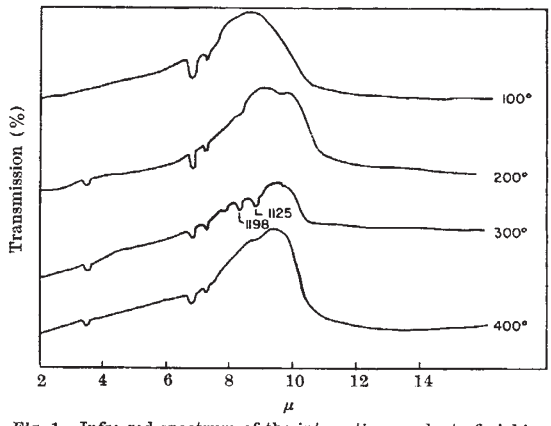

Fig. 1. Infra-red spectrum of the interaction product of niobium dioxide and nitrogen dioxide for various temperatures of interaction at a pressure of 65 cm. nitrogen dioxide

to the above stoichiometric ratio it was noted that a small amount of nitrogen was also incorporated in the oxide. At a pressure of 26·5 cm. mercury of NO_2 and in the temperature interval from 100 to 500° C. the stoichiometric ratio of nitrogen–niobium varied linearly with increasing temperature from 0·019 to 0·043 and at a $P_{NO_2} = 0·014$ cm. mercury the nitrogen content was within the limit of error of the method[2].

In an attempt to determine the origin of this incorporated nitrogen the infra-red spectra of the reacted material was obtained. This was done on a Perkin Elmer model 221 double-beam spectrophotometer. The spectra are partially reproduced in Fig. 1 for the interaction of NO_2 at 65·5 cm./mercury and Nb_2O_4 in the temperature-range of 100–500° C. Absorption peaks may be seen at ~ 3·5, 6·8, and 7·3μ due to interference from the 'Nujol' mulling agent. Secondly, a broad band is in evidence which begins at about 10·5μ. This is most probably due to the Nb–O stretching frequency[3,4]. Finally, bands may be seen at ~ 7·8, 8·3, 8·8 and 9·6μ. It is felt that the bands at 7·8 and 9·6 are probably due to the presence of some form of ionic nitrate[5] as these bands have been found to be characteristic of ionic nitrates in general. The bands at 8·3 and 8·8 appear to be due to the NO_2 group, in the form of strongly chemisorbed nitrogen dioxide or as the nitrite group[6]. It should be noted that in both these cases the presence of these species occurs at an extremely low concentration and thus does not demonstrate the inherent basic character in niobium dioxide.

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Dissociation Energy of Aluminium Monobromide

In a recent review[1] of the dissociation energies of the gaseous monohalides of boron, aluminium, gallium and thallium, it was concluded that the best value for D_0'' (aluminium monobromide) is 105 k.cal. mole^{-1}. Dr. P. Gross has now kindly directed my attention to the work of Semenkovich[2], who has determined the standard heat of formation of gaseous aluminium monobromide by a thermochemical method similar to that used by Gross, Campbell, Kent and Levi[3] for aluminium monofluoride and monochloride. Semenkovich obtains $Q_f(AlBr_g) = +1·1$ k.cal. mole^{-1}. With $\Delta_s H(Al) = 77·4$, $Q_f(Br_g) = 26·71$, and $D_{298}'' - D_0'' = 0·85$, $D_0''(AlBr) = 102·2$ k.cal mole^{-1}. As with AlF and AlCl, this value is a little lower than two of the spectroscopic estimates from the state $A\,^1\Pi$, which, for AlBr, are 106·9 k.cal. by extrapolation, and $>104·4$ k.cal. from the highest observed vibrational level: it is, however, consistent with a predissociation limit which leads to $D_0'' \leqslant 105·7$ k.cal.

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Triplet Bands of Carbon Monoxide: the System $e\,^3\Sigma^- - a\,^3\Pi$

Some years ago, in a study of the triplet system, $d(?^3\Pi) - a^3\Pi_r$ of carbon monoxide, Herman and Herman[1] observed a progression of bands of similar appearance which they assigned to a new system. They suggested that the upper state of this system was d and that the lower state was a new triplet-level, lying close to $a^3\Pi$. Later work[2,3] on the forbidden systems of carbon monoxide observed in the absorption spectrum in the Schumann region has provided detailed information about some of the triplet-levels, and the object of this communication is to show that the Herman system arises in fact from the transition $e\,^3\Sigma^- - a\,^3\Pi_r$.

In Table 1, the second column gives values of band-origins of the $e - X$ system[2]. Positions of the band-heads of the Herman system[1] are given in columns three and four. The results of subtracting column four from two are given in column five. These figures are as constant as could be expected, and indicate that the bands form a progression involving the levels $v' = 2$ to 7 of $e\,^3\Sigma^-$. The mean value for the height of the lower level above $v = 0$ in the ground-state $X\,^1\Sigma^+$ is 48,520·$_5$ cm.$^{-1}$.

Table 1

v	e–X ν_0	e–a λ	e–a ν	a–X ν
7	71,926·5	4,270·8	23,408·3	48,518·2
6	70,966·2*	4,454·5	22,442·9	523·3
5	69,986·4	4,657·2*	21,465·9*	—
4	68,987·9*	4,885·0	20,465·1	522·8
3	67,970·3	5,140·3	19,448·7	521·6
2	66,933·3	5,428·3	18,416·9	516·4

* Interpolated value.

The measurements of band-heads given in Table 1 refer to the longest wave-length heads of groups of three. For the $v' = 2$ and $v' = 3$ bands, further measurements are available[4]: