New Interpretation of the $^1\Sigma_u^+$ and $^1\Pi_u$ Rydberg- and Valence

States of Nitrogen below the first Ionization Limit

by

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The longest-wavelength allowed transitions in the absorption spectrum
of cold molecular nitrogen appear as a complex spectrum of strong bands in
the region shortward of 1000 A. Worley has ordered some of these bands
into Rydberg series, while approximately fifty bands remaining in the re-
gion 1015 to 800 A have been grouped into 13 short vibrational progressions
with intervals indicative of very shallow potential curves. The great in-
tensity of the bands leaves no doubt that the corresponding excited states
must be of species either $^1\Sigma_u^+$ or $^1\Pi_u$. Additional information on
states of these species has been obtained through studies of emission bands
to the ground electronic state (Birge and Hopfield, Watson and Koontz,
Tschulanowsky, Setlow, Wilkinson and Houk, Tilford and Wilkinson), and of
emission bands to the state a $^1\Pi_g$ (Gaydon, Herman, Janin, Lofthus).

The currently accepted interpretation of the $^1\Sigma_u^+$ and $^1\Pi_u$ levels
observed in the interval 98000 - 120000 cm^{-1} in terms of as many as 15
valence states of these same two species is not in accordance with elemen-
tary molecular orbital predictions. Furthermore, the assignment of observed
levels of Rydberg type to the expected pair of Rydberg $^1\Sigma_u^+$, $^1\Pi_u$ states
of configuration $(N_2^+ \; X \; ^2\Sigma_g^+) \; 3p \; \sigma_u$, π_u has not been clear at all. These

difficulties of interpretation disappear when the spectrum is analyzed as one showing strong homogeneous perturbations, thus leading to an interpretation in terms of deperturbed electronic states of pure Rydberg and pure valence type, with configuration interaction accounting for the actually observed complexities. A deperturbation study similar to the one employed in the analysis of the NO spectrum (Miescher, Lagerqvist, Dressler) leads to the assignments of observed levels to electronic states as shown in Table 1. The deperturbation has been based on and is consistent with 1. recent isotope shift measurements in the absorption spectrum (Ogawa and Tanaka and Jursa) and in some emission spectra terminating in the $\underline{a}$ state (Carroll and Mahon-Smith), 2. studies of vibrational shifts and spacings, and of B-values and perturbed rotational structures, 3. intensity distributions and absolute intensities, and 4. close comparison with the Rydberg energy structures of NO and CO and their theoretical interpretations. Absolute f-values for some of the bands have been obtained experimentally at Princeton, and additional intensity information has been extracted from the electron energy loss spectra of several investigators.

The resulting picture (cf. Table 1) shows one excited valence state of each species, $\underline{b'}$ $^1\Sigma_u^+$ and $\underline{b}$ $^1\Pi_u$, whose levels show strong interactions with the levels of the Rydberg states $\underline{c'}$ $^1\Sigma_u^+$ and $\underline{c}$ $^1\Pi_u$ of configuration $(N_2^+ X)$ $3p$ σ_u, $3p$ π_u. The energy separation between the two Rydberg states $\underline{c'}$ and $\underline{c}$, after deperturbation, is probably less than 100 cm^{-1}. The $\underline{b'}$ - $\underline{c'}$ interaction is strongest between the levels $\underline{b'}$ 7 and $\underline{c'}$ 2, giving rise to the observed perturbed levels $\underline{g}$ and $\underline{k}$, while the $\underline{b}$ - $\underline{c}$ interaction between $\underline{c}$ 0 and the whole group of levels $\underline{b}$ 2,3,4,5 is so strong that the presence of a Rydberg-type level $\underline{c}$ 0 can

only be recognized through a detailed deperturbation study of the $\underline{b}$, $\underline{l}$, and $\underline{d}$ levels. The Rydberg state $\underline{o}$ $^1\Pi_u$ of configuration $(N_2^+ A\ ^2\Pi_u)$ $3s\ \sigma_g$ appears to be free of strong perturbations.

