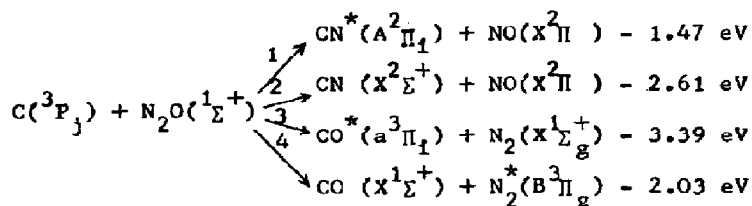


CN\*(A<sup>2</sup>Π<sub>1</sub>) CHEMILUMINESCENCE FROM C + N<sub>2</sub>O → CN\*(A<sup>2</sup>Π<sub>1</sub>) + NO

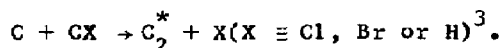
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At room temperature, the reaction C + N<sub>2</sub>O is very fast and may proceed along the following pathways<sup>1,2</sup> :



We have undertaken a spectroscopic study of this reaction to try to detect emission from electronically excited products. A gas phase flow reactor was used and chemiluminescent spectra were recorded between 200 and 1100 nm. Carbon atoms were produced by mixing, on a multihole diffuser, a flow of atomic hydrogen diluted in helium with a flow of halomethane (CHCl<sub>3</sub>, CHBr<sub>3</sub> or CCl<sub>4</sub>). This mixing gave intense C<sub>2</sub><sup>\*</sup> bands of Swan, Phillips and Ballik-Ramsay systems from the reaction :

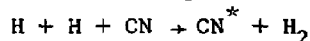


The CN red bands of A<sup>2</sup>Π<sub>1</sub> → X<sup>2</sup>Σ<sup>+</sup> transition arose readily when N<sub>2</sub>O was added to the flow of halomethane while the intensities of C<sub>2</sub><sup>\*</sup> bands decreased so much that the overlapping of CN<sup>\*</sup> red bands by C<sub>2</sub><sup>\*</sup> bands became negligible for P<sub>N<sub>2</sub>O</sub> > 0.02 torr. Furthermore in the red and near infrared no emission from N<sub>2</sub><sup>\*</sup>(B<sup>3</sup>Π<sub>g</sub>) could be detected. Thus for P<sub>N<sub>2</sub>O</sub> > 0.02 torr, CN<sup>\*</sup> red bands appearing alone, it was possible from the measurement of their intensities to determine the relative vibrational populations of CN<sup>\*</sup>(A<sup>2</sup>Π<sub>1</sub>). Between 200 and 250 nm Cameron bands from CO<sup>\*</sup>(a<sup>3</sup>Π<sub>1</sub>) were not detected.

About CN chemiluminescence, three main features can be pointed out:

1 - for constant operating conditions, the distribution of relative vibrational populations of A<sup>2</sup>Π<sub>1</sub> state was independent of the nature of halomethane.

2 - the increasing of power in the microwave cavity, which produced H atoms by dissociating  $H_2$  diluted in He, did not affect this distribution, even for H concentration ten times greater (determined by H + NO chemiluminescence). Thus energy transfers leading to  $CN^*(A^2\Pi_1)$ , from :



or collisions of CN with excited species produced either in the microwave cavity or in the diffusion flame, had no detectable influence on the observed distribution.

3 - If we suppose that reaction 1 has no activation energy and accounted for  $N_2O$  is a linear molecule, the mean total energy available on products, for reactants at temperature T is :

$$\bar{\epsilon}_{tot} = 1.47 \text{ eV} + \frac{5}{2} kT$$

$$\text{For } T = 300 \text{ K it is } \bar{\epsilon}_{tot} = 1.53 \text{ eV}$$

Vibrational levels  $v' = 7$  and  $v' = 8$  are lying, respectively, 1.48 and 1.68 eV above  $v' = 0^4$ . Production of  $CN^*(A^2\Pi_1)$  up to  $v' = 7$  must be expected from this reaction. In our experiments, bands from vibrational levels up to  $v' = 7$  were actually observed. We never detected any band corresponding to  $v' \geq 8$ .

