Reaction dynamics of $CN+O_2 \rightarrow NCO+O(^3P_2)$

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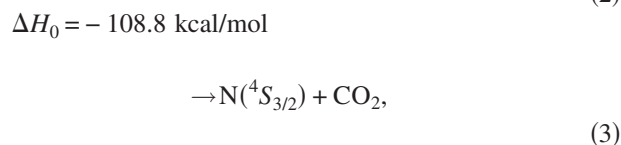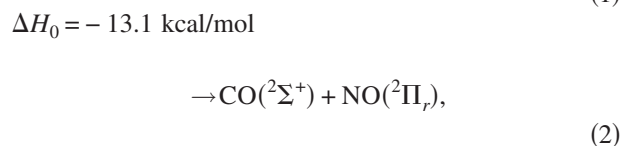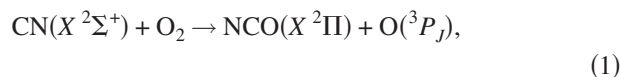
We have used oxygen Rydberg time-of-flight spectroscopy to carry out a crossed molecular beam study of the $CN+O_2$ reaction at collision energies of 3.1 and 4.1 kcal/mol. The $O(^3P_2)$ products were tagged by excitation to high-n Rydberg levels and subsequently field ionized at a detector. The translational energy distributions were broad, indicating that the NCO is formed with a wide range of internal excitation, and the angular distribution was forward-backward symmetric, indicating the participation of NCOO intermediates with lifetimes comparable to or longer than their rotational periods. Rice-Ramsperger-Kassel-Marcus modeling of the dissociation of NCOO to NCO+O suggests that $Do(NC-OO) \geqslant 38$ kcal/mol, which is consistent with several theoretical calculations. Implications for the competing CO+NO channel are discussed. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2173261]

I. INTRODUCTION

The oxidation reactions of CN and NCO radicals can lead to the formation of NO_x and are therefore relevant to combustion processes.[1,2] The reaction of $CN+O_2$ has been studied thoroughly over the last 30 years[3–8] and the rate constants for reaction are accurately known over the temperature range from 13 K (Refs. 9 and 10) to 3800 K.[11,12] The reaction exhibits a mild negative temperature dependence, suggesting that it proceeds on a barrierless attractive potential energy surface (PES), possibly involving a long-lived complex. This has led some to consider $CN+O_2$ as a model for radical-radical reactions, where long range attractive potentials are often encountered. A clear and thorough review of the kinetics and dynamics of the title reaction was published by Smith in 1995.[13]

Using enthalpies of formation based on the most recent theoretical[14] and experimental[15] work, three exothermic product channels are possible as follows:[13]

$$CN(X\ ^2\Sigma^+) + O_2 \rightarrow NCO(X\ ^2\Pi) + O(^3P_J), \quad (1)$$

$$\Delta H_0 = -13.1 \text{ kcal/mol}$$

$$\rightarrow CO(^2\Sigma^+) + NO(^2\Pi_r), \quad (2)$$

$$\Delta H_0 = -108.8 \text{ kcal/mol}$$

$$\rightarrow N(^4S_{3/2}) + CO_2, \quad (3)$$

$$\Delta H_0 = -85.1 \text{ kcal/mol}.$$

A considerable amount of work has gone into determining the thermodynamics and branching ratios for channels (1)–(3). The $NCO+O(^3P_J)$ yield is dominant over the entire

range of temperatures studied, comprising as much as 78% of the total product yield at room temperature.[3,16,17]

A number of questions about the NCO+O product state distributions remain. Dagdigian and co-workers have studied the reaction at room temperature in a static gas cell.[18,19] Their studies indicated that NCO was produced over a wide range of vibrational energies, with a substantial fraction of the available energy appearing in NCO bending excitation. Phillips *et al.* studied the reaction in a gas cell at room temperature and also found evidence for a broad range of NCO internal energies.[20] Liu and co-workers, who studied the reaction in crossed pulsed beams, found that the NCO product was formed rotationally and vibrationally cold and suggested that most of the excess energy likely appeared in product translational energy.[21,22] The striking difference between the NCO bending excitation in the gas cell and crossed beam experiments suggests that the vibrational energy disposal in the $CN+O_2$ reaction may depend strongly on the amount of initial rotational energy in the CN reactant.[13] If this hypothesis is correct, the $CN+O_2$ reaction could be an important prototype system in which reactant rotational energy plays a significant role in the product energy disposal.

