VOLUME 60, NUMBER 10 PHYSICAL REVIEW LETTERS 7 MARCH 1988

Electric-Field–Hindered Vibrational Autoionization in Molecular Rydberg States

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(Received 9 December 1987)

The vibrational autoionization process of the Na_2 *nd* Rydberg states has been studied in the presence of an electric field. The autoionization lifetime is shown to increase as a function of the electric field. This effect is interpreted in terms of Stark mixing with the high-angular-momentum hydrogenic complex. Moreover, it is shown that the autoionization lifetime grows with the field even in the inter-*n*-mixing region.

PACS numbers: 33.80.Eh

In the absence of external field, the vibrational autoionization process of molecular Rydberg states has been widely studied in the past decade. The most extensive study concerns the H_2 molecule[1,2] where precise linewidths and autoionization rates have been measured. The experimental results have been fairly interpreted in the framework of multichannel quantum-defect theory (MQDT),[3] which has been extended to rovibrational interactions by Jungen and co-workers.[4] Investigations of molecular Rydberg states in an electric field began quite recently. The influence of the electric field **F** on the ionization threshold[5-9] was reported, and the $-2\sqrt{F}$ law was observed experimentally. We have obtained[10] the Stark structure of Na_2 Rydberg states. We have also experimentally demonstrated[8] that a small electric field can indeed induce the rotational autoionization. Because of mixing induced by the field, a Rydberg level with a high J value ($J \simeq 20$) can autoionize to the $N^+=0$ rotational level of the $Na_2{}^+$ ion. Our experiments are in agreement with independent results obtained by Gallagher and co-workers on Li_2.[7]

We report in this Letter the first observation of the influence of the electric field on the vibrational autoionization process. The experiment concerns the Na_2 $nd\,{}^1\Lambda_g$ Rydberg series which have been analyzed in detail by MQDT.[11,12] By measuring the autoionization lifetimes of the $\Delta v=1$ process, we demonstrate that vibrational autoionization is appreciably reduced by the applied electric field.

Our experimental setup is very similar to the one described in previous papers[12] except for details concerning the time-resolved detection. A supersonic sodium beam is crossed at right angles by two superimposed counterpropagating tunable dye lasers pumped by the harmonics of a pulsed yttrium-aluminum-garnet laser. The first dye laser selects a well defined level (v',J') of the $A\,{}^1\Sigma_u^+$ intermediate state of Na_2. The second one is tuned to the autoionizing Rydberg states. We observe mainly the $nd\,{}^1\Sigma_g^+$ and $nd\,{}^1\Pi_g$ series; $nd\,{}^1\Lambda_g$ lines appear when angular mixing occurs. These two lasers are of grazing-incidence design. Both of them have typical linewidths of 3 GHz (0.1 cm^{-1}). Laser pulse duration is about 6 ns. The electric field F is applied in the interaction region between two parallel plates 1 cm apart. In addition, this electric field collects the produced electrons which are then detected by an electron multiplier. The electron current is recorded in a microcomputer through a boxcar integrator with a variable gate aperture time.

In Na_2, the vibrational autoionization process cannot be investigated from linewidth measurements because of the finite experimental resolution (0.1 cm^{-1}). However, the lifetimes can be measured since they are expected to range from 1 to 100 ns. Using different gate aperture times of our boxcar integrator, we are able to measure the lifetimes of each line. The recorded signal S is proportional to the integral of the electron current during the gate aperture. Taking into account the duration of the laser pulse T_0 (about 5 ns) one can easily show that

$$S=k[T_0+\tau e^{-T/\tau}(1-e^{T_0/\tau})], \qquad (1)$$

where T is the gate aperture time, τ is the lifetime of the Rydberg state, and k is a factor depending on the population of the Rydberg state. Because of experimental limitations, we can estimate that 5 ns is the minimum value of the lifetime which can be precisely measured. Under these conditions, this method is more powerful than a measurement of individual lifetime of each line for three reasons. (i) There is congestion of the spectra and superimposition of different lines just below the ionization threshold where field effect is predominant. (ii) The Stark spectra are not well resolved and assigned.[10] (iii) This method offers the possibility of our measuring the lifetimes of each line (or group of lines) of an entire spectrum directly, by varying the gate aperture time. Finally, we must mention that the experiment intrinsically imposed restrictions on the applied electric field strengths. In fact, for weak field, the emitted electrons are accelerated too slowly in the interaction region and the time-resolved signal is distorted. On the other hand, a high value of F lowers the ionization threshold so much that field effects are no longer measurable. It is well known[5,8] that F lowers the ionization threshold by an energy $\Delta E=-2\sqrt{F}$ (a.u.). These two effects limit the values of interest of F to the range 1 to 20 V/cm in our case.

