

## THE LOCATION OF NO( $b^4\Sigma^-$ ) AND THE EXCITATION MECHANISM OF NO $\beta$ BANDS

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### Summary

The mechanism for NO( $B^2\Pi$ ) population associated with the combination of N( $^4S$ ) + O( $^3P$ ) atoms is considered. Evidence is obtained from observations of the kinetic behaviour of nitric oxide  $\beta$  and Ogawa bands in the nitric oxide afterglow.

The proposed population route involves the formation of NO( $a^4\Pi$ ) and ( $b^4\Sigma^-$ ) states as precursors, in agreement with previous workers. However, the evidence favours a reassignment of the vibrational  $v'$  numbering scheme for NO( $b^4\Sigma^-$ ) with respect to that currently accepted. The revised  $v'$  are shown to be consistent with both spectroscopic evidence and the mechanism for population of NO( $B^2\Pi$ ) levels. This allows NO( $b$ ) ( $v' = 0$ ) to be the immediate precursor of NO( $B$ ) ( $v = 0$ ). Calculation of the  $b^4\Sigma^-$  potential energy curve according to the revised scheme gives a  $D_e$  value of  $275.6 \pm 1.6$  kJ mol $^{-1}$ , and indicates that the highest level so far observed is  $v' = 6$ .

The negative temperature coefficient observed for the  $\beta$  bands is also explained in relation to that observed for the overall three-body combination N + O + M.

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### 1. Introduction

In the afterglow associated with combining N( $^4S$ ) and O( $^3P$ ) atoms the conspicuous blue colouration is due to NO  $\beta$  bands from the transition  $B^2\Pi-X^2\Pi$ . Since the NO( $B^2\Pi$ ) state does not correlate with the ground state atoms, the route(s) by which the vibrational levels are populated have long been of interest, with a view to extension of our knowledge of intermolecular and intramolecular energy transfer processes. Young and Sharpless [1, 2] proposed the general features of the mechanism. Since NO( $a^4\Pi$ ) appears to be the only excited state correlating with N( $^4S$ ) + O( $^3P$ ), it must be initially populated; however, in view of the substantial separations of NO( $a^4\Pi$ ) and NO( $B^2\Pi$ ) potential energy curves it was proposed that NO( $b^4\Sigma^-$ ) served as a "bridge" between the two. We have recently studied [3] the Ogawa band emission

$\text{NO}(\text{b}^4\Sigma^- \rightarrow \text{a}^4\Pi)$  associated with  $\text{N} + \text{O}$  and have obtained evidence of preassociation in the highest  $v'$  observed which served to locate the energetic position of that level with respect to the first dissociation limit of  $\text{NO}$ . In this paper we consider the apposition of energy levels in  $\text{NO}(\text{b}^4\Sigma^-)$  and  $(\text{B}^2\Pi)$  and how the collision-induced crossing may be interpreted in the light of the available kinetic and spectroscopic evidence. This has led us to propose that the currently accepted  $v'$  numbering scheme for  $\text{NO}(\text{b}^4\Sigma^-)$  given by Gilmore [4] must be revised in order to reconcile this evidence.

The paper is divided into four main sections. In Section 2 we summarize briefly the available evidence pertinent to a deduction of the excitation mechanism. In Section 3 the role of  $\text{NO}(\text{a}^4\Pi)$  and  $(\text{b}^4\Sigma^-)$  as intermediates in the population of  $\text{NO}(\text{B}^2\Pi)$  is discussed. Then in Section 4 we propose and justify our numbering scheme for  $v'$  levels of  $\text{NO}(\text{b}^4\Sigma^-)$  and finally in Section 5 we reconcile this with the observed kinetic behaviour of  $\beta$  band emission.

For ease hereafter, we shall use a state letter with a subscript vibrational quantum number to denote a given level of an electronic state. Thus  $\text{B}_0, \text{B}_1, \text{B}_2, \text{B}_3$  denote  $\text{NO}(\text{B}^2\Pi)$   $v' = 0, 1, 2, 3$  respectively and  $\text{a}_v$  and  $\text{b}_v$  denote levels of  $\text{NO}(\text{a}^4\Pi)$  and  $\text{NO}(\text{b}^4\Sigma^-)$  respectively.

## 2. Summary of experimental observations on $\text{NO}$ $\beta$ bands

The available kinetic behaviour from  $\text{N} + \text{O}$  system studies is restricted to the pressure range 0.1 - 1.4 kPa, the practical range of the discharge flow systems serving as the only controlled source. Moreover, only the levels  $\text{B}_0, \text{B}_1, \text{B}_2$  and  $\text{B}_3$  give rise to emission intensities  $I$  sufficient for kinetic studies.

### 2.1. Pressure dependences and quenching

$I(\text{B}_0), I(\text{B}_1)$  and  $I(\text{B}_2)$  increase linearly with increasing pressure in nitrogen carrier gas [5]. In contrast  $I(\text{B}_3)$ , although also increasing with increasing pressure, shows evidence of quenching by nitrogen [5]. In carrier gas mixtures of nitrogen plus a quenching gas  $\text{Q}$  ( $\text{Q} = \text{CO}_2, \text{N}_2\text{O}$  or  $\text{H}_2\text{O}$ ) it was shown [5] that  $\text{Q}$  acted directly on  $\text{NO}(\text{B}^2\Pi)$  itself and quenching on the precursor(s) was insignificant.

