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NO($B\ ^2\Pi_r$ and $A\ ^2\Sigma^+$) chemiluminescence from the reaction $C+NO_2 \rightarrow CO+NO$ at 300 K

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The $C + NO_2 \rightarrow CO + NO$ reaction at 300 K has been shown to exhibit a strong ultraviolet chemiluminescence from NO ($B\ ^2\Pi_r$) and a weak one from NO($A\ ^2\Sigma^+$). The NO ($B\ ^2\Pi_r$)$v' = 0$ production rate was found to be approximately ten times greater than that of NO ($A\ ^2\Sigma^+$)$_{v'=0}$. No chemiluminescence either from NO($C\ ^2\Pi_r$) or NO ($D\ ^2\Sigma^+$), however energetically accessible, could be observed. These features are in close agreement with the C_s symmetry correction diagram for this reaction. The nascent vibrational distribution of NO($B\ ^2\Pi_r$) was found to be much cooler than the prior statistical one.

I. INTRODUCTION

The reactions of atomic carbon giving CO as a product are often very exoergic since the CO bond is the strongest in chemistry (dissociation energy: $D_0 = 11.09$ eV).[1] For a few reactions, such as $C + OCS \rightarrow CO + CS$[2] and $C + SO_2 \rightarrow CO + SO$,[3,4] the exoergicity allows the production of electronically excited products giving ultraviolet chemiluminescence.

Taking a value for the dissociation energy of the NO–O bond, $D_0 = 3.12$ eV,[1] the $C + NO_2 \rightarrow CO + NO$ reaction is exoergic by 7.97 eV for reactants and products in their ground electronic states. Each electronic state of CO or NO whose energy lies below 7.97 eV has thus a chance to be produced and among them, four NO radiative states: $A\ ^2\Sigma^+$, $B\ ^2\Pi_r$, $C\ ^2\Pi_r$, and $D\ ^2\Sigma^+$ whose energies above the ground state $X\ ^2\Pi_r$ are, respectively, 5.48, 5.64, 6.49, and 6.60 eV.[5] The corresponding transitions to the ground state, called, respectively, the γ, β, δ, and ϵ bands, lie in the ultraviolet (γ: 220–300 nm, β: 240–450 nm, δ and ϵ: 190–220 nm).[6]

It must be pointed out that the NO($B\ ^2\Pi_r$) chemiluminescence could be of interest for a chemical laser in the ultraviolet for two reasons. Firstly the transitions from $B\ ^2\Pi_r$ terminate on high vibrational levels of $X\ ^2\Pi_r$ state which are almost unoccupied at 300 K, so that population inversions between rovibronic states of $B\ ^2\Pi_r$ and $X\ ^2\Pi_r$ could be achieved, if necessary, by means of a slight collisional vibrational relaxation in $X\ ^2\Sigma^+$. Secondly the radiative lifetime of NO($B\ ^2\Pi_r$), 3.1 μs,[7] is a good compromise between two necessary but opposing conditions for lasing, i.e., the shortest possible lifetime to get an appreciable gain in the ultraviolet and the longest one, at least greater than 1 μs, to allow the chemical pumping to give a sufficient excited state density.[8]

II. EXPERIMENTAL

In our previous experiments on $C + N_2O$,[9,10] $C + OCS$,[2] and $C + SO_2$[4] reactions, ground state atomic carbon was produced by mixing a flow of halomethane diluted in helium with a flow of atomic hydrogen also diluted in helium. N_2O, OCS, or SO_2 were then added to the halomethane to obtain their reaction with atomic carbon at 300 K. The pressures were typically: 3 Torr He, 200 mTorr H_2 before microwave dissociation, and a few mTorr for both halomethane and the molecule to react with atomic carbon. We tried this procedure for the reaction $C + NO_2$. We observed an intense signal from the CN violet bands at 388 nm ($B\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$ transition) and a signal from the NO β bands ($B\ ^2\Pi_r \rightarrow X\ ^2\Pi_r$ transition) which was unfortunately too weak for a spectral analysis since only the bands originating from $v' = 0$ were distinguishable. Such a weak signal was due to the almost complete consumption of NO_2 by the extremely fast $H + NO_2 \rightarrow NO + OH$ reaction ($k = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}),[11] since atomic hydrogen was in large excess. The NO produced by $H + NO_2$ then reacted with C_2, produced by the H + halomethane diffusion flame to give the observed CN($B\ ^2\Sigma^+$) chemiluminescence.[12–15] We were thus obliged to use another atomic carbon source.

The simplest alternative was the dissociation of CO diluted in He through a microwave discharge. Such a discharge also produces excited atomic carbon which, fortunately, disappears downstream faster than ground state carbon. The products of the discharge were expanded into a Teflon coated chamber. NO_2 was then mixed with the incoming flow, through an array of 12 small holes drilled along the side of a vertical Teflon tube inside the chamber, 25 cm downstream from the discharge. At such a distance excited carbon was negligible while ground state carbon still had an appreciable density allowing the spectral analysis of its chemiluminescent reaction with NO_2. Pressure conditions were typically: 3 Torr for He, 40 mTorr for CO, and 1 mTorr for NO_2. The flow speed was 3 ms^{-1}. Chemiluminescence was observed through a

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quartz window at right angles to the direction of the flow using a 0.6 m scanning monochromator (Jobin–Yvon HRS1) with a grating blazed at 250 nm. The output current of the photomultiplier (E.M.I. 9789 QBM) was amplified (Keithley 427) and recorded on a strip chart recorder. The spectral response from 220 to 430 nm was determined by comparing the distribution of recorded NO band intensities in a progression $v' \rightarrow v''$ with the actual distribution, in arbitrary units proportional to photons $\times$ nm^{-1} $\times$ s^{-1}, given by the corresponding Einstein emission probabilities.[16] The progression $v' = 0 \rightarrow v'' = 4$–12 was used for the range 260–400 nm and the progressions $v' = 2$ and $v' = 3 \rightarrow v'' = 2$–6 for the range 220–260 nm. For CO dissociation we used the microwave cavity at 2450 MHz designed by Vidal and Dupret[17] because it offers both efficiency and stability over a wide range of pressures.

