Evidence for Predissociation of N_2 into $N(^2D) + N(^2D)$ from New High-Resolution Vacuum-Ultraviolet Emission Bands

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The use of a low-pressure discharge lamp has permitted us to discover many new emission bands of N_2 at short wavelengths, in the vacuum ultraviolet. Strong evidence of predissociation is afforded by the sharp breaking off in the rotational structure of some bands corresponding to transitions originating from an electronic state different in $^{14}N_2$ and $^{15}N_2$. The respective limits give, directly, an improved upper limit for the dissociation into $N(^2D) + N(^2D)$, furnishing clear-cut evidence for setting definitely the dissociation energies of N_2.

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The determination of the dissociation energy of N_2 is a long story, masterfully told in Gaydon's book,[1] and even now, when looking at the well documented monograph by Lofthus and Krupenie,[2] one is surprised to discover to what extent previously reported vacuum ultraviolet (vuv) emission spectra led to controversial conclusions about predissociation in N_2. It is said that "the preponderance of evidence supports the higher value of the dissociation energy of N_2 (9.759 eV), though direct evidence is still lacking." We are going to show that the presently reported spectra eventually afford further support to that value.

The last emission work in the vuv, dating more than twenty years back, was performed by Tilford and Wilkinson at modest resolution and many results were inconclusive.[3] When one remembers that an emission spectrum is the more sensitive test

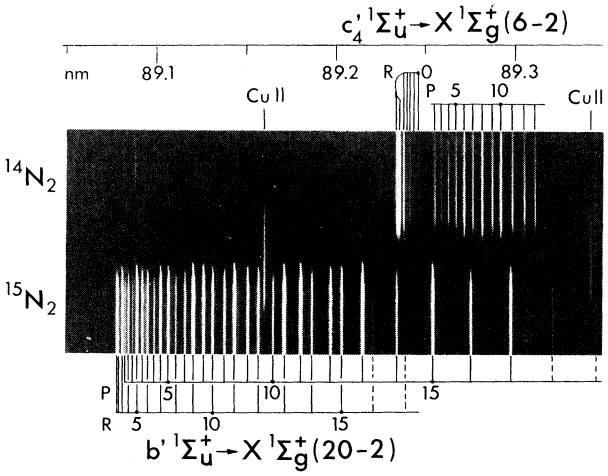

FIG. 1. Emission spectrum of $^{14}N_2$ and $^{15}N_2$ near 89.2 nm. Very weak (predissociated) spectral lines are indicated by broken lines.

TABLE I. Wave numbers (in inverse centimeters) of the emission lines $R(J)$ and $P(J)$ of the bands (6-1) and (6-2) of the transition $c_4' {}^1\Sigma_u^+ \rightarrow X {}^1\Sigma_g^+$ of $^{14}N_2$. Very weak (predissociated) lines are in parentheses.

	$v'=6, v''=1$		$v'=6, v''=2$	
J	$R(J)$	$P(J)$	$R(J)$	$P(J)$
0	114480.47		112179.19	
1	114483.55	114472.97	112182.44	
2	114486.39	114468.57	112185.34	112167.55
3	114488.70	114463.76	112187.87	112162.87
4	114490.60	114458.63	112189.69	112157.94
5		114453.10		112152.48
6		114447.50		112146.66
7		114440.62		112140.44
8		114433.70		112133.83
9		114426.92		112126.50
10		114419.80		112120.14
11		114411.10		112112.21
12		114402.20		112103.68
13		114394.16		112096.11
14		(114384.36)		(112086.64)
15		(114374.31)		(112077.62)

TABLE II. Same as Table I for the bands (20-0), (20-1), and (20-2) of $b'\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$ of $^{15}N_2$. Anomalously weak lines are in parentheses.

	v'=20, v"=0		v'=20, v"=1		v'=20, v"=2	
J	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
0			114619.19		112393.99	
1			114619.19	114613.24	112393.99	112388.22
2			114618.34	114607.88	112393.24	112382.77
3			114615.15	114601.02	112390.11	112375.91
4				**114592.20**	112385.84	112367.50
5			114604.35	114582.01	112379.77	112357.37
6			114596.78	114570.07	112372.10	112345.59
7		116807.93	114587.17	114556.60	112362.91	112332.22
8		116792.31	114576.04	114541.31	112352.05	112317.30
9	116814.11	116775.26	114563.45	114524.63	112339.59	112300.81
10	116799.65	116756.54	**114549.17**	114505.94	112325.68	112282.64
11	116783.44	116736.23	114533.34	114486.12	112310.17	112262.95
12	116765.63	116714.17	114515.95	114464.44	112293.10	112241.70
13	116746.45	116690.61	114497.13	114441.28	112274.74	112219.02
14	116725.88	116665.36	114477.01	114416.55	112254.98	112194.70
15	116703.74	116638.82	114455.27	114390.51	112233.89	112168.93
16		116610.71	(114432.52)	114362.97	(112211.57)	112141.44
17		116581.14	(114409.06)	114334.00	(112187.84)	112113.44
18		(116550.26)		(114303.74)		(112083.91)
19						(112052.90)

for detecting even weak predissociation the need for further investigation is very understandable.