As mentioned in the introduction, we will limit our discussion to the $\Delta v = 1$ process. General considerations about molecular couplings[13] have shown that the $\Delta v = 1$ autoionization lifetime scales as $1/\sqrt{v}$. Under these conditions, it is interesting to conduct experiments with the vibrational series of greatest lifetime—that is to say, with the $v = 1$ series. The results presented here are thus all obtained for $v = 1$ series. The $A\,^1\Sigma_u^+$ $(v' = 1, J' = 6)$ level was chosen to be the intermediate state. The observed Rydberg levels are mainly $v = 1$ (because of Franck-Condon factors close to $\delta_{vv'}$), $J = 5$, 6, and 7 (respectively, P, Q, and R lines) converging towards the $v^+ = 1$, $N^+ = 3$, 5, 7, and 9 limits of the ion. (The energy difference between the limits $N^+ = 3$ and $N^+ = 9$ is only 9 cm^{-1}.)

Each state observed in that kind of spectra autoionizes directly ($\Delta v = 1$ process) leading to a Na_2^+ ion in its vibrational ground state plus a free electron. For each field strength, we simultaneously record two spectra: one with a large integration time (200 ns), the second with a short integration time (10 ns). Figure 1 shows such spectra recorded with $F = 2$ V/cm. The upper spectrum is recorded with a 200-ns gate, the lower one with a 10-ns gate. The lower spectrum shows clearly the region of long-lived states located just below the ionization limits ($v^+ = 1$, $N^+ = 3$, 5, 7, and 9) lowered by the quantity $\Delta E = -2\sqrt{F}$ mentioned above. In order to show more clearly the variation of the lifetime versus the electric field, it is possible to extract from the two spectra the average lifetime in a limited energy range. We proceed as follows. The two spectra are smoothed, then by dividing the spectra recorded with the wide gate T_1 by the one recorded with the short gate T_2 we obtain a new spectrum, which, according to (1) is proportional to

$$S' = \frac{T_0 + \tau e^{-T_1/\tau}(1 - e^{T_0/\tau})}{T_0 + \tau e^{-T_2/\tau}(1 - e^{T_0/\tau})}. \qquad (2)$$

It is then possible to deduce the value of τ which is now an average value of the lifetime as a function of the energy instead of the real lifetime of each individual line.

As the identical procedure is followed with calculated spectra, we are able to make valuable comparisons with experimental results. Figure 2 shows experimental spectra treated in that way for different values of the electric field (2, 5, and 20 V/cm). It is clear from Fig. 2 that increasing the electric field causes the lifetime to increase. This figure also shows the lowering of the direct ionization threshold through a deep decrease in the lifetime (this threshold is not very sharp, probably because of rotational autoionization[8]).

Let us compare these experimental results with theoretical lifetimes in zero electric field. As shown by Jungen and co-workers,[4] the MQDT is the method best

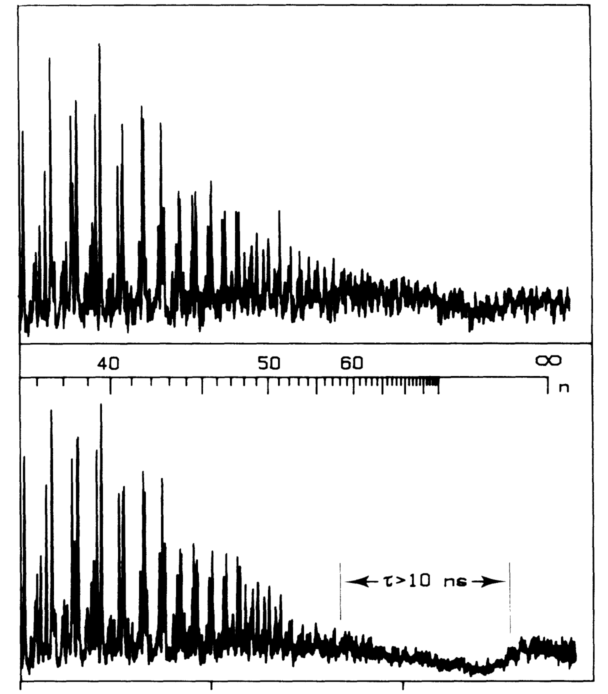

FIG. 1. Two spectra recorded with the intermediate level $(v' = 1, J' = 6)$ and $F = 2$ V/cm. Upper spectrum: $T_1 = 200$ ns. Lower spectrum: $T_2 = 10$ ns. The n values correspond to the $v^+ = 1$, $N^+ = 6$ limit of the ion (the true ionization limits are in fact $v^+ = 1$, $N^+ = 3$, 5, 7, and 9). The region of long-lived states appears clearly in the lower spectrum.