III. RESULTS

A. Chemiluminescence spectrum

In the range 190–500 nm the emission spectrum of the discharge products, 25 cm downstream from the discharge was characterized by two of the C_2 "high pressure" bands, at 436.9 and 468.0 nm, and a faint emission of the CN violet system at 388 nm (Fig. 1). The so-called C_2 high-pressure bands characterize exclusively the progression $(d\,^3\Pi_g)_{v'=6} \rightarrow (a\,^3\Pi_u)_{v''}$. The bands, attributed to the exoergic reaction $C + C_2O \rightarrow C_2 + CO$,[18–20] are often observed in CO discharges since C_2O is produced by the consecutive reactions: $C + O + M \rightarrow CO + M$ followed by $C + CO + M \rightarrow C_2O + M$. The faint violet CN bands $(B\,^2\Sigma^+ \rightarrow X\,^2\Sigma^+)$ are certainly due to atomic nitrogen generated by the microwave dissociation of an N_2 impurity in the CO and He. It could yield $CN(B\,^2\Sigma^+)$ by the $C + N + M \rightarrow CN + M$ recombination reaction[21] and the reaction $N + C_2O \rightarrow CN(B\,^2\Sigma^+) + CO$ which has an exoergicity of 2.5 eV.

The addition of NO_2 decreased the C_2 emission and simultaneously a strong chemiluminescence of NO β bands, $(B\,^2\Pi_r \rightarrow X\,^2\Pi_r)$ degraded to the red, was observed from 220 to 450 nm (Fig. 2). A strong chemiluminescence of the CN violet bands $(B\,^2\Sigma^+ \rightarrow X\,^2\Sigma^+)$ at 388 nm also appeared. Between 220 and 290 nm extremely faint NO γ bands, $(A\,^2\Sigma^+)_{v'=0} \rightarrow X\,^2\Pi_r$, degraded to shorter wavelengths, were also observed superimposed on the NO β bands from $(B\,^2\Pi_r)_{v'=1,2,3}$. Such bands are more clearly distinguishable in Fig. 3 where it is also shown that no emission was seen below 214 nm. This indicates that there is no chemiluminescence from the NO δ bands, $C\,^2\Pi_r \rightarrow X\,^2\Pi_r$, and from the NO ϵ bands, $D\,^2\Sigma^+ \rightarrow X\,^2\Pi_r$, both of which have their strongest bands lying between 190 and 210 nm.

1. *The origin of NO β and γ band chemiluminescence*

In our flow reactor only three reactions can produce NO: $C + NO_2 \rightarrow CO + NO$, $O + NO_2 \rightarrow O_2 + NO$, and $C_2 + NO_2 \rightarrow C_2O + NO$. However the exoergicities of $O + NO_2$ and $C_2 + NO_2$ are, respectively (and relative to ground state products) 2.0 and 4.06 eV. Therefore neither of these two reactions can produce $NO(B\,^2\Pi_r$ or $A\,^2\Sigma^+)$. Only $C + NO_2$ can do it.

One could also imagine that the NO β and γ emissions could be due to an excitation of ground state NO, produced by the above reactions, by excited metastable species coming from the discharge such as $CO(a\,^3\Pi)$ and $He(^3S)$. In order to test for this possibility, NO was introduced, instead of NO_2, in the flow of discharge products. The emission spectrum is given in Fig. 4. A strong CN violet emission due to the $C_2 + NO \rightarrow CN(B\,^2\Sigma^+) + CO$ reaction was observed but not the faintest emission of NO β or γ bands could be detected. Thus the observed chemiluminescence when adding NO_2 can only be explained by the reaction between atomic carbon and NO_2.

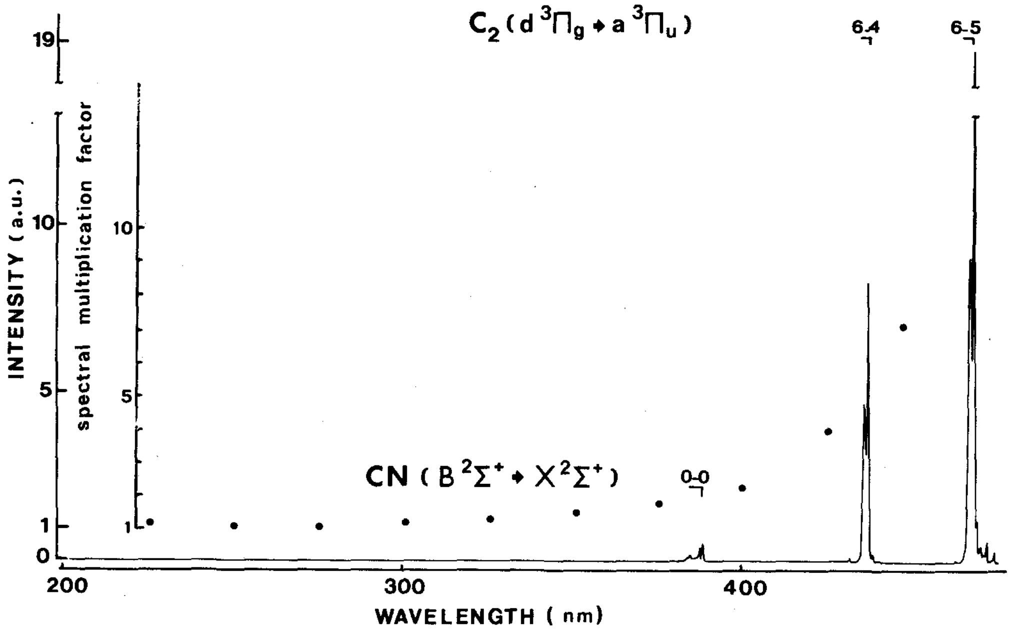

FIG. 1. Emission of CO discharge products 25 cm downstream from the discharge. P_{CO}: 40 mTorr, P_{He}: 3 Torr. The spectral multiplication factors by which the intensity at each wavelength should be multiplied to obtain intensity units proportional to photons nm^{-1} s^{-1} are given by the envelope of full circles. Spectral width: 0.1 nm.

