

Determination of Vibrational Energy Distributions of CN ($A^2\Pi_i$) and ($X^2\Sigma^+$) from the C + N₂O Reaction by Chemiluminescence and Laser Induced Fluorescence

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The CN ($A^2\Pi_i$) and ($X^2\Sigma^+$) vibrational distributions from the C + N₂O → CN + NO reaction at 300 K were determined in a low pressure flow reactor. From the chemiluminescence $A^2\Pi_i \rightarrow X^2\Sigma^+$ the vibrational distribution of $A^2\Pi_i$ was found to peak at $v' = 1$. From the laser induced fluorescence $B^2\Sigma^+ \rightarrow X^2\Sigma^+$, the vibrational distribution of $X^2\Sigma^+$ was found to peak at $v'' = 4$.

A C₂H₂–N₂O combustion flame, stabilized at 2.8 torr with a temperature of 2500 K, gave a CN ($A^2\Pi_i$) vibrational distribution peaking at $v' = 2$ which can be attributed to the C + N₂O reaction at 2500 K. However the CN ground state vibrational distribution was found to be relaxed.

INTRODUCTION

Reactions sufficiently exoergic to give electronically excited products involve two rather interesting features. The first one concerns the electronic branching related to non-adiabatic transitions between potential energy surfaces connecting products and reactants. The second one pertains to the rovibrational distribution of products when the involved potential energy surface contains a well. Usually such a well characterizes an intermediate “long lived complex” (actually,

according to the terminology of unimolecular reactions, it is a chemically activated molecule). Owing to its long life, energy randomization occurs before it dissociates into the products, which have an energy distribution given by the statistical theories of unimolecular processes. This distribution depends only on the total energy of the reaction and not on the way it was initially distributed in the reactants. Such reactions, called "statistical" or "complex-mode" reactions, are the opposite, dynamically, of direct reactions which present no potential energy well and are characterized by the dependence between the products and reactants energy distributions (state-to-state chemistry). However between these two limiting cases, one must consider an intermediate activated molecule which has a total energy far in excess of its dissociation energy to the products. Its lifetime is rather short so that energy randomization has not completed and a statistical formalism cannot be applied. Such a behavior is likely to occur in very exoergic reactions exhibiting a potential well.

The energy profiles for the exoergic $C + N_2O \rightarrow CN + NO$ reaction have been recently calculated. On each pathway leading to the two CN energetically accessible states, $A^2\Pi_i$ and $X^2\Sigma^+$, there is a potential well.¹ It was thus interesting to determine the vibrational distribution of both states to see whether or not energy randomization is complete. These distributions have been determined in a low pressure flow reactor at 300 K. They were also determined in a low pressure $C_2H_2-N_2O$ self-sustained flame since such a flame exhibits a very strong CN ($A^2\Pi_i \rightarrow X^2\Sigma^+$) chemiluminescence.

EXPERIMENTAL

C+N₂O reaction at 300 K

Atomic carbon was produced at 300 K in an H+halomethane ($CHBr_3$, $CHCl_3$ or CCl_4) diffusion flame. An initial mixture of H_2 diluted in He was flowed through a microwave cavity (2450 MHz).² The products of the discharge were then mixed with the halomethane and N_2O in a chemical laser type Teflon throat to provide a reaction volume exhibiting a species density gradient only in the direction of gas pumping. A two stage mechanical pump (Alcatel 2060) gave an estimated flow speed of 20 ms^{-1} .

