

THE KINETICS OF OGAWA BAND CHEMILUMINESCENCE IN THE NITRIC OXIDE AFTERGLOW

I. M. CAMPBELL and R. S. MASON

School of Chemistry, University of Leeds, Leeds LS2 9JT (Gt. Britain)

(Received March 8, 1976)

Summary

Nitric oxide Ogawa band chemiluminescences emanating from $\text{NO}(\text{b}^4\Sigma^-) v' = 4, 3$ and 2 , associated with combining $\text{N}(^4\text{S})$ and $\text{O}(^3\text{P})$ atoms in a discharge flow system, have been detected photoelectrically. In N_2 carrier the intensities ($I_{v'}$) followed relationships $I_{v'} = k_{v'}[\text{N}][\text{O}]$ with $k_{v'}$ independent of $[\text{N}_2]$ in the range $(4 - 15) \times 10^{-5} \text{ mol/dm}^3$ at both 195 K and 298 K. The temperature coefficients of $k_{v'}$, expressed as $T^{-n_{v'}}$, were $n_3 = 1.8 \pm 0.4$, $n_2 = 1.5 \pm 0.8$ and $n_3 - n_4 = 0.62 \pm 0.20$. Addition of Ar ($\leq 76\%$) had no effect upon $k_{v'}$ but distinct quenching of k_3 and k_2 occurred when N_2 was partly replaced with CO_2 , N_2O and H_2O ($\leq 46\%$). On the simplest basis CO_2 was about twice, N_2O about four times and H_2O about six times as effective as N_2 in removing $\text{NO}(\text{b}^4\Sigma^-) v' = 2, 3$. Only with H_2O was any quenching detected for k_4 and that ~ 3 times less than for k_3 .

The results for $v' = 4$ were interpreted in terms of the lowest rotational level being within 5 to 10 kJ/mol of the first dissociation limit of NO, so that preassociation/predissociation operates in the mechanism.

Absolute intensity measurements gave $I/\text{photons dm}^{-3} \text{ s}^{-1} = 1.4 \times 10^3$ ($[\text{N}][\text{O}]/\text{mol}^2/\text{dm}^6$) for the bands observed between 700 and 1000 nm. A lower radiative lifetime limit of $6 \times 10^{-6} \text{ s}$ is deduced for $v' = 3$ on the basis of a mechanism where depopulation is dominated by collisional removal and quenching in mixed carriers.

Introduction

The combination of $\text{N}(^4\text{S})$ and $\text{O}(^3\text{P})$ atoms in the gas phase gives rise to several associated chemiluminescent emissions. Nitric oxide $\beta(\text{B}^2\Pi \rightarrow \text{X}^2\Pi)$, $\gamma(\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi)$ and $\delta(\text{C}^2\Pi \rightarrow \text{X}^2\Pi)$ bands appear in the ultra-violet region of the spectrum (above 190 nm wavelength), with the

extension of β bands into the visible giving rise to the characteristic blue-violet afterglow. In each system only vibrational levels of the electronically excited states below the first dissociation limit of NO (627.2 kJ/mol) are populated. The kinetics of these ultra-violet emissions have received considerable study and it is generally accepted that intermediate quartet states, $\text{NO}(a^4\Pi)$ and $\text{NO}(b^4\Sigma^-)$, are involved in the mechanism [1, 2]. However, there is little information on the kinetics governing the populations of these quartet states in the afterglow.

The only gas phase chemiluminescence involving the quartet states is the Ogawa band system [$\text{NO}(b^4\Sigma^- \rightarrow a^4\Pi)$] appearing in the near infra-red region of the spectrum. Most studies of this emission have been performed with detection by photographic plates [3 - 5]. Ogawa [4] observed bands in the region of 780 nm and 860 nm, which were relatively strong, together with a very weak structure in the vicinity of 720 nm. The bands were six headed. In a subsequent study Brook and Kaplan [5] found additional bands around 960 nm and compiled a Deslandres table listing the wavelengths of prominent band heads. In all, seven bands were detected and a vibrational numbering scheme was proposed. Gilmore [6] drew on the expected similarity to the spectroscopic parameters available for the equivalent ($b^4\Sigma^-$) state of the iso-electronic species O_2^+ . As a result he proposed that Brook and Kaplan's numbering of vibrational levels of $\text{NO}(b^4\Sigma^-)$ be increased by one. On this basis the Ogawa bands detected emanated from $\text{NO}(b^4\Sigma^-) v' = 4, 3, 2, 1$. Young and Sharpless [1] have claimed photoelectric detection of Ogawa band emission intensities in a discharge flow afterglow system but did not identify the bands concerned.

The potential energy curves for the quartet states of NO drawn by Gilmore [6] are ascribed uncertainties of ≤ 19 kJ/mol (≤ 0.2 eV). The problem arises because the rotational structure of bands corresponding to transitions involving these states have not been analyzed and because no spectrum corresponding to the forbidden transition $\text{NO}(a^4\Pi \rightarrow X^2\Pi)$ has ever been detected in the gas phase. An indication of the energetic location of $\text{NO}(a^4\Pi)$ levels relative to $\text{NO}(X^2\Pi) v = 0$ has been provided by the observation of the transition in emission when NO, frozen down in argon or krypton matrices, was excited by X-rays [7]. However, the wavelength location of the bands (appearing between 220 and 260 nm) varied by some 0.5 nm between the two matrices; at the same time the NO β band excited with a head at 220.6 nm in the argon matrix was displaced upwards by 0.8 nm compared to the same band in the gas phase afterglow. Accordingly this solid environment work cannot provide an accurate excitation energy for $\text{NO}(a^4\Pi)$ as a gas phase species, thus adding to the uncertainty in the excitation energies of $\text{NO}(b^4\Sigma^-)$ levels. The identification of population routes for the NO β band chemiluminescence in particular has been hindered by the energetic uncertainty attaching to the likely precursors [2].

We report here upon the first resolved photoelectric detection of the stronger Ogawa bands. We also present kinetic evidence on the energetic

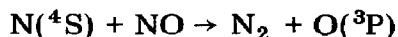
location of $\text{NO}(b^4\Sigma^-)$ vibrational levels, together with a lower limit for the radiative lifetime of $v' = 3$.

Experimental

The work was performed in a discharge flow system similar to that described by Campbell and Neal [2] in a study of the ultra-violet chemiluminescences. Accordingly only significant differences will be pointed up in detail.

$\text{N}(^4\text{S})$ atoms were produced by microwave discharging of N_2 with flowrates between 100 and 1000 $\mu\text{mol/s}$ and total pressures in the range 0.1 to 1.6 kN/m^2 . Under typical conditions a flowtime of about 0.1 s elapsed between the discharge region and the observation tube, sufficient to ensure the decay of electronically excited species generated therein. Potential heating effects in the observation tube resulting from the presence of vibrationally excited N_2 were eliminated by addition of a small flow of CO_2 just below the discharge region. This procedure is sufficiently effective [8] for the temperature of the gas in the observation tube to be taken as that of the walls.