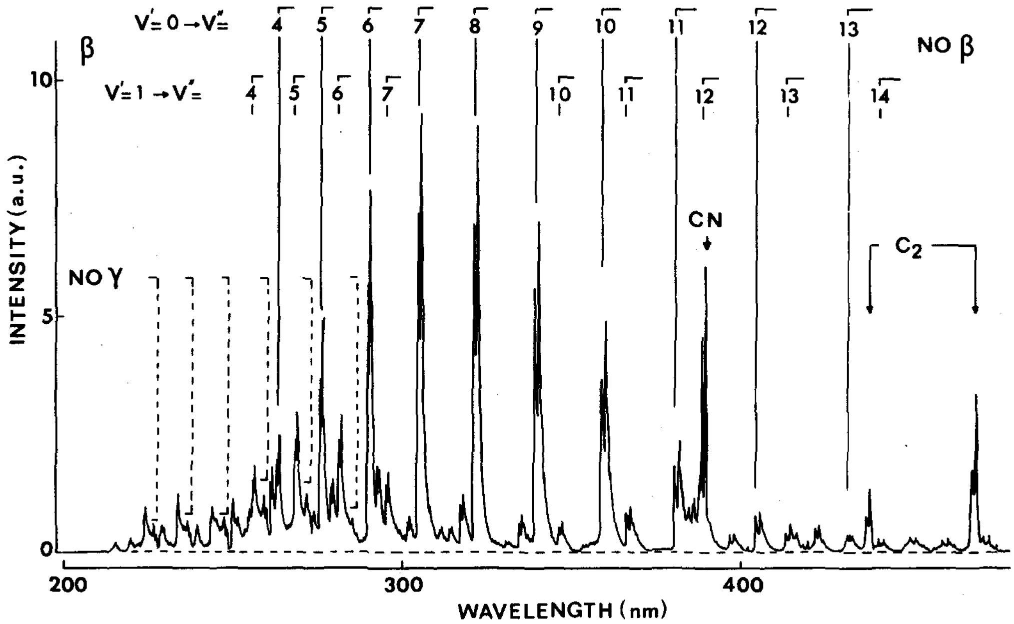

FIG. 2. Emission spectrum when NO_2 was added to CO discharge products 25 cm downstream from the discharge. Same conditions as for Fig. 1 with $P_{NO_2} = 1$ mTorr. The NO $\beta(B\,^2\Pi_r \rightarrow X\,^2\Pi_r)$ and CN violet $(B\,^2\Sigma^+ \rightarrow X\,^2\Sigma^+)$ emission are clearly visible.

However, metastable $C(^1D)$ or even $C(^1S)$ could have been still of importance at 25 cm from the discharge and could have reacted with NO_2 to give the observed chemiluminescence. To verify if the reactions of the excited carbon atoms contributed significantly to the NO chemiluminescence, CH_4 was added to NO_2 since at 300 K CH_4 reacts very fast with singlet atomic carbon (^1D and ^1S) but not with the triplet ground state (^3P).[22,23] We did not observe any modification of the spectrum, either in intensity or distribution, when CH_4 was added in equal amounts to NO_2 (typically 1 mTorr). On increasing the CH_4 pressure we still did not see any modification of the spectrum. This clearly indicates that excited atomic carbon did not contribute to the observed chemiluminescence.

In conclusion the NO β and γ band chemiluminescence can be definitely attributed to the ground state C + NO_2 reaction at 300 K.

2. *The origin of CN violet chemiluminescence*

$CN(B\,^2\Sigma^+)$ could be produced in three ways:

$$C + NO_2 \rightarrow CN(B\,^2\Sigma^+) + O_2 \quad \Delta\epsilon_0 = -0.1 \text{ eV},$$

$$C_2 + NO_2 \rightarrow CN(B\,^2\Sigma^+) + CO_2 \quad \Delta\epsilon_0 = -5.2 \text{ eV},$$

$$C_2 + NO \rightarrow CN(B\,^2\Sigma^+) + CO \quad \Delta\epsilon_0 = -2.9 \text{ eV}.$$

The contribution of the two first reactions, if any, must be negligible relative to that of the third one for the following reasons:

