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Decay dynamics of high Rydberg states in atoms and molecules

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Decay dynamics of high Rydberg states above the first ionization limit have been studied. The decay rate to the ionization continuum, due to spin orbit coupling for atoms (Ar), or coupling to the dense manifold of available rovibronic states in polyatomic molecules, was measured. This decay is non-exponential and can be influenced by external fields. The stabilization of very high (ZEKE) states is demonstrated and possible mechanisms accounting for these very long lived states are discussed.

1. Introduction

High Rydberg states (characterized by principle quantum number $n = 10\text{--}300$) have been found in most excited atoms (NBS 1949; Stebbing & Dunning 1983), many diatomic molecules (Lefebvre-Brion & Field 1986; Reiser *et al.* 1988; Bordas 1988; Pratt 1993) and some polyatomic molecules (Whetten *et al.* 1985; Muller-Dethlefs & Schlag 1991; Fujii *et al.* 1983; Consalvo 1993). Rydberg states are also found at energies that are above the first ionization limit of atoms or molecules, and decay to lower states is possible. The loosely bound electron can couple to the nuclear core, and its orbit can be perturbed by external fields. The study of the dynamics of the competition between the internal processes (spin orbit induced autoionization for atoms (Ernst *et al.* 1988; Klar 1992; Muhlfordt & Even 1995), autoionization predissociation, and internal conversion for molecules (Fano 1961; Mulliken 1969; Jortner & Morris 1969; Berry & Nielsen 1970; Jungen & Dill 1980; Gilbert & Child 1991)), and the external process (applied and stray electric or magnetic fields or fields produced by ions), is an interesting and challenging problem to both experiment and theory (Bordas 1988; Ernst *et al.* 1988; Fielding & Softley 1992; Merkt *et al.* 1993; Merkt & Zare 1994; Rabani *et al.* 1994, 1995*b*; Baranov *et al.* 1994; Bixon & Jortner 1995*b*, 1996*a*). It is expected that the lifetime of the metastable Rydberg states will scale as n^3 , where n is the principle quantum number (reflecting the square of amplitude of the wave function at the core (Stebbing & Dunning 1983; Bethe 1957)). On the other hand much longer lifetimes than can be expected from this simple extrapolation have been found in atoms and in molecules (Pratt 1993; Muller-Dethlefs & Schlag 1991; Mahon *et al.* 1990; Merkt & Softley 1993; Bahatt *et al.* 1993*b*; Even *et al.* 1994). It has been argued that an external electric field will cause Stark splitting of the different l states belonging to a given n ‘diluting’ the oscillator strength for the transition since only low- l states will couple to the core, thus lengthening the lifetimes by an additional factor of n (Rabani *et al.* 1994; Chupka 1993*a*; Bixon & Jortner 1994). A similar argument can be applied to m_l degeneracy