The five-times-larger resolution available at Meudon Observatory makes the analysis of the whole spectrum more reliable. Besides, as in the case of H_2, another limitation comes, most of the time, from the use of ordinary discharge lamps, in which the pressure is high enough to give rise to noticeable self-absorption at short wavelengths, a complaint of astrophysicists.[4] By contrast, in our lamp the presence of a magnetic field permits us to lower the pressure by two orders of magnitude,[5] thus reducing greatly self-absorption and allowing many new bands to show up at short wavelengths.

In $^{14}N_2$ a progression of bands is readily assigned to the transitions $3p\sigma c'_4\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$ ($v'=6$, $v''=1, 2, 5, 7$) as the band $c'_4 \rightarrow X$ (6-0) is known from the absorption work of Carroll, Collins, and Yoshino.[6] The bands (6,3), (6,4), and (6,6) are either overlapped or too weak to be measured. Until recently the subscript 4 was taken as a value of the principal quantum number of the *np* Rydberg series. In the recent work of Stahel, Leoni, and Dressler,[7] the state c'_4, designated simply, c', appears as the term $n=3$, forming a complex with the other Rydberg state $c\,^1\Pi_u$ of the same electron configuration

formerly named c_3. If the subscript 4 has to be retained, in order to avoid a misleading new change of designation, it should be considered as only a running index, as suggested to us by Yoshino and Freeman.[8] In $^{15}N_2$ the only data, available from a low-resolution absorption study,[9] are the bandheads but presently R and P branches are so nicely developed that it is straightforward to identify the bands to the transitions $b'\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$ ($v'=20$, $v''=0,1,2$). In Fig. 1 the bands ($v', v''=2$) are shown for both isotopes. It is clearly seen that the breaking off occurs beyond $R15$ and $P17$ for $^{15}N_2$ and beyond $P13$ for $^{14}N_2$, the R branch forming a head at high J in the last case. However, the R branch of (6,7) breaks clearly after $J=11$. The occurrence for the two isotopes of the breaking off, in two distinct electronic states, very close to an expected dissociation limit is strongly in favor of predissociation.

Tables I and II list the wave numbers of lines for each isotope. Starting from the Raman data of Bendtsen,[10] and using the term value method,[11] we have calculated the band origin $T_v(0)$ and the rotational constant B' of the upper states, and vibrational spacings $T_v(0)$ and rotational constants B_v of the ground state, as reported in Table III.

Some intensity anomalies are not yet well understood at this stage. The intensity alternation, typical of nuclear spin statistics, is not respected by $P4$ and $P12$ of $c_4' \rightarrow X$ for any $(6, v'')$, probably on account of predissociation in the last case. Stranger is the absence of $P1$ of $c_4' \rightarrow X$ (6,2) and $P4$ of $b' \rightarrow X$ (20,1) and the weakness of $P9$ of $c_4' \rightarrow X$ (6,1) and $P3$ and 10 of $b' \rightarrow X$ (20,1). As these anomalies do not occur in all bands of same v' and different v'', it cannot be excluded that some fortuitous self-absorption and/or parasitic absorption reduce greatly the intensity of some lines. Moreover, the bands $c_4' \rightarrow X$ $(6, v'')$ are not observed at all in $^{15}N_2$ while $b' \rightarrow X$ $(19, v'')$ appears weakly in $^{14}N_2$ and not at all in $^{15}N_2$, because of vibronic coupling.

The limit of dissociation is set halfway between the first predissociated and the last unpredissociated level. This leads to a value slightly smaller, therefore better, than that of the expected limit of dissociation into $N(^2D)+N(^2D)$, calculated by adding to a well-known predissociation limit into $^4S+^2D$ the value of the excitation energy of the ^2D state of the N atom.[13] It is known that $c_4'\,^1\Sigma_u^+$ and $b'\,^1\Sigma_u^+$ on the one hand and $c_3\,^1\Pi_u$ and $b\,^1\Pi_u$ on the other hand are configurationally mixed. Besides, c_4' and c_3 form the terms of a complex $3p\lambda$ ($\lambda=\sigma$ and π) and have their potential energy curves almost superimposed. Therefore it is not surprising that all

TABLE III. Molecular constants for $c_4'\,^1\Sigma_u^+(6)$ and $X\,^1\Sigma_g^+(v'')$ of $^{14}N_2$ and $b'\,^1\Sigma_u^+(20)$ and $X\,^1\Sigma_g^+(v'')$ of $^{15}N_2$. All entries in inverse centimeters.