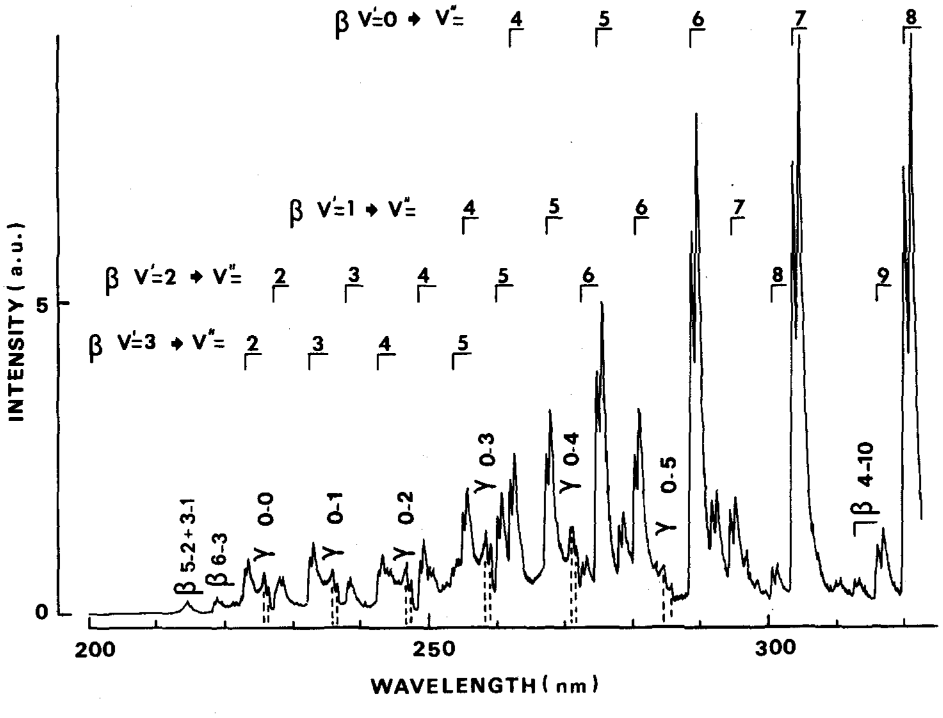

FIG. 3. A more detailed spectrum than that of Fig. 2 showing the faint NO γ bands $(A\,^2\Sigma^+ \rightarrow X\,^2\Pi_r)$, and $B\,^2\Pi_r$ emission from vibrational levels up to $v' = 4$. δ and ϵ bands, which occur below 210 nm, cannot be observed.

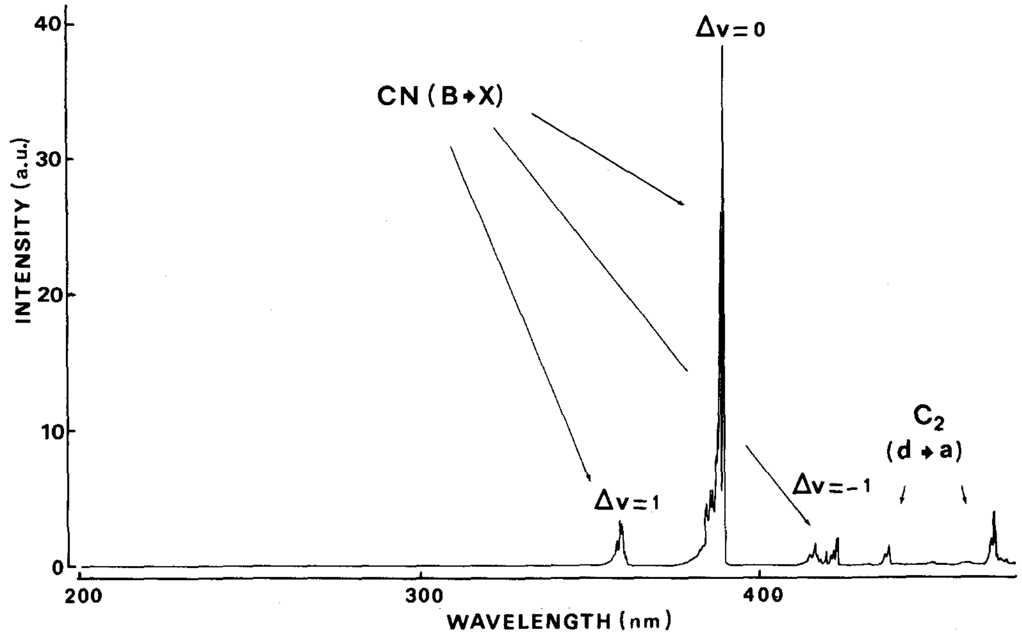

FIG. 4. Emission spectrum when NO was introduced instead of NO_2 into the discharge products flow. No emission from excited NO could be detected. However, strong CN violet emission arose.

The $C + NO_2$ reaction is just sufficiently exoergic to produce $CN(B\ ^2\Sigma^+)_{v'=0}$. Thus it cannot explain the emission from higher vibrational levels. Furthermore the $CN(B\ ^2\Sigma^+)_{v'=0}$ signal itself did not follow a constant ratio to the NO γ and β signals, while the experimental conditions were varied, as should have been the case if it originated from the $C + NO_2$ reaction.

The $C_2 + NO_2 \rightarrow CN + CO_2$ reaction requires the breaking of three bonds (the C_2 bond and two NO bonds) and the formation of three new bonds (the CN bond and two CO bonds). It appears reasonable to speculate that it occurs at a lower rate than the $C_2 + NO_2 \rightarrow C_2O + NO$ reaction which needs only the rupture of one bond and the creation of another.

The $C_2 + NO$ reaction is more likely since NO can be produced by the $C + NO_2 \rightarrow NO + CO$, and $O + NO_2 \rightarrow NO + O_2$ ($k = 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1})[24–26] reactions and perhaps by the $C_2 + NO_2 \rightarrow C_2O + NO$ reaction, whose rate constant is unknown, since C, O, and C_2 are discharge products. At 300 K both $C_2(X\ ^1\Sigma^+)$ and $C_2(a\ ^3\Pi_u)$ can react with NO since these two states differing in only 0.07 eV are populated in the proportion of 70% and 30%. However, according to the C_s correlation diagram,[13] it is the reaction $C_2(a\ ^3\Pi_u) + NO$ which should populate $CN(B\ ^2\Sigma^+)$, the overall rate constant for this reaction being[12] 7.5×10^{-11} cm^3 molecule^{-1} s^{-1}. On replacing NO_2 by an equal pressure (1 mTorr) of NO, reaction with the discharge products produced a CN signal eight times greater (Fig. 4).