### 2.2. Relative intensities

The relative intensities of emission from  $\text{B}_v$  ( $v = 0, 1, 2$  or  $3$ ) have been measured by Campbell and Neal [6] taking account of  $\text{N}$  and  $\text{O}$  atom quenching/enhancement effects. The results are listed in Table 1. It should be noted that in order to convert relative intensities into relative populations it is necessary to know the radiative lifetimes of the particular levels; these were taken from Jeunehomme and Duncan [7] for consistency with our earlier paper on quenching behaviour [5].

TABLE 1

Relative populations  $P$  of  $\text{NO}(B^2\Pi)$  levels at 298 K

$v'$	0	1	2	3
$P$	$1.0 \pm 0.3$	$0.09 \pm 0.03$	$0.09 \pm 0.03$	$0.20 \pm 0.06$

Values taken from ref. 6.

TABLE 2

Temperature coefficient indices ( $n_v$ ) for  $\text{NO } \beta$  bands

$v$	0	1	2	3
$-n_v$	$1.6 \pm 0.2$	$0.18 \pm 0.05$	$0.15 \pm 0.05$	$1.5 \pm 0.2$

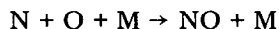
Values taken from ref. 6.

### 2.3. Temperature dependences

The temperature variation of the emission rate constant  $k_v$ , for a particular vibrational level  $v$ , has been defined by the relation [6]

$$\frac{I(B_v)}{[N][O][N_2]} = k_v \propto T^{-n_v}$$

and the results are shown in Table 2. This presents a major problem, in that the temperature coefficients of  $B_1$  and  $B_2$  are evidently much less than those of  $B_0$  and  $B_3$ . Moreover, the temperature coefficient of the overall reaction



is different again with measured values of  $n$  being  $-0.65$  [8] and  $-0.5$  [9].

### 2.4. Atom quenching/enhancement effects

It has been shown that N and O atoms quench emission from  $B_0$  while increasing [O] leads to spectacular parallel enhancements of rate constants for emissions from  $B_1$  and  $B_2$  [6, 10]. The emission rate constant from  $B_3$  is largely unaffected by [N] and [O]. However, these effects do not have a bearing on the present discussion and a detailed interpretation of the effects will be published shortly [11].

## 3. The role of the quartet states

### 3.1. Vibrational relaxation in the $a^4\Pi$ state

Emission from  $\text{NO}(a^4\Pi)$  has never been observed in the gas phase, reflecting the forbidden nature of the  $a^4\Pi-X^2\Pi$  transition. However, this transition has been observed in a solid argon matrix [12], and of course the  $a$  state gives rise to the lower of the Ogawa bands.

Statistically one would expect two-thirds of N + O combinations to populate NO(a) initially, with the ground state accounting for the remainder. At 298 K the rate constant for the overall combination reaction has been measured as  $3.3 \times 10^9 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  ( $M = \text{N}_2$ ) [8], while measurements of the absolute intensity of the total  $\beta$  band emission have yielded a population rate constant of  $1.1 \times 10^8 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  [13]. Thus only about 3% of combinations pass through NO(B<sup>2</sup>Π). At the same time the measurement of the absolute intensity of the Ogawa (b → a) emission [3], which is pressure independent, has yielded a rate constant for emission of  $1.4 \times 10^3 \text{ einstein dm}^{-3} \text{ s}^{-1}$ . The lack of pressure dependence of Ogawa band emissions down to  $[\text{N}_2] = 4 \times 10^{-5} \text{ mol dm}^{-3}$  was shown to indicate that at most only 10% of NO(b) molecules formed are removed by radiation under these conditions. However, strong evidence was presented that the overwhelming component of the pressure-dependent removal process was collision-induced crossing back to NO(a) and on this basis Ogawa band radiation amounts to only 1% at most loss of molecules from the NO(a) manifold. Thus there is a clear case for regarding the major flux in the excited states as vibrational relaxation down the NO(a) state. In the vicinity of the dissociation limit, vibrational relaxation in NO(a) would be expected to be very rapid in view of the small wavenumber ( $\bar{\omega}$ ) spacing of adjacent levels. However, at  $v = 20$  it can be calculated that  $\bar{\omega} \approx 30\,000 \text{ m}^{-1}$  and at  $v = 9$   $\bar{\omega}$  has become about  $65\,000 \text{ m}^{-1}$  so that vibrational relaxation would be expected to become less rapid as  $v$  decreased. In the absence of any other net removal processes of significant rate for a particular level denoted  $a_v$  the population will be governed by the initial combination rate constant  $k$  into NO(a) and the rate constant  $k_v$  for vibrational relaxation out of this level, *i.e.*

$$[a_v] = \frac{k[\text{N}][\text{O}]}{k_v}$$

In this case the temperature dependence of  $[a_v]$  will be governed by that of the ratio  $k/k_v$ . It is known that, except in special cases [14, 15], the rate constant  $k_v$  will be likely to have a small positive temperature coefficient [14, 16] while it is likely that  $k$  will have a negative temperature coefficient close to that for the overall combination (about  $T^{-0.6}$ , see Section 2.4). Accordingly we would expect  $[a_v]/[\text{N}][\text{O}]$  to have a sharper negative temperature coefficient than the overall combination rate constant.

This is an important point since Ogawa band emissions [3] and  $\beta$  band emissions from B<sub>0</sub> and B<sub>3</sub> vary with temperature approximately as  $T^{-1.5}$ , which is evidently sharper than the overall combination rate constant. Thus we interpret these as reflecting directly the population kinetics of the NO(a) levels serving as precursors. The implication is that for levels below  $a_{17}$  (approximately isoenergetic with b<sub>3</sub> (Gillmore numbering)) the  $k_v$  have similar temperature coefficients.