Of the chemical species present in the diffusion flame, H, CH, CBr or CCl, C₂, C, . . . only atomic carbon can react with N₂O at 300 K, the other reactions being either endoergic or exhibiting a high activation energy. For example as the C+N₂O activation energy is about 0.07 eV (1.5 kcal mol⁻¹) that of the very exoergic reaction H+N₂O → OH+N₂ is 0.8 eV (17 kcal mol⁻¹).³ The CN (A ²Π_i → X ²Σ⁺) chemiluminescence occurring mainly in the near infrared was analyzed through a 0.6 m monochromator (Jobin-Yvon HRS 1) with an InGaAsP photocathode photomultiplier (Varian 159) allowing detection down to 1130 nm. The vibrational distribution in the CN (X ²Σ⁺) ground state was determined from the laser induced fluorescence of the B ²Σ⁺ → X ²Σ⁺ violet system (Figure 1). Excitation was performed

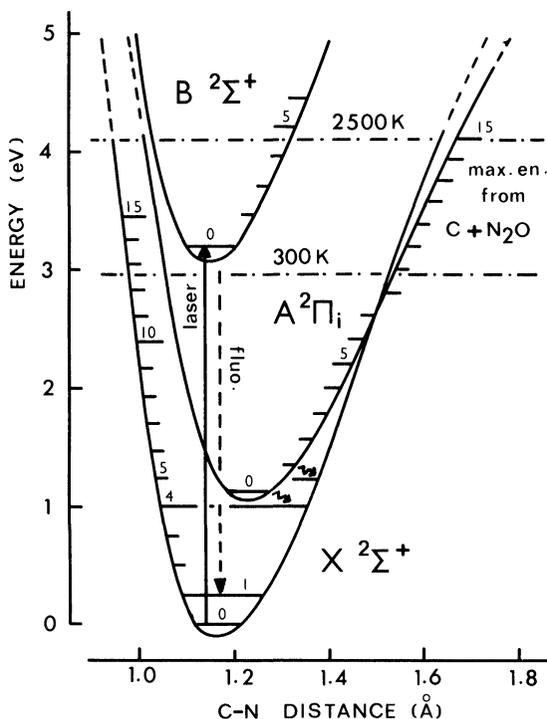


FIGURE 1 CN potential energy diagram. Transitions for laser induced fluorescence are indicated. The maximum energy available to CN, from the C+N₂O reaction at 300 and 2500 K, is also given.

with a nitrogen laser pumped dye laser (Sopra) on $\Delta v = 0$ transitions between 382 and 389 nm using the B.B.Q. dye. Fluorescence on $\Delta v = -1$ transitions was detected between 412 and 422 nm through an interference filter centered at 417 nm (10 nm FWHM) in order to eliminate scattered laser light. The signal from the photomultiplier was amplified (Keithley 427), averaged by a boxcar integrator (Tekelec Airtronic 9870) and displayed on a strip chart recorder.

C₂H₂–N₂O self-sustained flame

A rectangular burner (5 × 20 cm) was designed to provide low pressure flames for spectral studies (emission, absorption, laser-induced fluorescence). The gases were premixed through a bed of glass balls and then flowed into a bundle of 437 small tubes (2 mm diameter) embedded and sealed at both ends on a plate, one plate being the top of the burner. The plates and the tubes were water cooled, minimizing the radial temperature gradient in the preheating zone. As a result it was possible to get both a good flame stabilization and a large optically homogeneous zone inside the flame. The laser beam crossed the flame at its upstream limit. Fluorescence was observed at right angles through a solid angle allowing only the observation of the homogeneous part of the flame. In such a flame a rather intense $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ chemiluminescence was observed. The laser-induced fluorescence signal, coming only from two fluorescent lines, could not be seen through the interference filter because it was negligible compared to the multiline chemiluminescence of $B^2\Sigma^+$ transmitted by the filter. To get a negligible chemiluminescent signal the fluorescence was detected through a monochromator, scanned synchronously with the laser.