Prior to the entry throat of the Pyrex glass observation tube (0.3 m long \times 22 mm i.d.) the N atoms could be partly titrated with NO added through a pepper-pot jet. The familiar fast titration reaction:



then produces a controlled mixture of $\text{N}(^4\text{S})$ and $\text{O}(^3\text{P})$ atoms in the observation tube. In experiments involving mixed carrier gases (Ar , CO_2 , N_2O , $\text{H}_2\text{O} + \text{N}_2$) the other gases were added to the flowing N_2 through a sidearm upstream of the pepper-pot jet. The methods of flowrate measurement and purification were as described before [2, 9]. For experiments at 195 K the observation tube was surrounded by a tank filled with finely crushed Cardice.

It was important that decays of atomic concentrations down the observation tube should be insignificant. The achievement of this condition was established using a secondary titration jet located at the exit throat. The above titration reaction, coupled with photometric measurements of the N_2 First Positive (1+) and $\text{NO } \beta$ band intensities, using an R.C.A. 1P28 photomultiplier fitted in turn with Wratten 22 and Chance OV1 filters, yielded concentrations of atoms in both entry and exit tubes as before [2]. Decays of $\leq 5\%$ were regarded as tolerable, a condition achieved by adjustment of total flowrates.

Chemiluminescent emission intensities were measured along the axis of the observation tube from both ends. At the upstream end the light passed through an evacuated chamber between a double Pyrex window, was collimated by passage through a bundle of uniform bore stainless-steel tubes (80 mm long \times 1.5 mm i.d.) coated with camera black

and finally passed through a filter assembly before impinging upon the photocathode of an E.M.I. 6256 B photomultiplier. $N_2(1+)$ intensity ($\propto [N]^2$ [10]) was isolated using a Wratten 22 filter. The photomultiplier output was displayed as a deflection on a Pye Scalamp galvanometer. The nitric oxide titration procedure [10] then allowed this signal to be calibrated as a direct measure of $[N]^2$ and hence $[N]$ in the observation tube.

At the downstream end of the observation tube the glowing gas was prevented from diffusing into the dead space between the exit throat and a Spectrosil quartz window using a ballast flow of CO_2 (<10% of the total flowrate) as described before [2]. After passage through this window the light was focused by a condensing lens onto the entry slit of the monochromator (McPherson Model 218). A Wratten 22 filter (lower wavelength transmission limit ~ 550 nm) was interposed between the lens and slit and absorbed NO chemiluminescence which, in second order reflection from the monochromator grating, would otherwise have overlapped the Ogawa bands in first order. This grating had 1200 grooves mm^{-1} and was blazed for 1000 nm. The light emerging from the exit slit entered a refrigerated photomultiplier chamber (Model TE-114, Products for Research, Inc.) cooled to ~ 170 K by liquid N_2 , before detection using an E.M.I. 9659 B photomultiplier tube (extended S-20). The double pane of Plexiglass at the entry to the chamber was electrically heated to prevent frosting. This photomultiplier output was displayed on a Honeywell Elektronik 194 potentiometric recorder.

Results

Detection of Ogawa bands

Figure 1 shows a slow scan over the regions $775 - 800$ nm and $835 - 880$ nm. The profile labelled (a) was obtained when the observation tube contained both N and O atoms while the profile (b) was produced under identical conditions with the same $[N]$ but in the absence of O atoms.

The Ogawa bands (4, 1), (3, 0), (4, 2), (3, 1) and (2, 0) are clearly developed over the background N_2 emissions. However, the weak structure near 725 nm detected by Ogawa [4] and corresponding to the (4, 0) band could not be observed, even though our detection system had its highest sensitivity in this region.

We also attempted to detect the (2, 1) and (1, 0) Ogawa bands found by Brook and Kaplan [5] in the $940 - 980$ nm region. Unfortunately our detection sensitivity fell by a factor of ~ 150 from 750 to 900 nm (see next section) mainly on account of the fall-off in response of the extended S-20 photocathode. Nevertheless, with slits opened up to $1000 \mu m$ and conditions adjusted to maximize afterglow intensities, we could detect the (3, 3) (~ 970 nm) and (2, 2) (~ 994 nm) $N_2(1+)$ bands, showing that our system retained some sensitivity out to 1000 nm. When

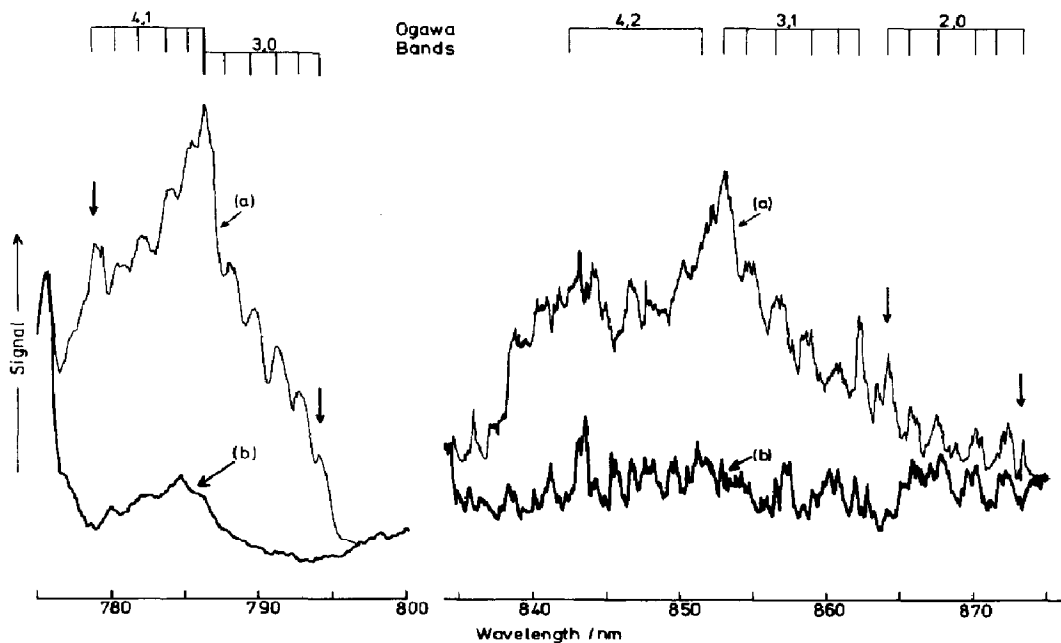


Fig. 1. Slow scan spectrum over the Ogawa bands at 298 K (a), superimposed on the background N_2 spectrum (b) for conditions of $[N_2] = 1 \times 10^{-4} \text{ mol/dm}^3$, $[N] = 1.9 \times 10^{-7} \text{ mol/dm}^3$ and for (a) $[O] = 1.3 \times 10^{-6} \text{ mol/dm}^3$.

the nitrogen afterglow was partly titrated with NO, these $N_2(1+)$ band intensities decreased without the appearance of any other features in this spectral region. To test the possibility that the (3, 3) $N_2(1+)$ band was masking the (1, 0) Ogawa band, the signal with the monochromator set to 970 nm (I_{970}) was measured as a function of $[N]$ in the presence of larger $[O]$. A plot of I_{970} versus $[N]^2$ gave a straight line. Within the random variations it was concluded that these Ogawa bands could have intensities no more than 10% of that of the observed (3, 3) $N_2(1+)$ band under the most favourable conditions which could be produced in our system.