### 3.2. Crossing to the B<sup>2</sup>Π state

There is a substantial separation of NO(a<sup>4</sup>Π) and B<sup>2</sup>Π potential energy curves, particularly at energies below B<sub>3</sub> where the inner limbs of the two

curves diverge rapidly. It is therefore unlikely that the B state could be populated by direct  $a \rightarrow B$  crossing. Indeed, if this were the major route we would expect  $B_0$  to have the lowest relative abundance because it is the furthest removed from the a state, whereas in fact  $B_0$  has the highest relative abundance (Table 1).

However, as can be seen in Fig. 1, the  $b^4\Sigma^-$  state curve has an inner limb close to that of the a state, thereby greatly assisting a  $\rightarrow$  b crossing, and it also crosses the B state. It is expected that  $b \rightarrow B$  crossing will occur much more readily than  $a \rightarrow B$  because the  $b$ -B overlap of vibrational wavefunctions should be much more favourable than the  $a$ -B overlap. Two factors contribute to the enhanced  $b$ -B overlap. First, the overlap is between levels of low  $v$  numbers in both states where the wavefunctions are not closely confined to the classical turning points. This is not the case for  $a$ -B overlap, since very high  $v$  levels ( $v \geq 9$ ) of the a state are involved. Second, of course, the b state inner limb lies between that of the a and B states.

The b state must therefore be regarded as a necessary precursor of the  $\beta$  band emission. It is generally accepted that such crossing processes will occur most rapidly between nearly isoenergetic levels and thus it becomes important to locate the energy levels of the b state in particular in an attempt to explain the relative populations of  $B_0$ ,  $B_1$ ,  $B_2$  and  $B_3$  shown in Table 1.

#### 4. Location of $\text{NO}(b^4\Sigma^-)$ vibrational levels

Direct spectroscopic evidence on the energetic location of  $\text{NO}(b)$  comes from the Ogawa bands ( $b \rightarrow a$ ). Brook and Kaplan [17] assigned the  $v'$ ,  $v''$  numbering scheme shown in column 1 of Table 3. Gilmore [4] amended this scheme by the addition of 1 to  $v'$  as in column 2 of Table 3. The justification for this came from the relative intensities of the bands as far as they could be judged from the published spectrograms. In our recent paper [3], Gilmore's numbering scheme (G) was adopted and the  $b_4$  (G) level was located energetically to within 5 - 10  $\text{kJ mol}^{-1}$  below the first dissociation limit ( $D_0^0(\text{NO})$ ). Further evidence supporting this location is to be found in work by Kley [18]. Using the large spherical vessel described by Becker *et al.* [19], Kley observed Ogawa bands at very low pressures (1.3 Pa) and a band in the 830 - 842 nm region was newly identified as the (5,3) (G) band. This band and the neighbouring (4,2) (G) band were the dominant emission features under these conditions. However, when the operating pressure was increased to 13 Pa, the Ogawa band intensity distribution became similar to that which we observed at 133 Pa [3] when the  $v' = 3$  (G) bands are the most intense. At the lowest pressure Kley found that the (5,3) (G) band had a pressure-independent intensity, whilst the other bands in the  $\Delta v = -2$  sequence ((4,2), (3,1) and (2,0) (G)), grouped for the purposes of measurement, had pressure-dependent intensities. These observations are a clear indication that  $b_5$ (G) is populated entirely by preassociation (two-body)

TABLE 3  
Observed Ogawa bands

Assignment ( $v'$ , $v''$ )			Wavelength (nm)	Relative intensity
Revised (R)	Gilmore (G)	Brook and Kaplan (BK)		
2,0	1,0	0,0	968 <sup>a</sup>	
3,1	2,1	1,1	950 <sup>a</sup>	
3,0	2,0	1,0	869	0.65
4,1	3,1	2,1	858	1.00
5,2	4,2	3,2	847	0.47
6,3	5,3	4,3	836 <sup>b</sup>	~0.15
4,0	3,0	2,0	790	0.25
5,1	4,1	3,1	782	0.28
5,0	4,0	3,0	~726 <sup>c</sup>	

<sup>a</sup> Observed by Brook and Kaplan [17] only.

<sup>b</sup> Identified by Kley [18].

<sup>c</sup> Observed by Ogawa [27] only.

combination), while our work [3] showed that  $b_4(G)$  is populated by a combination of two-body and three-body processes. Taking as reference point  $b_4(G)$ , which lies 5 - 10  $\text{kJ mol}^{-1}$  below  $D_0^0(\text{NO})$ ,  $b_5(G)$  must lie 3 - 8  $\text{kJ mol}^{-1}$  above  $D_0^0(\text{NO})$ . In the nitrogen afterglow  $\text{N}_2(\text{B}^3\Pi_g) v' = 13$  is also populated by a preassociation process and this level lies 5.8  $\text{kJ mol}^{-1}$  above  $D_0^0(\text{N}_2)$ . Since this is the largest energy gap so far known over which such a mechanism can operate, the upper limit above for  $b_5(G)$  is probably too high and might more realistically be 6  $\text{kJ mol}^{-1}$  above  $D_0^0(\text{NO})$ . In this event the  $b_v$  energy levels are now located to within an uncertainty of 3  $\text{kJ mol}^{-1}$  with respect to  $D_0^0(\text{NO})$ . The most recent spectroscopic measurement [20] places  $D_0^0(\text{NO}) = 626.0 \pm 0.1 \text{ kJ mol}^{-1}$  and is adopted in this paper.

