Doubly Excited Rydberg States of the Na_2 Molecule

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We report here the first observation of Na_2 Rydberg states with an excited Na_2^+ $1\,^2\Pi_u$ core. The principle of our experiment is to prepare a Rydberg state associated with the ion in its ground state and then to excite the Na_2^+ core with a tunable laser. The autoionization processes occurring in these states as well as the internal energy redistribution of the singly excited Rydberg states are discussed. Finally, the energy levels of the $1\,^2\Pi_u$ state of Na_2^+ are deduced.

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The doubly excited states of atoms or molecules have been a field of increasing interest in recent years. This is mainly due to the fact that these states exhibit strong correlations between the two excited electrons which lead to specific and very new effects. In atomic physics, doubly excited states have been widely studied both theoretically[1,2] and experimentally, especially in the case of s^2 configurations such as in helium[3] or barium.[4] In diatomic molecules, doubly excited states are generally built up from two monoexcited atoms. The main consequence of this feature is that the regions of singly and doubly excited states widely overlap in molecules while this situation is unusual for atoms. Hence, stable doubly excited states of diatomic molecules exist well below the first ionization limit, such as in H_2,[5] K_2,[6] or Na_2.[7] However, in molecules, new phenomena are expected when the doubly excited states lie above the first ionization limit. For example, many continua may interact with these doubly excited states and dissociation to three particles (atom, ion, and electron) may occur. We think that an interesting approach to this problem is to consider doubly excited molecules where one electron is in a low-lying state, and the other one is in a highly excited Rydberg state. Probably the best known example of such a system is discussed in previous works concerning the Worley and the Hopfield series of N_2[8,9] in the vacuum-ultraviolet (VUV) domain which has stimulated much experimental and theoretical development.[10] However, up to now, all doubly excited Rydberg states of molecules have been studied by single optical resonance in the VUV range. As a consequence, the selectivity and resolution of these experiments were severely limited. We have circumvented these difficulties by performing a three-phonon-three-color experiment on Na_2, where the starting level to probe the doubly excited states is a well-characterized $nd\,^1\Lambda_g$ Rydberg state selected by optical-optical double resonance.[10]

It has been pointed out in previous papers that Na_2 doubly excited states were involved in two-color-three-photon ionization of Na_2.[11,12] The Rydberg series converging toward the $1\,^2\Pi_u$ or $1\,^2\Sigma_u^+$ excited states of Na_2^+ was invoked to explain the dissociative ionization[12] obtained in these three-photon processes. However, in these experiments, the third photon was not scanned toward the doubly excited states and was *a priori* off resonance. Our three-color experiment offers the possibility to probe directly the Rydberg series converging to the Na_2^+ excited states.

The principle of our experiment is shown schematically in Fig. 1. A first laser, $h\nu_1$ (oxazine 720), excites a well-defined v'',J'' level of the $A\,^1\Sigma_u^+$ state of Na_2, and then a second laser, $h\nu_2$ (diphenylstilbene), reaches a highly excited $nd\,^1\Lambda_g$, v',J' Rydberg state, well characterized in previous works,[10] which belongs to a series converging toward the $v^+=v'$, N^+ level of the ground state of Na_2^+. We choose to excite long-lived Rydberg states lying below the $v^+=0$ level of the ion. The third laser $h\nu_3$ is delayed by about 45 ns to avoid the transition induced by $h\nu_3$ starting from the A state. The 12-ns lifetime of the $A\,^1\Sigma_u^+$ state ensures that there are almost no molecules left in the A state when the third laser is on.

The Na_2 molecules are produced in a free molecular beam[10] and are excited at right angles by three superim-