In a number of the previous experimental studies of this system, the NCO products were probed by laser-induced fluorescence (LIF) in the $A\ ^2\Pi$-$X\ ^2\Pi$ system.[23,24] While the excited bending levels ($v_2=534$ cm^{-1}) of NCO have been characterized spectroscopically, the higher energy symmetric (v_1) and asymmetric (v_3) stretch modes, which lie at 1266 and 1921 cm^{-1}, respectively,[18] are relatively difficult to study via NCO LIF for v_1 or $v_3 > 1$.[18] This is because each vibrational level is split both by spin-orbit coupling and Renner-Teller effects, both of which can be hard to account for when relating line intensities to relative populations. In addition, the use of band head intensities to approximate the whole contribution from a given vibrational mode is often required, making the analysis imprecise.

The thermodynamic stability of the likely reaction inter-

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mediate, NCOO, has been the subject of a number of theoretical studies. Using G2 (MP2), Vallance *et al.* calculated a well depth of 42.4 kcal/mol relative to $CN+O_2$ reactants.[10] Using this value and assuming that dissociation to NCO $+O(^3P_J)$ occurs over a tight transition state with no significant barrier above the endothermicity for O–O bond fission, calculated reaction rate constants were found to be in fair agreement with the experiment.[10] Using Moller-Plesset perturbation theory, Klippenstein and Kim calculated a NC–OO binding energy of 45.2 kcal/mol.[25] The most recent published calculations were carried out by Qu *et al.*[26] They concluded that the C_s NCOO well lies at 32.0 kcal/mol below the reactants; using their calculated reaction exothermicity, dissociation of NCOO to NCO+O would involve a barrier of only 12.2 kcal/mol.[27] Recent, unpublished calculations by Carpenter yielded 298 K NC–OO bond dissociation enthalpies of 38.5 kcal/mol (CBS-QB3) and 38.7 kcal/mol (CBS-APNO).[28]

The negative temperature dependence of the reaction rate constant is a strong evidence that the first step in the mechanism involves $CN+O_2$ association. However, none of the experimental studies to date have been able to provide insight into the lifetime of the NCOO complex. Although there is no question that NCOO represents the lowest energy region of the PES, for an appreciably exothermic reaction involving only four atoms, the lifetime of the complex will depend critically upon the well depth and the nature of the transition state for O–O bond fission forming NCO $+O(^3P_J)$.

Whether or not energy is fully randomized within the complex prior to decomposition remains an open question.[29] The highly internally excited NCO products observed by Dagdigian and co-workers[18,19] and by Phillips *et al.*[20] would seem to favor a mechanism in which there is some energy randomization prior to O–O bond fission. Although it was not possible to extract detailed product state distributions, a comparison with phase space theory calculations by Phillips *et al.* suggested that the energy randomization was not complete.[20] A strong correlation between incident CN rotational energy and product NCO bending excitation would imply that reactant rotational energy correlates adiabatically with NCO product rotation, favoring a mechanism in which energy is not randomized within an intermediate complex.[13,22] A cold rotational and vibrational NCO product internal energy distribution with a preference for NCO+O translational energy release[22] also suggests a nonstatistical partitioning of available energy into the products.

A number of studies have shown that channel (2) plays a significant role, with a quantum yield of 0.22 ± 0.02 at 296 K, with this value likely increasing at lower temperatures.[3] Since a four-center transition state in reaction (2) is thought to be energetically inaccessible, Mohammad *et al.* proposed that for some dissociation pathways, after the formation of NCOO, the departing $O(^3P)$ associated with channel (1) might undergo a secondary collision with the N atom within the complex, leading to NO+CO.[16] This mechanism is analogous to that proposed by Townsend *et al.* in recent studies of the $CO+H_2$ channel from H_2CO photodissociation near threshold for the formation of H+HCO.[30]

Difficulties associated with converting NCO LIF signals to relative populations have made it hard to fully unravel the product vibrational energy distribution. Using oxygen Rydberg time-of-flight (ORTOF) spectroscopy to detect the $O(^3P_2)$ products of the reaction, we were able to measure both the angular distribution and translational energy release simultaneously. A direct determination of the product angular distribution could shed light on the question of complex formation. Although the translational energy distributions do not yield state specific information, through energy conservation they do provide insight into the overall level of NCO product internal energy.

II. EXPERIMENT

These experiments were carried out using a fixed source, rotatable detector crossed molecular beam apparatus.[31] Both beams were generated in separately pumped chambers and collimated by nickel skimmers (Precision Instruments Inc.) before crossing at fixed 90°, 7.0 cm away from each pulsed nozzle.

The CN molecular beam was produced by 193 nm photodissociation of various C_2N_2 mixtures directly in front of the orifice of a pulsed nozzle.[32,33] By choosing different seeding gases, backing pressures, and excimer-pulsed valve delays, we had a control over the CN beam velocity and, to some degree, its rotational temperature. LIF via the CN $B\,^2\Sigma^+\leftarrow X\,^2\Sigma^+$ transition[34] was used to measure the rotational temperature of the CN beam, as well as to determine its velocity. For example, a 10% mixture of C_2N_2 in He with a backing pressure of 10 psi was used to generate a fast CN beam ($\langle v\rangle=1400$ m/s) characterized by a rotational temperature of 55 K for $J=0-7$ for both $v=0$ and $v=1$. Under these conditions, the fraction of CN in $v=1$ was about 17%, slightly less than the nascent $v=1$ distributions determined in the earlier beam experiments.[32] By expanding a mixture consisting of 5% C_2N_2, 15% N_2, and 80% H_2 at 150 psi, we generated a CN beam with approximately the same velocity, but rotationally cooler, with a temperature of 20 K and 12% $v=1$.