These features indicate that the observed chemiluminescence of CN red bands must proceed by a unique mechanism, likely to be reaction 1. Distributions of relative vibrational populations of  $CN^*(A^2\Pi_1)$  for different pressures of  $N_2O$  are given in the figure. The collisional relaxation by  $N_2$ , chemically unreactive, is also shown. Let us call  $R = k_1/k_1 + k_2$  the ratio of the rate of production of  $CN^*(A^2\Pi_1)$  to the total rate of production of CN. Let us define  $R_e = N'/N' + N''$  the ratio of the effective steady density  $N'$  of  $CN^*(A^2\Pi_1)$  to the total steady density of CN on both electronic states  $A^2\Pi_1$  and  $X^2\Sigma^+$ . Owing to relaxation we have  $R_e < R$ . We applied the criterion of Sutton and Suchard<sup>5</sup>, determining minimal value of  $R_e$  to get amplification on a vibronic transition, to transitions with important Franck-Condon factors. For operating conditions of case d in the figure, the lowest value was got on 1-3 transition with  $R > R_e > 0.17$ . Thus chances for an electronic transition chemical laser based on  $C + N_2O$  reaction can be investigated from the transition  $CN^*(A^2\Pi_1)_{v'=1} \rightarrow CN(X^2\Sigma^+)_{v''=3}$ .

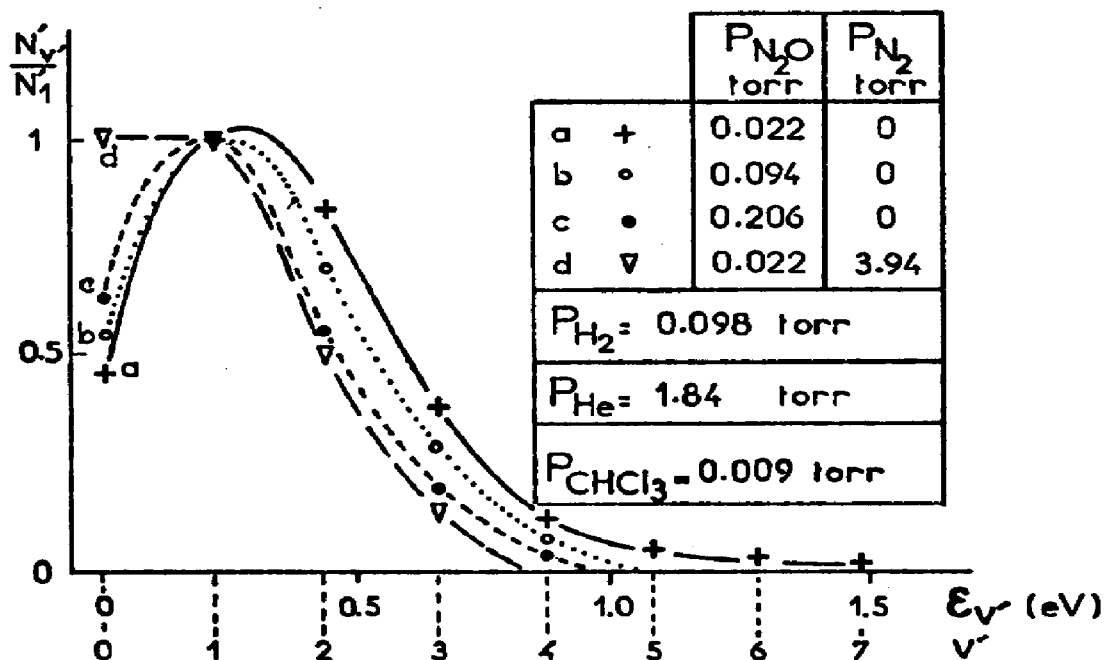
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$CN^*(A^2\Pi_1)$  vibrational distributions from  $C + N_2O \rightarrow CN^*(A^2\Pi_1) + NO$  under different pressures of  $N_2O$ . Relaxation by  $N_2$  is shown. The origin of vibrational energy is taken at  $v' = 0$  since available energy on reaction products at  $T = 300$  K,  $\epsilon_{tot} = 1.53$  eV, is given relatively to their lowest vibrational level.