RESULTS

C + N₂O reaction at 300 K

CN ($A^2\Pi_i$) vibrational distribution H + halomethane flames gave fairly strong C₂ chemiluminescences attributed⁴ to the exoergic reaction



When N_2O was added the spectra showed a strong decrease of C_2 emission indicating a consumption of atomic carbon and the simultaneous appearance of intense CN red bands (Figure 2). For partial pressures of N_2O greater than 20 mtorr the quasi-complete disappearance of those C_2 bands which overlap the CN red bands allowed the calculation of relative vibrational populations of CN ($A^2\Pi_i$) from the accurate measurement of band areas. The vibrational distribution peaks at $v'=1$ and extends up to $v'=8$ (Figure 3). The maximum energy available to CN corresponds to the mean total energy available to the reaction products. For the thermal reaction it is given through the relationship:

$$\varepsilon_{\text{tot}}(T) = -\Delta\varepsilon_0 + \varepsilon_A(T) + \varepsilon_R(T)$$

$\Delta\varepsilon_0$ = energy difference between zero point levels of products and reactants. From recent values of $D(C-N)^{5,6}$ and $D(N-NO)^6$ $\Delta\varepsilon_0$ can be estimated to 2.88 eV relative to ground state products and 1.75 eV relative to CN ($A^2\Pi_i$) + NO, since the energy difference between zero point levels of CN ($A^2\Pi_i$) and CN ($X^2\Sigma^+$) is 1.13 eV.⁷ $\varepsilon_A(T)$ = Arrhenius activation energy. It can be estimated to about 0.07 eV from the rate constant value at 300 K.⁸ $\varepsilon_R(T)$ = thermal

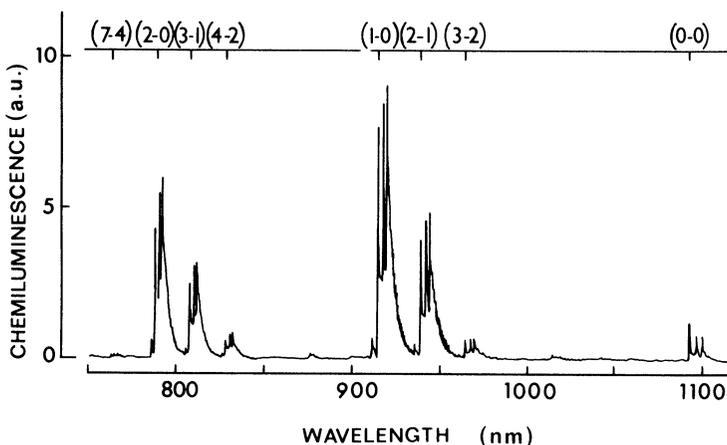


FIGURE 2 CN ($A^2\Pi_i \rightarrow X^2\Sigma^+$) chemiluminescence spectrum from the reaction $C+N_2O$ at 300 K. Pressure conditions; He: 3.68 torr, H_2 (before dissociation): 200 mtorr, $CHCl_3$: 20 mtorr, N_2O : 40 mtorr.

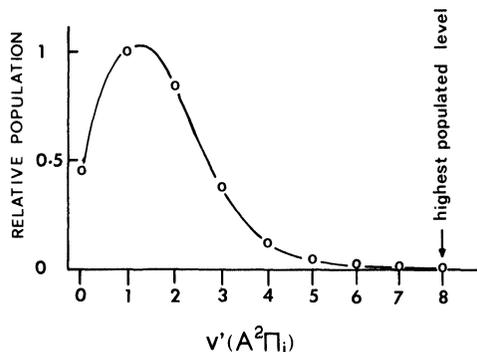


FIGURE 3 Vibrational distribution of CN ($A^2\Pi_i$) from the reaction $C+N_2O$ at 300 K.

energy of reactants relatively to their zero point levels. The thermal translational energy is given by $3/2 kT$ and the rotational one is given by kT since N_2O is a linear molecule. As for thermal vibrational energy it is given by

$$\sum_i k \frac{\theta_i}{e^{\theta_i/T} - 1} \quad \text{with} \quad \theta_i = \frac{hc}{k} \omega e_i$$

ωe_i = vibrational constant of i th vibrational mode, θ_i = characteristic vibrational temperature of i th mode.