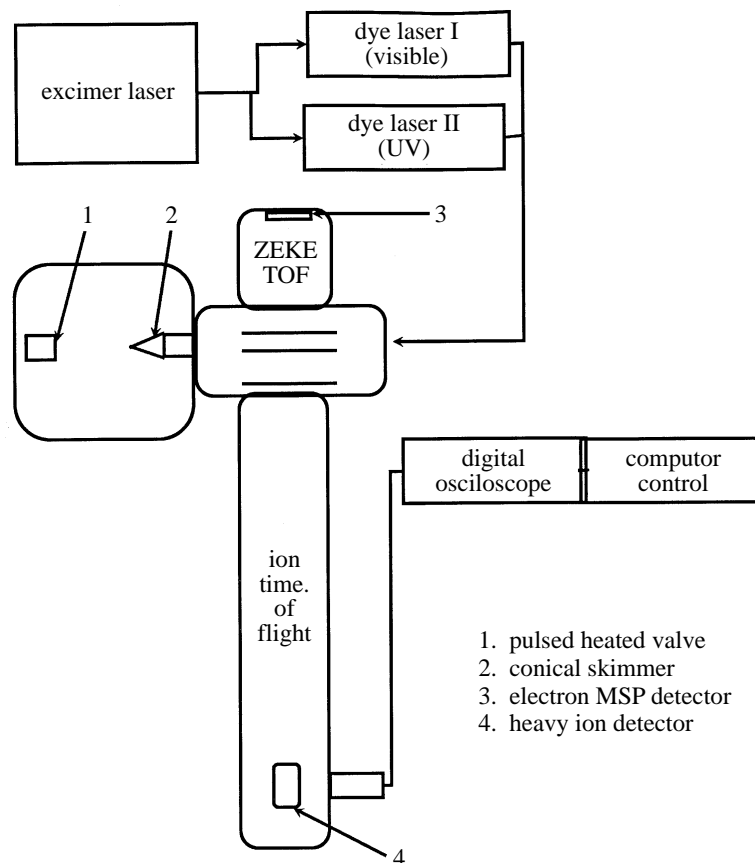


Figure 1. Schematics of the experimental system layout. The supersonic beam is generated by a heated pulsed valve and is excited by counter propagating two colours tunable photons. Ar atoms were excited by an electrical discharge near the valve nozzle to a metastable state, and ionized by one UV photon only. Ions were collected by a 1 m time of flight mass spectrometer. Electrons were detected in an imaging ZEKE spectrometer described here. Base pressure was 10^{-2} Pa, 10^{-4} Pa and 10^{-5} Pa at each chamber, respectively. Ionization volume was a cylinder of 2 mm diameter and 10 mm length, where the mildly focused laser beams overlapped. Ion density was less than 10 ions mm^{-3} . Ionization pulse was delayed after the laser pulse so that ionization occurred under field free (less than 0.1 V cm^{-1}) conditions.

removal by magnetic fields (Rabani *et al.* 1995*b*; Chupka 1993*b*), neighbouring ions (Merkt & Zare 1994; Alt *et al.* 1994, 1995; Zhang *et al.* 1993) or the anisotropy of the molecular core (Rabani & Even 1994; Rabani *et al.* 1995*a*; Remacle & Levine 1996*b*) causing a further lengthening of the lifetime. We wanted to clarify the different possible mechanisms contributing to the experimentally found long lifetimes of the very high Rydberg states (Scherzer *et al.* 1994) (known now as 'ZEKE' states, an acronym for 'zero electron kinetic energy' (Muller-Dethlefs & Schlag 1991; Krause & Neuser 1993)). We present here experimental data on the lifetimes of the autoionizing np' Rydberg series for the Ar atom as well as data for a predissociating polyatomic molecule (1,4-diazobicyclo2,2,2octane, DABCO) taken under similar conditions. A discrepancy of 2–3 orders of magnitude is found from the extrapolated n^3 lifetime of the low Rydberg states ($n = 10$ – 20) to the measured high 'ZEKE' states lifetime ($n = 100$ – 200).