#### 4.1. Vibrational level renumbering scheme

There is a need for reconsideration of the vibrational level numbering scheme in  $\text{NO}(b)$  arising from difficulties in explaining how  $\text{NO}(B)$  levels are populated. Brook and Kaplan's assignment would place  $b_0(\text{BK})$  close in energy to  $B_3$ . Gilmore's numbering scheme would place  $b_0(G)$  approximately midway between  $B_1$  and  $B_2$ . In neither case is there an apparently easy route for population of  $B_0$  on the basis that almost isoenergetic crossing processes are liable to be the most efficient. The large relative population of  $B_0$  in Table 1 might suggest on this basis that crossing to  $B_0$  involved the least conversion of energy into other forms. This postulation leads to a consideration of whether the true  $b_0$  might lie one vibrational spacing again below  $b_0(G)$ , in which case the mechanism for population of  $B_0$  would be much more obvious. This proposal then requires that the Ogawa  $v'$  numbering scheme be revised so that  $v' = v'(G) + 1 = v'(\text{BK}) + 2$ . Such a revised assignment of

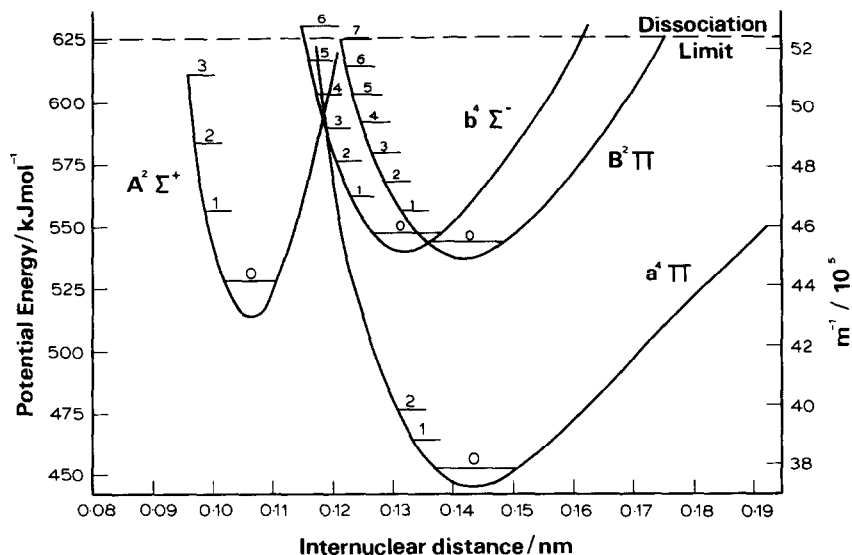


Fig. 1. Potential energy curves of excited states of NO below the first dissociation limit showing the relocation of the  $b^4\Sigma^-$  state.

observed bands is shown in column 3 of Table 3. The potential energy curves would then appear as shown in Fig. 1 (see the Appendix for the calculation of the a and b state curves and Table A1 for the parameters used). It must now be shown that the renumbering scheme for the Ogawa bands is reasonable on spectroscopic grounds.

#### 4.2. Comparison of predicted and observed Ogawa band intensities

It was by comparison of band intensities (estimated by eye from the published spectra) that Gilmore [4] concluded that Brook and Kaplan's numbering scheme was incorrect. The relative intensities of some of these bands were measured recently in this laboratory using a quantitative photoelectric method [3] and the relative intensities are shown in Table 3.

A major factor determining the relative intensities of the Ogawa bands would be expected to be the Franck-Condon overlap between the b state upper vibrational level and the a state lower vibrational level. For Ogawa bands up to  $v', v'' = 3$ (BK) Franck-Condon factors have been calculated by Nicholls [21] using the parameters indicated in Table A1. This table shows that the parameters vary by a few per cent depending on the numbering scheme adopted, but Nicholls' values of the Franck-Condon factors should not be too sensitive to these small differences and are used here to compare the predicted intensity variations between bands with those actually observed. For  $v' > 3$  there are no available calculated Franck-Condon factors; however, without resorting to a full calculation, the order of intensity for bands with the same value of  $v'$  but varying  $v''$  ( $v'' > 0$ ) can be predicted by comparison of values of  $\Delta r$  given by

$$\Delta r = r_{\max}(b_v) - r_{\max}(a_{v'})$$

where the  $r_{\max}$  are the classical turning points on the outer limbs of the potential energy curves. It is in the vicinity and on the same side of the classical outer turning points that the vibrational wavefunctions of levels with  $v'$  or  $v''$  greater than zero have their maximum amplitude. There is in general an intensity maximum for those transitions in which the  $r_{\max}$  of the lower state lies vertically below the  $r_{\max}$  for the upper state [22, 23] (evidently a reflection of the Franck-Condon principle). Only  $r_{\max}$  criteria are important (not  $r_{\min}$ , the inner turning point) for the Ogawa bands concerned here (see Fig. 1).

Therefore, depending on the value of  $v'$ , either Nicholls' table or the  $\Delta r$  value has been used to predict the expected order of band intensities. The order is set out in Table 4 for each numbering scheme and compared with available measured relative intensities  $I$ . Since the  $b_v$  levels are not necessarily equally populated, it is only possible strictly to compare bands originating from the same  $v'$ .

According to the BK scheme only the bands (3,1) and (3,2) with (2,0) and (2,1) can be considered. There is evidently no correspondence between predicted and observed orders of intensity. Using the Gilmore scheme the above bands are reassigned as (4,1), (4,2), (3,0) and (3,1) respectively, while in our revised scheme they become (5,1), (5,2), (4,0) and (4,1) respectively. It can be seen in the table that correspondence between predicted and observed orders of intensity is strongest for the revised numbering scheme. If there are no sharp population differences between the adjacent  $b$  levels concerned here, the (4,1) (R) (R = revised) band is actually predicted to show the intensity maximum observed [3].

