

# A crossed beam study of the reaction $C(^3P) + N_2O$ : energy partitioning between the $NO(X^2\Pi)$ and $CN(X^2\Sigma^+)$ products

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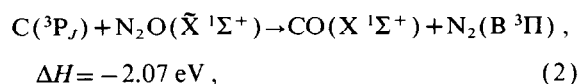
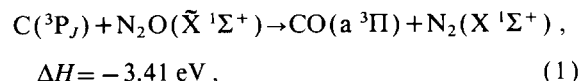
The reaction of  $C(^3P)$  with  $N_2O$  is studied at a collision energy of  $0.9 \pm 0.4$  eV in a crossed, pulsed molecular beam arrangement using laser ablation for carbon atom production. Nascent  $CN(X^2\Sigma^+)$  and  $NO(X^2\Pi)$  products are detected by laser-induced fluorescence. In accord with previous studies, the  $CN(X^2\Sigma^+)$  product is found to be vibrationally inverted (maximum at  $v=3$ ) and possesses substantial rotational excitation. Product  $NO(X^2\Pi)$  is formed vibrationally "cold" (maximum at  $v=0$ ) but rotationally "hot", with a maximum population found at  $J=49.5$  for both spin-orbit states. The implications of these results for the reaction dynamics are assessed.

## 1. Introduction

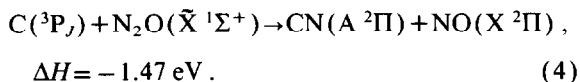
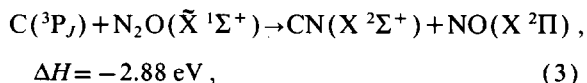
The reactions of ground-state atomic carbon ( $^3P$ ) are important in combustion environments, hydrocarbon synthesis, electric discharges, and graphite ablation, in addition to their fundamental interest. In contrast to the corresponding reactions of ground-state  $O(^3P)$ , relatively few studies have examined reactions of  $C(^3P)$ , due mainly to difficulties in source preparation. The formation of electronically and/or vibrationally excited products in the reactions of  $C(^3P)$  with  $SO_2$  [1],  $NO_2$  [2],  $OCS$  [3],  $N_2O$  [4] and  $O_2$  [5] have allowed determination of state distributions of chemiluminescent products under rotationally relaxed conditions. In addition, detection by laser-induced fluorescence (LIF) has been employed to study the  $CN(X^2\Sigma^+)$  product from the reactions  $C(^3P) + N_2O$  and  $C(^3P) + NO$  under both rotationally relaxed [6] and single-collision [7,8] conditions. As demonstrated in the latter studies, the combination of laser ablation with pulsed crossed molecular beams is an attractive method for studying reactive scattering of atoms under single-collision

conditions with well-defined collision energies. In this Letter, we report preliminary results on the  $C(^3P) + N_2O$  reaction at a collision energy of  $\approx 0.9$  eV obtained with a crossed beam apparatus, employing free laser ablation for production of the atom beam. This reaction is especially intriguing in that LIF detection is possible for both  $CN$  and  $NO$  products. While four-atom reactions with detection of both diatomic products have been previously studied (e.g.,  $H + NO_2$  [9,10]), they have primarily involved light-atom attack or light-atom transfer reactions, whose dynamics are strongly influenced by kinematic constraints.

Assuming the validity of spin conservation and symmetry correlation rules and an intermediate of  $C_s$  symmetry, the reaction of ground-state atomic carbon with nitrous oxide may proceed through the following allowed pathways:



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Chemiluminescence from the electronically excited products of reactions (1) and (2) has not been observed, while  $\text{CN}(A \rightarrow X)$  chemiluminescence from reaction (4) has been observed in one study [4] but not in another [6] and remains a source of controversy.