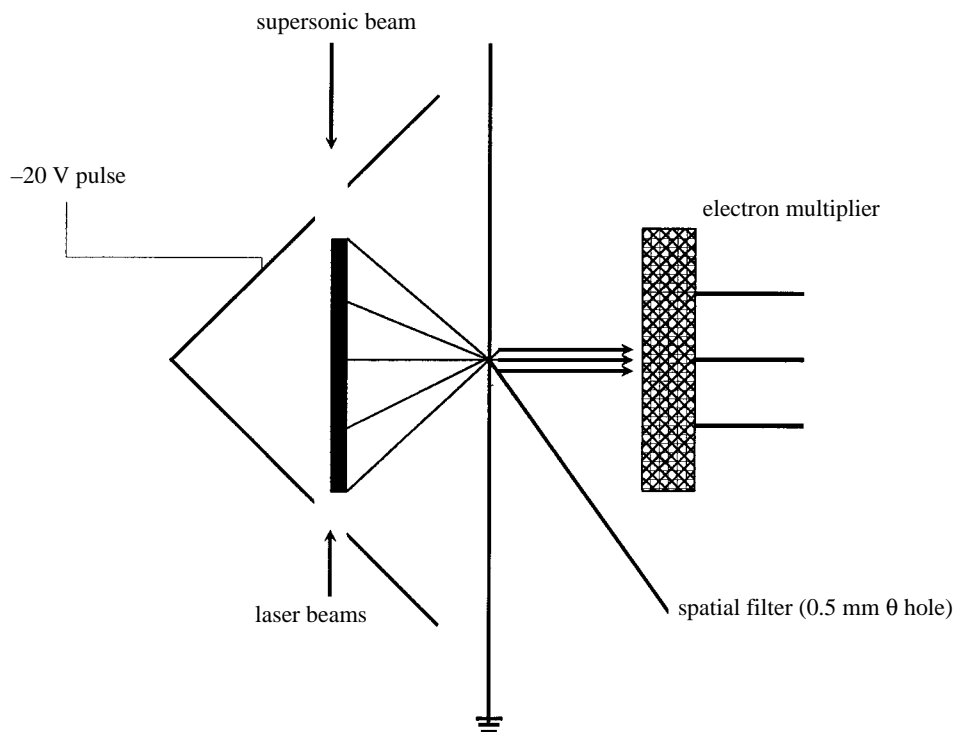


Figure 2. Electrons are produced by the intersection of the overlapping laser beams and the molecular beam. The narrow (2 mm diameter) cylinder of electrons is allowed to expand before the application of a negative fast (10 ns) 20 V pulse to the conical lens (shown in cross section here). This voltage creates a field of approximately 2 V cm^{-1} and focuses the electrons through the exit hole (0.5 mm diameter) to the multi channel plate detector. The focusing properties of the conical lens are such that expansion of the electron cloud by only a few mm is enough to exclude their exit from the spatial filter hole. This is translated to a time delay that can be shorter than 100 ns. Prompt electrons produced at the lens surface or in the beam are thus eliminated quickly. Two pairs of Helmholtz coils (external to the vacuum system and not shown) reduced the earth magnetic field to less than 0.1 gauss.

2. Experimental

Ion and electron were created in a differentially-pumped three-chambers vacuum system. Sample molecules were introduced using a home built heated pulsed nozzle. The system was described in detail previously (Bahatt *et al.* 1987, 1993a) and its schematics are shown in figure 1. Ions and ZEKE electrons were used to follow the decay dynamics of the populated Rydberg states.

Ion detection was used when following the low Rydberg states population prepared by the laser excitation, since they are slow enough, and remain where created, and thus can be detected even when the decay was fast. The lifetime was determined by measuring the spectral width of the excited Rydberg level. The finite laser width (0.2 cm^{-1}) limited this method to decay times shorter than approximately $5 \times 10^{-11} \text{ s}$. Time dependent ZEKE spectroscopy was used to measured lifetime longer than approximately $5 \times 10^{-8} \text{ s}$. This method probes the surviving population of a prepared Rydberg state by delayed pulse ionization. We developed an imaging ZEKE spectrometer for this purpose with a time resolution that is better than 50 ns (figure 2). The Ar atoms were excited to a meta stable (triplet) state using a hollow

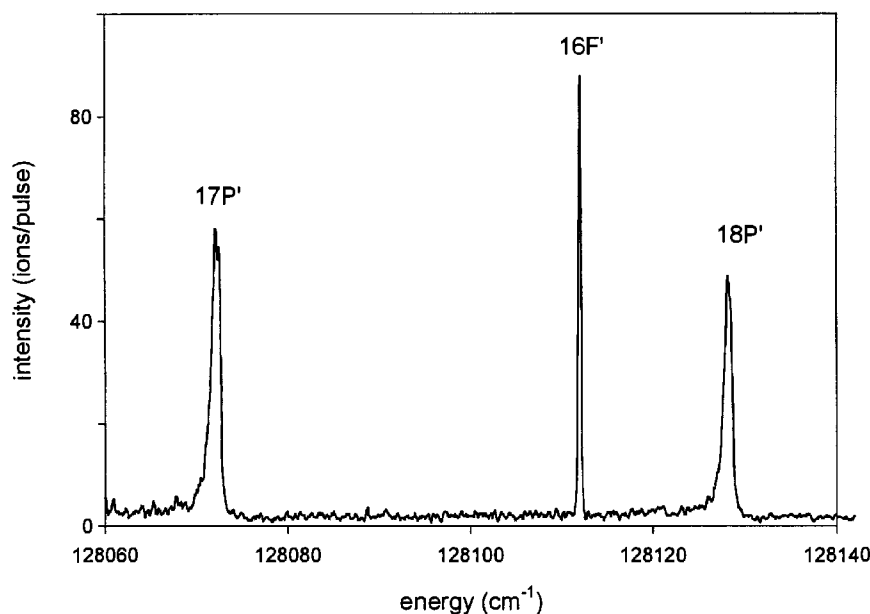


Figure 3. Ion spectra of Ar showing two members of the p series and one of the f lines. The transitions were induced by single UV photon absorption of the meta-stable atoms produced by electrical discharge near the nozzle exit. The p series are lifetime broadened while the f line width is laser limited.

cathode pulse discharge near the nozzle exit. A 600 V pulse was applied to a short cylinder (approximately 10 mm diameter and 10 mm length) placed inside a ring magnet (producing 600 Gauss field). A single UV photon was used to excite these metastable atoms to the Rydberg states reported here. Molecular Rydberg excitation was achieved by two tunable photons, adjusted to an intermediate state resonance (S1) in the molecule.

