Stark Multiplets in Molecular Rydberg States

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The Stark splitting in molecular Rydberg states has been observed for the first time in the Na_2 molecule. At high electric field, very simple hydrogenic structures appear, corresponding to the field-induced decoupling between electronic and nuclear motion. At low field strengths core interaction and molecular rotation cause departure from this hydrogenic model.

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Photoionization in electric fields has been the subject of great interest as it has enabled a number of fundamental processes to be studied: measurements of Stark structure, Fano line profiles due to the interaction of discrete level and ionization continua, departure from hydrogenic behavior as a result of the interaction between penetrating electronic orbitals and the ionic core, etc.[1-4] Nevertheless, experiments in this field have so far been limited to atoms; to our knowledge, except the works of Seaver *et al.*[5] on NO and of Cooper *et al.*[6] on H_2 (where Stark structure was not resolved), no molecular Rydberg Stark spectra have yet been recorded. A possible explanation for this situation may be the high congestion of molecular Rydberg states, congestion which is expected to increase with the Stark splitting.

We report in this paper the observation of photoionization spectra of Na_2 molecules in an electrostatic field whose strength varies up to 3 kV/cm. Surprisingly, some regions of these spectra are much simplified at high field, the spectra being reduced to a simple periodic structure. The variation of this structure with field strength, principal quantum-number values n, and molecular rotation is studied and discussed in this paper.

The experimental setup has been described in detail elsewhere.[7] Briefly, Na_2 molecules in a supersonic beam interact at a right angle with two counterpropagating laser beams. The spectral width of the two pulsed tunable dye lasers is about 0.2 cm^{-1}. In order to perform a two-step excitation, the first laser $h\nu_1$ is fixed to select a given v,J level in the intermediate A state. The second laser $h\nu_2$ is then scanned to explore the ionization region. Three series of experiments were conducted with $v=2$, $J=12$; $v=4$, $J=6$; and $v=4$, $J=18$. In the third perpendicular direction, a dc electric field is applied between two circular parallel plates that are 1 cm apart. The photoelectrons are extracted through a grid at the center of the positive plate, then enter a secondary electron multiplier for amplification. The electron signal is averaged with a boxcar integrator before being recorded and stored in a microcomputer.

The Stark structure is well established for hydrogen-atom Rydberg states; the application of an electric field to a system with Coulomb field symmetry results in a splitting into $n-|m_l|$ components for each (n,m_l) level. In alkali-metal atoms, departure from the hydrogenic model is characterized by the breaking off of Coulomb field symmetry because of the penetration of low-l orbitals in the ionic core; the quantum defect accounts for this. Consequently a no-crossing rule between Stark sublevels holds in the inter-n-mixing region, and leads to more complicated spectra.[1]

In molecular Rydberg states, the spectrum is already rather complicated in the absence of an electric field.[7] This is due to the rotational structure and to the splitting between the various Λ components in an nl complex. In principle, the electric field introduces an additional splitting of the M_J components and this could lead to extremely congested spectra in which the structure may no longer be resolved. However, the observed Stark spectra (Fig. 1) for increasing field values display very simple periodic structure which correspond roughly to hydrogenic Stark splittings.

Let us first consider high electric fields for which the total Stark splitting in an n complex is large as compared to the rotational structure. Under such conditions, the Rydberg electron tends to be decoupled from the molecular axis and the eigenfunction can be written at first approximation as a product $\psi_{N^+v^+}\psi_{el}$, where N^+,v^+ are, respectively, the rotational and vibrational quantum numbers of the molecular core Na_2^+, $\psi_{N^+v^+}$ is the Na_2^+ eigenfunction, and ψ_{el} is the Rydberg electron eigenfunction. ψ_{el} can be calculated by use of a Stark Hamiltonian and a Coulomb potential except in the ionic core, as in alkali atoms. In this approximation, the energy levels of the hydrogenic complex can be easily obtained[8]:

$$E_{tot}=E_{v^+N^+}+W_a+W_1, \tag{1}$$

where $E_{v^+N^+}$ is the energy of the Na_2^+ molecular ion,

$$W_a=(2n^2)^{-1}, \tag{1a}$$

$$W_1=\tfrac{3}{2}n(n_1-n_2)F. \tag{1b}$$

W_a and W_1 are expressed in atomic units. $n_1+n_2=n-|m_l|-1$ are quantum numbers deduced by our solving the Schrödinger equation after separation in parabolic coordinates. Consequently, the energy difference