	$^{14}N_2$ c'4 → X (6-v")		$^{15}N_2$ b' → X (20-v")	
	Present work	previous work	present work	previous work
T_v (0)	116806.82(8)	116806.8[a]	116868.03(22)	116869.0[b]
B_v	1.7681(12)	1.769[a]	1.0311(13)	
T_1"(0)	[c]	2329.9168(3)[e]	2251.88(27)	2252.1249(3)[e]
T_2"(0)	4631.06(11)	4631.23[d]	4476.65(25)	
T_5"(0)	11362.66(12)	11362.61[f]		
T_7"(0)	15705.97(12)	15707.7 [d]		
B"$_0$		1.989574(12)[e]	[c]	1.857624(16)[e]
B"$_1$	[c]	1.972189(82)[e]	1.8430(16)	1.841956(96)[e]
B"$_2$	1.9563(14)		1.8298(15)	
B"$_5$	1.9035(15)	1.9022[d]		
B"$_7$	1.8674(15)			

[a]Carroll, Collins, and Yoshino, Ref. 6.
[b]Ogawa, Tanaka, and Jursa, Ref. 9.
[c]Constrained.
[d]Lofthus and Krupenie, Ref. 2.
[e]Bendtsen, Ref. 10.
[f]Miller, Ref. 12.

TABLE IV. Steps leading to refined values of $D_0(^4S+^4S)$ and $D_0(^2D+^2D)$. Entries in inverse centimeters unless otherwise indicated.

	$^{14}N_2$	$^{15}N_2$
$D_0(^2D+^2D)$	117105.3 ± 22.7[a]	117167.0 ± 18.0[a]
$2\times E(^2D)-E(^4S)$	38449[b]	38449
$D_0(^4S+^4S)$	78656.3	78718.0
$\frac{1}{2}\omega_e-\frac{1}{4}\omega_e x_e$	1175.7[c]	1136.9[d]
$D_e(^4S+^4S)$	79832.0 ± 22.7	79854.0 ± 18.0
$D_e(^4S+^4S)$ refined	79844 ± 9	
$D_0(^4S+^4S)$ refined	78669 ± 9 (9.7537 eV)	78708 ± 9 (9.7766 eV)
$D_0(^4S+^4S)$ previous	78714 ± 40[e]	78824 ± 45[f]
$D_0(^2D+^2D)$ refined	117118 ± 9 (14.5208 eV)	117157 ± 9 (14.5258 eV)

[a]Present work.
[b]Moore, Ref. 13.
[c]Huber and Herzberg, Ref. 14.
[d]Calculated from isotopic shift.
[e]Grapical extrapolation, Buttenbender and Herzberg, Ref. 15.
[f]Graphical extrapolation, Frackowiak, Ref. 16.

of the states lying above the limit $^2D+^2D$ are subject to indirect predissociation by vibronic coupling with the continuum of the state $b\ ^1\Pi_u$ whose limit of dissociation is into $^2D+^2D$. That we have not detected any emission band that could originate from levels lying above this limit is a further argument in support of predissociation.

The derived values of the dissociation energy can be further refined by taking into account that the value D_e of the dissociation energy with respect to the bottom of the potential energy curve has to be the same for both isotopes.[1] Table IV indicates the successive steps leading to improved values of $D_0(^2D+^2D)$ and subsequently of $D_0(^4S+^4S)$. It has to be remarked that for $^{14}N_2$ our value falls within the error limit of the admitted value of D_0 whereas for $^{15}N_2$ the presently reported value is too high and cannot lead to a common D_e value for the two isotopes.

Until now, the only two firmly established dissociation limits of $^{14}N_2$ were those into $^4S+^2D$ at 97938 cm^{-1} and into $^4S+^4S$ at 78714 cm^{-1} (9.759 eV), separated by the excitation energy of the ^2D state of the N atom. Now that we have found a clear limit at 117118 cm^{-1}, i.e., separated from 97938 cm^{-1} by about the same excitation energy, we can say that the three limits $^2D+^2D$, $^2D+^4S$, and $^4S+^4S$ are well settled and the long-alleged limit at 7.373 eV can be definitely ruled out.

In conclusion it can be said that the presently reported new emission bands afford the first clear-cut evidence of a predissociation into $^2D+^2D$, thus establishing firmly and refining the value of the first dissociation energy of N_2.

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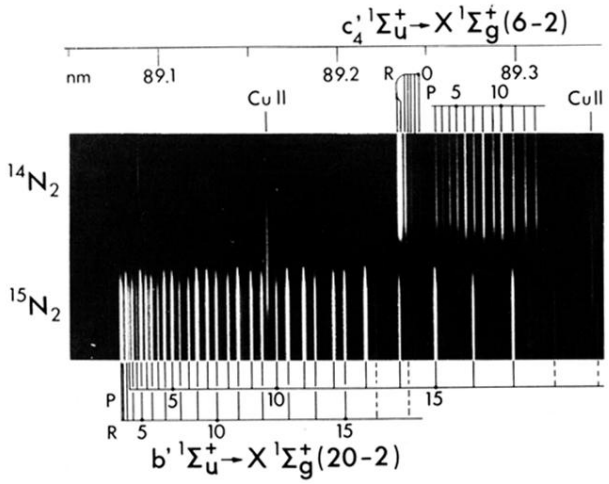

FIG. 1. Emission spectrum of $^{14}N_2$ and $^{15}N_2$ near 89.2 nm. Very weak (predissociated) spectral lines are indicated by broken lines.