

APPENDIX A

We evaluate the allowed beta-decay matrix element $|\mathcal{J}\sigma|^2$ for image transitions. Trigg¹⁴ has shown that

$$|\mathcal{J}\sigma|^2 = [(I+1)\alpha^2 - I(1-\alpha^2)]^2 / [I(I+1)]. \quad (\text{A1})$$

Introducing α^2 from Eq. (33), we get

$$\begin{aligned} |\mathcal{J}\sigma|^2 &= I/(I+1), & I = j = l + \frac{1}{2} > \frac{1}{2}, \\ &= [I/(I+1)]^2, & I = j = l - \frac{1}{2} > \frac{1}{2}. \end{aligned} \quad (\text{A2})$$

Thus, the coupling to the core leaves the ratio for $l + \frac{1}{2}$ and $l - \frac{1}{2}$ unchanged relative to the values for pure *LS* coupling, but reduces both by the factor $I^2/(I+1)^2$. An alternative derivation starts from the equivalence relation,

$$\sigma \sim I \frac{2I}{I+1} \frac{(-1)^{l+\frac{1}{2}-i}}{2l+1}. \quad (\text{A3})$$

Then

$$\left| \int \sigma \right|^2 = \frac{I^3}{I+1} \frac{1}{(I+\frac{1}{2})^2}, \quad (\text{A4})$$

in agreement with Eq. (A2).

APPENDIX B

The diagonal matrix elements of $(\mathbf{I}-\mathbf{j})^2$ and $(\mathbf{I}-\mathbf{j})^4$ can be evaluated with the aid of Eqs. (16), (17), and (40). Results are

$$\begin{aligned} (\frac{1}{2}M | (\mathbf{I}-\mathbf{j})^2 | \frac{1}{2}M) &= (j+\frac{1}{2})[j+\frac{1}{2} - (-1)^{i-\frac{1}{2}}]; \\ (IM | (\mathbf{I}-\mathbf{j})^2 | IM) &= 2I, \quad I > \frac{1}{2}; \\ (IM | (\mathbf{I}-\mathbf{j})^4 | IM) &= 2(2I)^2, \quad I > \frac{1}{2}. \end{aligned}$$

For $I = \frac{1}{2}$, Eq. (16) shows that $(I-j)^2$ is a constant of motion.

A Third Rydberg Series of N_2

R. EDWIN WORLEY

Department of Physics, University of Nevada, Reno, Nevada

(Received October 31, 1952)

A third series of Rydberg bands, converging to the ${}^2\Pi$ state of N_2^+ , has been identified in the far ultraviolet absorption spectrum of nitrogen. Its interpretation substantiates an assignment of vibrational numbers for the ${}^2\Pi$ state, and indicates that this state is derived from the o state of N_2 .

TWO series of Rydberg terms have previously been identified for N_2 , one^{1,2} converging to the $X \ 2\Sigma$ state of N_2^+ , the other^{3,4} to the excited $B \ 2\Sigma$ state. I shall refer to these as the $X-X$ and the $B-X$ series, and discuss here a third, or $A-X$, series that converges to the $A \ 2\Pi$ state, about 1 eV above the ground state. Some years ago Professor Mulliken suggested I examine my spectrograms of the far ultraviolet absorption of N_2 , with the object of identifying the corresponding bands and thus locating the ${}^2\Pi$ state. However, due to overlying absorption on the best plates (nitrogen pressure too high), this proved unfeasible.

The recent identification of ${}^2\Pi-2\Sigma$ bands of N_2^+ by Meinel,⁵ in auroral spectra, affords an approximate value for the limit of the anticipated Rydberg series. I have accordingly re-examined my plates, and have found five distinct bands⁶ which fit the following Ryd-

berg formula with residuals of +1, -2, +2, +2, -2 cm^{-1} .

$\nu_m = 136\,607 - R/(m - 0.0441 - 0.018/m)^2$; $m = 2$ to 6, $R = 109\,735 \text{ cm}^{-1}$. The bands are rather narrow, are shaded to longer wavelengths, and show but one head. Starting with the first member, intensities progressively decrease in a normal manner, the values being comparable to those of corresponding $X-X$ bands. The upper term for the first band is the $v=1$ level of state o .

Dalby and Douglas⁷ have photographed the ${}^2\Pi-2\Sigma$ bands of N_2^+ at large dispersion, using a laboratory source. From preliminary results of the analysis, kindly supplied by Dr. Douglas, the empirical series limit, above, is found to correspond to the $v=1$ level of the ${}^2\Pi$ state, and apparently to its upper component ${}^2\Pi_{1/2}$. The position of this component, as found by adding $\nu_{00} + \Delta G(\frac{1}{2}) + \frac{1}{2}A$ to the limit of the $X-X$ Rydberg series,² is $136\,597 \text{ cm}^{-1}$ above the ground state of N_2 . In fact, if the heads of the higher members of the $X-X$ series represent origins—that is, if they are of Q -form as is suggested by the extreme narrowness of the bands—and if a computed origin-to-head interval is added

¹ R. E. Worley and F. A. Jenkins, *Phys. Rev.* **54**, 305 (1938).