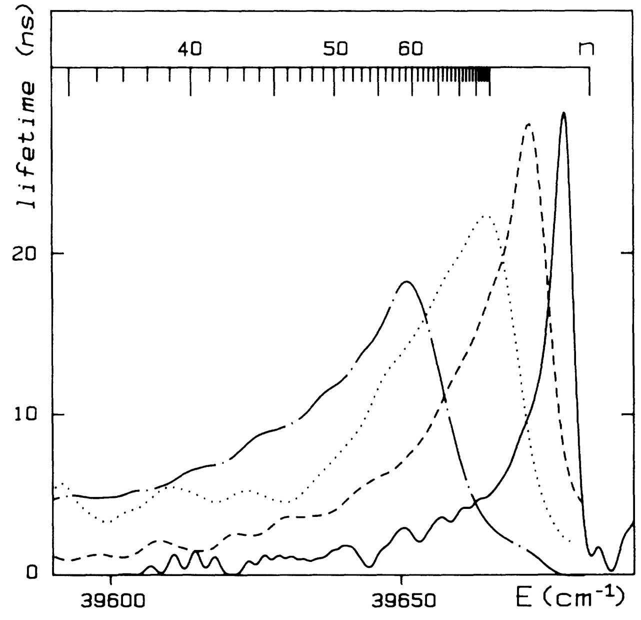

FIG. 2. Average values of the autoionization lifetime vs energy. Solid curve: MQDT calculation. Dashed curve, experiments with $F = 2$ V/cm; dotted curve, $F = 5$ V/cm; dashed-dotted curve, $F = 20$ V/cm (n is defined as in Fig. 1).

suited to solve this problem. To take into account both rotational and vibrational interactions, we have to introduce quantum defects as a function of the internuclear separation $\mu_\Lambda(R)$ and open channels. The reaction matrix used in the MQDT treatment is

$$R_{v^+N^+,v^{+\prime}N^{+\prime}}=\sum_\Lambda \langle N^+|\Lambda\rangle \left[\int \chi_{v^+}\tan\pi\mu_\Lambda(R)\chi_{v^{+\prime}}dR\right]\langle\Lambda|N^{+\prime}\rangle, \tag{3}$$

where (v^+,N^+) are the ionization channels and the χ's are the vibrational wave functions of the ionic core.

The relevant quantities $\mu_\Lambda(R)$ are derived from previous analysis of vibrational perturbations on energy levels. The detailed spectroscopic study leading to these quantities is to be published elsewhere.[14] It can be seen from expression (3) that the precise treatment of $\Delta v=1$ autoionization requires only first-order expressions of the μ_Λ's as functions of R. The values used in the calculations are reported in Table I. Notice that in the limit of only one Λ channel the expression (3) leads to the well-known approximate values[14] for the lifetime of a Rydberg series $(v=1)$:

$$\tau=6.3\times10^{-7}[d\mu_\Lambda(R_e)/dR]^{-2}\nu^3, \tag{4}$$

where the lifetime τ is expressed in nanoseconds and R in angstroms, and ν is the effective quantum number (defined by $E=E_{\text{ion}}-1/2\nu^2$ in atomic units). In fact, because of the interchannel mixing, the lifetime depends not simply on the energy. The theoretical spectrum calculated in zero electric field following the MQDT procedure described above is shown in Fig. 2. The electric field is clearly demonstrated to increase the autoionization lifetime and its influence appears quite drastic.

This result can be qualitatively interpreted as follows: The role of the field is to mix the low-l states $(l\le 2)$ of an n manifold with the high-angular-momentum hydrogenic complex. The high-l states are nonpenetrating and so they do not interact with the ionic core and thus have very low autoionization rates. This mixing leads to an increase of the autoionization lifetime because the coupling between the core and the electron, due to the low-l components, is shared by all the components of the n manifold. In fact, the different l components are more and more mixed as the field increases leading to approximately pure parabolic eigenstates labeled (ν,n_1,m) where ν replaces the hydrogenic principal quantum number n.