Absolute band intensities

The sensitivity of our detection system as a function of wavelength was calibrated using the emission intensities of nitrogen afterglow bands in the range 750 - 900 nm in the absence of O atoms. Bayes and Kistiakowsky [11] have measured the relative $N_2(1+)$ band intensities under similar conditions. Thus a relative sensitivity factor, $F_\lambda = I_{BK} / I_M$, where I_{BK} is the relative intensity of a band given by Bayes and Kistiakowsky and I_M is the peak area on our chart paper measured with a radial planimeter, was obtained. The areas between matched slow scans of types (a) and (b) shown in Fig. 1 were measured and the areas of the Ogawa bands were converted to relative intensities by multiplying by the average F_λ within the wavelength spread of each band. One problem

TABLE 1

Values of k_L for Ogawa bands at 298 K in N_2 carrier

Band (ν' , ν'')	(4, 1)	(3, 0)	(4, 2)	(3, 1)	(2, 0)	(2, 1) (1, 0)
k_L	80	85	308	634	280	≤ 80

evident in Fig. 1 is the overlap of adjacent bands under our relatively low resolution conditions compatible with obtaining measurable intensities. As a reasonable approximation for one such overlap situation, a vertical line was drawn midway between the known wavelengths [5] of the lowest head of the one band and the highest wavelength head of the other. Fortunately there is no instance where the heads of adjacent Ogawa bands cross over. Justification for this procedure is that the intensity fall-off at the edge of the outer heads is sharp; this may be seen on the right hand edge of the (3, 0) band and the left hand edge of the (4, 1) band in Fig. 1. Moreover we may anticipate Fig. 5 where the preferential quenching of the (3, 0) band by water vapour reveals clearly the sharp right hand edge of the (4, 1) band.

The relative intensities of the Ogawa bands were converted to absolute values on the basis of the absolute intensities measured by Campbell and Thrush [10] for $N_2(1+)$ emission in the nitrogen afterglow. Their result for the total intensity, $I(1+)$, expressed in photons $dm^{-3} s^{-1}$, was $I(1+) = 8 \times 10^3 [N]^2$, with $[N]$ expressed in mol/dm^3 . The absolute chemiluminescent rate coefficients for each Ogawa band, k_L , thus derived are shown in Table 1, where the intensity of each band in photons $dm^{-3} s^{-1}$ is expressed as $k_L [N][O]$, with the concentrations in mol/dm^3 . This form anticipates the total pressure independence of k_L values in N_2 carriers under our conditions, as shown in the next section. Upper limits are given in the Table for the (2, 1) and (1, 0) bands which could not be detected.

The total Ogawa band intensity detected here then gives a total chemiluminescent rate coefficient $\Sigma k_L \approx 1.4 \times 10^3$. This is then less than the comparable total chemiluminescent rate coefficient for the NO δ bands under the same conditions, given as $(9 \pm 2) \times 10^3$ in the same units [12].

Intensity variations in N_2 carriers

The relatively weak intensities of the Ogawa bands forced the use of slit widths of $400 \mu m$ to produce sufficiently large signals for kinetic measurements. We used the peak height at selected wavelengths as measures of the total band intensities; there were no indications of changes in band profiles over our range of conditions. Under these low resolution situations it was essential to ascertain that the signal at a chosen wavelength represented only one band and was not overlapped by the wing of another.

In experiments on the kinetics of emissions emanating from $\text{NO}(\text{b}^4\Sigma^-)$ $v' = 4$ and 3 (Gilmore's numbering scheme [6]), the signals with the monochromator set to 778.9 nm and 794.0 nm respectively were monitored. These are indicated by arrows in Fig. 1 and it can be seen that overlap is unlikely and that the variation of peak heights reflects the kinetics of $v' = 4$ and $v' = 3$ separately. On the other hand, for study of $v' = 2$ the signal at the preferred wavelength of 873.3 nm is very weak (arrowed in Fig. 1); accordingly under conditions involving higher degrees of quenching the stronger head at 864.1 nm was monitored as a supplement. This latter head is evidently more susceptible to interference by the wing of the adjacent $(3, 1)$ band. However, comparative experiments at these two $v' = 2$ wavelength settings under moderate quenching conditions revealed no significant differences in behaviour. But it is difficult to say whether or not the signal at 864.1 nm contains a component of the $(3, 1)$ band in view of the similarity of quenching effects on the emissions from $\text{NO}(\text{b}^4\Sigma^-)$ $v' = 3$ and 2 (see below).

Before a flow of NO was added at the pepper-pot jet, a weak nitrogen afterglow was established in the observation tube and a background signal, I_B , was measured at each of the selected wavelengths. A considerably stronger nitrogen afterglow was then partly titrated with NO to leave a residual $[\text{N}]$ the same as before. A signal I_m was measured at each monochromator setting. The Ogawa band intensity from a particular vibrational level, v' , of $\text{NO}(\text{b}^4\Sigma^-)$ is then measured by $I_{v'} = I_m - I_B$.

In N_2 carriers at both 298 K and 195 K, in experiments where total pressure and $[\text{N}]$ were kept constant but $[\text{O}]$ was varied in the range $(1 - 12) \times 10^{-7}$ mol/dm³, the ratios $I_{v'}/[\text{O}]$ showed only small random variations. In an intensive series of experiments where $[\text{N}]$, $[\text{O}]$ and $[\text{N}_2]$ were varied, the ratios $I_{v'}/[\text{N}][\text{O}]$ for each v' were constant to within 10% with no significant trend for $[\text{N}_2]$ variation. Typical results are shown in Fig. 2 in the form of plots of $[\text{N}][\text{O}]/I_{v'}$ versus $[\text{N}_2]^{-1}$; results for 195 K and 298 K are combined by dividing the former set by the established temperature enhancement factors for each v' , given below. Relationships of the form $I_{v'} = k_{v'}[\text{N}][\text{O}]$ summarize this behaviour, with each $k_{v'}$ constant for a given temperature. This is in accord with the observations of Young and Sharpless [1].