As mentioned above, product CN from channel (3) has been detected by LIF under both rotationally relaxed and single-collision conditions. The qualitative conclusions regarding vibrational excitation were similar; a vibrational population inversion was observed in each case with the maximum population around  $v=3$  and bandheads up to  $v=6$  identified. Spectra obtained under single-collision conditions suggested that the rotational excitation of the CN fragment was also high [7,8], and although the distributions were non-Boltzmann, temperatures as high as 11000 K were inferred from the mean rotational energies [7]. The observed CN excitation limit, which corresponded to approximately half of the available energy, led to the suggestion that a large amount of energy must reside in the NO fragment [8]. This suggestion was reasonable in light of the deep well obtained in the calculated potential energy surface (PES), which implied the possible formation of an intermediate CNNO complex, the lifetime of which could be long compared to the time required for intramolecular energy redistribution (IVR) [11]. Determination of the NO state distributions should therefore be valuable in clarifying the mechanism of the reaction and revealing added details of the PES associated with the reaction channel leading to  $\text{CN}(X^2\Sigma^+)$  and  $\text{NO}(X^2\Pi)$ . The preliminary results reported here show that while both CN and NO are born with high degree of rotational excitation, the vibrational excitation of NO is much lower than that of CN.

## 2. Experimental

The crossed molecular-beam apparatus employed

in these studies consists of an octagonal stainless-steel reaction chamber and an ablation chamber containing the carbon source, each separately pumped by a liquid-nitrogen trapped diffusion pump (Varian VHS-4), giving average background pressures with both beams on of  $\leq 3 \times 10^{-5}$  and  $\leq 8 \times 10^{-5}$  Torr for the source and main chambers, respectively. This apparatus will be described in detail elsewhere [12].

The atomic beam is generated by free laser ablation of a spectroscopic-grade graphite rod. The free ablation produces a pulsed beam of short temporal duration (10–20  $\mu\text{s}$  fwhm) at the interaction region, which is translationally "hot" compared to beams produced by atom entrainment in the expansion of a carrier gas from a pulsed nozzle [7]. Although the spread in atom velocities is larger than in beams produced by the latter method, free ablation is advantageous in that near complete destruction of cluster species is achieved at moderate laser energies. In this work, approximately 20 mJ of 355 nm radiation from a Nd:YAG laser (14 ns fwhm) is focused to a 1 mm spot at the graphite rod surface with a 50 cm fused silica lens. To ensure good shot-to-shot stability the rod is maintained in constant helical motion. The position of the rod relative to the skimmer and chamber center is adjustable over a 4.5 cm range using an XY translator. In our current configuration the rod is placed 6.6 cm from the center of the chamber, and the atom beam is collimated to  $\approx 10^\circ$  by a stainless-steel skimmer (3 mm diameter). Removal of ionic species is accomplished by a pair of deflection plates located inside the skimmer mount; however, no differences were observed in spectra taken with the field on and off.

The neutral beam is generated by expansion of a 10% mixture of  $\text{N}_2\text{O}$  (MG Industries, 99.9%, used without further purification) in He (Spectra, 99.999%) through the 0.5 mm orifice of a pulsed nozzle (Lasertechnics LPV-1) at a typical stagnation pressure of 10 psig (0.7 atm). The nozzle is oriented perpendicular to the atomic-beam centerline and its position is adjusted with an XYZ translator. Typically the nozzle orifice is set 20 mm (40 nozzle diameters) above the chamber center. A series of scans taken at varying stagnation pressures and nozzle distances verified that single-collision conditions are met under these conditions. In the current configuration this beam is uncollimated.

The experimental timing sequence is controlled by

a master pulse/delay generator with 10 ns resolution. Pulses from this generator trigger the pulsed nozzle and the ablation laser so that the carbon and  $N_2O$  beams overlap temporally at the center of the chamber. The probe laser pulse is delayed by 15  $\mu s$  with respect to the ablation pulse. In the current experimental geometry, the probe laser beam propagates in a direction orthogonal to the photomultiplier tube (PMT) axis and oriented at  $45^\circ$  to the axis of the atomic beam and  $90^\circ$  to the molecular beam. The probe laser (Lambda Physics MSC 201 + FL3002) is operated on either QUI or C460 dyes. Product detection is achieved by excitation of the  $\Delta v=0, -1$ , and  $-2$  sequences of the  $B^2\Sigma^+ \leftarrow X^2\Sigma^+$  transition of CN and the  $\Delta v=0$  sequence of the  $A^2\Sigma^+ \leftarrow X^2\Pi$  transition of NO (for which the dye laser output is frequency doubled in a BBO crystal). A fraction of the resulting fluorescence is imaged through appropriate filters onto either a GaAs (Hamamatsu R943-02) or a solar blind (Hamamatsu RU166H) PMT. The PMT signals are digitized and passed to computers which control the data acquisition and processing.