The parabolic eigenfunctions $\psi_{\nu n_1 m}$ can be expanded in the set of spherical functions[15-17] $\psi_{\nu lm}$:

$$\psi_{\nu n_1 m}=\sum_{l=m}^{\infty}U^{\nu m}_{n_1 l}\psi_{\nu lm}. \tag{5}$$

TABLE I. Values of the quantum defects $\mu_\Lambda(R_e)$ and of the first derivative $d\mu_\Lambda/dR$ (in reciprocal angstroms) used in the MQDT treatment (nd series). The precision is better than 0.01 for the quantum defects and 0.05 Å^{-1} for the first derivatives.

Λ	$\mu_\Lambda(R_e)$	$(d\mu_\Lambda/dR)_{R_e}$
Σ	0.205	0.15
Π	−0.03	0.20
Δ	0.41	0.05

When $l=m=0$, $U^{\nu m}_{n_1 l}=1/\sqrt{\nu}$. When $l\neq0$ the expression of the U matrix is more complex, but the magnitude of each term is of the order of $1/\sqrt{\nu}$. As a consequence, when the Stark mixing is complete, the eigenstates are superpositions of all the l sublevels having approximately the same weight. In other words, the autoionization rate being the sum of the contribution of each sublevel, it is divided by a factor which increases linearly with ν to a first approximation. This means that at a given energy the autoionization lifetime increases as a function of the field. We indeed observe the increasing of the autoionization lifetime in this region as qualitatively illustrated by Fig. 2. This effect has been calculated by Sakimoto[17] in the case of atomic resonance scattering. Harmin[18] has discussed the inverse process (dielectronic recombination) which exhibits a similar behavior. It was shown theoretically in this reference that the enhancement of dielectronic recombination saturates above the critical value $F=1/3\nu^5$.

Although our problem is quite different, the autoionization lifetime lengthening is expected to saturate at a value independent of the field for F larger than a critical value F_c. This critical field corresponds to the beginning of the complete Stark mixing. However, this quantity is not well defined but is expected to be of the order of the point of n-manifold crossing: $F_c=\nu^{-5}/3$. In fact, Table II shows that the autoionization lifetime continues to increase with F beyond this value. This character evidences that the point of n-manifold crossing does not denote complete Stark mixing. Clearly this model must be improved and at least two kinds of effects could explain the observed results: First, the measured lifetime is in fact an average of many Stark sublevels. Beyond the inter-n-mixing region, anticrossings occur leading to interference effects on the lifetime. In principle, the average value $\langle\Gamma\rangle=\langle1/\tau\rangle$ remains the same as that obtained without interference effect. However, the intensities of the various lines are also affected by the interference effects and it is difficult to predict the influence of these effects without precise calculation. Second, our rough model does not take into account the various rotational channels $N^+=3$, 5, 7, and 9 which are mixed by the electric field. It is very difficult to predict the influence of all these effects without detailed calculations.

TABLE II. Average values of the autoionization lifetime vs electric field for different values of the effective quantum number ν (relative to the $v^+=1$, $N^+=6$ level of the ion). The lifetime increases as a function of the electric field below and above $3\nu^5F=1$ (see text).

F (V/cm)	38		50		60		70	
ν	τ (ns)	ν^5F (a.u.)	τ	ν^5F	τ	ν^5F	τ	ν^5F
2	<5	0.03	<5	0.12	8	0.30	13	0.65
3	<5	0.05	6	0.18	11	0.45	15	0.98
5	5	0.08	8	0.30	15	0.76	20	1.63
20	6	0.31	12	1.22				

In conclusion, we have observed the reduction of vibrational autoionization by the electric field. This effect can be qualitatively interpreted as due to the mixing with the hydrogenic complex and has been studied in detail for the $\Delta v=1$ autoionization process. (It can also indirectly influence $\Delta v>1$ autoionization. For example, in the $\Delta v=2$ process part of the autoionization rate comes from the coupling with the $v-1$ series which autoionizes by a $\Delta v=1$ process.) A quantitative interpretation of observed effects requires a complete MQDT treatment of molecular Rydberg states in electric field. This work is in progress in our laboratory.

We are grateful to Professor G. Jalbert for fruitful discussions and suggestions. Laboratoire de Spectrométrie Ionique et Moléculaire is Laboratoire No. 171 associé au Centre National de la Recherche Scientifique.

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