3. Results for an atom (Ar)

np' and nf' Rydberg series for Ar, obtained by ion detection, are depicted in figure 3. The np' series show lifetime broadening and its profile could be fitted to a Fano (1961, 1975) line shape quite accurately. These data complement the published ns' and nd' series for Ar (Fujii *et al.* 1983; Klar 1992; Huffman *et al.* 1963; Hudson & Carter 1968). The nf' series width is laser limited (0.2 cm^{-1}) and could not be measured.

The fitted width for the np' series could be described by a scaling law:

$$W_n = \frac{2100(\pm 100)}{n^3} (\text{cm}^{-1}).$$

Similar spectra can be obtained when electrons are used instead of ions for detection. The main difference is that the very fast autoionization and large (1431 cm^{-1}) kinetic energy carried by the electrons required a magnetic bottle (Bahatt *et al.* 1993a) or DC electric field to guide the electrons to the detector. Figure 4 depicts the obtained spectrum if we allow a delay of 40 ns between the laser pulse and the electric field pulse. All the low Rydberg states, and their emitted electrons have disappeared

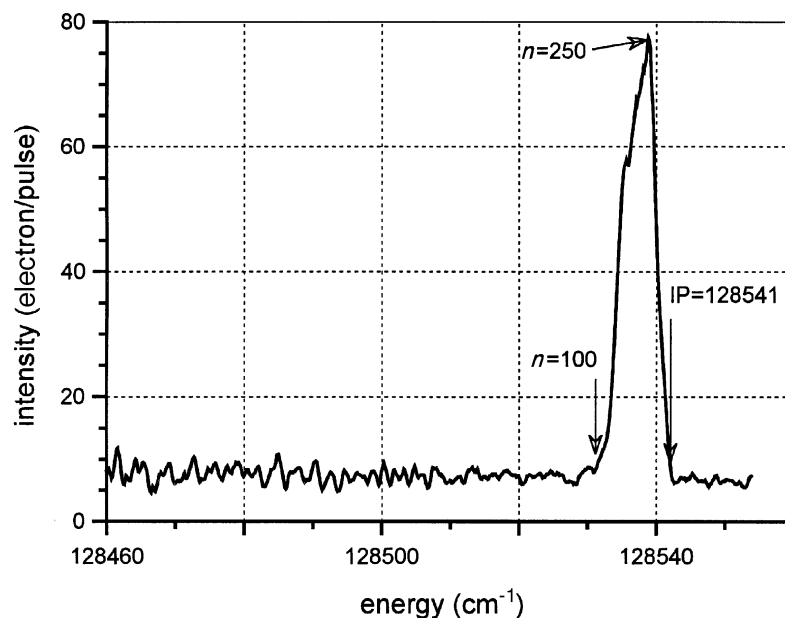


Figure 4. Ar ZEKE spectrum taken with a delay of 40 ns between the laser pulse and the electric field pulse. All the low lying Rydberg states have decayed. Only Rydberg states with $n > 100$ could be detected.

from the observation window and only the very high, unresolved, Rydberg states have survived (Muhlfordt & Even 1995; Fielding & Softley 1992; Yoshino 1970).

We can plot the surviving population of these high Rydberg states as a function of the delay of the applied electric field pulse for a given photon energy (exciting an unresolved narrow group of Rydberg states). The population exhibits a non exponential decay with time and the shorter components of these decay times are plotted in figure 5, together with the lifetimes obtained by the spectral width measurements of the lower np' Rydberg series. The quoted n values for the high Rydberg states are an average based on the known ionization potential of Ar ($IP = 128\,541\text{ cm}^{-1}$) and the laser photon energy (E_n)

$$n^2 = \frac{R_y}{(IP - E_n)}.$$

4. Results for molecules

Several molecular species were studied. Long Rydberg series could be detected for two of the molecules we studied (diazacyclooctane (DABCO) and bis(benzene)chromium (BBC)) but all molecules exhibited ZEKE spectra indicating long lived very high Rydberg states that can be ionized by a delayed pulsed electrical field. The long resolved series ($n = 10\text{--}70$) for the two mentioned molecules show similar behaviour to the Ar Rydberg series in figure 3. That is several Rydberg series can be identified and the spectral lines can be fitted to a Fano shape indicating finite lifetimes of the excited Rydberg states (Even *et al.* 1994). The long series allowed us to determine the series limit (IP) with an accuracy of approximately 1 cm^{-1} , and fix the scale for the quantum number n . Let us concentrate for the moment on the