All the Ogawa bands showed negative temperature coefficients, *i.e.* the $k_{v'}$ were increased at 195 K compared to 298 K. It is assumed that $k_{v'}$ is proportional to $T^{-n_{v'}}$, where $n_{v'}$ is a constant for each $v' = 2, 3$ and 4 . k_2 was the most difficult to evaluate, since $I_{v'}$ had to be taken at $\lambda = 873.3$ nm to preclude any possibility of overlap by the $(3, 1)$ band; Fig. 1 shows the low sensitivity and consequent small signal which led to a substantial uncertainty in the value of n_2 . The result $n_2 = 1.5 \pm 0.8$ represents the best which could be achieved. More definitive results of $n_3 = 1.8 \pm 0.4$ and $n_4 = 1.2 \pm 0.4$ were obtained from the much stronger I_3 and I_4 signals. The apparent overlap potential of the error limits of these two indices is unreal, representing more systematic variation from

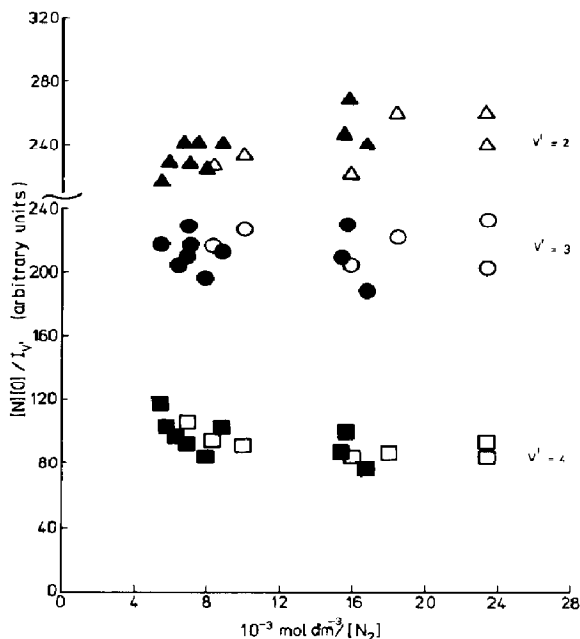


Fig. 2. Plots of $[N][O]/I_{v'}$ vs. $[N_2]^{-1}$ in pure N_2 carriers. \square , \circ and \triangle represent results for $v' = 4, 3$ and 2 respectively at 298 K . \blacksquare , \bullet and \blacktriangle represent results for $v' = 4, 3$ and 2 at 195 K , rendered comparable with the 298 K results using the established temperature coefficients for each v' .

one experiment to the next than random. In confirmation of this point, the ratios I_3/I_4 showed an index difference $n_3 - n_4 = 0.62 \pm 0.20$, showing clearly that k_4 had a distinctly smaller temperature coefficient than did k_3 . Attempts to treat I_2/I_3 similarly were inconclusive since the variation of this ratio was more random and could not exclude possible coincidences of n_2 with either of n_3 or n_4 .

Intensity variations in mixed carriers

When N_2 was replaced by up to 76% argon (the maximum consistent with measurable signals on account of dilution effects), no significant trends were found in any of the $k_{v'}$ parameters.

On the other hand, when CO_2 , N_2O or H_2O vapour were added in separate experiments, distinct decreases were found in k_3 and k_2 . However, only in the case of H_2O vapour was any effect on k_4 observed and that much reduced compared to the effects of H_2O vapour on k_2 and k_3 . These quenching effects are shown in Figs. 3 and 4, the former indicating that CO_2 effects are much the same at 195 K and 298 K . A Stern-Volmer form is adopted where $(k_{v'})_0/k_{v'}$ is plotted against mol fraction, $[Q]/[M]$, with $(k_{v'})_0$ the value in pure N_2 carrier and $Q = CO_2, N_2O$ or H_2O . The slopes of these Stern-Volmer type plots were constant within experimental error when $[M]$ was varied across the range $(0.6 - 2.5) \times 10^{-4}\text{ mol/dm}^3$, with the values listed in Table 2.

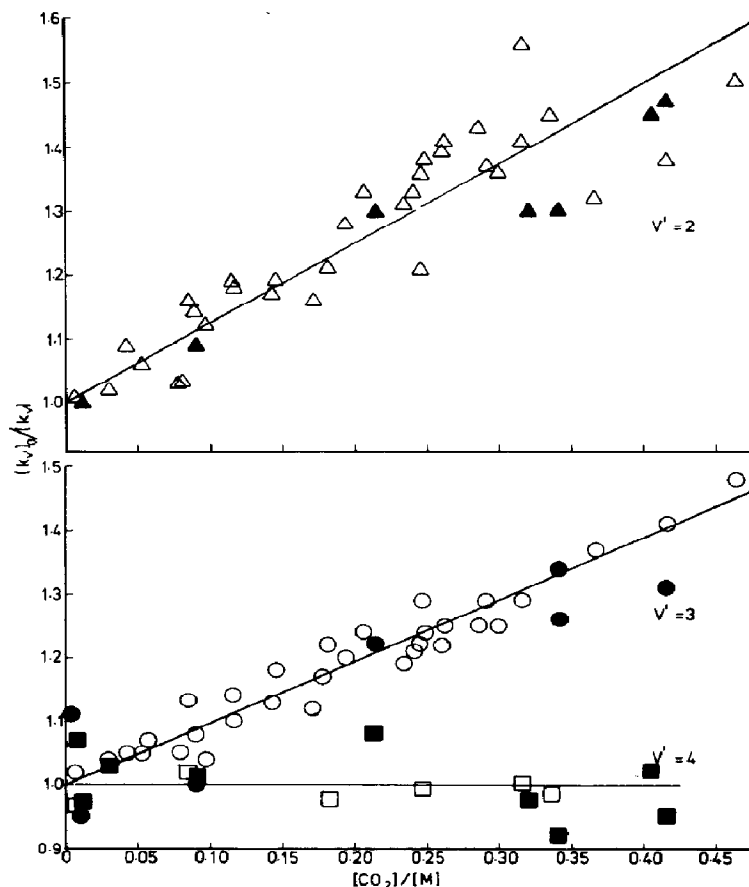


Fig. 3. Plots of $(k_{v'})_0/k_{v'}$ vs. mol fraction of CO_2 in N_2 carrier. \square , \circ and \triangle represent $v' = 4, 3$ and 2 respectively at 298 K ; \blacksquare , \bullet and \blacktriangle represent $v' = 4, 3$ and 2 respectively at 195 K .

TABLE 2

Slopes of $(k_{v'})_0/k_{v'}$ vs. $[Q]/[M]$ plots

Q	v'		
	4	3	2
CO_2	≤ 0.1	0.97 ± 0.07	1.25 ± 0.23
N_2O	≤ 0.3	2.4 ± 0.2	3.6 ± 0.4
H_2O	1.15 ± 0.15	5.5 ± 0.6	4.3 ± 0.7

Figure 5 shows a spectacular demonstration of the lower quenching susceptibility of emission from $v' = 4$ compared to $v' = 3$ with high mol fraction of H_2O vapour. The scans cover the band widths of the overlapping (4, 1) and (3, 0) bands. The profile labelled unquenched was obtained in pure N_2 carrier and shows the strong peak in the middle of the structure