For N_2O we have two degenerate vibrational modes with $\theta = 845$ K, the two other modes being characterized by temperatures of 1840 and 3190 K.⁹

At 300 K the maximum energy available to CN ($A^2\Pi_i$) is thus found to be 1.89 eV. As vibrational levels $v' = 8$ and $v' = 9$ lie respectively 1.81 and 2.00 eV above $v' = 0$,⁷ an excitation up to $v' = 8$ is expected. The agreement with experimental observation demonstrates that the observed chemiluminescence proceeds actually from the $C(^3P) + N_2O(^1\Sigma^+)$ reaction and that $C^*(^1D) + N_2O(^1\Sigma^+)$ reaction is negligible in our system, since such a reaction should have populated much higher levels.

The (2-0) band was sufficiently intense to be rotationally resolved. A rotational temperature of 347 K was found on $v' = 2$ indicating a significant relaxation of rotational levels.

CN ($X^2\Sigma^+$) vibrational distribution A typical CN ($X^2\Sigma^+$) excitation spectrum under conditions of low collisional relaxation is given in Figure 4. Rotational lines assignment was made from Engleman's table¹⁰ of the $\Delta v = 0$ CN violet spectrum. The rotational distribution is thermalized at 322 K indicating that relaxation of rotational levels is complete. Using the known Einstein coefficients for excitation and fluorescence⁵ it was then possible to determine from rotational lines intensities the relative populations shown in Figure 5. In this figure is also shown the least relaxed distribution we could get. Such a distribution is consistent with the vibrational excitation limit at $v' = 12$. The rather strong population inversion indicates that the intermediate complex is too short-lived to allow energy randomization.

The increase of collisional relaxation did not result in a Boltzmann-type distribution (Figure 6) since $v'' = 4$ appears as a smooth secondary peak after $v'' = 0$. This peak could be explained by the collisional transfer from CN ($A^2\Pi_i$) $v' = 0,1$ to CN ($X^2\Sigma^+$) $v'' = 4,5$ (Figure 1) which has been shown to be very efficient.¹¹ In such a case we could conclude that the production of CN ($A^2\Pi_i$) should not be negligible compared to that of CN ($X^2\Sigma^+$).

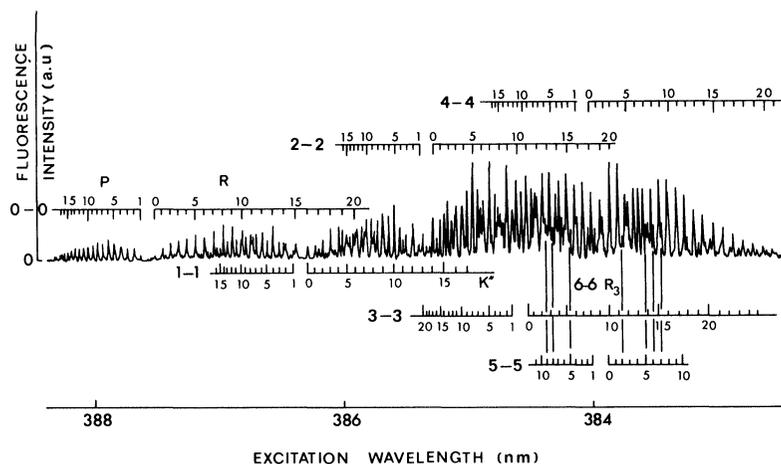


FIGURE 4 CN ($X^2\Sigma^+$) excitation spectrum. Pressure conditions; He: 3.80 torr, H₂: 180 mtorr, CHBr₃ = 11 mtorr, N₂O: 30 mtorr.