² R. E. Worley, *Phys. Rev.* **64**, 207 (1943).

³ J. J. Hopfield, *Phys. Rev.* **36**, 789 (1930). See also Takamine, Suga, and Tanaka, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo* **34**, 854 (1938).

⁴ R. S. Mulliken, *Phys. Rev.* **46**, 144 (1934).

⁵ A. B. Meinel, *Astrophys. J.* **114**, 431 (1951); **112**, 562 (1950).

⁶ Most bands referred to herein are listed in Table I, reference 2. Omitted were the following (cm^{-1}): 123 995* ($m=3$); 124 069* (footnote 8). Recently measured for use in Table I herein were 122 068; 133 995; 135 361 cm^{-1} .

⁷ F. W. Dalby and A. E. Douglas, *Phys. Rev.* **84**, 843 (1951). See also R. Herman, *Compt. rend.* **233**, 926 (1951); N. D. Sayers, *Proc. Phys. Soc. (London)* **65**, 152 (1952).

TABLE I. Values of ΔG for the Rydberg terms.

m	$\Delta G(1/2)$	$\Delta G(3/2)$
2	1962	1917
3	(1927)	...
4	...	1863
5	1886	(1860)
6	1883	(1853)
${}^2\Pi(N_2^+)$	1872	1843

to the figure just given, the limit predicted for the present series is $136\,609\text{ cm}^{-1}$.

Professor Mulliken (private communication) points out, however, that this feature is readily explained if the upper terms of the $A-X$ absorption bands are ${}^1\Sigma$, as is suggested by their appearance. ${}^3\Sigma$ terms of the same electron configuration will then converge to ${}^2\Pi$, and observable transitions to these terms from $X\ {}^1\Sigma(N_2)$ are not expected for $m \leq 4$. But absorption may become discernible for higher values of m , due to the mixing of wave functions of the singlet and triplet states with change in coupling of the excited electron. Very weak, hence somewhat doubtful, heads are indeed found for $m=5$ and 6 , displaced to lower wave numbers by about 110 cm^{-1} and 90 cm^{-1} , respectively. If we accept convergence of this series to ${}^2\Pi_{3/2}$, no absorption bands converging to the ${}^2\Pi_{3/2}$ component, which lies about 80 cm^{-1} below ${}^2\Pi_{3/2}$, were evident.⁸

The $B-X$ and the strongest $X-X$ absorption series of N_2 consist of bands for which $v'=0$. That the $A-X$ bands correspond to $v'=1$ is attributed to a somewhat greater internuclear distance of the excited terms of

⁸ An alternative interpretation of these details is suggested by the presence of second heads lying 74 cm^{-1} and 70 cm^{-1} , respectively, to shorter wavelengths from the bands for $m=3$ and 4 . May not the observed series converge to ${}^2\Pi_{3/2}$, while these other bands converge to ${}^2\Pi_{1/2}$? The bands for $m=5$ and 6 are unobscured, but no double heads are found here; nor is there a second head for $m=2$ (state o).

these bands, as compared to those of the other two series (Franck-Condon principle). A larger internuclear distance is clearly indicated by the low intensity of the $v'=0$ band of the $o-X$ progression. For the higher Rydberg terms, a few heads have been found that correspond to $v'=0$, and it appears that their intensities increase relative to bands with $v'=1$. (A similar trend with increase of m is seen in the $X-X$ bands.) A few possible heads are found also for $v'=2$. The corresponding $\Delta G(\frac{1}{2})$ and $\Delta G(\frac{3}{2})$ values are shown in Table I. Because of overlying diffuse absorption, some of these identifications for $v'=0$ and 2 are questionable, but the more reliable ΔG intervals show a reasonable correlation between the o term of N_2 ($m=2$) and the ${}^2\Pi$ term of N_2^+ .

TABLE II. Data and vibrational analysis, state o of N_2 .

Int.	ν_H (cm^{-1})	Vibrational constants (from band heads)
1	105 694.5	$\omega_e = 2020.00 \pm 0.07\text{ cm}^{-1}$
6	7657.0	$\omega_e x_e = 32.28 \pm 0.03\text{ cm}^{-1}$
5	9574.4	$\omega_e y_e = 2.167 \pm 0.004\text{ cm}^{-1}$
3	111 459.8	
$\frac{1}{2}$	3326.1	

In conclusion, this assignment and identification of bands in the absorption spectrum confirms the vibrational numbering for the ${}^2\Pi$ state of N_2^+ as proposed by Dalby and Douglas,⁷ and by Meinel.⁵ It also identifies the o state of N_2 as the parent term from which ${}^2\Pi$ is derived by removal of an electron. Table II lists the intensities and wave numbers of the $o-X$ absorption bands,⁹ and gives the vibrational constants of state o , as derived from these data by a least-squares solution.¹⁰

⁹ The weak head for $v'=4$ is not listed in reference 2, as it was incorrectly attributed to a rotational perturbation in an overlying band. (In Table II, the v' values run from 0 to 4.)

¹⁰ R. T. Birge and J. W. Weinberg, *Revs. Modern Phys.* **19**, 298 (1947).