### 3. Results

LIF signals were obtained for both  $CN(X^2\Sigma^+)$  and  $NO(X^2\Pi)$ . A typical  $CN(B^2\Sigma^+ \leftarrow X^2\Sigma^+)$  LIF spectrum, corrected for probe power variations, showing the  $\Delta v=-2$  sequence is displayed in fig. 1. The CN product is rotationally and vibrationally "hot" with bandheads of  $v \leq 7$  clearly identified and the maximum population is in  $v=3$ . The observed rovibrational excitation is in good agreement with the work of Costes et al. [8] who, using the  $\Delta v=-1$  sequence, reported rotational temperatures up to 11000 K (based on mean energies) and an inverted vibrational distribution which peaked at  $v=3$  and extended to  $v=6$ . The  $\Delta v=-2$  progression allows the detection of higher vibrational levels due to reduced spectral congestion. The high rotational excitation is clearly evident in fig. 2, which shows part of the P branch of the (0, 0) band. Rotational levels  $\leq 60$  are significantly populated and easily identified before the onset of the (1, 1) bandhead.

In this work, state-resolved detection of  $NO(X^2\Pi)$  is reported for the first time. A representative sec-

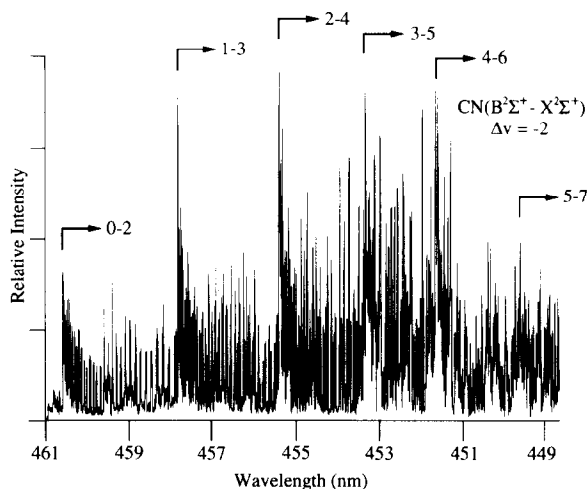


Fig. 1. Nascent  $CN(B^2\Sigma^+ \leftarrow X^2\Sigma^+)$  LIF spectrum observed from the reaction of  $C(^3P)$  with  $N_2O$ . The  $\Delta v=-2$  sequence was excited and fluorescence was observed on the  $\Delta v=0$  sequence.

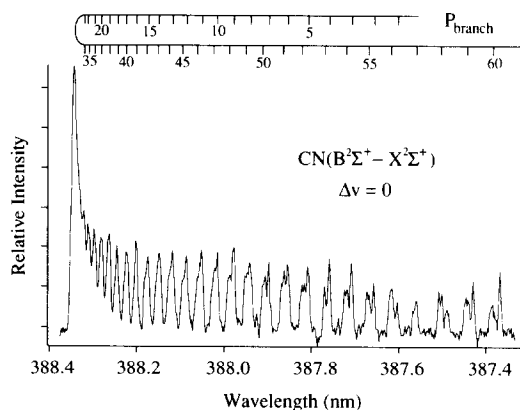


Fig. 2. Nascent  $CN(B^2\Sigma^+ \leftarrow X^2\Sigma^+)$  LIF spectrum displaying the P branch of the (0, 0) bandhead. The  $\Delta v=0$  sequence was excited and fluorescence was observed on the  $\Delta v=0$  sequence. This spectrum was taken under partially saturated conditions (probe laser energy  $\approx 50 \mu J$  in 7 mm beam). The high rotational levels are broader than the adjacent low levels due to the increased separation between their spin-rotation components.

