



## CN(X 2 $\Sigma$ +) vibrational population inversion from the C+N2O $\rightarrow$ CN+NO reaction at 300 K

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Citation: The Journal of Chemical Physics **74**, 6523 (1981); doi: 10.1063/1.440998 View online: http://dx.doi.org/10.1063/1.440998 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/74/11?ver=pdfcov Published by the AIP Publishing

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The observed frequencies agree well with the frequencies of the E modes calculated by Luty, <sup>14</sup> which were 75, 69, and 60 cm<sup>-1</sup>. Unfortunately, Luty did not present his eigenvectors, so no clue to the source of the intensity disparity is available. It is less easy to compare the experimental frequencies with the values recently calculated by Windsor *et al.*, <sup>15</sup> because the Emodes are not readily identified in their figures and no tabulation was given. However, their frequencies are all between 80 and 110 cm<sup>-1</sup>, well above the observed values.

After our attempt to observe the Raman spectrum was finished, Jenkins and Lewis<sup>16</sup> reported the Raman spectrum of adamantane II at 100 °K but did not list their frequencies. From their figure, they observed peaks at (relative intensities in brackets) 29(s), 36(m), 45(s), 53(m), 61(s), 68(m), 78(s), 84(m), 93(m), 100(w), 109(w), and 118(m) cm<sup>-1</sup>, all measured from their figure to  $\pm \sim 1$  cm<sup>-1</sup>, with possible additional weak shoulders, in particular at 74  $\text{cm}^{-1}$ . At 100 °K the intense infrared line is at 74 cm<sup>-1</sup> and the weaker ones can be estimated to be at 62 and 52 cm<sup>-1</sup>, so the expected appearance of the Emodes in the infrared and Raman spectra is observed. The uncertainty with this Raman spectrum is, of course, that at least 12 features were observed but only five are expected, and the dipole moment derivatives are far too small to give additional peaks due to the E modes through longitudinal optic-transverse optic splitting. Luty calculated the  $A_1$  active rotational vibration and the inactive  $A_2$  one to be at 54 and 47 cm<sup>-1</sup> and the  $B_1$  translational vibration to be at 123 cm<sup>-1</sup>. Thus, the "extra peaks" in the Raman spectrum are largely

above 80 cm<sup>-1</sup> according to the calculation that best fits the infrared frequencies.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support and for a 1967 Science Scholarship to B. F. F.

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## $CN(X^{2}\Sigma^{+})$ vibrational population inversion from the $C+N_{2}O\rightarrow CN+NO$ reaction at 300 K

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In H + halomethane + N<sub>2</sub>O diffusion flames at 300 K, the C + N<sub>2</sub>O - CN + NO excergic reaction produces a strong CN( $A^{2}\Pi_{i}$ ) chemiluminescence, this species exhibiting a vibrational distribution peaking at v' = 1 and extending to v' = 7, in agreement with the excitation limit expected from the reaction excergicity.<sup>1,2</sup> To complete the results reported so far, it was necessary to determine the vibrational distribution in the CN( $X^{2}\Sigma^{+}$ ) ground state. This was accomplished using the laser induced fluorescence of the  $B^{2}\Sigma^{+} + X^{2}\Sigma^{+}$  CN violet system.

An initial mixture of  $H_2$  diluted in He was flowed through a microwave cavity (2450 MHz). The products of the discharge were then mixed with a halomethane  $(CHBr_3, CHCl_3, \text{ or } CCl_4)$ , and  $N_2O$  in a chemical laser type Teflon throat<sup>3</sup> to provide a reaction volume exhibiting a species density gradient only in the direction of gas pumping. The excitation laser beam was directed tangentially to the upstream limit of the reaction zone in order to excite the least vibrationally relaxed CN radicals. The fluorescence from  $B^2\Sigma^*$  was observed at right angles through the incoming flow of H + He. A two-stage mechanical pump gave an estimated flow speed of 20 ms<sup>-1</sup> in the reactor. Excitation was performed with a tunable nitrogen laser pumped dye laser (Sopra) on  $\Delta v = 0$  transitions between 382 and 389 nm using the BBQ dye. Fluorescence from  $\Delta v = -1$  was detected between



FIG. 1. Uncorrected excitation spectrum of  $CN(X^2\Sigma^*)$ produced by  $C + N_2O \rightarrow CN + NO$ at 300 K with  $H_2 = 0.18$  Torr, He = 3.80 Torr,  $CHBr_3 = 11$ mTorr, and  $N_2O = 30$  mTorr. Unoverlapped rotational lines from v'' = 5 and v'' = 6 are indicated.

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 (EMI 9789 QB) was amplified (Keithley 427), averaged by a boxcar integrator (Tekelec Airtronic 9870), and displayed on a strip chart recorder.

A typical excitation spectrum obtained under conditions of low collisional relaxation is given in Fig. 1. Rotational lines assignment was made from Engleman's table<sup>4</sup> of  $\Delta v = 0$  CN violet system. Seven rotational lines can be clearly resolved for the (5-5) transition, and one R(3), for the (6-6) transition. Rotational lines from v'' > 6, strongly overlapped and certainly much weaker than those of lower vibrational levels, cannot be distinguished. The rotational distribution appears thermalized at 300 K. Thus, it was easy to deduce the vibrational distribution from intensities of unoverlapped rotational lines. These intensities were determined by correcting spectrum intensities for the wavelength variation of laser intensity for excitation, for the filter transmission, and for the photomultiplier response for fluorescence. Using the known Einstein coefficients<sup>5</sup> for excitation and fluorescence it was then possible to determine the relative vibrational populations shown in Fig. 2.