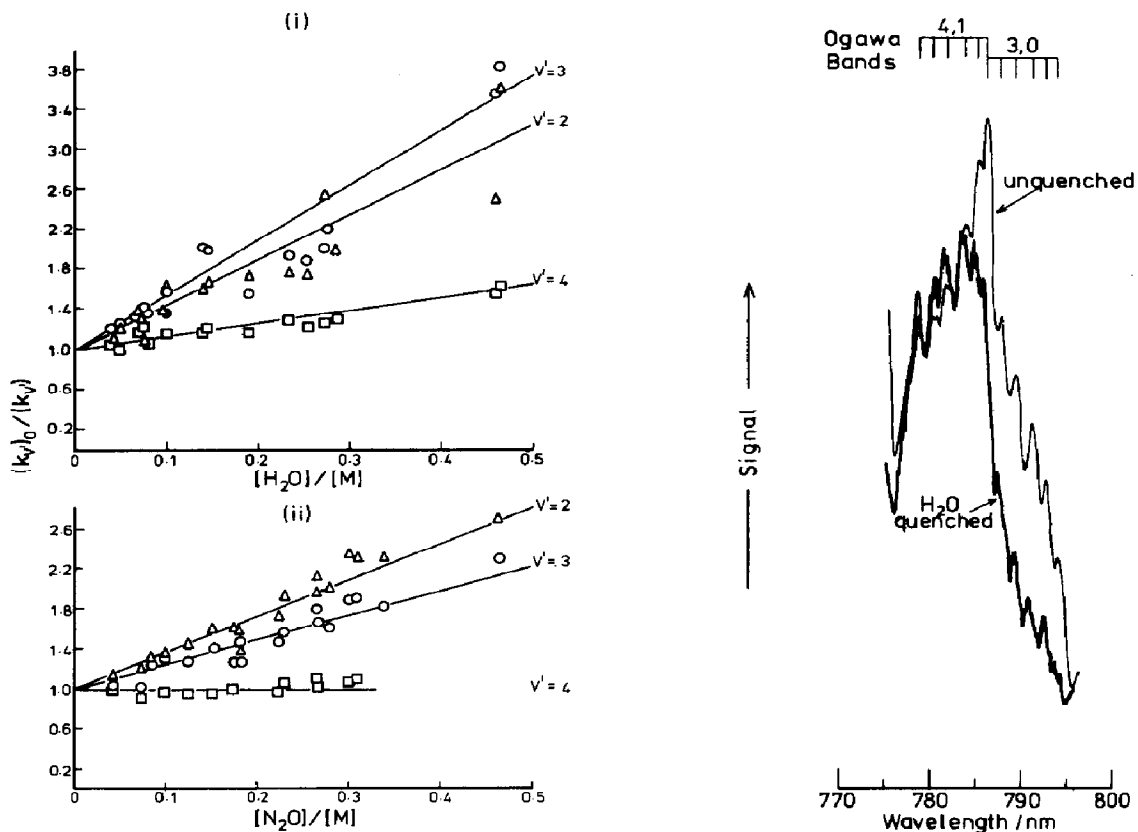


Fig. 4. Plots of $(k_{v'})_0/k_{v'}$ vs. mol fraction of H_2O (i) and N_2O (ii) in N_2 carrier gas. \square , \circ and \triangle represent $v' = 4, 3$ and 2 respectively, all at 298 K .

Fig. 5. Comparative spectral scans over the $(4, 1)$ and $(3, 0)$ Ogawa bands in pure N_2 (unquenched) and in N_2 carrier gas containing 46% H_2O vapour (quenched) at 298 K .

arising from reinforcement of the highest wavelength head of the $(4, 1)$ band by the lowest wavelength head of the $(3, 0)$ band. The profile labelled quenched, which has been carefully matched to produce the same $(4, 1)$ band intensity as in the unquenched plot, was obtained when the N_2 carrier was partly replaced with 46% H_2O vapour. The $(3, 0)$ band intensity is heavily suppressed, revealing the true structure of the $(4, 1)$ much more clearly. In particular the six-headed appearance becomes better developed and the peak at the centre of the structure in N_2 carriers is revealed as composite.

Discussion

The generally accepted mechanism for population of the electronically excited states of $\text{NO}(\text{A}^2\Sigma^+, \text{B}^2\Pi, \text{C}^2\Pi$ and $\text{b}^4\Sigma^-)$ which do not correlate with ground state N and O atoms is that the $\text{NO}(\text{a}^4\Pi)$ state, which does

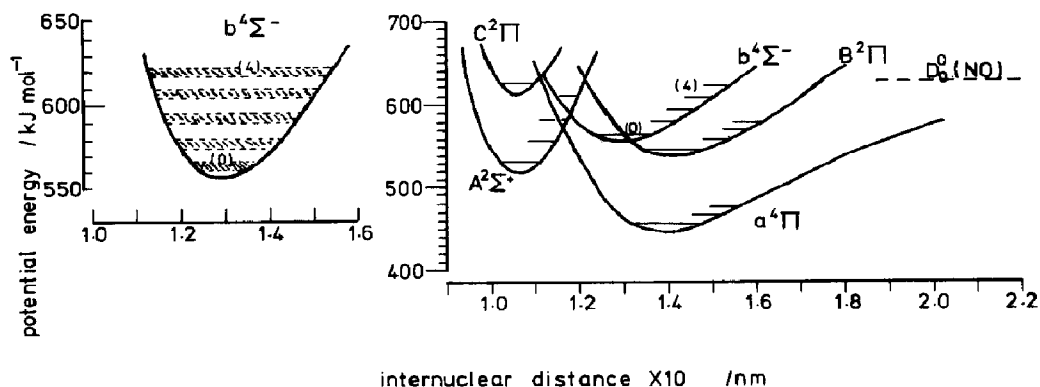
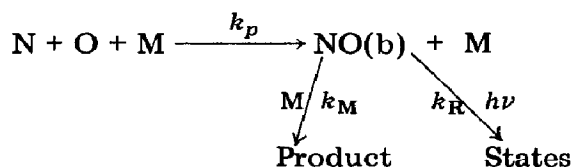


Fig. 6. The relevant potential energy curves of nitric oxide (after Gilmore [6]). The uncertainty in the energetic location of the vibrational levels of $\text{NO}(b^4\Sigma^-)$ is indicated by bands in the inset at the left.

correlate, serves as the intermediate. Collision induced crossings (*i.e.* with rates proportional to $[M]$), in competition with vibrational relaxation, are considered to lead to the other states. $\text{NO}(b^4\Sigma^-)$ (hereafter referred to simply as *b* state) has a potential energy curve which approaches closely to that of $\text{NO}(a^4\Pi)$ (hereafter referred to as the *a* state) on the inner limbs, as may be seen in Fig. 6, which should aid such crossing.

In all of our experiments the Ogawa band intensities were independent of total pressure. It follows that the *b* state levels cannot be depopulated predominantly by radiation since this would lead to $I_{\nu'}/[N][O]$ ratios proportional to $[M]$, reflecting the collisional nature of the population process. Thus the overwhelming modes of depopulation under our conditions must be pressure dependent processes also; these could be reverse crossings back to the *a* state or physical or chemical quenchings. Thus we may write the simplified general mechanism:

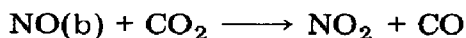


where k_R is the radiative rate constant for Ogawa emissions. Application of the stationary state approximation to $\text{NO}(b)$ leads to the predicted kinetic expression:

$$I_{\nu'}/[N][O] = k_R k_p / k_M \quad (i)$$

in agreement with the pressure independence found experimentally, under the condition that $k_M[M] \gg k_R$.