tion of the  $(A^2\Sigma^+ \leftarrow X^2\Pi)$  spectrum, again corrected for probe power variations, showing the (0, 0) bandhead can be seen in fig. 3. Individual peaks have been assigned with reference to the tabulated line positions of Deezsi [13]. In analogy to CN, a high degree of rotational excitation is observed with levels in excess of  $J=60.5$  being detected. Close examination of

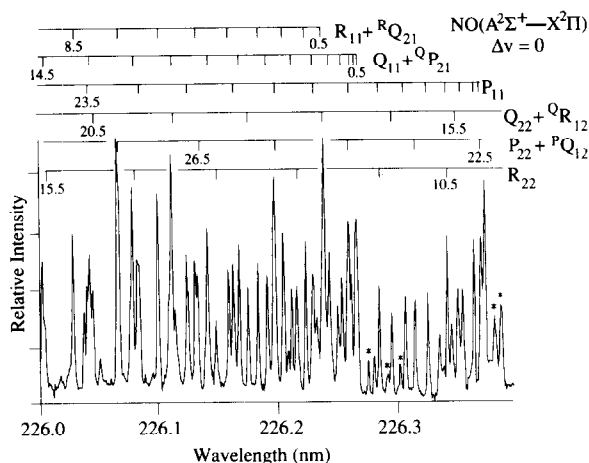


Fig. 3. Nascent NO( $A^2\Sigma^+-X^2\Pi$ ) LIF spectrum displaying the region of the (0, 0)  $Q_{11}$  bandhead. The  $\Delta v=0$  sequence was excited and fluorescence was observed on the  $\Delta v=0-7$  sequences. Checks of P/R line intensity ratios revealed no evidence of saturation at probe energies  $\leq 100 \mu\text{J}$  in a 7 mm beam.

the NO spectra reveals a number of weak features not attributable to NO( $A^2\Sigma^+-X^2\Pi$ ). In the spectral region displayed in fig. 3 these "spurious" lines are indicated by asterisks. A possible source of these peaks is excitation of the Mulliken bands ( $D^1\Sigma_u^+-X^1\Sigma_g^+$ ) of  $C_2$ , which is a minor product of free graphite ablation [14]. By performing scans with only the ablation source operating, signals were observed in the (0, 0) and (1, 0) bandhead regions which are definitely assignable to the  $C_2$  Mulliken bands. However, overlap is observed only with rotational levels of the NO(0, 0) band higher than those shown in fig. 3. Clearly, further studies are necessary to unambiguously determine the origin of the spurious spectral features, which fortunately present little hindrance to analysis of the NO product state distributions. It should be pointed out that neither  $C_2$ ,  $C_3$ , nor higher order clusters have sufficient exoergicity on reaction with  $N_2O$  to result in the observed CN and NO excitations. In fact, the removal rate coefficients of  $C_2$  and  $C_3$  by  $N_2O$  are  $\leq 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [15] and we have not observed  $C_3$  LIF signals although the Swing bands ( $A^1\Pi_u-X^1\Sigma_g^+$ ) have a strong absorption in the region of the CN( $B^2\Sigma^+-X^2\Sigma^+$ )  $\Delta v=0$  sequence.

Metastable carbon singlet states ( $^1D$  and  $^1S$ ) are also possible byproducts of the ablation process.

Checks were made for the presence of  $C(^1D)$  in the ablated beam by seeding  $N_2O$  in  $H_2$  as a 10% mixture.  $C(^1D)$  is known to react efficiently with  $H_2$  to yield  $CH(X^2\Pi)$  ( $k=(3.7\pm 0.2)\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [16],  $\Delta H=-0.26 \text{ eV}$ ), whilst reaction with  $C(^3P)$  is endoergic. No intensity attributable to  $CH(X^2\Pi)$  was detected. Contribution from  $C(^1S)$  is assumed unimportant in light of the absence of  $C(^1D)$ , 1.42 eV lower in energy. In addition, Costes et al. were unable to detect  $C(^1S)$  by LIF at 247.9 nm in their graphite ablation source [7].