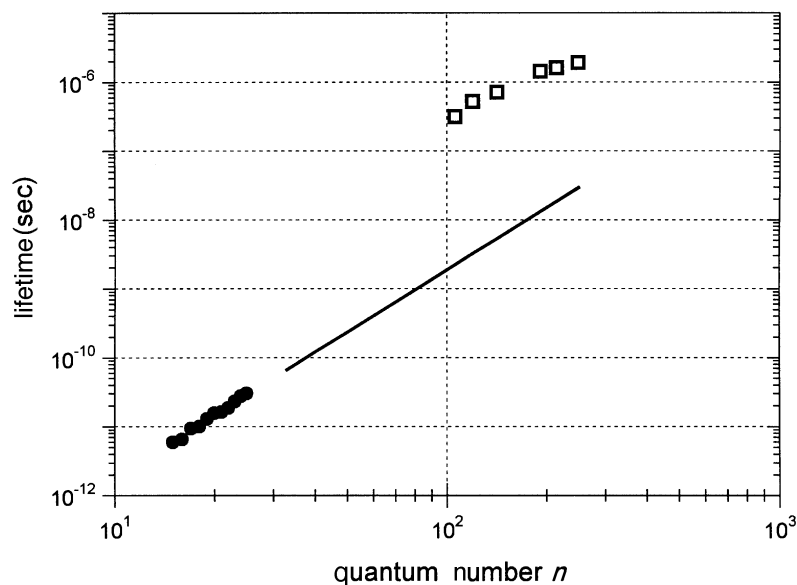


Figure 5. Low and high Rydberg states lifetime for Ar np series. A gap exists between the highest resolved width measurements ($n = 27$) and lowest time resolved ZEKE measurements ($n = 100$). The simple n^3 extrapolation does not hold.

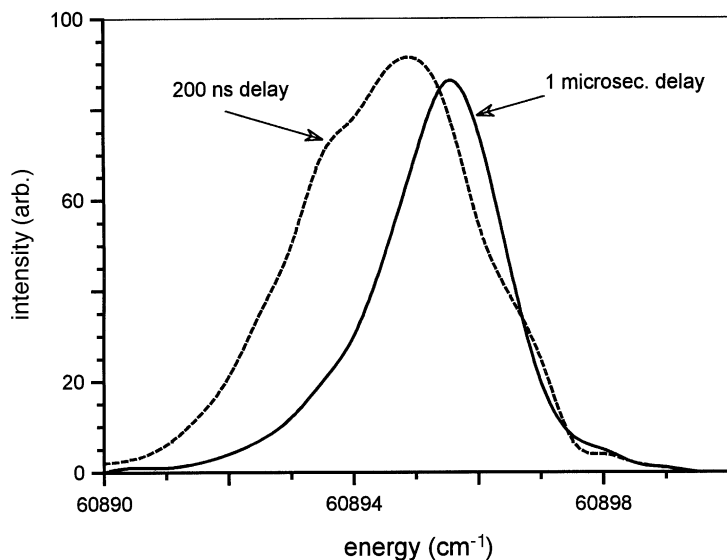


Figure 6. Intensity profile of the ZEKE peak of dichloroanthracene taken at two delays of the field ionizing pulse. The faster decay of the 'red' part of the spectrum is apparent.

unresolved high Rydberg series ($n = 100$ – 250) hiding under the 'ZEKE' peaks in all studied molecules.

Figure 6 is a typical example of the shape of this peak appearing below the ionization threshold for many molecules (Dichloroanthracene in this case).

We would like to stress that this typical time response is for an excitation below the first ionization potential for the molecule and the electron cannot carry kinetic energy upon ionization. The decay in time of the excited Rydberg states must be