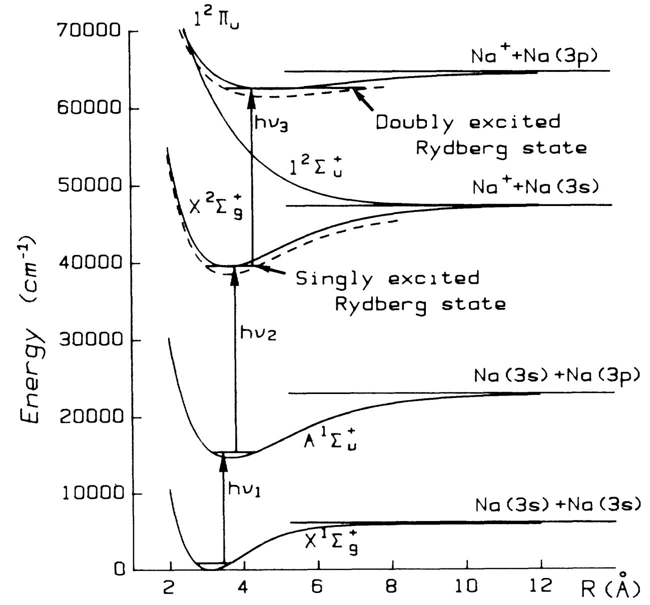

FIG. 1. Principle of the optical excitation of doubly excited Rydberg states.

posed pulsed dye lasers (7-ns pulse duration, 5 GHz FWHM). The Na^+ and $Na_2{}^+$ ions produced by the autoionization or dissociation of the doubly excited states are detected by means of a time-of-flight mass spectrometer.[13] In the interaction region, the accelerating electric field is pulsed and delayed by about 100 ns with respect to the optical excitation in order to avoid the Stark effect. Because of that pulsed field (53 V/cm), the apparent ionization threshold is lowered by about 45 cm^{-1} and the nonautoionizing Rydberg states may produce $Na_2{}^+$ ions by forced ionization.[14,15] This ion signal is used to set $h\nu_2$ resonant with the intermediate Rydberg state. Thus, three cases are possible. If the intermediate Rydberg state lies below the forced-ionization threshold, we can detect either Na^+ or $Na_2{}^+$ ions produced by the fragmentation of the doubly excited molecules. If the Rydberg state lies between the forced-ionization and the field-free-autoionization threshold, only Na^+ ions can be detected since the $Na_2{}^+$-ion signal produced by the third laser is embedded in the strong ion current produced by forced ionization. Finally, if the Rydberg level is above the autoionization threshold, it has generally a very short lifetime (less than 1 ns for $v'=1$ levels) and only $Na_2{}^+$ $v^+=0$ ions remain present in the interaction zone when the third laser is on. In this last case, doubly excited states cannot be studied.

A typical doubly excited-state spectrum is shown in Fig. 2. The first laser excites the $v''=1$, $J''=10$ level of the $A\,{}^1\Sigma_u^+$ state while the second one excites the $v'=1$, $J'=10$, $n=27$ d ${}^1\Pi_g^-$ Rydberg level located in the forced-ionization region. Then, the third laser is scanned between 23 370 and 24 100 cm^{-1}. The whole spectrum of Fig. 2(a) clearly exhibits a long vibrational progression while an enlarged portion of this spectrum is displayed in Fig. 2(b). At first glance, this spectrum calls for three remarks. First, the lines are quite sharp (about 0.2 cm^{-1}) which is remarkable for doubly excited states and makes possible a rotational analysis by using the B_v values deduced from previous pseudopotential calculations of the $Na_2{}^+$ $1\,{}^2\Pi_u$ state.[12,16] Second [see Fig. 2(b)], all the rotational levels from $N^+=0$ to 12 are populated in the singly excited Rydberg states. This is surprising since we have excited the level $J'=10$ and we have assumed that the excited electron has an angular momentum $l=2$ which implies that the core kinetic momentum N^+ lies between $J'-l$ and $J'+l$, that is to say, between 8 and 12. Moreover, each vibrational band has two components which correspond to the fine structure of the ${}^2\Pi_u(\Omega=\frac{3}{2},\Omega=\frac{1}{2})$ excited state of $Na_2{}^+$ (10.9 cm^{-1}). Third, comparison with spectra recorded with different intermediate states, having different quantum defects, shows that the observed line positions are independent of n, Λ, and J' but depend only on v'. However, the linewidth depends sensitively on n. For exam-