LIF signal intensities, corrected for probe power fluctuations, were converted to populations by taking account of the appropriate Hönl-London line-strength factors, calculated using the formulae of Earls [17]. Intensities were obtained from peak heights, averaged over several scans, due to the large number of merged lines and hence difficulty in determining peak areas. The rotational distribution for the  $v=0$  level of NO( $^2\Pi_{1/2}$ ) is displayed in fig. 4, and a similar distribution is obtained for NO( $^2\Pi_{3/2}$ ). The distribution is inverted with a maximum population in  $J=49.5$ .

A measure of the vibrational partitioning is generally determined by summation over the observed rotational levels of each vibrational state. In our case this was not practical due to a significant reduction in signal intensity for  $v=1$  and 2 relative to  $v=0$  and the extensive spectral overlap of the bands. For these reasons, a series of scans were obtained under conditions of partial rotational but negligible vibra-

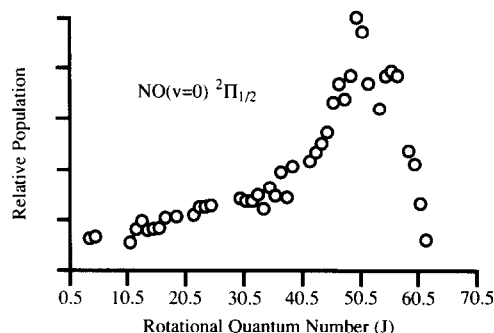


Fig. 4. Nascent rotational distribution of the  $v=0$  level of NO( $^2\Pi_{1/2}$ ) produced in the  $C(^3P)+N_2O$  reaction. While error bars are not shown, random measurement error is  $\leq 7\%$ . Possible systematic errors affecting this distribution are discussed in the text.

tional relaxation. This was achieved using a stagnation pressure of 40 psig (2.7 atm). Rotational relaxation of NO by He is much more efficient than vibrational relaxation ( $k_R(v=2) \approx 2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [18],  $k_v(v=1) = 1.05 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [19]). Since comparable rotational distributions were observed for all vibrational levels in the nascent spectra, we assume similar relaxed distributions for each vibrational level, and thus the vibrational population ratios were obtained by comparing intensities in the bandheads of each level. The vibrational population in  $v=0:1:2$  was found to be 1:0.45:0.12. These ratios have been corrected for the Franck-Condon factors associated with both excitation and emission to  $v''=0-7$  [20] convoluted with the wavelength response of the filter/PMT combination. Although the random measurement error is  $\leq 7\%$ , the quoted ratios should be taken as upper limits, since corrections for systematic errors would lower the population of vibrationally excited levels, as discussed below.

Quantities measured by LIF are, of course, number densities. In order to extract the cross section associated with formation of a specific product quantum state one must employ a number density-to-flux transformation. Energy conservation requires that product internal excitation correlates inversely with recoil velocity, fragments with a higher level of internal excitation being preferentially detected. In addition, in experiments utilizing a probe volume much smaller than the crossed-beam interaction region, products formed outside the irradiated volume may scatter into it thus contributing to the signal.

For this preliminary report no attempt was made to correct for density-to-flux effects, but we believe that the transformation will not affect the conclusions regarding the relative internal energy deposition in the CN and NO fragments. The CN( $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ ) LIF spectra obtained in our work are in good qualitative agreement with those obtained by Costes et al. under conditions where density-to-flux corrections were small even for highly excited CN fragments [7,8]. Also, since the NO vibrational population distribution is determined under relaxed conditions, we assume that translational equilibration among the levels is achieved. The NO ( $v=0$ ) rotational distribution is probably biased in favor of high rotational levels; however, since the excitation

in the accompanying CN fragment is very broad, we expect a rather broad translational energy distribution for each NO rotational level, making the differences between levels not as sharp as for a narrow translational distribution. We thus expect a density-to-flux correction (employing, for example, the model recently proposed by Naulin et al. [21]) to neither significantly affect the NO state distributions presented here nor the qualitative conclusions regarding the relative energy deposition in the CN and NO fragments.