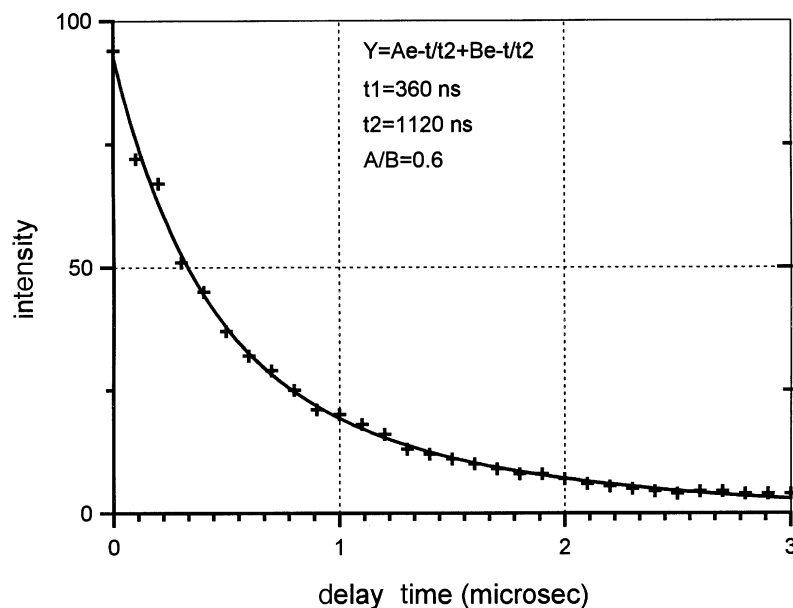


Figure 7. Decay of the ZEKE signal for tetracene as a function of the time delay between the laser pulse and field ionization. A fitted two-exponential decay with a long component (approximately $1.1 \mu\text{s}$) and a short component (approximately 360 ns) is typical. Two photons were used, the first one is in resonance with the S_0-S_1 (o-o) transition and the second photon is tuned just below the threshold for ionization. The decay curve depends on the laser excitation energy within the line profile.

by converting electronic energy to internal molecular modes (predissociation, intersystem crossing or direct fragmentation). We can tune the laser to a particular energy in this broad (8 cm^{-1}) profile and follow the time evolution of the group of (unresolved) excited Rydberg states. A typical time decay is shown in figure 7 for another molecule (tetracene) together with its fitted two-exponential decay curve. Such non-exponential decay was found for many of the molecules investigated by us (Rabani *et al.* 1994, 1995a; Bahatt *et al.* 1993b).

The decay curves of these high Rydberg states depend on the specific energy of the (second) laser photon. Figure 8 shows the dependence of the short time component on the total photon energy (sum of two photons). As can be seen there is a rapid decrease in the lifetime as we go to lower energies from the ionization threshold, denoting the increased coupling to the molecular core as we reduce the quantum number n . Since the exact ionization potential was not determined for this molecule we cannot assign an accurate scale for this n . Such a scale can be established only for molecules that exhibit very long Rydberg series from which we can establish the series limit (IP). Only molecules with weak coupling of the Rydberg states to the core will show such a long series, and these are exceptions to the general case. We found two molecules with the required long series (DABCO and BBC) and wish now to examine the results we obtained.

Figure 9 is part of the ion spectrum of the DABCO molecule taken with a two-photon excitation. The first photon is tuned to a vibronic state in the S_1 manifold (823 cm^{-1} vibration at an energy of $36\,614 \text{ cm}^{-1}$ (Consalvo 1993)) and the second photon brings the molecule to the Rydberg states. It is noteworthy that these Rydberg states can only be detected when the DABCO is excited with excess vibrational

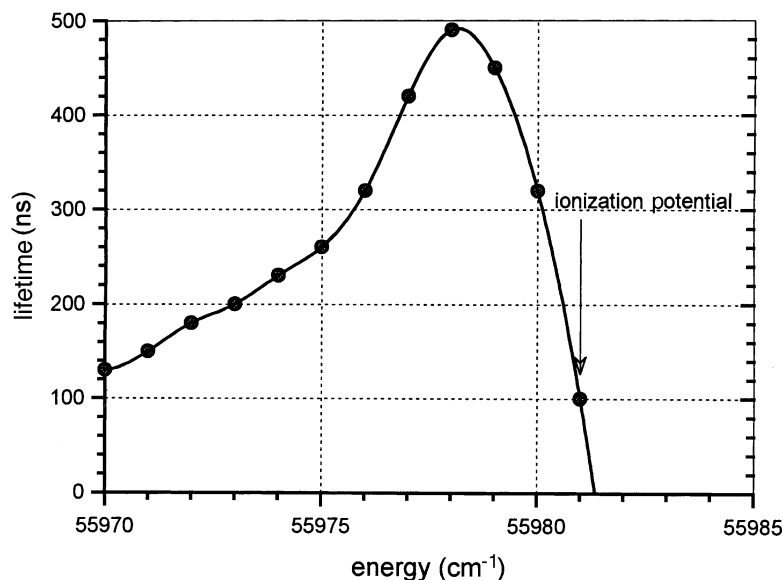


Figure 8. Behaviour of the short time component of tetracene as a function of the laser excitation energy. Ionization potential is estimated from the ZEKE spectra at low fields. Signal above the ionization limit are due to the finite laser width of 0.2 cm^{-1} .