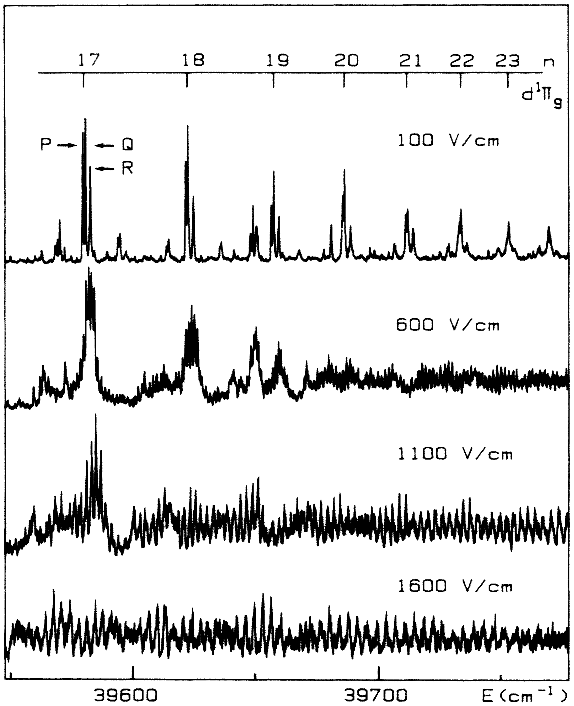

FIG. 1. Stark spectra obtained with the intermediate state A, $v=4$ and $J=6$ for various F values. At $F=100$ V cm^{-1}, the rotational structure is observed at low n values. At $F \geq 600$ V cm^{-1}, the Stark splitting δ is observed.

between Stark sublevels is

$$W_1(n_1) - W_1(n_1 - 1) = 3nF \tag{2}$$

for a given $|m_l|$ value; it is $\frac{3}{2}nF$ when odd and even values of $|m_l|$ are considered simultaneously.

If we express W_1 in inverse centimeters and F in volts per centimeter, formula (2) becomes

$$W_1(n_1) - W_1(n_1 - 1) = 1.280 \times 10^{-4} nF. \tag{3}$$

In fact, formulas (1a), (1b), and (2) are true for all m_l values in the hydrogen atom only. In the sodium atom, Fabre *et al.*[9] have shown that $|m_l| = 0,1,2$ sublevels of the hydrogenic complex have the same energies. If we limit ourselves to these m_l values, the observed Stark splitting δ is no longer equal to $\frac{3}{2}nF$ but to $3nF$. Using a simple model based on a truncated Stark basis, Fabre *et al.*[9] have demonstrated that this degeneracy is general when few Rydberg levels have nonzero quantum defects: In the lithium atom only *ns* levels have a large quantum defect, and levels with $|m_l| = 0$ and $|m_l| = 1$ are degenerate. This is the case for *ns* and *np* levels in the sodium atom, and the levels with $|m_l| = 0$, 1, and 2 are degenerate. In Na$_2$, *ns*, *np*Λ, and *nd*Λ have nonzero quantum defects,[10] and we expect the levels $|m_l| = 0,1,2,3$ to be degenerate.

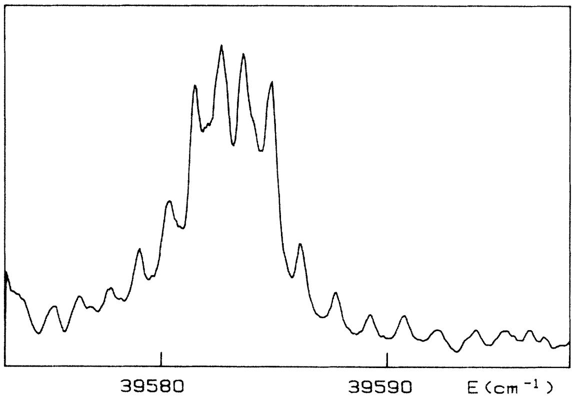

FIG. 2. Stark multiplet for $v=4$, $J=6$, $n=17$, and $F=600$ V cm^{-1}.

In our Na$_2$ experiment, the intermediate A state has a strong $3p$ character and the second laser reaches states with $|m_l| = 0,1,2$. Consequently the observed Stark splitting δ is expected to be $\delta = 3nF$ in Na$_2$. Figure 2 shows an example of a Stark multiplet in $v^+ = 4$, $n=17$ for $F=600$ V cm^{-1}. The observed splitting ($\delta = 1.33$ cm^{-1}) agrees well with formula (2). In Fig. 3, we have reported the Stark splittings measured for various Na$_2$ Rydberg levels as a function of nF. Within experimental error, the points are well aligned and a least-squares fit leads to $\delta = (1.27 \pm 0.02) \times 10^{-4} nF$, in good agreement with formula (2).