If the  $b_v$  (R) scheme is correct, then the as yet unseen (0,0) and (1,0) (R) bands would be expected to appear in the regions of 1263 nm and 1094 nm respectively, little examined as yet. Kley [18] has a poorly resolved and low intensity spectrum extending to about 1100 nm, taken at low pressure, in which an unresolved and unidentified NO band system is seen near 1100 nm. The critical region is difficult to study and the (0,0) (R) band may be obscured by the  $\text{NO}(C^2\Pi-A^2\Sigma^+)$  band centred on 1223 nm [24] unless the resolution is very high. Moreover, it is possible that  $b_0$  and  $b_1$  (R) are relatively weakly populated in view of the increased separation of the  $a$  and  $b$  potential curves at lower energies (Fig. 1).

It is concluded that the R assignment of the Ogawa bands fits the spectroscopic data better than the BK or G schemes. Henceforth only the R assignments are referred to unless otherwise indicated.

## 5. The mechanism of $\beta$ band excitation

The main factors which would be expected to determine the rate of collision-induced crossing between potential energy curves are (i) spin



TABLE 4  
Comparison of measured relative intensities  $I$  for Ogawa bands for the different ( $\nu'$ ,  $\nu''$ ) assignments

Column 1 (BK)			Column 2 (G)			Column 3 (R)			
Band	FC	$I$	Band	FC	$\Delta r$ (nm)	$I$	Band	$\Delta r$ (nm)	$I$
1,0	0.415	0.65	4,1*		$-4 \times 10^{-4}$	0.28	4,1 <sup>†</sup>	$-8 \times 10^{-4}$	1.00
3,1*	0.334	0.28	3,1 <sup>†</sup>	0.334	$-4 \times 10^{-3}$	1.00	3,0	$+>1.9 \times 10^{-3}$	0.65
2,0 <sup>†</sup>	0.254	0.25	2,0	0.254		0.65	5,2*	$-2.6 \times 10^{-3}$	0.47
2,1 <sup>†</sup>	0.137	1.00	4,2*		$-5.6 \times 10^{-3}$	0.47	5,1*	$+2.6 \times 10^{-3}$	0.28
3,2*	0.004	0.47	5,3		$-6.6 \times 10^{-3}$	$\sim 0.15$	6,3	$-3.7 \times 10^{-3}$	$\sim 0.15$
4,3		$\sim 0.15$	3,0 <sup>†</sup>	0.071		0.25	4,0 <sup>†</sup>	$<5.6 \times 10^{-3}$	0.25

The bands are listed in order of expected decreasing intensity.

\* <sup>†</sup>, Comparable pairs. FC, Franck-Condon factor.  $\Delta r$ , see text.

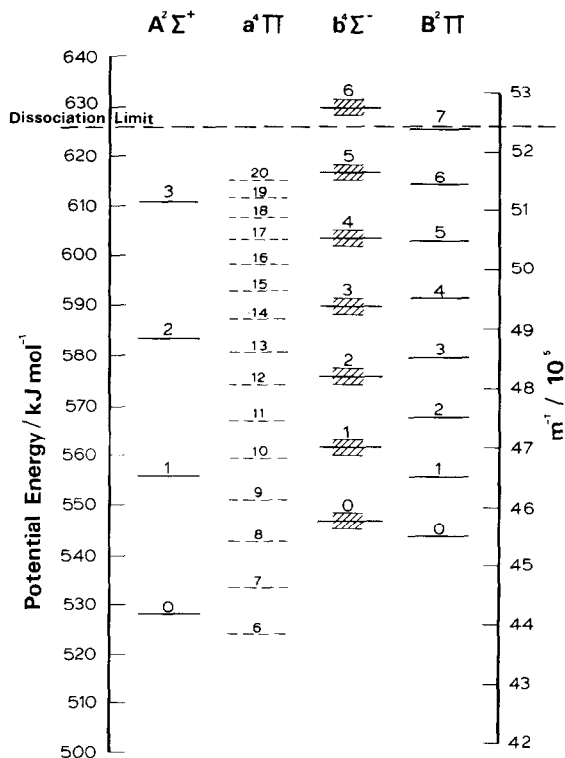


Fig. 2. Energy level diagram showing rotationless vibrational levels in the  $a^4\Pi$  and  $b^4\Sigma^-$  states in relation to those in the  $B^2\Pi$  state. The broad banding shown for  $b^4\Sigma^-$  levels indicates the uncertainty ( $\pm 1.5 \text{ kJ mol}^{-1}$ ) in their position. Levels in the  $a^4\Pi$  state (broken lines) are tied to the b state to within  $\pm 0.7 \text{ kJ mol}^{-1}$ .

conservation, (ii) the degree of wavefunction overlap (henceforth referred to as Franck–Condon overlap since similar principles appear to apply here as for optical transitions) and (iii) the modulus of the energy defect  $|\Delta E|$ , which is the magnitude of the energy gap between the lowest rotational level of the vibrational level of the initial state and that of the vibrational level of the product state.