It would be expected that the triatomic gases, CO_2 ($D_0^0 = 531.3$ kJ/mol), N_2O ($D_0^0(\text{NN-O}) = 167.4$ kJ/mol) and H_2O ($D_0^0 = 497.9$ kJ/mol) would be able to dissociatively quench the $\text{NO}(b)$ levels concerned here. Alternatively they might react chemically in highly exothermic processes such as:



This type of reaction has been proposed for the NO(a) state [13]. The third possibility is that the triatomic species merely act as does M in the above mechanism, producing other electronic states. In any event, separation of the depopulation rate parameter, $k_M [M]$, into the sum of components, $k_{N_2} [N_2] + k_Q [Q]$, produces the expanded form of eqn. (i):

$$k_{v'} = I_{v'} / [N] [O] = k_R k_p [M] / (k_{N_2} [N_2] + k_Q [Q]) \quad (\text{ii})$$

The prediction then is that the reciprocal of $k_{v'}$ is a linear function of the mol fraction $[Q] / [M]$, provided that k_p is largely independent of the nature of M. This is in agreement with the forms of Figs. 3 and 4. A dependence upon $[Q]$ itself rather than the mol fraction would have been expected if the population mechanism of NO(b) had been a pressure independent radiationless crossing process from NO(a), which is allowed by the radiationless crossing selection rules.

The absence of any significant trend in $k_{v'}$ with up to 76% replacement of N_2 carrier by Ar suggests that the rates of the principal removal processes for NO(b) $v' = 4, 3$ and 2 have a rather non-specific dependence upon the nature of these M species. Such would be expected if the processes induced by N_2 and Ar were reverse transitions back to almost isoenergetic levels of NO(a) but not if substantial amounts of energy were being exchanged. In contrast the $N_2(1+)$ emission intensity in the nitrogen afterglow shows sharp enhancement when N_2 carrier is replaced by Ar [10], because N_2 quenches the emitting $N_2(B^3\Pi_g)$ state electronically, a mechanism not available to Ar.

The obvious quenching effects on Ogawa intensities from NO(b) $v' = 2, 3$ induced by CO_2 , N_2O and H_2O then strongly suggest the transfer of substantial amounts of energy from NO(b) to these molecules, particularly as the three have very different efficiencies in this.

Single vibrational level relaxation within NO(b) in N_2 carriers is unlikely to be rapid in view of the wide difference between vibrational level separations in this state ($\sim 115,000 \text{ m}^{-1}$) and that in N_2 ($233,070 \text{ m}^{-1}$). Moreover if single vibrational relaxation was reasonably efficient, then the quenching effects on $v' = 2$ emission in mixed carriers would be expected to be larger than those for $v' = 3$ emission. Not only would the $v' = 2$ state be quenched in its own right, but the population rate by vibrational relaxation from $v' = 3$ would reflect the quenching there and the total effect would be cumulative. In fact in the case of $Q = \text{H}_2\text{O}$, the results in Table 2 show a lesser quenching effect on $v' = 2$ than on $v' = 3$.

However, there is a near resonance for double vibrational relaxation of NO(b) in N_2 carrier. The wavenumber separation of $v' = 4$ and $v' = 2$ is $225,900 \text{ m}^{-1}$, a difference of only about 7000 m^{-1} from the wavenumber separation in N_2 . Such double relaxation processes have been shown to occur in the lower vibrational levels of $N_2(A^3\Sigma_u^+)$ in N_2 with a

TABLE 3

Approximate populations of NO(b) levels
($T = 298$ K, $M = N_2$)

v'	4	3	2	1
Relative population	1	2	1	<0.3

limiting collisional efficiency of 10^{-2} [14]; the wavenumber difference in this case was about four times larger than that for the potential NO(b) relaxation in N_2 with $\Delta v' = 2$. Although our error limits are too wide for unequivocal differentiation of the temperature coefficient of k_2 from that of k_3 , nevertheless the average value of n_2 is less than that of n_3 . Double quantum relaxation could provide an explanation; part of the population rate at least of NO(b) $v' = 2$ would then reflect the distinctly lower n_4 compared to n_3 . However, the lack of any substantial effect on the relative populations of $v' = 2$ and $v' = 3$ with up to 76% Ar may argue against such a double relaxation process associated with N_2 molecules unless the rate is a strongly non-linear function of the mol fraction. CO_2 and N_2O have fundamental wavenumbers also in near resonance ($234,930\text{ m}^{-1}$ and $222,400\text{ m}^{-1}$ respectively) but H_2O induces no obvious effects associated with the absence of any such match.

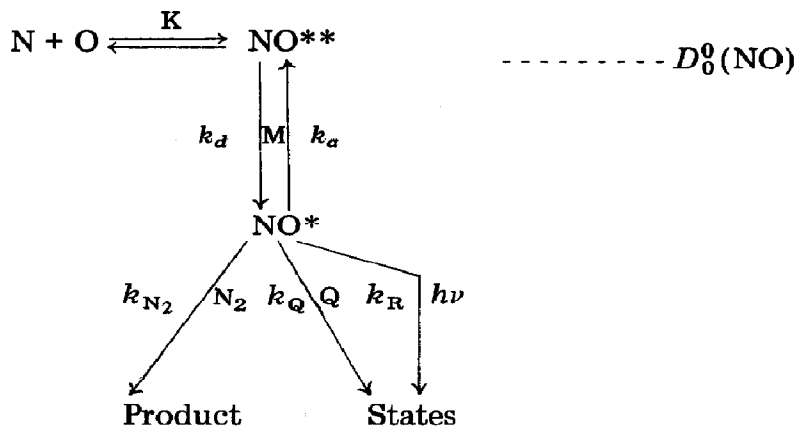
Our failure to detect Ogawa bands emanating from NO(b) $v' = 1$ has allowed us to impose an upper limit upon the population of this level under our conditions. We have calculated approximate Franck-Condon factors for the Ogawa transitions on the simplified basis proposed by Nicholls [15], using the widths and internuclear separations of the NO(a) and NO(b) potential curves given by Gilmore [6]. Combined with the ν^3 factor, these suggest that the (1, 0) Ogawa band should be a major radiative channel for $v' = 1$. On the further assumption that the bands which we have detected represent the major radiative channels for NO(b) $v' = 2, 3$ and 4 and taking into account the ν^3 factor in the Einstein coefficient for spontaneous radiation, the approximate populations are as shown in Table 3 at 298 K in N_2 carrier. It must be recognized that there will be a considerable extension of Ogawa band emission to wavelengths above 1000 nm, but with decreasing radiative transition probabilities due to the ν^3 factor. Despite this we can be reasonably confident that $v' = 3$ has the largest population, greater than that of $v' = 2$ or 4 and with the likelihood that that of $v' = 1$ is less than any of these. Two factors may contribute to this last feature. The inner limbs of the a and b states become increasingly separated as v' decreases (see Fig. 6), which is likely to discourage a \rightarrow b crossing. Also the potential curves of the b state and the $B^2\Pi$ state come into close proximity near $v' = 1$, creating the strong possibility for b \rightarrow B depopulation of $v' = 1$ with resultant production of the observed NO β band emission.