In contrast with the atomic case,[1-4,11] this Stark splitting $\delta = 3nF$ is observed even in the inter-n-mixing region. For example, at $F=1600$ V cm^{-1} (Fig. 1) some

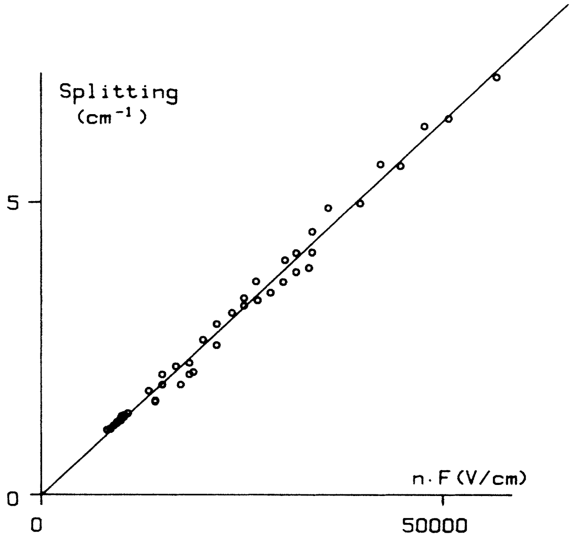

FIG. 3. Splitting between Stark sublevels vs nF.

parts of the spectrum are complicated, but there are also regions where the $3nF$ splitting emerges. The exact theory of molecular Rydberg states in high electric field is very difficult. We have to use the multichannel quantum defect theory in parabolic coordinates introduced by Harmin.[12] This theory has been applied only to alkali-metal atoms and its extension to atoms, to date, with fine structure[11] and to molecules is very complicated, though in principle possible. However, the regular structures we have observed could be very stimulating for theoreticians.

In contrast to the above, at low electric field, the total angular momentum **J** of the molecule remains a good quantum number and the Stark splitting is expected to be quadratic. The linewidth of our laser ($\simeq 0.2$ cm^{-1}) is too high for us to be able to resolve all the M_J components and we can observe only a broadening of the lines (Fig. 1).

In principle, the study of the passage from quadratic to linear Stark effect contains interesting information about the perturbing states. In our spectra we observe only $nd\,^1\Lambda_g$ states. As the Stark Hamiltonian is odd, the perturbing states are $np\,^1\Lambda_u$ and $nf\,^1\Lambda_u$ states, but their quantum defects are not known.[13] The p orbitals are expected to penetrate the ion core and to have nonzero quantum defects, while the f orbitals are less penetrating. For example in the NO molecule,[14] all the quantum defects of the nf complex are smaller than 0.02. But in Na_2, the larger molecular ion core can lead to larger quantum defects for the f complex, the internuclear distance being 3.6 Å for Na_2^+ as compared to 1.06 Å for NO^+.

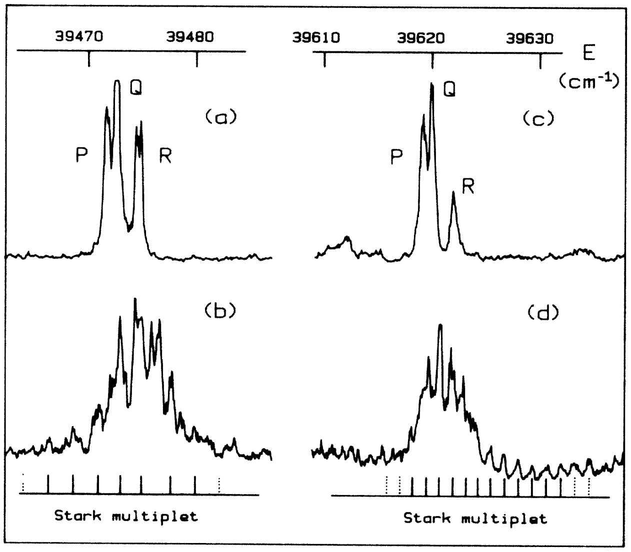

FIG. 4. Photoionization spectra for various n and F values with $v=4$, $J=6$. (a) $n=15$, $F=600$ V cm^{-1}, (b) $n=15$, $F=1300$ V cm^{-1}, (c) $n=18$, $F=200$ V cm^{-1}, (d) $n=18$, $F=500$ V cm^{-1}. $3nF$ is the same for (a) and (d) but the structures are completely different (see the text). The Stark manifold begins to appear in (b) and (d).

