JOURNAL OF MOLECULAR SPECTROSCOPY 61, 92-99 (1976)

Predissociation and Λ-Doubling in the Even-Parity Rydberg States of the Nitrogen Molecule

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Predissociations in the $y\,^1\Pi_g$ and $x\,^1\Sigma_g^-$ Rydberg states of N_2 (configurations $1\sigma_u^{-1}4p\sigma$ and $1\sigma_u^{-1}3p\pi$, respectively) and their likely causes, are discussed. Peaking of rotational intensity at unusually low J values, without sharp breaking off, is interpreted as due to case c^- or case c' predissociation. A doubling in the y state, attributed to interactions with the $x\,^1\Sigma_g^-$ state and with another, $^1\Sigma^+$, state of the same electron configuration as x, is analyzed. From this analysis the location of the (unobserved) $^1\Sigma_g^+$ state, here labeled x', is obtained. It is concluded that the predissociation in the Π^+ levels of the y state is an indirect one mediated by the interaction with x' coupled with predissociation of x' by a $^4\Sigma_g^-$ state dissociating to $^4S + {}^2P$ atoms; combined, however, with perturbation of the y state by the $k\,^1\Pi_g$ Rydberg state (configuration $3\sigma_g^{-1}4d\pi$), whose Π^+ levels are completely predissociated.

I. INTRODUCTION

Among the Rydberg states of the nitrogen molecule above 13.0 eV, just two of even parity have long been known, $x\,^1\Sigma_g^-$ and $y\,^1\Pi_g$. A third, $k\,^1\Pi_g$, has recently been discovered (*1*). These states are known from emission bands as follows: $x\,^1\Sigma_g^- \rightarrow a'\,^1\Sigma_u^-$ (fifth positive bands), $y\,^1\Pi_g \rightarrow a'\,^1\Sigma_u^-$ (Kaplan's first system), $y\,^1\Pi_g \rightarrow w\,^1\Delta_u$ (Kaplan's second system), $k\,^1\Pi_g \rightarrow a'\,^1\Sigma_u^-$ (Carroll–Subbaram second system), and $k\,^1\Pi_g \rightarrow w\,^1\Delta_u$ (Carroll–Subbaram first system). All these systems show evidences of predissociation.

For brevity the various systems will be referred to as x–a', y–a', y–w, k–a', and k–w. A consideration of electron configurations leaves no reasonable doubt that states x, y, and k have the respective electron configurations $A\,3p\sigma_u$, $A\,4p\sigma_u$, and $X\,4d\pi_g$, where A refers to the first excited state $\cdots 1\pi_u^4 3\sigma_g^1\,{}^3\Pi_u$, and X to the ground state $\cdots 1\pi_u^4 3\sigma_g^2\,{}^1\Sigma_g^+$, of N_2^+, and united-atom n values are used for the Rydberg MO's. Potential curves for the x, y, k, and certain other even-parity states relevant to the following discussion are shown in Fig. 1.

The $y\,^1\Pi_g$ state shows anomalous behavior in the spacings of its rotational and vibrational levels (*2*). These anomalies have now been fully explained as the results of a homogenous mutual (vibronic) perturbation between the y and $k\,^1\Pi_g$ states. Carroll and Subbaram (*1*) have carried out a deperturbation analysis which shows the rotational and vibrational constants of the unperturbed y and k levels to be close to those of their respective parent ions X and A, a relation which is somewhat disguised in the observed perturbed states.

In the $y\,^1\Pi_g$ state two vibrational levels $v = 0$ and 1 have long been known, but recently $v = 2$ has also been discovered (*1*). For the $k\,^1\Pi_g$ state, only $v = 0$ and 1 have

Salient features of the follow-up work by Professor R.S. Mulliken on the Nitrogen Molecule that provided the theoretical spine to the experimental work.

Extract from the above original publication of Professor R.S. Mulliken

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