#### 4. Discussion

The total energy available for partitioning between the internal degrees of freedom and recoil velocity of the reaction fragments is given by

$$E_{\text{avail}} = E_{\text{trans}} + E_{\text{int}} - \Delta H_0,$$

where  $E_{\text{trans}}$  is the relative translational energy of the reactants,  $E_{\text{int}}$  is the rotational and vibrational energy of  $\text{N}_2\text{O}$  and  $\Delta H_0$  the enthalpy change or the difference between the zero-point energies of reactants and products.  $\Delta H_0$  is calculated to be 2.88 eV [22]. The velocity of the molecular beam is taken to be  $\approx 1500 \text{ m s}^{-1}$  (10%  $\text{N}_2\text{O}/\text{He}$ ) and that of the C( $^3\text{P}$ ) is estimated in the range 3000–5000  $\text{m s}^{-1}$  from the appearance time of the signal and the translational distributions determined by time-of-flight following 351 nm graphite ablation [14].  $E_{\text{trans}}$  is thus estimated to be  $0.9 \pm 0.4 \text{ eV}$ . Since  $\text{N}_2\text{O}$  is cooled to  $\approx 10 \text{ K}$  in the supersonic expansion,  $E_{\text{int}}$  is negligible and we estimate that  $E_{\text{avail}} = 3.9 \pm 0.4 \text{ eV}$ .

The CN excitation limit observed by Costes et al. and ourselves suggests that nearly half of  $E_{\text{avail}}$  is deposited as internal energy of CN. Of the remaining  $\geq 50\%$ , significantly less appears as internal excitation of the NO fragment, which is formed vibrationally cool;  $\langle f_i \rangle \approx 5\%$  while  $\langle f_R(\text{NO}) \rangle \approx \langle f_R(\text{CN}) \rangle$ , where  $f_i$  is the fraction of energy deposited in the  $i$ th degree of freedom. Such non-statistical energy partitioning with one vibrationally "hot" and one vibrationally "cold" product is indicative of a reaction mechanism with substantial "direct" character. For pseudo-triatomic systems ( $A+BC$ ) Polanyi showed that product vibrational excitation can be correlated with reaction barrier location [23] and

height [24]. Exoergic reactions such as the one under investigation were found to have early barriers located in the entrance valley of the PES. In direct interactions on such surfaces, "attractive" energy released as the reactants approach was channeled into product vibration. Translational energy was found to be effective in overcoming barriers positioned early along the reaction coordinate. Attractive energy release has also been associated with forward scattering of the diatomic product, and in its limit the system can be thought of in terms of stripping dynamics. Here, the time scale of the interaction is so short that the C moiety behaves as a "spectator", the momentum of A carrying B towards a forward peaked angular distribution. Clearly, in the  $C(^3P) + N_2O$  reaction the NO species is not a true spectator and some level of energy flow into the N-O bond occurs. This suggests an attractive interaction between the CN and NO and the formation of a short lived intermediate which falls apart before complete energy randomization over all internal degrees of freedom.

Classical trajectory calculations of reaction (3) were run on a PES constructed using a MNDO semi-empirical CI SCF calculation [11,25]. The calculations assumed a pseudo-triatomic  $CNN'$  intermediate leaving no provision for partitioning of energy into the NO fragment. The surface, presumably a triplet of  $A''$  symmetry, showed a deep well favoring the formation of a long-lived intermediate. High CN vibrational excitation was found, and the calculated vibrational distribution was strongly inverted with maximum population in  $v=11$  and 12 (cf. experimentally  $v_{max}=3$ ). Vibrational inversion despite the presence of a deep well was attributed to the high exoergicity of reaction, and it was concluded that the reaction, although indirect, possessed some direct character. It has been shown that for surfaces with deep wells, the intermediate lifetime will fall dramatically at high collision energies with the interaction tending towards direct [26]. However, a more detailed theoretical study providing for energy flow into the third bond (i.e. NO) is clearly required. At the large collision energies employed in this work we suggest that the  $C(^3P) + N_2O$  reaction is predominantly direct and attractive in nature although exhibiting some indirect character. An interaction between CN and NO induced by the presence of the well corresponding with the  $CNNO$  complex inter-

mediate, allows some transfer of energy into the NO bond before the fragments separate permanently. Such complex effects are well known on attractive surfaces [26].