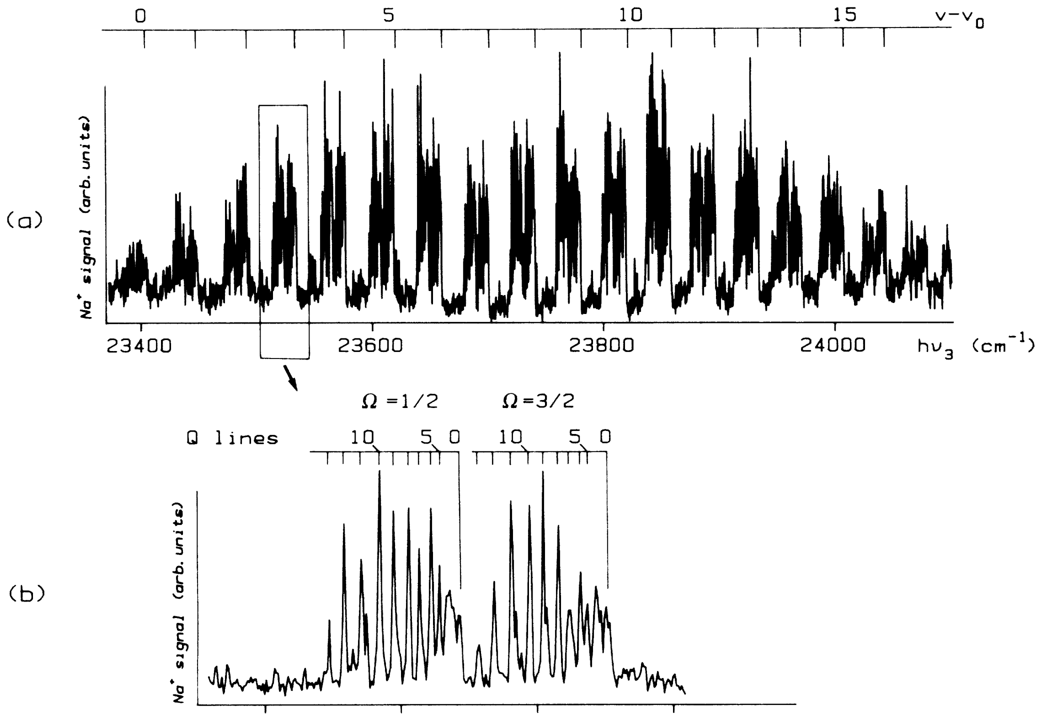

FIG. 2. Typical doubly excited Rydberg states spectrum recorded with $n=27$ d ${}^1\Pi_g^-$, $v'=1$, $J'=10$ as an intermediate state. (a) Whole spectrum showing a long vibrational progression. Vibrational levels are indicated with reference to v_0, the lowest observed level. (b) Enlarged portion of (a). We see clearly two groups of lines corresponding, respectively, to the $\Omega=\frac{1}{2}$ and $\frac{3}{2}$ fine-structure components of the $1\,{}^2\Pi_u$ state. The Q lines of the $X\,{}^2\Sigma_g^+ \rightarrow 1\,{}^2\Pi_u$ transition are indicated.

ple, when the intermediate Rydberg state is $v'=2$, $J'=10$, $n=20$ d $^1\Pi_g^-$, the rotational structure is no longer seen. This means that the linewidth is greater than 1 cm^{-1}, under the same optical conditions, or that the number of lines in that last case is much more important than in $v'=1$, $J'=10$, $n=27$, precluding the observation of the rotational structure. The third point seems to indicate that the observed transitions (in the limit of our experimental resolution) are intrinsic to the $\mathrm{Na_2}^+$ core and correspond to the $X\,^2\Sigma_g^+ \rightarrow 1\,^2\Pi_u$ absorption lines.

Another important experimental result is the branching ratio between the Na^+ and $\mathrm{Na_2}^+$ ions produced by the deexcitation of the doubly excited states. For this purpose, the intermediate level is chosen below the forced-ionization threshold so that the ions produced result from the dissociation or autoionization of the doubly excited state only. Figure 3 shows such spectra recorded with the $v'=1$, $J'=10$, $n=24$ d $^1\Pi_g^-$ intermediate Rydberg level. The upper spectrum corresponds to the Na^+ ions while the lower one corresponds to $\mathrm{Na_2}^+$. It is clear that the ratio $I(\mathrm{Na}^+)/I(\mathrm{Na_2}^+)$ is roughly constant and close to unity (0.8 ± 0.1). In fact, the doubly excited Rydberg states have many possibly decay channels.

