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A New Band System of N_2^+ Excited from Impact by Hydrogen Ions on a Nitrogen Target

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A new molecular spectrum has been observed in the 3820–3920 Å region by submitting nitrogen molecules to the impact of hydrogen ions in the 5–30 KeV energy range. The most intense band may be attributed to the (0–0) transition of a new system $^4\Sigma_u^+ \rightarrow X\,^2\Sigma_g^+$ of N_2^+. The following molecular constants have been determined: T_e = 3,16 eV, r_e = 1,077 Å, $3\,\varepsilon$ = 0,7 cm^{-1} for the quartet state.

The $B\,^2\Sigma_u^+ \rightarrow X\,^2\Sigma_g^+$ first negative system (F.N.S.) of N_2^+ has been extensively used in experimental work, for the determination of rotational temperatures as well as reaction mechanisms in the upper atmosphere [1–13]. Measurements are generally performed with instruments having low resolution ($\sim$30 000). The rotational structure is thus incompletely resolved, and the results are altered by overlapping of the R-branch lines by those of the folded-back portion of the P-branch [6, 10, 11, 14–17]. Moreover, extra lines may produce the same effect, which depends upon the excitation conditions [18].

A detailed analysis of the F.N.S. has been made, using a $f/8$ crossed-grating spectrograph with a resolving power of 180 000 at 4000 Å. Atomic and molecular hydrogen ions from a HF discharge have been accelerated in the energy range 5–30 KeV and focused into a collision chamber filled with nitrogen at pressures near $5 \cdot 10^{-3}$ Torr. Collision-induced spectra were recorded on Kodak 103 a-0 films with exposures of several hours.

A new molecular spectrum, with more than 150 strong lines, has been observed under these conditions in the region of the (0,0) and (1,1) bands of the F.N.S. (3820–3920 Å). In general, the lines of the most intense band are doubles regularly distributed between the components of the (0,0) band. This spectrum is not excited during collisions with atomic ion beams (Li^+, Na^+) or in microwave discharges. Because of the low target pressure and the flowing type of the experiment, no impurity in sufficient amount was present in the collision vessel.

The spacing between the strong lines of this new transition, which is very close to that of the (0,0) band of the F.N.S., as well as its even multiplicity give strong support to its attribution to N_2^+.

The analysis of the most intense band leads to a value of the lower rotational constant which is very close to that of the ground state of N_2^+. Assuming that $X\,^2\Sigma_g^+$ is actually the lower state of this new system, the upper state may be a new state, unless the extra lines belong to a transition $A\,^2\Pi_u \rightarrow X\,^2\Sigma_g^+$ induced by the electronic perturbation of $B\,^2\Sigma_u^+$ $(v=0)$ by $A\,^2\Pi_u$ $(v=10)$. Such a perturbation has been already observed [19–25]. From the rotational constants of the levels involved, the wave numbers of the (10,0) band belonging to the $A\,^2\Pi_u \rightarrow X\,^2\Sigma_g^+$ transition have been calculated. No agreement exists between the latter values and the observed ones. Accordingly, the hypothesis of such a transition must be rejected.

The observed transition has an energy very close to that of the (0,0) band of the F.N.S. The upper level of the former should thus be in the vicinity of $B\,^2\Sigma_u^+$ $(v=0)$, if the lower level is the ground state of N_2^+, as stated above. The only stable yet unknown states in this region are quartet states, first predicted by Mulliken [26], later calculated by Gilmore [27] and recently by Andersen [28]. Among these states, $^4\Sigma_u^+$ lies very near to $B\,^2\Sigma_u^+$. Taking into account the presence of several branches – often in coincidence – having P or R character, and the absence of a strong Q branch, we have attributed the intense lines to the (0,0) band of a new $^4\Sigma_u^+ \rightarrow X\,^2\Sigma_g^+$ transition of N_2^+. This assumption is further supported by the expressions of the rotational term values belonging to a $^4\Sigma$ state, first given by Budo [29]. They show that two levels F_1 and F_4 coincide, as do also F_2 and F_3 for not too small values of the rotational quantum number. Thus the spectrum consists mainly of doublets, as we have observed. Their spacing gives the value of the spin-spin interaction constant ε. We have found that $3\,\varepsilon = 0{,}7$ cm^{-1}. The rotational analysis of the most intense band leads to the following constants (in cm^{-1}):

$$\nu_{00} = 25563{,}3; \quad B' = 2{,}064; \quad D' = 5 \cdot 10^{-6}.$$

Other lines also appear, in the region of the (1,1) band of the F.N.S.

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They may belong to the (1,1) band of the new $^4\Sigma \rightarrow {}^2\Sigma$ system. In this case, the vibrational constants of the $B\,{}^2\Sigma_u{}^+$ and $^4\Sigma_u{}^+$ states are very close to one another. Assuming for these two states the same value of $\alpha_e = 0{,}0195\ \text{cm}^{-1}$ deduced from the study of the $B\,{}^2\Sigma_u{}^+ \rightarrow X\,{}^2\Sigma_g{}^+$ system, it is possible to calculate the equilibrium internuclear distance for the $^4\Sigma_u{}^+$ state. In the following table the values derived from our analysis are compared with those calculated by Andersen and Gilmore.

	(1)	(2)	(3)
T_e (eV)	3,16	3,6	5,4
r_e (Å)	1,077	1,40	1,15

(1) Experimental values deduced from the present results;
(2) Values from Andersen's calculations (1973);
(3) Values from Gilmore's estimates (1965).

The $^4\Sigma_u{}^+ \rightarrow X\,{}^2\Sigma_g{}^+$ transition is forbidden by the selection rule $\Delta S = 0$. But the upper state is metastable and has therefore a long lifetime, nearly 10^{-5} second [30–32]. The low pressure in the collision chamber is not favourable for the deexcitation of the $^4\Sigma$ metastable level by collision. The observation of the transition from this state to the ground state is then more probable. For that reason the new sysem has not been discovered in electric discharges, where the secondary collision processes are of importance.

The following mechanism may be assumed for the $N_2{}^+(^4\Sigma)$ ion formation:

$$N_2(X\,{}^1\Sigma_g{}^+) + H_2{}^+ \rightarrow N_2{}^+(^4\Sigma_u{}^+) + H + H\,.$$

Molecular hydrogen ions (produced in our source by H.F. discharge) are taken into account (rather than protons), in order to respect the Wigner spin conservation rule [33–35]. That is why the new system was not observed under the impact of atomic ions such as Li^+ and Na^+.

A more detailed report of our results is being prepared.

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