Figure 2 shows the energetic location of the vibrational levels of excited states of NO. It is clear that all the  $b_v$  levels lie sufficiently close to the  $a_v$  levels for almost isoenergetic  $a \rightarrow b$  crossing to occur (the  $a_v$  levels are anchored to the  $b_v$  levels to within  $\pm 0.73 \text{ kJ mol}^{-1}$ ; see the Appendix). In addition this transition satisfies spin conservation (whereas both  $a \rightarrow B$  and  $b \rightarrow B$  are spin forbidden transitions). Therefore, since no substantial change in internuclear separation is required either, it seems reasonable to regard  $a \leftrightarrow b$  crossing as a non-determining factor for  $\beta$  band intensities. In fact our studies [5] of the quenching behaviour of  $\beta$  band emission from  $B_0$  showed that  $\text{H}_2\text{O}$  did not lead to a significantly increased rate of removal of precursor(s) compared with nitrogen, which implies that the main process

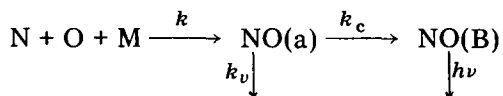
TABLE 5

Energy defects  $|\Delta E|$ , relative population  $[B_v]$  and temperature coefficient indices  $n_v$  for levels of  $\text{NO}(B^2\Pi)$

Crossing $b_{v'} \rightarrow B_v$ $v' \quad v''$	Mean $\Delta E$ ( $\text{kJ mol}^{-1}$ )	$[B_v]$	$-n_v$
2 $\rightarrow$ 3	+3.3	0.2	1.6
2 $\rightarrow$ 2	-8.0	0.09	0.18
1 $\rightarrow$ 2	+5.4		
1 $\rightarrow$ 1	-6.7	0.09	0.15
0 $\rightarrow$ 1	+8.8		
0 $\rightarrow$ 0	-2.9	1.0	1.5

concerned has a non-specific dependence on  $M$ . This can only be the reverse  $b \rightarrow a$  crossing, as opposed to other quenching mechanisms involving larger amounts of energy. This is also consistent with the  $\text{H}_2\text{O}/\text{N}_2$  quenching behaviour observed for emission from  $b_3(\text{R})$ , the lowest level observed in our study of Ogawa band chemiluminescence [3].

Clearly  $b \rightarrow B$  crossing does occur, violating spin conservation, and in Fig. 2 we see that the  $|\Delta E|$  criterion is of potentially much more significance. It can be seen in Figs. 1 and 2 that  $b_0$  is now the logical precursor of  $B_0$  only, with a good overlap of the wavefunctions. At the same time  $b_1$  is likely to be the common direct precursor of  $B_1$  and  $B_2$ , while  $b_2$  will populate  $B_3$ . Table 5 shows the  $\Delta E$  quantities calculated using the mean  $b_v$  energies within the remaining uncertainty of  $\pm 1.5 \text{ kJ mol}^{-1}$  in their location in comparison with relative populations of  $B_v$  and the temperature coefficients of the corresponding  $\beta$  bands. There appears to be a reasonably good correlation. Population of  $B_0$  and  $B_3$  appears to involve a  $|\Delta E| \approx 3 \text{ kJ mol}^{-1}$  and these levels have the highest populations and sharpest temperature coefficients. It is notable perhaps that average kinetic energies of molecules approach  $3 \text{ kJ mol}^{-1}$  at the temperatures 196 and 269 K used in our studies of  $\beta$  band chemiluminescence so that there should be little difficulty in effecting any energy conversion. The factor of approximately 5 between the populations of  $B_0$  and  $B_3$  may reflect a better wavefunction overlap for  $b_0$  with  $B_0$ . However, for  $B_1$  and  $B_2$  the  $|\Delta E|$  is about  $6 \text{ kJ mol}^{-1}$  and this sort of energy defect is well above the average kinetic energy. Accordingly it seems not unreasonable to regard these crossings as more difficult to accomplish and the possible consequence, indicated by the lesser negative temperature coefficients, is that a small activation energy applies to the corresponding  $b \rightarrow B$  crossing rate constants. Within the  $\pm 1.5 \text{ kJ mol}^{-1}$  uncertainty  $|\Delta E|$  can be the same (but of opposite sign) for  $b_1 \rightarrow B_1$  and  $b_1 \rightarrow B_2$  which could explain the near identical populations and temperature coefficients. On the basis of the simple mechanism



the combination of rate constants  $kk_c/k_v$ , can be shown to govern the population of NO(B) and the temperature coefficient of  $\beta$  band emission. Thus  $E_{\text{obs}} = E - E_v + E_c$  where  $E_{\text{obs}}$  is the observed activation energy for  $\beta$  band emission and  $\exp(-E_{\text{obs}}/RT) \approx T^{-n_v}$ . Thus if the activation energy for the  $b \rightarrow B$  crossing process is positive, the corresponding  $n_v$  will be lower.

### 5.1. Population of levels above $B_3$

The potential curves of Fig. 1 show the inner limbs of the a and b states to be almost equidistant from the B state potential curve at and above  $B_3$ . Nevertheless because the vibrational quantum numbers of the b state are much lower than those of the a state the Franck-Condon overlaps will remain more favourable for  $b \rightarrow B$  crossings. Moreover, above  $B_3$  the  $b_v$  energy levels move into closer resonance with the  $B_v$  levels. It is then surprising that there should be a dramatic decrease in population of  $B_4$  and  $B_5$  compared with the lower levels.