Collisional relaxation efficiency decreased in the following order: halomethane  $\gg N_2O \gg H_2 > He$ . Flames could be stabilized at lower pressure with CHBr<sub>3</sub> than with CHCl<sub>3</sub> or CCl<sub>4</sub>. From a preliminary analysis of collisional relaxation it seems unlikely that under the experimental conditions of Fig. 1 the collisional transfer from  $CN(A^2\Pi_i)v' = 0, 1, \ldots$  to  $CN(X^2\Sigma^*)v'' = 4, 5, \ldots$ could be of importance. The maximum observed for v'' = 4 is likely to proceed intrinsically from the pathway of the C + N<sub>2</sub>O reaction leading to  $CN(X^2\Sigma^*)$ . The energy of the highest vibrational level which can be populated corresponds to the mean total energy  $\overline{\epsilon}_{tot}$  available to reaction products, as follows:

$$\overline{\epsilon}_{tot} = -\Delta \epsilon + \epsilon_A + \frac{5}{2}kT$$
,

 $\Delta \epsilon = energy difference$ 

between products and reactants,

 $\boldsymbol{\epsilon}_{\textit{A}} = activation \ energy$  .

From the rate constant value at 300 K,  ${}^{6} \epsilon_{A}$  can be estimated to be  $0.07 \pm 0.01$  eV. From recent values of  $D(C-N)^{5,7}$  and D(N-NO),  ${}^{7} \Delta \epsilon$  can be estimated to 2.88  $\pm 0.05$  eV so that at 300 K we get  $\overline{\epsilon}_{tot} = 3.01 \pm 0.06$  eV. As vibrational levels v'' = 12 and v'' = 13 lie, respectively, 2.82 and 3.04 eV above v'' = 0, <sup>8</sup> the production of  $CN(X^{2}\Sigma^{*})$  up to v'' = 12 can be expected. The experimental distribution shown here, which is the intrinsic distribution from the C + N<sub>2</sub>O reaction at 300 K modified by a rather slight collisional relaxation, is consistent with such a vibrational excitation limit. It should be noted that less relaxed distributions were obtained with weaker spectrum intensities; the maximum remained at v'' = 4.

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## Growth of structurally different oxide layers of the same stoichiometry on metals by multispecies diffusion

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It is sometimes found that oxides growing on metals have a distinctly different structure adjacent to the parent metal than adjacent to the reactive oxygen.<sup>1</sup> The purpose of this note is to examine one possible implication of this phenomenon, namely, that of an interior reaction zone for new oxide formation.

For simplicity, consider the case in which a cation interstitial particle current flows through the oxide adjacent to the parent metal, while an anion interstitial particle current flows through the oxide adjacent to the reactive oxygen. Then it is conceivable that the reaction zone for new oxide formation is neither the metaloxide interface nor the oxide-oxygen interface, as usually assumed for cases of a single mobile ionic defect species,<sup>2</sup> but instead is within the interior of the oxide. Although new oxide formation could possibly occur throughout the existing oxide as the cation and anion interstititals come into contact, this does not seem too likely because the microscopic volumes available for motion of the diffusing defects are too small to accommodate two defects side by side so that chemical reaction and recombination<sup>3</sup> can occur. It seems more probable that there is a discrete reaction zone located somewhere in the interior of the oxide where the diffusing cations and anions meet and react to form more oxide (Fig. 1). For planar metal surfaces, the planar oxide layers experimentally observed as being structurally different<sup>1</sup> indicate a planar reaction zone at the boundary separating the two layers. In fact, the structure differences of the individual layers may well be closely related to the different species diffusing through these layers.

If oxide growth is taking place under conditions appropriate for the thick-film parabolic growth law, <sup>4</sup> each diffusion current  $J_s$  (s = 1 for cation interstitials and s = 2 for anion interstitials) varies inversely with the thickness  $L_s$  of the layer in question, namely,

$$J_s = \gamma_s / L_s \ (s = 1, 2) ,$$
 (1)

where the constants  $\gamma_s$  are determined from the respective thick-film parabolic rate constants.<sup>5</sup> (It can be argued convincingly that the coupled-currents condition<sup>2</sup> holds independently for each layer.) Considering the formation of new oxide having chemical composition  $Me_{\rho}O_{q}$  for both layers (the two layers differing only in structure and not stoichiometry<sup>1</sup>), then the steady-state defect currents satisfy the relation (growth under fixed experimental conditions is assumed)

$$|J_1/p| = |J_2/q|$$
 . (2)

Substituting Eq. (1) then leads to the following prediction for the thickness ratio for the layers:

$$L_2/L_1 = \left| \not P \gamma_2/q \gamma_1 \right| . \tag{3}$$

A knowledge of the stoichiometry of the oxide and the thick-film parabolic rate constants thus allows a prediction for the thickness ratio. Alternatively, an experimental determination of the stoichiometry and the thickness ratio allows one to infer the ratio  $|\gamma_2/\gamma_1|$  involving the thick-film parabolic rate constants. This is important because it yields information on the diffusion coefficients and defect concentrations in the layers.<sup>5</sup> It is noteworthy that Eq. (3) predicts that the thickness ratio  $L_2/L_1$  should be independent of the individual layer thicknesses  $L_1(t)$  and  $L_2(t)$  which steadily increases with time t of oxide growth. It would be interesting to check this prediction experimentally.



FIG. 1. Growth of an oxide layer on a metal by the diffusion of two different defect species.