Let us first assume that quantum defects of all the $nf\,^1\Lambda_u$ states are zero (or close to zero). In this case, as the $nd\,^1\Pi_g$ states also have quantum defects close to zero ($\mu_{d\Pi}=-0.01$), we might expect the hydrogenic Stark manifold to appear at very low electric field strengths, with the $d\Pi$ level being directly coupled through the $nf\Lambda$ levels to the hydrogenic complex. Such a situation is encountered in the xenon[11] atom for the Stark effect of the nf states. The field F_c at which the Stark manifold should appear on the spectrum can be roughly estimated by the equation

$$(1/n^3)\mu_{d\Pi}=\tfrac{3}{2}n^2F_c, \qquad (4)$$

where $\frac{3}{2}n^2F_c$ is the half width of the hydrogenic Stark manifold and $(1/n^3)\mu_{d\Pi}$ the energy difference between the $nd\Pi$ level and the hydrogenic complex. Equation (4) would lead to $F_c \approx 50$ V cm^{-1} for $n=15$.

Figure 4(a) shows the PQR lines of the $15d\Pi$ level at $F=600$ V cm^{-1}. These lines are broadened (full width at half maximum ≈ 1 cm^{-1}); but the Stark manifold is not observed. In fact, for $n=15$, the Stark manifold begins to be observed for fields larger than 1200 V cm^{-1} [Fig. 4(b)]. This means that the $nf\,^1\Lambda_u$ states ($\Lambda=0,1,2$), coupled through the Stark Hamiltonian to the $nd\,^1\Pi_g$ states, probably have nonzero quantum defects. If this is the case, the Stark manifold which contains only electronic angular momenta l larger than 3 cannot be directly excited from the $A\,^1\Sigma_u^+$ intermediate state, which has a strong $3p$ character. Therefore the Stark manifold can only be observed when it is mixed with the $nd\Pi$ level through a component of the nf complex. The electric field F_c can then be roughly estimated by our transposing Eq. (4) to the nf complex

$$(1/n^3)\mu_{f\Lambda_0}=\tfrac{3}{2}n^2F_c, \qquad (5)$$

where $\mu_{f\Lambda_0}$ is the smallest quantum defect among $\mu_{f\Sigma}$, $\mu_{f\Pi}$, and $\mu_{f\Delta}$ (the level $nf\varphi$ is not coupled to the $nd\Pi$ level).

Equation (5) implies that n^5F_c is constant. The measured F_c values are shown in Table I for $15 \le n \le 20$. The determination of F_c is not very precise because we observe in fact a rather gradual transition from the rota-

TABLE I. F_c and n^5F_c values (see the text). n^5F_c is roughly constant.

n	F_c	n^5F_c
15	1200 ± 100	9.1×10^8
16	700 ± 70	7.3×10^8
17	550 ± 50	7.8×10^8
18	450 ± 50	8.5×10^8
19	400 ± 40	9.9×10^8
20	300 ± 30	9.6×10^8

tional structure (P, Q, R lines) to the Stark manifold. However, the law $n^5F_c \approx$ const is well verified within the experimental error. Figure 4 also illustrates the n^{-5} dependence of F_c. For $n=18$, $F_c=450$ V cm^{-1}, while for $n=15$, $F_c=1200$ V cm^{-1}. It must be noticed that for $n=15$, $F=600$ V cm^{-1} [Fig. 4(a)], and for $n=18$, $F=500$ V cm^{-1} [Fig. 4(d)], the Stark splitting $3nF$ is the same but the spectrum is completely different because of the n^5F_c dependence. Figure 4 corresponds to $J=6$, but the experiment was also performed for $J=12$ and 18, and we obtained the same F_c values inside the experimental incertitude. This indicates that the rotational structure alone cannot explain the high value of F_c.

The comparison between Eq. (5) and Table I leads to $\mu_{f\Lambda_0} \approx 0.2$. This result is only qualitative and a complete multichannel quantum-defect treatment is necessary if the interpretation is to be carried further. We can only conclude that, unlike in the NO molecule where all the $f\Lambda$ quantum defects are less than 0.02, the Na_2 $nf\Lambda$ states ($\Lambda=0,1,2$) are not clustered in the hydrogenic complex.

In conclusion, we have observed for the first time Stark multiplets in highly excited molecular Rydberg states. The main features of our spectra have been interpreted in both strong and weak fields. A detailed multichannel quantum-defect–theory analysis of our spectra will be very interesting, but it requires knowledge of the quantum defects of the $np\Lambda_u$ and $nf\Lambda_u$ series. These can be found from microwave transitions between molecular Rydberg states, and such experiments are in progress in our laboratory.

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