The explanation may be indicated by the quenching behaviour of  $B_3$  bands. Of the lowest four B levels,  $B_3$  was the only one seen to be quenched by nitrogen over the pressure range investigated [5]. Since states below  $B_5$  have insufficient energy to excite  $N_2(X^1\Sigma_g^+)$  to  $N_2(A^3\Sigma_u^+)$ , the only feasible mechanism was argued to be reverse crossing back into the b state from  $B_3$  [5]. The  $B_3$  level is the lowest one for which such a collisional process becomes relatively easy on the basis of a low energy defect to  $b_2$ . Since  $b_0$  lies 2–3  $\text{kJ mol}^{-1}$  above  $B_0$  with no b level below and  $B_1$  and  $B_2$  are substantially separated from  $b_1$  and  $b_0$ , these reverse crossings appear less likely, in line with the experimental evidence. Figure 2 makes it particularly clear that reverse crossings for  $B_4$  and  $B_5$  are near-resonance processes and accordingly would be expected to be fast. At the same time it can be noted in Fig. 1 that the a state inner limb actually lies closer to that of the B state above  $B_3$  than does that of b. The relatively high density of a state levels may also then promote both forward and reverse crossings, with emphasis on the latter in the light of the low intensities of corresponding  $\beta$  bands. This argument then predicts that the intensities of  $\beta$  bands emanating from  $B_4$  and  $B_5$  should be substantially pressure independent for the pressure range concerned since these levels must be removed more efficiently by collisional processes than  $B_3$  in order to account for their very low intensities. However, there is no reliable experimental evidence as yet with which to compare this prediction. Taking the overall view, it would seem that the reverse crossing processes  $B \rightarrow b(a)$  must be more sensitive to energy defect considerations than the forward  $b \rightarrow B$  processes.

## 6. Conclusion

We have set out evidence favouring a reassignment of the vibrational numbering scheme for NO( $b^4\Sigma^-$ ) with respect to that currently accepted. The revised NO( $b^4\Sigma^-$ ) potential energy levels are shown to be consistent

with both spectroscopic evidence and the mechanism for population of  $\text{NO}(B^2\Pi)$  levels in the nitric oxide afterglow.

## References

- 1 R. A. Young and R. L. Sharpless, *Discuss. Faraday Soc.*, **33** (1962) 228.
- 2 R. A. Young and R. L. Sharpless, *J. Chem. Phys.*, **39** (1963) 1071.
- 3 I. M. Campbell and R. S. Mason, *J. Photochem.*, **5** (1976) 383.
- 4 F. R. Gilmore, *J. Quant. Spectrosc. Radiat. Transfer*, **5** (1965) 369.
- 5 I. M. Campbell and R. S. Mason, *J. Photochem.*, **8** (1978) 321.
- 6 I. M. Campbell and S. B. Neal, *Discuss. Faraday Soc.*, **53** (1972) 72.
- 7 M. Jeunehomme and A. B. F. Duncan, *J. Chem. Phys.*, **41** (1964) 1692.
- 8 I. M. Campbell and C. N. Gray, *Chem. Phys. Lett.*, **18** (1973) 607.
- 9 I. M. Campbell and B. A. Thrush, *Proc. R. Soc. London, Ser. A*, **296** (1967) 222.
- 10 I. M. Campbell, S. B. Neal, M. F. Golde and B. A. Thrush, *Chem. Phys. Lett.*, **8** (1971) 612.
- 11 I. M. Campbell and R. S. Mason, to be published.
- 12 H. P. Broida and M. Peyron, *J. Chem. Phys.*, **32** (1960) 1068.
- 13 R. W. F. Gross and N. Cohen, *J. Chem. Phys.*, **48** (1968) 2582.
- 14 A. B. Callear and J. D. Lambert, in C. H. Bamford and C. F. H. Tipper (eds.), *Formation and Decay of Excited Species, Comprehensive Chemical Kinetics*, Vol. 3, Elsevier, Amsterdam, 1969, p. 182.
- 15 J. Billingsley and A. B. Callear, *Trans. Faraday Soc.*, **67** (1971) 257.
- 16 R. L. Taylor, *Can. J. Chem.*, **52** (1974) 436.
- 17 M. Brook and J. Kaplan, *Phys. Rev.*, **96** (1954) 1540.
- 18 D. Kley, *Habilitationschrift, Univ. Bonn, Bonn*, 1973.
- 19 K. H. Becker, W. Groth, P. Harteck and D. Kley, *Forschungsbericht SHA/1, Inst. Phys. Chem., Univ. Bonn*, 1968.
- 20 A. B. Callear and M. J. Pilling, *Trans. Faraday Soc.*, **66** (1970) 1618.  
T. W. Dingle, P. A. Freedman, B. Gelernt, W. Jones and I. W. M. Smith, *Chem. Phys.*, **8** (1975) 171.
- 21 R. W. Nicholls, *J. Res. Nat. Bur. Stand., Sect. A*, **68** (1964) 535.
- 22 G. Herzberg, *Spectra of Diatomic Molecules* (2nd edn.), Van Nostrand, New York, 1950.
- 23 R. W. Nicholls, *J. Res. Nat. Bur. Stand., Sect. A*, **65** (1961) 451.
- 24 W. Groth, D. Kley and U. Schurath, *J. Quant. Spectrosc. Radiat. Transfer*, **11** (1971) 1475.
- 25 A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, Chapman and Hall, London, 1968.
- 26 J. T. Vanderslice, E. A. Mason and W. G. Maisch, *J. Chem. Phys.*, **31** (1959) 738.
- 27 M. Ogawa, *Sci. Light* (Tokyo), **3** (1954) 39.