B. $NO(B\ ^2\Pi_r)_{v'=0}$ and $NO(A\ ^2\Sigma^+)_{v'=0}$ rate production ratio

The observed steady state density of a vibronic level results from the balance between its production by the $C + NO_2$ reaction and its deactivation both by spontaneous emission and collisional quenching. The steady state density $N_{B,0}$, for example, can be approximated by:

$$N_{B,0} = \frac{k_{B,0}[C][NO_2]}{\tau_{B,0}^{-1} + k_{B,0}^{q}[M]}, \qquad (1)$$

where $k_{B,0}$ is the rate constant for $(B\ ^2\Pi_r)_{v'=0}$ production, $k_{B,0}^q$ is the rate constant for $(B\ ^2\Pi_r)_{v'=0}$ quenching and $\tau_{B,0}$ is the radiative lifetime of $(B\ ^2\Pi_r)_{v'=0}$. The Einstein coefficients are related to the radiative lifetime through the expression:

$$\tau_{B,0}^{-1} = \Sigma_{v''} A_\beta(0, v''). \qquad (2)$$

A similar expression for $N_{A,0}$ can be used.

Under our conditions, according to known data,[27] the collisional quenching of $(B\ ^2\Pi_r)_{v'=0}$ and $(A\ ^2\Sigma^+)_{v'=0}$ should be negligible. As a matter of fact by decreasing the pressures of NO_2, CO, and He below the typical values given in Figs. 1, 2, and 3, we did not observe any modification of the relative intensities of the γ and β bands with respect to each other, so that collisional quenching under our typical conditions was actually negligible. By neglecting collisional quenching in Eq. (1) the rate production ratio of these two vibronic levels can be thus determined from band intensities $I_\beta(0, v'')$ and $I_\gamma(0, v'')$, according to the relationship

$$\frac{k_{B,0}}{k_{A,0}} = \frac{I_\beta(0, v'')}{I_\gamma(0, v'')} \, \frac{\Sigma_{v''} A_\beta(0, v'')}{A_\beta(0, v'')} \, \frac{A_\gamma(0, v'')}{\Sigma_{v''} A_\gamma(0, v'')}. \qquad (3)$$

Nicholls' values[16] for the Einstein coefficients of the NO β and γ transitions were used. The $\beta(0, v'')$ band intensities were determined with a fairly good accuracy. This was not the case for the γ bands which are much weaker and strongly overlapped by the β bands. The $\gamma(0, 0)$, (0, 1), (0, 2), and (0, 3) band intensities have been determined by subtracting the roughly extrapolated β signals. The best estimation should be that of the $\gamma(0, 2)$ band since the band head is almost completely resolved, although the tail of the band is overlapped by β emission (Fig. 3). The worst case should be that of the $\gamma(0, 3)$

TABLE I. Steady state $N_{v'}$ and nascent $k_{v'}$ relative vibrational populations of NO($B\ ^2\Pi_r$) from the C + $NO_2 \rightarrow$ NO($B\ ^2\Pi_r$) + CO reaction at 300 K (from spectral analysis of Figs. 2 and 3). $\tau_{v'}$ is the radiative lifetime of vibrational level v' (Ref. 7), $P_{v'}$ is the probability of populating vibrational level v', and P^0_v is the prior statistical one.

v'	$N_{v'}$ (a.u.)	$\tau_{v'}$ (μs)	$k_{v'}$ (a.u.)	$P_{v'}$	$P^0_{v'}$
0	100	3.10	100	0.571	0.192
1	33	2.86	36	0.205	0.161
2	20	2.77	22	0.125	0.133
3	10	2.63	11	0.063	0.110
4	5	2.53	6	0.034	0.090

band since it is strongly overlapped on both sides, by the β(1, 4) and (2, 5) bands. From the uncertainties attached to the γ band intensities, the rate constant ratio for the production of NO($B\ ^2\Pi_r$)$_{v=0}$ and NO($A\ ^2\Sigma^+$)$_{v=0}$ can be estimated by $k_{B,0}/k_{A,0} = 10 \pm 2$.

C. Vibrational distribution of NO($B\ ^2\Pi_r$)

1. Experimental nascent distribution

The experimental nascent distribution refers to the distribution of rate constants $k_{v'}$ for production of vibronic levels. As the collisional relaxation of the vibrational distribution is negligible, the nascent distribution is deduced from the distribution of steady state densities of vibronic levels $N_{v'}$ through the relationship

$$k_{v'} \propto N_{v'} \frac{\tau_{v'=0}}{\tau_{v'}}, \qquad (4)$$

where $\tau_{v'}$ is the radiative lifetime of vibrational level v'. This distribution, given in Table I, can be fitted to a Boltzmann distribution with a vibrational temperature of 2200 K.

2. Prior statistical distribution

It is interesting to compare the experimental nascent vibrational distribution with the prior statistical one, to see if the reaction has some direct character, i.e., giving an experimental nascent distribution different from the prior statistical one, or a complex mode behavior, i.e., giving a close matching between the two distributions.

When two diatomic molecules AB and CD are produced by an exoergic reaction, the prior statistical probability of producing AB in a given vibrational level for a total energy available to products ϵ_{tot}, is given by[13]

$$P^0_{v(AB),\epsilon_{tot}} = \frac{X}{\sum\limits_{v(AB)}^{v^*(AB)} X} \qquad (5)$$

with

$$X = \sum_{v(CD)}^{v^*(CD)} [\epsilon_{tot} - \epsilon_{v(AB)} - \epsilon_{v(CD)}]^{5/2},$$

where $\epsilon_{v(AB)}$ and $\epsilon_{v(CD)}$ are the energies of AB and CD vibrational levels, v^*(AB) and v^*(CD) being the highest vibrational levels allowed energetically, i.e., whose energy cannot exceed the value of ϵ_{tot}.