(1) Electronic autoionization to the ground state:

$$\mathrm{Na_2}^{**} \rightarrow \mathrm{Na_2}^+(X\,^2\Sigma_g^+) + e^- \quad \text{(fast electron)}.$$

(2) Vibrational autoionization:

$$\mathrm{Na_2}^{**} \rightarrow \mathrm{Na_2}^+(1\,^2\Pi_u, v^+ \approx 0) + e^- \quad \text{(slow electron)}.$$

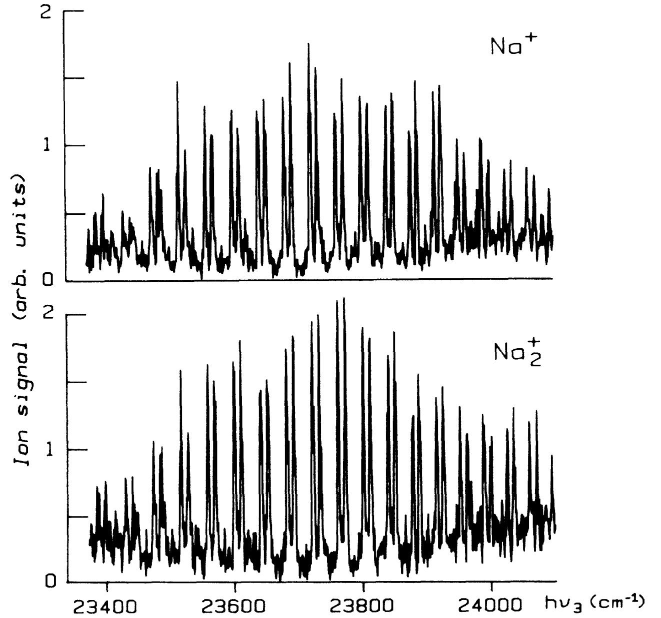

FIG. 3. Low-resolution spectra recorded on the Na^+ channel (upper) and $\mathrm{Na_2}^+$ channel (lower) with $n=24$ d $^1\Pi_g^-$, $v'=1$, $J'=10$ as intermediate state. The branching ratio $\mathrm{Na}^+/\mathrm{Na_2}^+$ is roughly constant (0.8 ± 0.1).

This channel may, in principle, produce Na^+ ions if the $1\,^2\Pi_u$ state is predissociated. However, experiments we have realized directly with $\mathrm{Na_2}^+$ ions in the ground state ($X\,^2\Sigma_g^+, v^+=0$) have demonstrated that the $1\,^2\Pi_u$ state is not predissociated in the spectral range of interest, which is in accordance with the fact that there is no overlap between $1\,^2\Pi_u$ and $1\,^2\Sigma_u^+$ vibrational wave functions in this region. Thus, process (2) produces only $\mathrm{Na_2}^+$ ions.

(3) Dissociative autoionization (electronic autoionization to the dissociative state):

$$\mathrm{Na_2}^{**} \rightarrow \mathrm{Na_2}^+(^2\Sigma_u) + e^-$$
$$\hookrightarrow \mathrm{Na}^+ + \mathrm{Na}(3s).$$

This process may also occur by interaction with doubly excited Rydberg states having low-n values and converging to the repulsive $\mathrm{Na}^+ + \mathrm{Na}(3p)$ core. These states cross the potential curves of the high-n-value doubly excited states produced in our experiment. After predissociation through these low-n-value doubly excited states, interaction with the repulsive curve of the $^2\Sigma_u^+$ state of $\mathrm{Na_2}^+$ may occur with large overlap and lead to $\mathrm{Na}^+ + \mathrm{Na}$. The role of these doubly excited states has already been pointed out in $\mathrm{H_2}$.[17]

(4) Dissociation in neutral fragments (not observable here):

$$\mathrm{Na_2}^{**} \rightarrow \mathrm{Na}(3s) + \mathrm{Na}(nl)$$

or

$$\mathrm{Na_2}^{**} \rightarrow \mathrm{Na}(nl) + \mathrm{Na}(n'l').$$

Our experimental setup does not allow us to discriminate between the autoionization processes (1) and (2) both of which produce $\mathrm{Na_2}^+$. All we can deduce from Fig. 3 is that the autoionization processes (1) and (2) are of the same order of magnitude as the dissociative autoionization (3). The calculation of this branching ratio, taking into account the possible influence of the low-n doubly excited Rydberg state, will be an interesting challenge for theoreticians.