It is interesting that all $^1\Sigma_u^+$ levels up to $\underline{b'}$ 9 ($\underline{f}$) and $\underline{c'}$ 4 ($\underline{h}$) are observed in emission while only a few selected $^1\Pi_u$ levels appear in emission. Several of the non-emitting Π levels are definitely moderately strongly predissociated, since they are observed to give rise to diffuse lines in absorption, even though the predissociation cannot be caused by a $^1\Pi_u$-, nor a $^1\Sigma_u$ - or $^1\Delta_u$-continuum. The predissociation of the $^1\Pi_u$ levels is probably caused by the same $^3\Pi_u$ continuum, associated with the $^4S + ^2D$ limit at 97940 cm^{-1}, which also predissociates the higher levels of the $\underline{C}$ $^3\Pi_u$ and $\underline{C'}$ $^3\Pi_u$ states, however, the singlet-triplet mixing is probably an indirect one, proceeding via mixing of individual singlet levels with excited levels of the $\underline{C}$ and $\underline{C'}$ states which in turn are strongly mixed with the $^3\Pi_u$ continuum. This would explain the erratic occurrence of predissociation along the sequence of $^1\Pi_u$ levels, i.e. the fact that several groups of emitting levels alternate with groups of predissociated levels over the interval 100000 - 110000 cm^{-1}, since the indirect process depends on accidental energy coincidences and rapidly fluctuating vibrational overlap integrals mixing the $^1\Pi_u$ levels with the higher levels of $\underline{C}$ or $\underline{C'}$. The absence of predissociation of the lower $^1\Sigma_u^+$ levels shows that the mixing of these levels with the $\underline{A}$ $^3\Sigma_u^+$ continuum and with the $^3\Sigma_u^+$ continuum of the limit $^4S + ^2D$ is much weaker, which in turn indicates that there is no shallow $^3\Sigma_u^+$ state available that could take the role of the $\underline{C'}$ state in providing the levels for an indirect process of mixing with the continuum.

Table 1. Correlation between the observed (perturbed) $^1\Sigma_u^+$ and $^1\Pi_u$ levels of N_2^{14} and the deperturbed vibrational levels of the valence states $\underline{b}$, $\underline{b}'$, and Rydberg states $\underline{c}$, $\underline{c}'$, $\underline{o}$

v($\underline{b}'$ $^1\Sigma_u^+$) B_v	($\underline{c}'$ $^1\Sigma_u^+$) B_v	v ($\underline{c}$ $^1\Pi_u$) B_v	v($\underline{b}$ $^1\Pi_u$) B_v	v($\underline{o}$ $^1\Pi_u$) B_v
13 r -			17 q 1.05	
	h 1.655	4 R -	16 q -	
12 r 1.07				
11 r -			15 q 1.07	
10 r -			14 q 1.09	3 o -
	s' 1.595	3 R -		
9 f 1.124			13 q 1.11	
8 * 1.18(v"=1)			12 q -	2 o -
7 g 1.356			11 p 1.21	
	k 1.435	2 d" 1.797		
6 b' -			10 p 1.21	
5 b' 1.159			9 p -	1 o -
4 b' -			8 m (em.N$_2^{15}$)	
	r' 1.711	1 R -		
3 b' 1.137			7 m 1.35	
2 b' 1.142			6 m 1.361	0 o 1.694
1 b' 1.146			5 d 1.47	3s σ_g
	p' 1.929	0 ℓ 1.494		
0 b' 1.152			4 b 1.41	N$_2^+$ A $^2\Pi_u$
	3p σ_u	3p π_u	3 b 1.40	
	N$_2^+$ X $^2\Sigma_g^+$		2 b 1.41 (i 2 = v"=1)	
			1 b 1.399 (i 1 = v"=1)	
			0 j 1.44 (i 0 = v"=1)	

Note: underlined levels observed in emission.

*   Interpretation of a band reported by Tilford and Wilkinson as terminating in v"=1.

8 m obs. in emission in N_2^{15} via interpretation of a band reported by Mahon-Smith and Carroll.