An upper limit to the radiative rate constant, k_R , for the level $v' = 3$ can be produced on the basis of data of the type shown in Fig. 2. Although there is no significant gradient evident, least squares analysis produced an upper limiting positive value by taking the plus sign standard deviation. The expanded form of eqn. (i) would have a denominator $k_R + k_M [M]$, so that the gradient to intercept ratio of plots like Fig. 2 is k_R/k_M . The $v' = 3$ data lead to $k_R/k_{N_2} \leq 3.2 \times 10^{-6} \text{ mol/dm}^3$. At the same time the H_2O quenching data of Table 2 show that on the simplest basis this species is about 6.5 times more effective than N_2 in removing $v' = 3$. Making the assumption that k_Q for $Q = H_2O$ is unlikely to exceed the upper limiting value of the order of $3 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ obtained for the quenching of $NO(B^2\Pi) v' = 0$ [16] or $NO(A^2\Sigma^+) v' = 0$ [17], we derive $k_{N_2} \leq 5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the b state $v' = 3$. This gives the upper limiting value of $1.6 \times 10^5 \text{ s}^{-1}$ for k_R when combined with the above ratio. Alternatively this may be expressed as a lower limiting radiative lifetime of $6 \times 10^{-6} \text{ s}$. A value of this order of magnitude might be predicted by comparison with the radiative lifetime of around $4 \times 10^{-6} \text{ s}$ for the lower levels of $N_2(B^3\Pi_g)$ [18], the emitting state of the $N_2(1+)$ system which appears in the same spectral region as the Ogawa bands and is similarly a fully allowed transition.

Evidence for preassociative formation of $NO(b^4\Sigma^-) v' = 4$

The kinetic behaviour of the Ogawa band emission originating from $NO(b) v' = 4$ is strikingly different from that emanating from $v' = 3$ or 2. The outstanding feature is that the chemiluminescent rate coefficient k_4 shows no trend upon addition of up to 46% of CO_2 or N_2O whereas k_3 and k_2 show considerable decreases. When the N_2 carrier was replaced with up to 46% of H_2O vapour even stronger reductions of k_3 and k_2 were found; in this case k_4 did show evidence of quenching but on a much reduced scale. Further the temperature coefficient of k_4 in N_2 carrier is significantly lower than that of k_3 . It is then clear that the general mechanism advanced for the Ogawa band emission from $v' = 2$ and 3 above must be modified to explain the different behaviour of the emission from $v' = 4$. There is no obvious reason why $v' = 4$ should have much lower rate constants than $v' = 2, 3$ for quenching processes acting upon it.

The apparently critical difference for the $v' = 4$ level is that it lies close to the first dissociation limit of NO and as such it might be expected that a predissociation/preassociation mechanism could govern the populations of rotational levels observed in emission. Under these circumstances a simplified mechanism can be advanced as below:



NO** represents an NO(b) $v' = 4$ species with sufficient rotational excitation for its total energy to slightly exceed $D_0^0(\text{NO})$. The concentration $[\text{NO}^{**}]$ is governed overwhelmingly by pressure independent preassociation and predissociation processes, presumably operating through the NO(a) continuum; it is controlled by a pseudo-equilibrium constant K and is expected to be rather small compared to $[\text{NO}^*]$. NO* represents a species with total energy slightly less than $D_0^0(\text{NO})$; this can only be produced by collisional abstraction of energy from species like NO**. But NO* is close enough to the dissociation limit for subsequent collisions with M species to donate sufficient energy to excite it back to NO** and hence achieve effective redissociation. It is expected that the predominant species giving rise to Ogawa emission from $v' = 4$ will be of the NO* type. For NO* species with energies sufficiently far below $D_0^0(\text{NO})$, it would be expected that the various interactions with N_2 and Q species would be similar to those for NO(b) $v' = 3, 2$.

Stationary state analysis generates an expression for the intensity of emission from NO* species:

$$I^* = k_R [\text{NO}^*] = \frac{k_R k_d K [\text{N}] [\text{O}] [\text{M}]}{k_a [\text{M}] + k_{\text{N}_2} [\text{N}_2] + k_Q [\text{Q}]} \quad (\text{iii})$$

comparable with expression (ii) for the lower vibrational levels. It is the appearance of the additional term $k_a [\text{M}]$, representing effectively the redissociation rate, which reduces the effect of the quenching term $k_Q [\text{Q}]$ in eqn. (iii) as opposed to (ii).

We therefore consider that sufficient of the emitting rotational levels within the $v' = 4$ assembly must be subject to such redissociation to explain the reduced quenching by Q species compared to $v' = 2$ and 3 (Table 2). This can only be expected if the lowest rotational level of NO(b) $v' = 4$ lies within a certain energy separation from $D_0^0(\text{NO})$.

The principal parameter in expression (iii) which would be expected to have a temperature dependence is k_a . It would not be unreasonable to consider this to be of the form $\exp(-\Delta E/RT)$, where ΔE approximates

to the energy difference between $D_0^0(\text{NO})$ and NO^* level. In this event the effective chemiluminescent rate constant, $I^*/[\text{N}][\text{O}]$, would be expected to show a variable negative temperature coefficient for the set of NO^* species. The upper limiting negative temperature coefficient would be expected to correspond to that observed for emission from $v' = 3$, where none of the populated rotational levels can be subject to a redissociation process. The Ogawa band intensities observed here are integrated necessarily over a substantial range of rotational energy levels. Accordingly the corresponding chemiluminescent rate coefficient for $v' = 4$ emission will show a weighted average over the NO^* species. But the fact that this is significantly less than the temperature coefficient for $v' = 3$ emission is interpreted as indicating that a substantial number of the emitting rotational levels of $v' = 4$ lie close enough to the first dissociation limit to show a reduced temperature coefficient, in accord with the arguments based on quenching efficiencies.

A predissociation mechanism is known to govern the intensities of the $\text{NO } \delta$ bands in $\text{N} + \text{O}$ systems. The lowest rotational level of the emitting $\text{NO}(\text{C}^2\Pi) v = 0$ state lies at an energy of 626.3 kJ/mol, some 0.9 kJ/mol below $D_0^0(\text{NO})$. The manifestation of this situation is that the chemiluminescent rate coefficient for δ band intensity has a temperature variation of around $T^{-0.35}$ [19], much less than the temperature coefficients attaching to β and γ bands with emitting states at considerably lower energies. Moreover, it has been shown that some 97% of the depopulation rate of $\text{NO}(\text{C}^2\Pi) v = 0$ under similar conditions to those of our work is accounted for by predissociation [20]. On the basis of the rather larger temperature coefficient attaching to emission from $\text{NO}(\text{b}) v' = 4$ found here ($T^{-1.2 \pm 0.4}$), the lowest rotational of this state must lie below 626.3 kJ/mol.