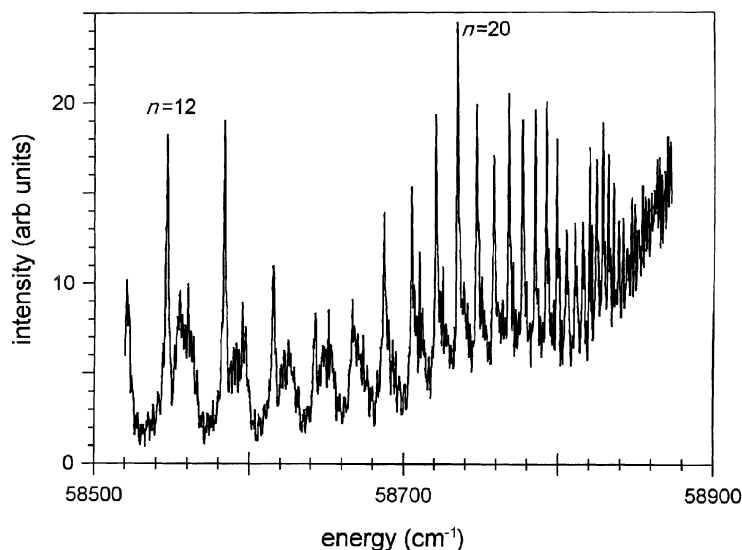


Figure 9. Rydberg series for DABCO excited through its 825 cm^{-1} vibration in the S_1 state. Several series are detected. Assigned quantum numbers are indicated for some of the lines in one of the series. Individual lines could be resolved up to $n = 70$.

energy (Consalvo 1993; Even *et al.* 1994; Fisanick *et al.* 1983; Fujii *et al.* 1983; Boogaart 1996). We tried several vibrations and could not detect any systematic differences in the width or intensity of the spectral lines. The autoionization is fast as indicated by the width of the lower Rydberg states ($n = 11\text{--}27$). As for the case of the Ar np' series the width in DABCO becomes progressively smaller with rising n approximately with an n^{-3} dependence. We could not resolve the width for $n > 27$.

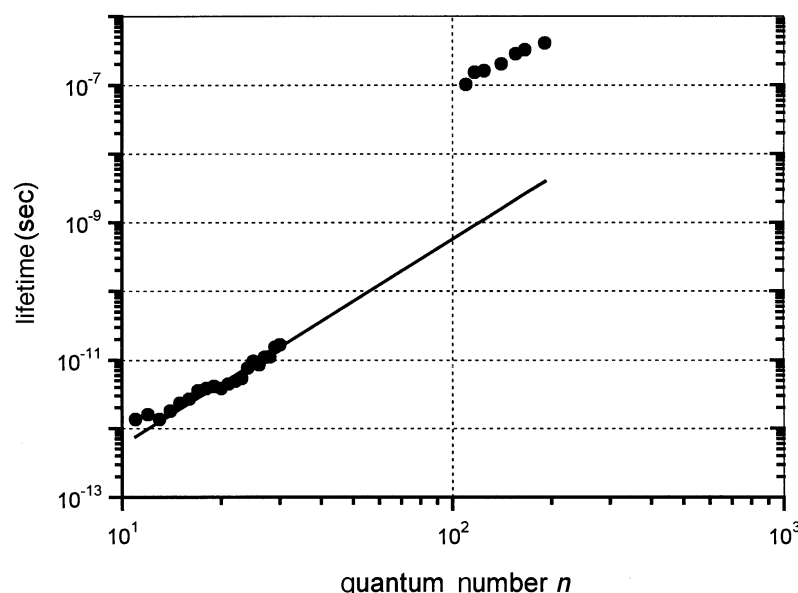


Figure 10. A plot of the lifetime obtained for DABCO, combining the lifetimes derived from width measurements at low n with the short lifetime component obtained by delayed ZEKE spectroscopy. A gap exists in our measurements' capabilities between the highest resolved line width ($n < 27$) and lowest measured ZEKE state ($n > 100$). A simple n^3 extrapolation is shown for comparison.

The long Rydberg series allowed us to determine the ionization limit with high accuracy (IP = $58\,862.3 \pm 0.2 \text{ cm}^{-1}$ for the ion in this vibronic state) allowing a precise determination of the n scale even when we lose resolution of individual spectral lines.

In contrast to the fast autoionization of the lower Rydberg states, the higher ones ($n > 100$) live long enough to be detected by time resolved ZEKE spectroscopy as is the case for other molecules. The lifetime of the short component of the decay was measured as a function of the excitation energy and the established n scale. The lifetime deduced from the width of the lower Rydberg states and those measured directly by pulsed field delay are shown in figure 10. As in the atomic case there is a gap in our measurement capability, but there seem to be a failure of the n^3 extrapolation law from low to high n' .

