LASER STARK SPECTROSCOPY OF MOLECULAR RYDBERG STATES

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As molecular Rydberg states are very sensitive to external influences, various effects are expected to appear when an electric field is applied. Lowering of ionization threshold, rotational autoionization [1], stabilization of high n levels in vibrational autoionization processes, molecular Stark structure [2] have been recently reported. We present here the Stark structure observed in photoionization spectra of Na_2 molecules in an electric field varying up to 6.5 kV/cm.

Na_2 molecules in a supersonic beam are excited up to autoionizing Rydberg states via a two-step optical-optical double resonance by means of two tunable dye lasers. The photoelectrons are collected by the applied electric field and give rise to the spectra shown in Fig.1 ; the dominant series correspond to $nd^1\Pi_g$ states.

In the low-field range (Fig.1), the two most striking features of the spectra are the progressive disappearance of the rotational structure and the emergence of a hydrogenoid Stark structure, characterized by the spacing $\delta=3$ nF between neighbouring Stark sublevels. Assuming that $nf\Lambda$ states which couple $nd\Pi$ to the hydrogenic complex have zero quantum defect, this Stark structure is expected when the $nd\Pi$ states are mixed by the field with the hydrogenic complex Stark manifold ; this should occur beyond a critical electric field F_c defined by

$$\frac{1}{n} \mu_{d\Pi} = \frac{3}{2} n^2 F_c$$

where $\mu_{d\Pi}$ is the $nd\Pi$ series quantum defect. Indeed, the F_c measured value corresponds to a quantum defect (0.2) larger than $\mu_{d\Pi}$ (0.01). This means that the nf perturbing states are not clustered in the hydrogenic complex in the low field range, and that, in Na_2 molecules, nf orbitals penetrate the ionic core [2].

Regarding the rotational components, it seems they completely disappear when emerges the Stark structure ; nevertheless a comparison with an atomic Stark multiplet (Fig.2) shows that the rotational structure strongly influences the shape of the Stark manifold. The calculation of this effect by Multichannel Quantum Defect Theory (M.Q.D.T.) including the core rotation is now in progress.

Fig.1. Stark spectra obtained via $A^1\Sigma_v^+$ $v=4, J=6$ as intermediate state.

Fig.2. a) Na_2 Stark multiplet for $v=4, J=6, n=17$, and $F=600 \text{ V.cm}^{-1}$.
b) Na Stark multiplet for $n=29, F=3.2 \text{ V/cm}$ [3].

Increasing the electric field (up to 6.5 kV/cm) we reach energy regions where the Stark manifolds arising from neighbouring n values overlap completely. In these inter- n mixing regions, the Fourier transforms of the spectra (Fig.3) show two dominant frequencies whose relative intensities depend on the electric field strength. In brief, the Stark frequency $\delta=3 \text{ nF}$ is dominant except when its second harmonic is close to the half rotation frequency of the core: $4B(J+1/2)$. The condition

$$4B \left(J + \frac{1}{2} \right) = \frac{1}{2} 3nF$$

is then approximately fulfilled and a frequency locking is observed on the $4B (J+1/2)$ frequency. As F increases, this coupling loosens and the 3 nF frequency becomes dominant again.

This result suggests a resonant phenomenon between the core rotation and the movement of the Rydberg electron induced by the electric field (let us remember that, for an atom, $3/2 \text{ nF}$ is the precession frequency of $\vec{L}$ around the external electric field in the low field approximation [4]). A more complete interpretation of this observation following a M.Q.D.T. treatment requires spectroscopic data on the np and nf series interacting with the nd series. They will be excited in a forthcoming experiment by a third microwave photon.

Fig.3. Fourier transform (in energy units) of Stark spectra for various high electric field (intermediate state $A^1\Sigma_u^+$ $v=4$, $J=6$).

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