Neglecting the activation energy, a value of 2.41 eV was thus taken for the mean total energy available to the products NO($B\ ^2\Pi_r$) + CO($X\ ^1\Sigma^+$). The corresponding prior vibrational distribution of NO($B\ ^2\Pi_r$) is given in Table I and it can be fitted to a Boltzmann distribution of 7200 K.

3. Surprisal

It is now usual to characterize the degree of discrepancy between the nascent distribution $P_{v'}$ and the prior statistical one $P^0_{v'}$ by the "surprisal" $I_{v'}$ defined by[28]

$$I_{v'} = -\ln \frac{P_{v'}}{P^0_{v'}}. \qquad (6)$$

If we label $f_{v'}$ the ratio of the energy of vibrational level v' to the total energy available on reaction products, it is often found in chemical dynamics that $I_{v'}$ is a linear function of $f_{v'}$:

$$I_{v'} = I_0 + \lambda f_{v'}. \qquad (7)$$

The linear surprisal factor therefore characterizes the discrepancy for the whole distribution. In the case of C

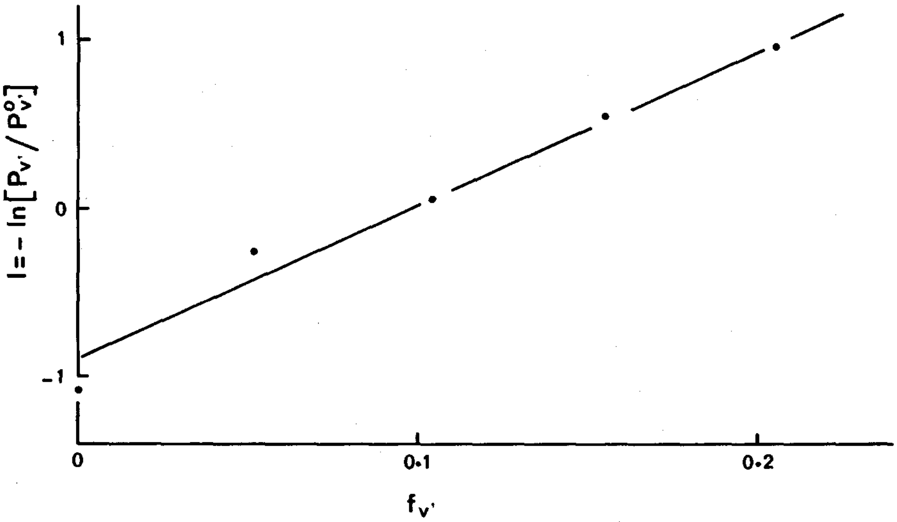

FIG. 5. NO($B\ ^2\Pi_r$) vibrational energy surprisal vs the vibrational energy expressed as a fraction of the total energy available to the products. The surprisal is approximately linear and leads to a positive linear surprisal factor $\lambda_{v'} = 7.4$.

+ $NO_2 \rightarrow NO(B\ ^2\Pi_r) + CO(X\ ^2\Sigma^+)$ at 300 K the linear surprisal factor for the vibrational distribution of $NO(B\ ^2\Pi_r)$ is found to be equal to 7.4, a rather large value (Fig. 5). It can be concluded that the reaction $C(^3P) + NO_2(\tilde{X}\ ^2A_1) \rightarrow NO(B\ ^2\Pi_r) + CO(X\ ^1\Sigma^+)$ has a marked direct character.

IV. DISCUSSION

The theoretical determination of the dynamics of an exoergic four atom reaction leading to electronically excited products still remains a challenge since the accurate determination of the corresponding potential energy surfaces is extremely difficult. Thus, the correlation diagram between reactant and product states is usually given for a qualitative discussion of the possible involved pathways, assuming both the weak spin-orbit coupling approximation and a planar collision complex (C_s symmetry). While this is not the "least symmetrical complex"[29] in the case of a four atom reaction, the use of C_s symmetry has been shown to be a sensible basis of discussing reactions of this type.

For a chemiluminescent reaction one must also consider whether the possible metastable states produced by the reaction are strongly interacting with the observed radiative state (for example, from a potential energy curve crossing or the existence of nearly resonant rovibronic levels). In such cases, a collisionally induced transfer from the metastable state to the radiative state can be very efficient if we are not strictly in single collision conditions. In our experiments the relaxation of vibrational levels of $NO(B\ ^2\Pi_r)$ is negligible but that of rotational levels has been completed to 300 K. We are thus far from single collision conditions and a collisionally induced chemiluminescence from a metastable species produced by the reaction cannot be excluded.

A. C_s Symmetry correlation diagram

It is given in Fig. 6. The products $NO(B\ ^2\Pi_r) + CO(X\ ^1\Sigma^+)$ are correlated to ground state reactants through one $^2A''$ potential energy surface. However, this surface crosses the surface connecting $C(^1D) + NO_2(\tilde{X}\ ^2A_1)$ to $NO(A\ ^2\Sigma^+) + CO(X\ ^1\Sigma^+)$ so that a branching must occur between the NO($B\ ^2\Pi_r$ and $A\ ^2\Sigma^+$) states. Ground state reactants cannot lead to NO($C\ ^2\Pi_r$ or $D\ ^2\Sigma^+$) either directly or by surface crossing. Thus the observation of intense NO β bands and weak γ bands without δ and ϵ bands is consistent with the correlation diagram.