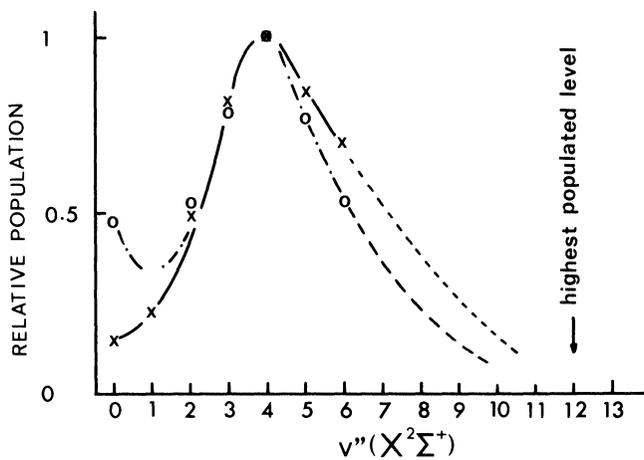


FIGURE 5 CN ($X^2\Sigma^+$) vibrational distribution. Circle: conditions of Figure 4. Cross: conditions of Figure 4 except $\text{CHBr}_3 = 10$ mtorr, and $\text{N}_2\text{O} = 10$ mtorr.

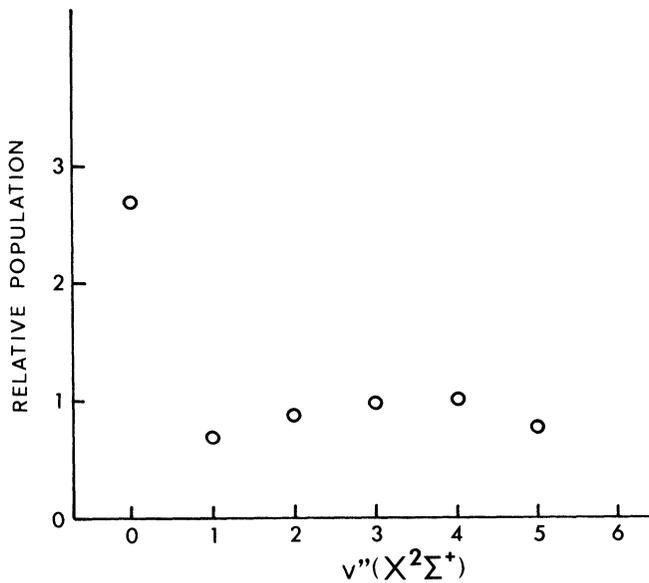


FIGURE 6 CN ($X^2\Sigma^+$) vibrational distribution. Pressure conditions, He: 3.80 torr, H_2 : 180 mtorr, CCl_4 : 25 mtorr, N_2O : 20 mtorr.

C₂H₂—4 N₂O self sustained flame at 2.8 torr

A C₂H₂—4 N₂O flame could be stabilized down to 2.8 torr. The emission spectrum from 600 to 1100 nm belongs exclusively to the CN ($A^2\Pi_i \rightarrow X^2\Sigma^+$) red system. Between 300 and 600 nm the usual combustion emissions of electronically excited OH, NH, CH and C₂ were detected in addition to the CN ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) violet system. The CN red system intensities appeared at least one order of magnitude greater than those of the violet system. This feature is to be noticed since the spontaneous emission probabilities for the red system are two orders of magnitude smaller than those of the violet system.^{5,12}

The rotational distribution of CN ($A^2\Pi_i$)_{v'=2} gives a temperature of 2500 K which is likely to be that of the heat bath. The vibrational distribution of CN ($A^2\Pi_i$) peaks at v'=2 and extends to higher vibrational levels than v'=8, the limit found for the C+N₂O reaction at 300 K (Figure 7). Such a distribution seems to be consistent with that of the C+N₂O reactions at 2500 K which gives an excitation limit of v'=14.