## Appendix

### *Calculation of $\text{NO}(b^4\Sigma^-)$ and $(a^4\Pi)$ potential energy curves*

#### *A1. The $b^4\Sigma^-$ state*

Conventionally the term values  $G(v)$  referred to the potential energy minimum are given by the expression [22, 25]

TABLE A1  
Spectroscopic parameters for NO quartet states

State	$\omega_e$ (m <sup>-1</sup> )	$x_e\omega_e$ (m <sup>-1</sup> )	$B_e$ (m <sup>-1</sup> )	$r_e$ (nm)	$D_e$ (kJ mol <sup>-1</sup> )
b <sup>4</sup> Σ <sup>-</sup>					
Revised	125 700	1410	128.729 <sup>a</sup>	0.132	275.6 ± 1.6
Gilmore [4]	122 900	1410			258.4 ± 1.6
Brook and Kaplan [18]	120 100	1410			246.2 ± 1.5
Nicholls [22]	116 800	1330	133.5	0.130	
a <sup>4</sup> Π <sup>b</sup>	101 800	1230	110.466	0.1425	179.4 ± 2.4

<sup>a</sup>Taken from O<sub>2</sub><sup>+</sup> data [26]. Reduced mass  $\mu_{\text{NO}} = 7.469785$ .

<sup>b</sup>For the a<sup>4</sup>Π state the anharmonicity constants were also determined:  $y_e\omega_e = -39$  m<sup>-1</sup>;  $z_e\omega_e = 0.745$  m<sup>-1</sup>.

$$G(v) = \left(v + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right)^2 x_e \omega_e + \left(v + \frac{1}{2}\right)^3 y_e \omega_e - \left(v + \frac{1}{2}\right)^4 z_e \omega_e$$

where  $hG(v)$  is the energy of the rotationless vibrational level,  $\omega_e$  is the fundamental vibrational frequency and  $x_e \gg y_e \gg z_e$  are the anharmonicity constants.

The Morse function  $U(r - r_e)$  for the potential energy as a function of internuclear separation  $r$  is [25]

$$U(r - r_e) = D_e \{1 - \exp(-2\beta\xi)\}^2$$

where  $\xi = (r - r_e)/r_e$  and  $\beta = \omega_e/4(B_e D_e)^{1/2}$ ,  $D_e$  is the dissociation limit referred to the curve minimum,  $B_e$  is the equilibrium rotational constant and  $r_e$  is the equilibrium internuclear separation given by the relation

$$r_e = \left(\frac{h}{8\pi^2 c \mu B_e}\right)^{1/2} = 4.0909 \times 10^{-10} (B_e \mu)^{-1/2} \text{ m}^{-1}$$

However,  $B_e$  is unknown because the Ogawa bands have never been seen with sufficiently high resolution for rotational analysis. As before [4, 25], however, the  $B_e$  value of the isoelectronic species O<sub>2</sub><sup>+</sup>(b<sup>4</sup>Σ<sup>-</sup>) has been adopted; the error introduced by this approximation should be less than 1% in view of the close similarity of the spectroscopic parameters for other corresponding states of O<sub>2</sub><sup>+</sup> and NO [26].

NO(b<sup>4</sup>Σ<sup>-</sup>) correlates with N(<sup>4</sup>S) + O(<sup>1</sup>D) so that  $D_e$  is determined by the location of b<sub>5</sub>(R), which is known to lie  $8.5 \pm 1.5$  kJ mol<sup>-1</sup> below  $D_0^0(\text{NO})$ , combined with the excitation energy of the O(<sup>1</sup>D) atom with respect to O(<sup>3</sup>P) (189.63 kJ mol<sup>-1</sup>). The average values of  $\omega_e$  and  $\omega_e x_e$  (terms above quadratic are insignificant) were re-estimated from the papers of Ogawa [27] and of Brook and Kaplan [17] since  $\omega_e$  will depend on the numbering scheme adopted for the Ogawa bands.

The potential energy curve parameters are summarized in Table A1 which includes the values obtained using the Brook and Kaplan [17] and the Gilmore [4] numbering schemes for comparison. The values adopted by Nicholls [21] in calculating the Franck-Condon factors are also shown.

#### A2. The $a^4\Pi$ state

The  $G(v)$  formula and the Morse function expression given above are used to calculate the potential curve of  $a^4\Pi$ , using the cubic and quartic terms of  $G(v)$  for the higher levels. The value of  $x_e\omega_e$  was estimated from the analysis of the Ogawa bands as above; however, it was necessary to use an iterative fitting procedure to find the pair of lowest values of  $y_e\omega_e$  and  $z_e\omega_e$  which caused the levels to converge at the dissociation limit. The resultant parameters shown in Table A1 converge to zero at  $a_{33}$ , giving  $D_e = 179.4$   $\text{kJ mol}^{-1}$ .

The location of the  $a^4\Pi$  curve minimum is tied to the  $b^4\Sigma^-$  state using the wavelengths of the Ogawa bands. However, since the position of the origin within the band is not known, there is an uncertainty of  $\pm 0.7$   $\text{kJ mol}^{-1}$  (the average spread of the (4,0) (R) band at about 790 nm). The  $a^4\Pi$  curve minimum is therefore located at  $452.9 \pm 2.4$   $\text{kJ mol}^{-1}$  above  $\text{NO}(X^2\Pi)v = 0$ . This is within the error limit of the value determined from the  $a \rightarrow X$  bands observed in a solid argon matrix [12]. These all emanate from  $a_0$  down to different  $v''$ . The highest band intensity will occur for the  $v''$  level for which the outer turning point lies nearest to vertically below the minimum  $r_e(a)$  in the  $a$  state curve. Our calculations yield  $r_e(a) = 0.1425$  nm which leads to a prediction that the (0,8) band should be the most intense since  $r_{\text{max}}$  for  $X^2\Pi v'' = 8$  is  $0.1425$  nm ( $\Omega = \frac{1}{2}$ ) and  $0.1410$  nm ( $\Omega = \frac{3}{2}$ ) [26]. In line with this prediction, Fig. 2 of ref. 12 shows that the (0,8) band is apparently the most intense.