

# Predissociation and $\Lambda$ -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  $1w_{g-}^{-1}4p_{g-}$  and  $1w_{g-}^{-1}3p_{g-}$ , 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  $a'$  predissociation. A doubling in the  $y$  state, attributed to interactions with the  $x\ ^1\Sigma_g^-$  state and with another,  $'\Sigma^+$ , state of the same electron configuration as  $x$ , is analyzed. From this analysis the location of the (unobserved)  $'\Sigma_g^+$  state, here labeled  $x'$ , is obtained. It is concluded that the predissociation in the  $\Pi^+$  levels of the  $y$  state is an indirect one mediated by the interaction with  $x'$  coupled with predissociation of  $x'$  by a  $'\Sigma_g^-$  state dissociating to  $'\Sigma + 'P$  atoms; combined, however, with perturbation of the  $y$  state by the  $k\ ^1\Pi_g$  Rydberg state (configuration  $3s_{g-}^{-1}4d_{g-}$ ), whose  $\Pi^+$  levels are completely predissociated.

## 1. 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:  $x\ ^1\Sigma_g^- \rightarrow a'\ ^1\Sigma_g^-$  (fifth positive bands),  $y\ ^1\Pi_g \rightarrow a'\ ^1\Sigma_g^-$  (Kaplan's first system),  $y\ ^1\Pi_g \rightarrow w\ ^1\Delta_u$  (Kaplan's second system),  $k\ ^1\Pi_g \rightarrow a'\ ^1\Sigma_g^-$  (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  $A\ 3p_{g-}$ ,  $A\ 4p_{g-}$ , and  $X\ 4d_{g-}$ , where  $A$  refers to the first excited state  $---1w_{g-}^{-1}3s_{g-}^{-1}\ ^1\Pi_g$ , and  $X$  to the ground state  $---1w_{g-}^{-1}3s_{g-}^{-1}\ ^1\Sigma_g^+$ , 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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