

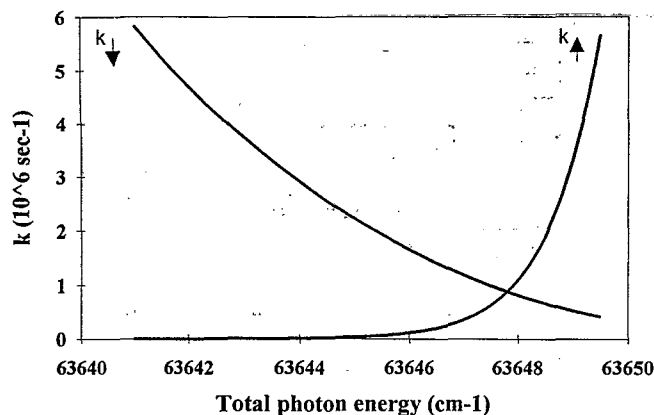


FIG. 3. The two decay rates, see Fig. 1, for *D*-phenanthrene (in  $10^6 \text{ s}^{-1}$ ) plotted vs the photon energy (in  $\text{cm}^{-1}$ ) using the equations and parameters quoted in the text. Note the rather steep frequency dependence of both rates near their threshold values.

pressure by over an order of magnitude and changing the carrier gas from He to Xe did not however show the effects expected if ionization is primarily due to collisions or to stray fields. Note that we are not necessarily assuming that all of the energy  $h\nu$  remains in the electron. It is to be expected that its motion is damped.<sup>3,18</sup> The essential point is that, for ionization to take place, energy in excess of the ionization potential  $I$ ,  $I > h\nu$ , must be made available in the orbital motion of the electron. When the electron is at the far end of its orbit the core is effectively a free ion. If the ion is not in its ground vibrational state, its excess energy can be made available to the electron at the other end of its orbit. This source of energy implies that the observed ionization potential  $I$  is somewhat higher than the strictly adiabatic value.

The electron acquires the excess energy required for ionization when it is near the core. Hence the rate  $k^1$  of ionization is  $k^1 = \bar{\nu} \exp(-(R/n^2)/\epsilon)$ . Here  $R/n^2$  is the threshold excess energy required for ionization, and  $\bar{\nu}$  is the orbital frequency factor.  $\epsilon$  is the mean vibrational energy per mode of the ionic core. The good fit to the data obtained with the theoretical value of  $\bar{\nu}$  confirms that collisional activation<sup>15,19</sup> of the Rydberg state which occurs by a lower rate is only a secondary process. The rotational temperature of the molecule (as estimated from the rotational contour of the  $S_1$  absorption) was varied between 1 and 6 K. Increasing the rotational temperature causes a significant broadening of the ZEKE spectrum but marginal change in the lifetime at the peak of the absorption. Of course, when  $kT < \hbar\omega$ , quantum statistics limits the energy per vibrational mode to be below that of the rotational modes.

The total decay rate of the Rydberg state is  $k_1 + k^1$ . Figure 1 shows the fit to the observed results. In obtaining the fit we regard the ionization potential  $I$ , range parameter  $\sigma$  and the mean energy  $\epsilon$  as variables. The limited number of data points means that the parameters of the fit can only be determined to within confidence intervals. Even so, it is clear that a good fit is obtainable when  $\bar{\nu}$  is the same for both isotopic variants. The fitted values of the ionization

potentials are  $63\,683 \pm 0.4 \text{ cm}^{-1}$  and  $63\,656 \pm 0.8 \text{ cm}^{-1}$  for phenanthrene and deuterated phenanthrene, respectively. The quoted limits are the confidence intervals from the data analysis. We emphasize that the fit does provide a tight value for the ionization limit, as well as for the range parameter ( $\sigma = 3.4 \pm 0.2$  and  $3.9 \pm 0.3$  for phenanthrene and deuterated phenanthrene, respectively). The excess internal energy per mode  $\epsilon$  is  $0.72 \pm 0.03$  and  $0.76 \pm 0.07 \text{ cm}^{-1}$ , respectively.

Similar behavior has also been found in aniline, 9,10-dichloroanthracene and perylene. On the other hand, the behavior is radically different for atoms. The detailed results will be presented elsewhere.

In our model, higher Rydberg states of polyatomic molecules are extensively diluted into a background continuum of rovibrational states and cannot therefore be easily seen in the spectra. Near to the ionization limit this intramolecular coupling, measured by  $k_1$  is weaker and distinct spectral features can be observed. Another way to compete with the fast dissipation of the Rydberg electron is by using vibrationally very hot molecules, e.g., by pumping via a vibrationally excited  $S_1$  intermediate state in a two photon excitation scheme. Rydberg progressions have indeed been reported<sup>19</sup> in such experiments, but are not seen when the intermediate  $S_1$  state is cold.

Our conclusions are summarized in Fig. 3. We propose that very high lying Rydberg states decay into the dissipative quasicontinuum<sup>20</sup> of rovibrational states of larger polyatomic molecules with a rate  $k_1$  which is very fast except just below the ionization limit. There, due to the electron being most of the time far away from the core, the rate of intramolecular dissipation when plotted vs frequency, Fig. 3, drops down steeply. On the other hand, just below the energetic threshold for ionization of a ground state molecule, the process of internal energy assisted ionization is rapidly switched on, Fig. 3. In that competing process, internal energy is being acquired by the electron and enables it to depart. As seen from Fig. 3, the competition between the two processes can serve as a sensitive probe of the dynamics of very high Rydberg states just below the ionization continuum.

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