B. The importance of other possible processes

The metastable $NO(a\ ^4\Pi_i)$ state can also be produced from ground state reactants. Since this occurs via a lower surface than that leading to $NO(B\ ^2\Pi_r)$, and therefore with a possible lower barrier, the rate of production of $a\ ^4\Pi_i$ may be greater than that of $B\ ^2\Pi_r$. The $a\ ^4\Pi_i$ state is known as an efficient precursor of the $A\ ^2\Sigma^+$ state (that it crosses), and of the $B\ ^2\Pi_r$ state through the $b\ ^4\Sigma^-$ state[30-34] (Fig. 7). Thus the question arose to determine whether the observed chemiluminescence proceeded from the surface leading directly from reactants to $NO(B\ ^2\Pi_r)$ or from the direct production of $a\ ^4\Pi_i$ followed by energy transfer to $B\ ^2\Pi_r$ and $A\ ^2\Sigma^+$. We could already point out

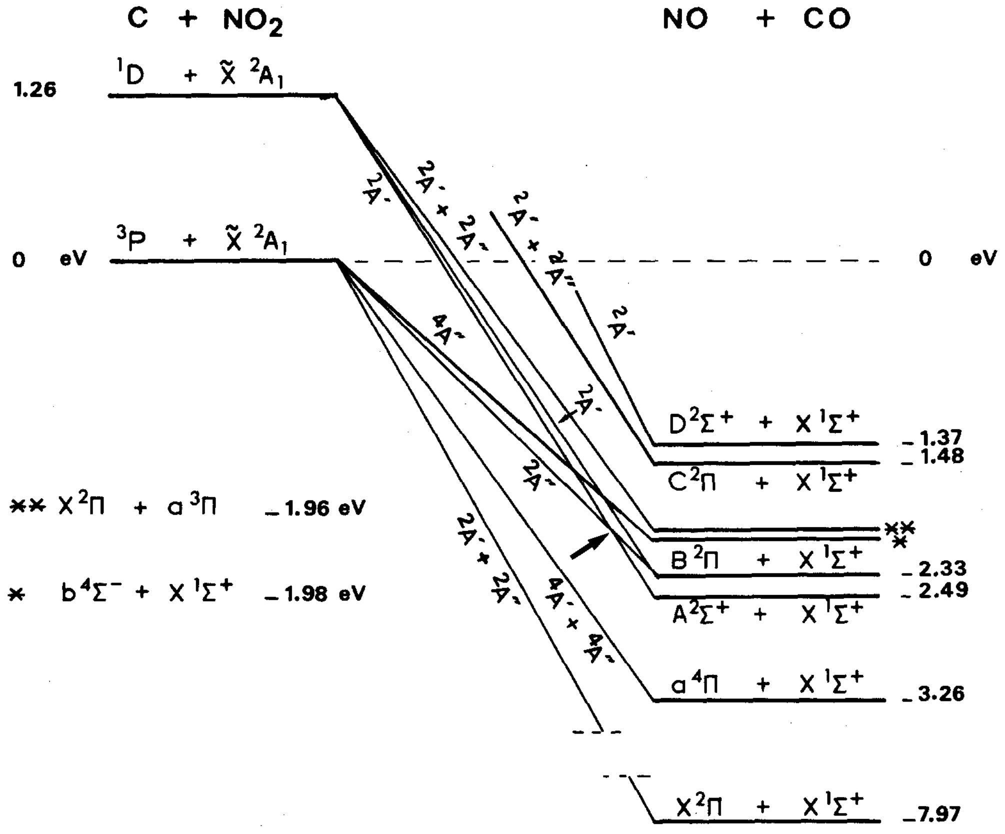

FIG. 6. Correlation diagram connecting the states of C + NO_2 with those of NO + CO assuming C_s symmetry in the collision complex. The crossing of potential energy surfaces explaining the observed production of the $NO(B\ ^2\Pi_r)$ and ($A\ ^2\Sigma^+$) states is indicated by an arrow.

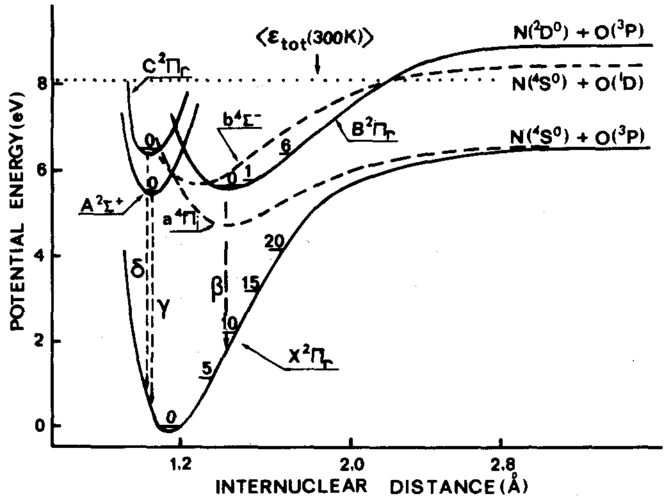

FIG. 7. Potential energy diagram of NO. The electronic transitions of interest, γ, β, δ are indicated by arrows. For the NO($b\ ^4\Sigma^-$) state, data from Refs. 33 and 34. For all other NO states data from Ref. 5. The mean total energy available to the products of the C + NO_2 → CO + NO reaction at 300 K, equal to the maximum excitation energy of NO, is indicated by an arrow.

that if the latter possibility were the case we should have seen the δ bands from $(C\ ^2\Pi_r)_{v'=0}$ since the $C\ ^2\Pi_r$ state is crossed by $a\ ^4\Pi_i$ at the level of $v' = 0$.[30] But it is possible that the δ bands were not observed owing to a lack of detection sensitivity.