Product rotational excitation must obey the conservation relationship

$$L + J = L' + J'.$$

Here  $L$  and  $L'$  are the orbital angular momenta of  $C(^3P)$  with respect to  $N_2O$  and CN with respect to NO, and  $J$  and  $J'$  are the internal angular momenta of  $N_2O$  and  $NO + CN$ . Since  $J$  is small, reactant orbital angular momentum is partitioned into product orbital and internal angular momentum. Classically,  $L = \mu vb$ , where  $\mu$  is the reduced mass of the reactants,  $v$  the relative velocity, and  $b$  the impact parameter. For this reaction, the large reduced mass, high collision energy, and large range of reactive impact parameters (evidenced by the large reaction cross section) suggest that fragment rotational excitation is not restricted by reactant orbital angular momentum. In such a case, the fraction of angular momentum appearing as product rotation is determined by details of the PES, namely the anisotropy in the potential or the geometry of the reactive path. The "hot" rotational distributions observed suggest a non-linear intermediate such that forces acting towards fragmentation impart a torque on the departing radicals. A shallow angular dependence of the potential for collinear C atom attack at  $NN'$  was determined theoretically [11], and the barriers to non-linear approach can be easily overcome by the translational energy of the reactants, suggesting that a broad distribution of  $CNN$  angles may lead to reaction.

The reaction of  $C(^3P)$  with  $N_2O$  can yield  $NO(X^2\Pi)$  via two pathways corresponding to CN in its ground ( $X^2\Sigma^+$ ) and first excited ( $A^2\Pi$ ) states. Costes et al. observed  $CN(A^2\Pi \rightarrow X^2\Sigma^+)$  chemiluminescence in a discharge flow system at total pressures of  $\approx 2$  Torr, utilizing the  $H + \text{halomethane}$  reaction to generate carbon atoms [4]. However, at lower pressures Sekiya et al., producing  $C(^3P)$  from dissociation of CO molecules with  $Ar(^3P_{2,0})$ , were unable to detect emission from  $CN(A^2\Pi)$  on addition of  $N_2O$  [6]. It was concluded that in the higher pressure work  $CN(A^2\Pi)$  was formed in secondary processes. Rayez and co-workers have shown that, assuming a planar intermediate configuration, re-

action to yield ground-state species can occur via an  $1A''$  or  $1A'$  surface [11]. It was postulated that  $CN(A^2\Pi)$  might be formed by a nonadiabatic transition from the  $1A'$  to  $2A''$  surface which correlates with  $N_2O$  in an excited triplet state and carbon  $^3P$  or  $^1D$ . Failure to detect  $CN(A^2\Pi)$  emission led Sekiya et al. to the conclusion that such a transition must occur with low probability. It is possible, however, that weak emission in their system was quenched by collisional equilibration between close-lying vibrational levels of the  $X^2\Sigma^+$  and  $A^2\Pi$  states which occurs with near gas-kinetic efficiency [27]. Conversely, such efficient collisional mixing between the  $X$  and  $A$  states may have been the source of the  $A \rightarrow X$  emission observed by Costes et al. The  $NO$  rotational excitations obtained in this work show no evidence for the involvement of two reaction channels. For example, no bimodality in the rotational distributions is observed, which might be expected if reaction (4), with 1.41 eV less available energy, was important.

In conclusion, we have presented preliminary results for  $NO$  state distributions in the  $C(^3P) + N_2O$  reaction. It is suggested that the reaction exhibits predominantly direct character while influenced by the attractive forces towards a  $CNNO$  intermediate. Although this work has gone some way in elucidating the reaction dynamics, it is apparent that many questions still remain. Investigation of the effect of translational energy on intermediate lifetime and thus relative energy deposition in the reaction fragments, analysis of fine-structure components and determination of vector correlations are now in progress in our laboratory. Improved calculations of the PES are clearly required.

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