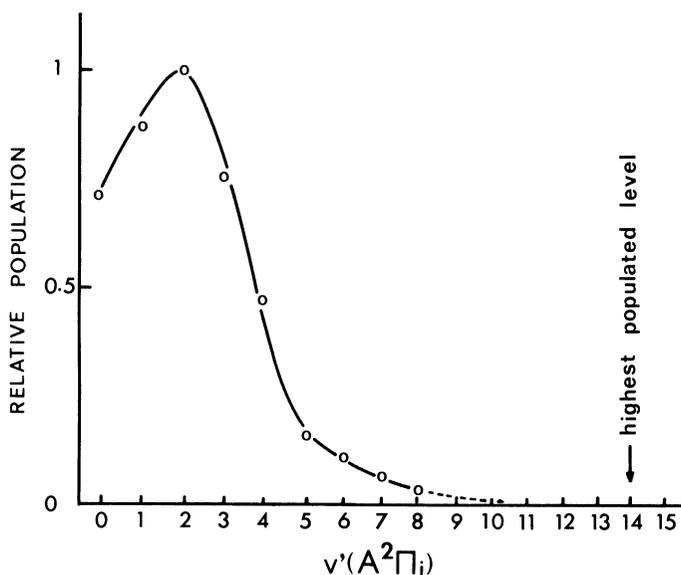


FIGURE 7 CN ($A^2\Pi_i$) vibrational distribution in a C₂H₂—4 N₂O flame at 2.8 torr and 2500 K. The excitation limit from the C+N₂O reaction at 2500 K is given.

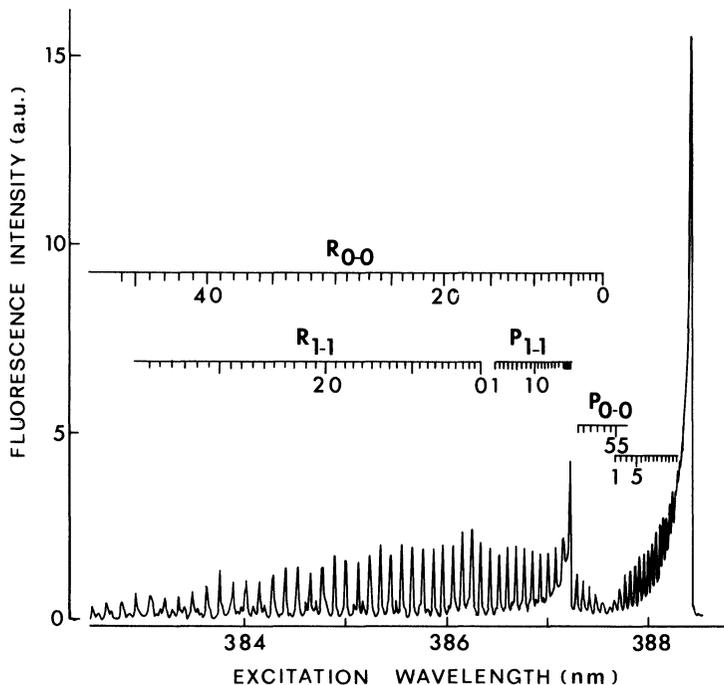


FIGURE 8 CN ($X^2\Sigma^+$) excitation spectrum in a $C_2H_2-4 N_2O$ flame at 2.8 torr.

The laser induced fluorescence of the CN ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) transition shows that the vibrational distribution of CN ($X^2\Sigma^+$) is relaxed (Figure 8).

Conclusion

The dynamics of the CN production from the $C+N_2O$ reaction at 300 K is characterized by vibrational populations inversions on both $A^2\Pi_i$ and $X^2\Sigma^+$ states indicating a short lived complex for each pathway. The low pressure combustion of $C_2H_2-4 N_2O$ flame gives a fairly strong CN ($A^2\Pi_i \rightarrow X^2\Sigma^+$) chemiluminescence which can be attributed to the $C+N_2O$ reaction, since the vibrational population of the $A^2\Pi_i$ state can be explained in terms of the $C+N_2O$ reaction

at 2500 K. However a relaxed vibrational distribution was observed in the CN ground state due to the unfavorable pressure conditions even though we had reached the lowest pressure compatible with a self sustained flame.

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