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New Interpretation of the $^1\Sigma_u^+$ and $^1\Pi_u$ Rydberg- and Valence States of Nitrogen below the first Ionization Limit

by

Kurt Dressler, Department of Astrophysical Sciences
Princeton University, Princeton, New Jersey 08540, U.S.A.

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 region 1015 to 800 A have been grouped into 13 short vibrational progressions with intervals indicative of very shallow potential curves. The great intensity 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 elementary 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 σ_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 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, b' $^1\Sigma_u^+$ and b $^1\Pi_u$, whose levels show strong interactions with the levels of the Rydberg states c' $^1\Sigma_u^+$ and c $^1\Pi_u$ of configuration (N_2^+ X) 3p σ_u, 3p π_u. The energy separation between the two Rydberg states c' and c, after deperturbation, is probably less than 100 cm^{-1}. The b' - c' interaction is strongest between the levels b' 7 and c' 2, giving rise to the observed perturbed levels g and k, while the b - c interaction between c 0 and the whole group of levels b 2,3,4,5 is so strong that the presence of a Rydberg-type level c 0 can

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

It is interesting that all $^1\Sigma_u^+$ levels up to b' 9 (f) and c' 4 (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 C $^3\Pi_u$ and 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 C and 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 C or C'. The absence of predissociation of the lower $^1\Sigma_u^+$ levels shows that the mixing of these levels with the 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 C' state in providing the levels for an indirect process of mixing with the continuum.

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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 b, b', and Rydberg states c, c', o

v(b' $^1\Sigma_u^+$)	B_v	(c' $^1\Sigma_u^+$)	B_v	v	(c $^1\Pi_u$)	B_v	v(b $^1\Pi_u$)	B_v	v(o $^1\Pi_u$)	B_v
13 r	-						17 q	1.05		
		h	1.655	4	R	-				
12 r	1.07						16 q	-		
11 r	-						15 q	1.07		
									3 o	-
10 r	-						14 q	1.09		
		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		
									0 o	1.694
2 b'	1.142						6 m	1.361		
1 b'	1.146						5 d	1.47		3s σ_g
		p'	1.929	0	ℓ	1.494				N_2^+ A $^2\Pi_u$
0 b'	1.152						4 b	1.41		
	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.