Band Spectra in the Schumann Region of NO and N₂⁺ with Enriched Nitrogen-15

IN connexion with the investigation of a new band system of the NO molecule $(B' - X^2\Pi)$[1] we photographed the emission spectra of ^{15}NO-gas. For the preparation of this gas we are very grateful to Prof. Clusius. The region investigated extends from 1300 to 2200 A. The spectrograph used was a 1-m. vacuum grating (8 A./mm. dispersion). An uncondensed discharge of 250 m.amp. through a tube 20 cm. in length and 4 mm. in diameter, containing circulating helium at a pressure of 4 mm. mercury, formed the source of light. To this a small amount of ^{15}NO was added. We observed bands of NO and N_2^+. A provisional measurement of the isotope splittings has been carried out.

(a) NO. ε-bands : Table 1 gives the observed and calculated isotope doublets and shows definitely that the ε-bands belong to a separate system. Herzberg and Mundie's[2] suggestion that the ε-bands might be a continuation of the γ-system with vibrational levels $v' \geqslant 4$ is therefore no longer valid.

Table 1. ISOTOPE SHIFTS, $\Delta \nu = \nu^i - \nu(\text{CM.}^{-1})$ IN ε-BANDS OF NO

v', v''	1·0		0·1		0·2	
	obs.	calc.	obs.	calc.	obs.	calc.
Head						
Q_1	− 44·1				+ 60·0	
P_1	− 42·6	− 43·7			+ 60·9	
Q_2	− 44·0		+ 28·7	+ 29·3	+ 59·8	+ 61·4
P_2	− 43·9		+ 31·1		+ 60·7	

β'-bands : The isotope shifts of the bands of this new system confirm the analysis already published[1] : B'-term : $\nu_e = 60{,}366$ cm.$^{-1}$, $\omega_e = 1{,}216$ cm.$^{-1}$, $x_e\omega_e = 16\cdot4$ cm.$^{-1}$.

Table 2. ISOTOPE SHIFTS, $\Delta \nu$ OF N_2^+-BANDS (SYSTEM $C - X$).
$\Delta \nu^i = \nu(^{14}N^{15}N) - \nu(^{14}N_2)$ (cm.$^{-1}$)
$\Delta \nu^{ii} = \nu(^{15}N_2) - \nu(^{14}N_2)$ (cm.$^{-1}$)

Watson-Koontz		Setlow			Observed values	
v', v''	$\Delta \nu^i$	v', v''	$\Delta \nu^i$	$\Delta \nu^{ii}$	$\Delta \nu^i$	$\Delta \nu^{ii}$
8,10	+ 42·9	3,10	+ 210·1	+ 424·8	+ 210	+ 417
9,11	+ 37·5	4,11	+ 203·4	+ 411·5	+ 203	+ 408
10,12	+ 31·4	5,12	+ 196·5	+ 397·7	+ 192	+ 393
11,13	+ 25·0	6,13	+ 190·1		+ 189	
8,9	+ 17·2	3,9	+ 184·4		+ 182	
9,10	+ 13·0	4,10	+ 178·9	+ 361·8	+ 174	+ 355
10,11	+ 8·3	5,11	+ 173·4	+ 350·9	+ 169	+ 346
11,12	+ 2·9	6,12	+ 168·0		+ 168	
8,8	− 9·6	3,8	+ 157·6		+ 155	

(b) N_2^+. Table 2 contains both the isotope displacements observed in the $C - X$ system and the theoretical values for the analysis of Watson and Koontz[3] on one hand, and the analysis of Setlow[4] on the other. It is seen that Setlow's analysis, originally based only upon the intensity distribution, is the correct one. The following data are now calculated for the $C^2\Sigma$-level of N_2^+ :

$\nu_e = 64{,}620$ cm.$^{-1}$, $\omega_e = 2{,}065$ cm.$^{-1}$, $x_e\omega_e = 7\cdot7$ cm.$^{-1}$, $y_e\omega_e = -0\cdot56$ cm.$^{-1}$.

Table 3. (i, HEADS OF ISOTOPE BAND OBSERVED)

$v'\backslash v''$	0		1		2		3		4		5		6
0	73,087	2,336	70,751	2,314	68,437i	2,276	66,161i	2,251	63,910	2,206	61,704i	2,187	59,517
1			1,559 72,310	2,311	1,562 69,999								

(c) New system. On the same spectrogram a new system was found. The wave-numbers of the heads are shown in Table 3. All bands are degraded to the red.

The analysis is based on the observed isotope shifts. The vibrational frequency of the lower level agrees with the frequency of the $X^1\Sigma$ level of the nitrogen molecule as well as with the frequency of the $A^2\Sigma$ level of the nitric oxide molecule. Since neither alternation of intensity in the rotational structure nor heads of nitrogen-15 ($^{15}N_2$) have been observed, no decision between these alternatives is possible at present.

Further details will soon be reported elsewhere.

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[1] Baer, P., and Miescher, E., Helv. Phys. Acta, 24, 331 (1951).
[2] Herzberg, G., and Mundie, L. G., J. Chem. Phys., 8, 263 (1940).
[3] Watson, W., and Koontz, P., Phys. Rev., 46, 32 (1932).
[4] Setlow, R. B., Phys. Rev., 74, 153 (1948).

Tellurite Glasses

IT has been noted previously[1] that the elements which, in the form of their oxides, are generally regarded as excellent glass formers have values of electronegativity on the Pauling scale[2] of 1·7–2·1. For example, boron, silicon, phosphorus and germanium with electronegativity values of 2·0, 1·8, 2·1 and 1·7 form borate, silicate, phosphate and germanate glasses. In addition. to these elements, others with values in the same range, according to Pauling, are arsenic and antimony (which form, for example, As_2O_3 and Sb_2O_3 glasses) and tellurium with an electronegativity value of 2·1, that is, the same as for phosphorus. These facts lead one to consider whether tellurium oxides or the tellurites or tellurates form glasses.

So far as I am aware, technologists have so far been quite unaware of the possibility of preparing tellurite and tellurate glasses, and yet a search of the literature soon revealed that Berzelius[3] had mentioned that clear, colourless glasses could be prepared from the molten tetratellurites of the alkali metals and of barium. More recently, Lenher and Wolesensky[4] confirmed the glass-making properties of sodium and potassium tellurites. Those observations, only briefly recorded in papers of wider chemical interest, appear to have escaped the attention of technologists.

An investigation of tellurite glasses was thought to be worth while, not only for its fundamental interest, but also because it could be expected that these glasses would have physical properties of value. For example, it could be estimated from the known cation radius of Te^{4+} (0·84 A. in its oxide) that the partial refractivity of tellurium oxide (TeO_2) in glass would be quite high[5] and that tellurite glasses would, therefore, have much higher refractive indices than corresponding silicate, borate, phosphate and germanate glasses.

The first glasses I studied were in the systems BaO—TeO_2 and PbO — TeO_2. They were found to