A lower limit to the energy of $\text{NO}(\text{b}) v' = 4$ may be estimated by comparison with the kinetic behaviour reported for $\text{N}_2(1+)$ emission in $\text{N} + \text{N}$ systems. One emitting level, $\text{N}_2(\text{B}^3\Pi_g) v = 12$, lies 10.4 kJ/mol below $D_0^0(\text{N}_2)$, but the kinetic behaviour of the corresponding chemiluminescent intensity, presumably integrated over the bulk of populated rotational levels, shows no characteristics associated with predissociative depopulation. For example, the temperature coefficients of $\text{N}_2(1+)$ bands emanating from $v = 12$ and $v = 11$ cannot be distinguished [21]. Therefore unless the degree of rotational excitation within $\text{NO}(\text{b}) v' = 4$ in the Ogawa system is unexpectedly very much higher than that within $\text{N}_2(\text{B}^3\Pi_g) v = 12$ in the nitrogen afterglow, it seems logical to postulate that the lowest rotational level of the former state lies closer than 10.4 kJ/mol to $D_0^0(\text{NO})$.

A further limitation can be derived on the more tenuous assumption that the variation of k_a in expression (iii) as a function of ΔE is held to be responsible itself for the reduced quenching efficiencies of Q species on $v' = 4$. Then the apparent slope of the plots of $(k_4)_0/k_4$ versus $[\text{Q}]/[\text{M}]$ in Figs. 3 and 4 is reduced compared to the others because of the

intervention of $k_a[M]$ in the denominator of eqn. (iii) in a weighted average over the populated rotational levels of $v' = 4$. If the rate constant $k_{\text{H}_2\text{O}}$ is in fact much the same for $v' = 4, 3$ and 2 , then the definite slope apparent in Fig. 4 for $(k_4)_0/k_4$ versus $[\text{H}_2\text{O}]/[M]$ suggests that k_a cannot be too much larger than $k_{\text{H}_2\text{O}}$ for the lowest rotational levels. On the other hand k_a must be considerably larger than $k_{\text{H}_2\text{O}}$ for rotational levels closer to the dissociation limit. Accordingly we must postulate that k_a must vary by at least an order of magnitude over the populated rotational assembly of $v' = 4$. If the variation of k_a is as $\exp(-\Delta E/RT)$, then the lowest rotational level must have $\Delta E \geq 2RT$ or 5 kJ/mol for $T \approx 300 \text{ K}$ to produce the required variation.

On the basis of a highly simplified mechanism admittedly, we consider that the kinetic evidence supports the location of $\text{NO}(b^4\Sigma^-) v' = 4$ in its lowest rotational level at within 5 to 10 kJ/mol below $D_0^0(\text{NO})$ *i.e.* at energies between 617.2 and 622.2 kJ/mol with respect to $\text{NO}(X^2\Pi) v = 0$.

Spectroscopic energy location of $\text{NO}(b^4\Sigma^-) v' = 4$

As pointed out in the introduction, the approximate energetic location of the $\text{NO}(b)$ state vibrational levels can be deduced from the wavelengths at which Ogawa bands appear coupled with the wavelengths at which the $\text{NO}(a^4\Pi \rightarrow X^2\Pi)$ bands appeared in the matrix experiments. The wavelength range covered by the Ogawa $(4, 0)$ band [5] corresponds to an excitation energy of $164.1 \pm 0.7 \text{ kJ/mol}$ for $\text{NO}(b) v' = 4$ with respect to $\text{NO}(a) v'' = 0$, on the assumption that the origin of the band lies within the outermost heads. An excitation energy of $455.2 \pm 1.5 \text{ kJ/mol}$ is derived for $\text{NO}(a) v = 0$ with respect to $\text{NO}(X^2\Sigma) v = 0$ from the report of Frosch and Robinson [7], noting that the frozen matrix environment tends to slightly lower the excitation energy compared to a gaseous environment. Together these predict that $\text{NO}(b) v' = 4$ lies in the range 617 to 622 kJ/mol , almost exactly in agreement with our deduction from kinetic evidence.

In conclusion therefore we produce Fig. 6, which shows the relevant potential energy curves of NO . The lowest rotational level of $\text{NO}(b) v' = 4$ has been put at its average excitation energy between the limits given above. The inset alongside shows the potential energy uncertainty of $\text{NO}(b)$ vibrational levels as bands on a twofold amplified scale.

References

- 1 R. A. Young and R. L. Sharpless, *Discuss. Faraday Soc.*, 33 (1962) 228.
- 2 I. M. Campbell and S. B. Neal, *Discuss. Faraday Soc.*, 53 (1972) 72.
- 3 M. W. Feast, *Can. J. Res.*, 28 (1950) 488.
- 4 M. Ogawa, *Science of Light (Tokyo)*, 2 (1953) 87.
- 5 M. Brook and J. Kaplan, *Phys. Rev.*, 96 (1954) 1540.
- 6 F. R. Gilmore, *J. Quant. Spectros. Radiat. Transfer*, 5 (1965) 369.

- 7 R. P. Frosch and G. W. Robinson, *J. Chem. Phys.*, 41 (1964) 367.
- 8 F. Kaufman and J. R. Kelso, *J. Chem. Phys.*, 28 (1958) 510.
- 9 I. M. Campbell and B. A. Thrush, *Trans. Faraday Soc.*, 64 (1968) 1275.
- 10 I. M. Campbell and B. A. Thrush, *Proc. R. Soc. (A)*, 296 (1967) 201.
- 11 K. D. Bayes and G. B. Kistiakowsky, *J. Chem. Phys.*, 32 (1960) 992.
- 12 M. Mandelman, T. Carrington and R. A. Young, *J. Chem. Phys.*, 58 (1973) 84.
- 13 N. Cohen and J. Heicklen, *J. Phys. Chem.*, 71 (1967) 558.
- 14 J. W. Dreyer and D. Perner, *J. Chem. Phys.*, 58 (1973) 1195.
- 15 R. W. Nicholls, *J. Quant. Spectros. Radiat. Transfer*, 13 (1973) 1059.
- 16 I. M. Campbell and B. A. Thrush, *J. Quant. Spectros. Radiat. Transfer*, 8 (1968) 1571.
- 17 N. Basco, A. B. Callear and R. G. W. Norrish, *Proc. R. Soc. (A)*, 260 (1961) 459.
- 18 A. W. Johnson and R. G. Fowler, *J. Chem. Phys.*, 53 (1970) 65.
- 19 R. F. Gross and N. Cohen, *J. Chem. Phys.*, 48 (1968) 2582.
- 20 A. B. Callear and I. W. M. Smith, *Discuss. Faraday Soc.*, 37 (1964) 96.
- 21 K. H. Becker, E. H. Fink, W. Groth, W. Jud and D. Kley, *Discuss. Faraday Soc.*, 53 (1972) 35.