The easiest way to eliminate the alternative possibility was to record the chemiluminescent spectrum of the N + O + M recombination, using our flow system. This recombination is known to give γ, β, and δ band chemiluminescence, not directly but from the $a\ ^4\Pi_i$ state which is the only excited state directly produced.[30–34] This spectrum is shown in Fig. 8. The first striking feature is the observation of the δ bands that we could not detect at all from the C + NO_2 reaction. A second feature is an enhancement of the γ band intensity relative to that of the β bands. These bands are ten times stronger than observed for the C + NO_2 reaction. Finally, the third feature concerns the β band distribution which exhibits an enhancement of transition from $(B\ ^2\Pi_r)_{v'=3}$ due to the interaction of $B\ ^2\Pi_r$ state with $b\ ^4\Sigma^-$.[33–34] The NO($B\ ^2\Pi_r$) vibrational distribution is given in Table II and fits that previously determined from N + O + M recombination where a secondary maximum at $v' = 3$ was observed.[33] From all these features the $a\ ^4\Pi_i$ state can be ruled out as a precursor state for the NO β and γ bands observed from the C + NO_2 reaction at 300 K.

One could consider that the $B\ ^2\Pi_r$ state, which is the most populated, should actually be directly produced along the $^2A''$ potential energy surface (Fig. 6) connecting ground state reactants to NO($B\ ^2\Pi_r$) and CO($X\ ^1\Sigma^+$). Furthermore, it might be thought that the $A\ ^2\Sigma^+$ state could be produced in two ways: firstly, by the surface crossing indicated by an arrow in Fig. 6 and secondly, once NO has been created in the $B\ ^2\Pi_r$ state, by an energy transfer process $B\ ^2\Pi_r \rightarrow A\ ^2\Sigma^+$ through the $b\ ^4\Sigma^-$ state. This latter process is actually very unlikely since it has been shown to be negligible[27] compared to the $B\ ^2\Pi_r$ state quenching to $X\ ^2\Pi_r$ which is itself negligible under our experimental conditions.

Thus it can be concluded that NO($B\ ^2\Pi_r$ and $A\ ^2\Sigma^+$) are directly produced by the C + NO_2 reaction and that the ratio of their rates of production must be ascribed to the crossing of the surface connecting $C(^3P)$ + $NO_2(\tilde{X}\ ^2A_1)$ to NO($B\ ^2\Pi_r$) + CO($X\ ^1\Sigma^+$) with that connecting $C(^1D)$ + $NO_2(\tilde{X}\ ^2A_1)$ to NO($A\ ^2\Sigma^+$) + CO($X\ ^1\Sigma^+$).

V. SUMMARY

The C + NO_2 → CO + NO reaction at 300 K has been shown to produce a strong ultraviolet chemiluminescence from the NO($B\ ^2\Pi_r$) state and a much weaker one from the NO($A\ ^2\Sigma^+$) state. The NO$(B\ ^2\Pi_r)_{v'=0}$ production rate was found to be approximately ten times greater than that of NO$(A\ ^2\Sigma^+)_{v'=0}$. Furthermore it has been shown that under our experimental conditions the

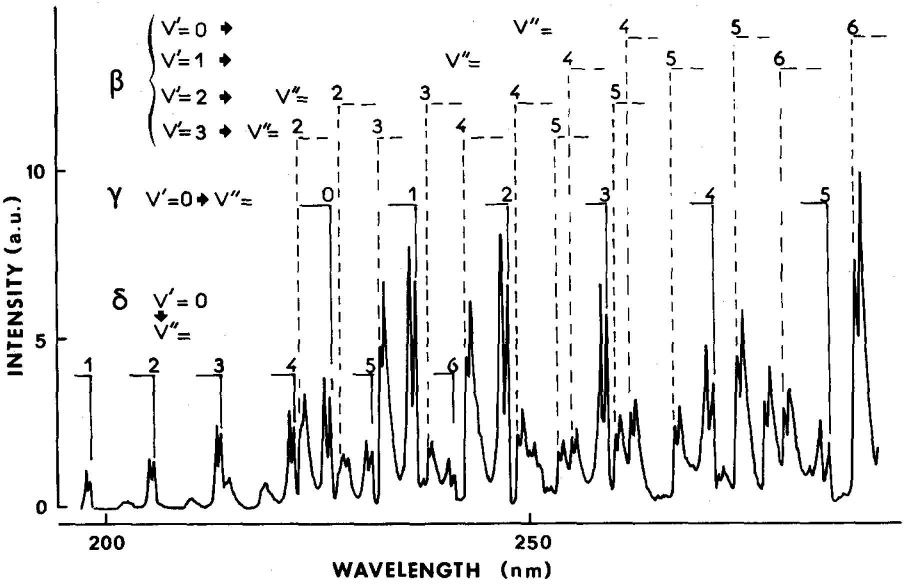

FIG. 8. NO chemiluminescence spectrum from N + O + M recombination. P_{N_2} (before dissociation): 250 mTorr, P_{O_2} (before dissociation): 40 mTorr. Carrier gas P_{He} = 2.5 Torr.

TABLE II. Steady state vibrational populations of NO($B\ ^2\Pi_r$) from the N + O + M reaction at 300 K given by the spectrum of Fig. 8.

v'	0	1	2	3	4
$N_{v'}$	100	37	43	64	25

observed NO($B\ ^2\Pi_r$ and $A\ ^2\Sigma^+$) states were directly produced from the reactants and not via the possible NO($a\ ^4\Pi_i$) precursor state. No chemiluminescence either from NO($C\ ^2\Pi_r$) and NO($D\ ^2\Sigma^+$) could be detected, despite the fact that they are energetically accessible. All these experimental features are consistent with the C_s symmetry correlation diagram for this reaction. The nascent vibrational temperature of the NO($B\ ^2\Pi_r$) state was found to fit a much lower temperature, 2200 K, than the prior statistical one, 7200 K. This corresponds to a linear surprisal factor equal to 7.4 and indicates a direct character for the pathway leading to NO($B\ ^2\Pi_r$) + CO($X\ ^1\Sigma^+$).

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