Let us now discuss the points mentioned above, namely, the sharpness of the lines, the independence of their positions relative to the intermediate level, and the presence of more rotational levels than allowed. This last point is probably the key point. As has been shown previously[14] in results concerning rotational autoionization, the rotational and electronic energies are partly redistributed in the Rydberg states. In fact, l is not an exact quantum number, so the rotational quantum number N^+ of the ion core, which, in principle, varies between $J-l$ and $J+l$, may vary over a larger range.

The process leading to this mixing with high-l values is complex. First, in molecules l, the orbital angular momentum of the Rydberg electron, is not conserved due to the nonspherical character of the potential energy experienced by the electron. This well-known effect was recently illustrated from the measurements of autoionization channels in H_2.[18] Moreover, in our experiment a stray electric field of about 0.5 V cm^{-1} is present. This small electric field does not directly influence the $n=27$, $v'=1$ N^+ levels, but those levels may be mixed by vibrational interaction with $n=60$–70, $v'=0$ N^+ levels. For such levels, a small electric field of 0.5 V cm^{-1} is not negligible and is known to induce N^+-l mixing. In Na_2, this effect was recently observed as well in forced rotational autoionization[14] and in hindered vibrational autoionization.[19]

The process discussed above allows us to give a possible explanation of the main observed features: After the optical excitation, the wave function of a singly excited Rydberg state is in fact a superposition of functions containing various N^+ and l values. The high-l ($l>3$) components lead to transitions very close to the intrinsic $Na_2{}^+$ transitions because their quantum defect is negligibly small. Since these states are nonpenetrating, the autoionization processes are slow and the lines are sharp. In contrast, transitions involving low-l-value wave functions as intermediate levels lead to a broad continuum which does not appear in our spectra. It is probable that these transitions, analogous to those observed in barium, for instance, are completely masked by the intense and sharp lines which emerge in our spectra. Incidentally, we can deduce from the observed transitions, precise measurements of the $Na_2{}^+(1\,^2\Pi_u)$ rovibrational levels. The spectroscopic constants of this state have been fitted on the assumption that the lowest observed vibrational level is $v_0=12$. This assignment, although arbitrary, gives the same vibrational spacing as the calculations of Bähring *et al.*[12] Obviously, the values of the equilibrium constants obtained for this state depend explicitly on the vibrational assignment. Accepting that the lowest level seen is $v_0=12$ we obtain $Y_{00}=62484.4\pm0.3$ cm^{-1} for $\Omega=\frac{1}{2}$ and $Y_{00}=62495.3\pm0.3$ cm^{-1} for $\Omega=\frac{3}{2}$, $\omega_e=50.25\pm0.03$ cm^{-1}, $\omega_e x_e=0.253\pm0.0006$ cm^{-1}, $B_e=0.0627\pm0.0014$ cm^{-1}, and $\alpha_e=(0.38\pm0.06)\times10^{-3}$ cm^{-1} (the indicated error is twice the standard deviation).

The fine structure of 10.9 ± 0.1 cm^{-1} is close to the 11.46-cm^{-1} spin-orbit splitting one would derive from $\frac{2}{3}$ of the asymptotic splitting between $Na(3\,^2P_{1/2})$ and $Na(3\,^2P_{3/2})$.

The last point concerning our results is the broadening of the observed lines as n decreases. As mentioned above, linewidths for $n=20$ are about 1 cm^{-1} although those for $n=27$ are about 0.2 cm^{-1}. This is not compatible with a simple $1/n^3$ law. However, as already noted, the results with $n=20$ may also be explained by a large number of lines which could be due to doubly excited states of $l=2$ superimposed on the observed levels. Other experiments on lower-n values are necessary to clarify this point.

As a conclusion, it must be emphasized that our experimental results prove the feasibility of studying doubly excited states as well as spectroscopy of the $Na_2{}^+$ ion. The detailed spectroscopy of these states as well as the deexcitation mechanism appears as a very interesting field of research.

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