5. Discussion and conclusions

Similarities and differences were found out in examining the molecular and atomic systems of the low and high Rydberg states as follows.

(1) Rydberg states of atoms below the ionization threshold are very stable in our system. We could easily detect them by field ionization even after a delay of $10 \mu\text{s}$ (Merkt & Zare 1994; Bahatt *et al.* 1993a). Interactions with the black body radiation field at room temperature (Stebbing & Dunning 1983) or near collisions with neighbouring ions do not play a major role in our time scale (few μs), ion densities (approximately 100 ions mm^3 (Alt *et al.* 1995)) and quantum numbers (10–300).

(2) Low molecular Rydberg states below the ionization threshold are not very common in large molecules, indicating fast decay to the dense rovibronic manifold

that is present at these high molecular excitation energies (Jortner & Morris 1969). Benzene (Whetten *et al.* 1985; Consalvo 1993), BBC (Berry & Nielsen 1970) and few others seem to be the exceptions while molecules like DABCO (Consalvo 1993; Even *et al.* 1994; Fisanick *et al.* 1983; Fujii *et al.* 1983) require vibrational excitation to enhance the autoionization rate and reveal its Rydberg series.

(3) Weak external fields seem to enhance the stability of autoionizing states in atoms and molecules. Breaking of the spherical symmetry and the ensuing degeneracy removal by Stark splitting can be invoked (Chupka 1993*a,b*) to explain this stabilization. The splitting of the energy levels by the external field reduces the transition probability to each sub level and causes an increase in the lifetime by a factor of n or n^2 . The same effect can be reproduced by classical trajectory calculation (Rabani *et al.* 1994, 1995*b*; Rabani & Even 1994). The effect of the external field can be seen as a 'time stretch' of the precessing electron orbit causing a slowing down of energy exchange with the core. An even simpler computational method is using a classical mapping method (Rabani *et al.* 1994). It is based on the 'kicked rotor' model to describe the electron interaction with the core and can give surprisingly accurate results containing the basic parameters of the problem. The electron motion is considerably slower than the rotating core and the interaction between the two is described in this model as random kicks. Detailed quantum model Hamiltonian predicts the non-exponential decay in atoms (Bixon & Jortner 1995*a*, 1996*a*) and shows the influence of even weak fields (0.1 V cm^{-1}) on the decay dynamics. The model Hamiltonian contains the interaction of the coulomb radial field with the external electric field in the full representation of the n , l and m quantum numbers. It can be diagonalized for atomic and also for simple molecular systems (Bixon & Jortner 1996*b*). This model predicts the deviation from a simple n^3 dependence and the 'jump' in the measured lifetimes for atoms and molecules.

(4) Coupling of the Rydberg electron to the molecular core can be influenced by the dipole or quadrupole moment of the molecule. Detailed calculations of this effect show that mixing of rotations can change the detection window in ZEKE experiments and bottlenecks in the coupling can cause the appearance of non-exponential decay mechanism (Baranov *et al.* 1997; Remacle & Levine 1996*a*) and lengthening of the lifetimes.

(5) It is still undecided whether external (stray fields, stray ions) or internal fields (quadrupolar or dipolar) dominate the decay behaviour of the high Rydberg states in all cases. The behaviour of an Atom (Ar) is similar to that of a large Molecule (DABCO or BBC) in the non-exponential time dependence and large deviation from the n^3 scaling law. This deviation is more pronounced in the examined Molecules than in an Ar atom. It is safe to assume that careful experimental design is necessary to reduce the external field effects for electrons at very high Rydberg states so that the internal interaction becomes dominant.

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Discussion

P. GUYON (*Université de Paris-Sud, France*). Professor Even mentioned the various perturbations that may destroy the value of the Rydberg state quantum number. In particular, ions or non-sphericity of the COR may destroy or mix the ML quantum numbers. Several recent experiments have been done on the role of ions to stabilize Rydberg states and several theoretical models have been proposed to explain the stability of the ZEKE states. Could he comment on the present status of this question?

U. EVEN. Our ion density is estimated to be too low to cause the estimated lengthening of the lifetime. We use unfocused laser beams and create no more than 10 ions mm⁻³. The role of the molecular core is in this problem is still being discussed and debated. I have no conclusive data to challenge the proposal that the influence of external fields (electric and magnetic) is dominant.