The O_2 molecular beam was formed by expanding 10 psi (gauge) of either neat O_2 or 20% O_2 in He from an identical piezoelectric pulsed valve. Although we were not able to measure the rotational and vibrational temperatures of the O_2 molecules, our experimental conditions should yield vibrational temperatures near 300 K and rotational temperatures in the 10–20 K range. The mean velocity and speed ratio of the pure O_2 beam were 650 m/s and 9, respectively. For the 20% mixture, the mean velocity was 1200 m/s, with a speed ratio of 12. We studied the reaction under three different sets of conditions: (1) E_{coll} =4.1 kcal/mol and T_{CN}=55 K, (2) E_{coll}=3.1 kcal/mol and T_{CN}=55 K, and (3) E_{coll}=3.1 kcal/mol and T_{CN}=20 K.

The use of ORTOF detection has been described in detail in previous work.[31] Briefly, the method is an extension of the hydrogen Rydberg time-of-flight (HRTOF) method devised by Schneider *et al.*[35] where the $O(^3P)$ products from a reaction are excited to high-lying Rydberg levels just below the ionization potential. The long-lived "tagged" O atoms fly to a

microchannel plate (MCP) where they are field ionized and counted as a function of arrival time. As in HRTOF, a two-color excitation scheme is used. Tunable vacuum ultraviolet (vuv) radiation near 130.2 nm is used to pump oxygen atoms from the O(^3P_J) state to their first excited state, O(^3S), followed by a 305 nm laser which excites the atoms to the high-n Rydberg state, in this case $n=19$. The vuv radiation used for product tagging was generated by resonance enhanced four-wave mixing ($\omega_{vuv}=2\omega_R-\omega_T$) in a krypton gas cell.[36] The wavelength of the frequency-doubled dye laser (ω_R) was fixed to the two-photon resonance transition to the $5p[1/2]_0$ level of Kr near 212 nm and that of the other dye laser (ω_T), operating near 578 nm, was varied to generate the tunable vuv light. The two laser beams were combined using a dielectric mirror and focused by a homemade air-spaced achromatic doublet ($f=30$ cm) into the gas cell. The generated vuv light passed through a MgF$_2$ collimating lens ($f=20$ cm) into the main chamber where it crossed the region where the molecular beams intersect, 4.5 cm away from the entrance to the rotatable detector. Excitation of O atoms to $n=19$ was accomplished using the doubled output of a third dye laser operating near 305 nm (Rydberg laser). The "tagged" O atoms flew 34 cm through a field-free region and were field ionized (2300 V/cm) and counted using a microchannel plate (Galileo). The ion signal was amplified by an EG&G VT120 preamplifier; time-of-flight (TOF) spectra were recorded by a Stanford Research Systems SR 430 multichannel scaler.

Under our current experimental arrangement, we have access to an angular range of 140° in the laboratory frame. Data were also recorded in which the excimer laser used to photolyze C$_2$N$_2$ was blocked. These scans were subtracted from the signal obtained with the excimer laser open, in order to account for the relatively strong O atom signal from O$_2$ photodissociation both at 130 nm (Refs. 37 and 38) and at 212 nm. Although at most laboratory angles the O atom signal arising from O$_2$ photodissociation arrives before that from the CN+O$_2$ reaction, at some angles there is some temporal overlap.

III. RESULTS AND DISCUSSION

Figure 1 shows the raw O atom TOFs both with and without the C$_2$N$_2$ photolysis laser at laboratory angles of 30° and 70°. The angles are referenced with respect to the CN beam in the laboratory frame. The trailing edge of the very large peak resulting from O$_2$ photodissociation at 130 nm is seen in all panels at arrival times less than 100 μs. This is earlier than the leading edge of the energetically allowed CN+O$_2$ signal. However, a small peak at a slightly later arrival time is also seen in the absence of the excimer laser and results from the 212 nm photodissociation of O$_2$. At a laboratory angle of 70°, this signal arrives at about 120 μs. Our analysis is based on the difference spectra between the TOFs with the excimer open and with the excimer blocked.

Some representative subtracted TOFs are shown in Fig. 2 (open circles), along with the fits (solid line). The signal at short times ($<$100 μs) results from an imperfect subtraction of signal from O$_2$ photodissociation at 130 nm. For this data
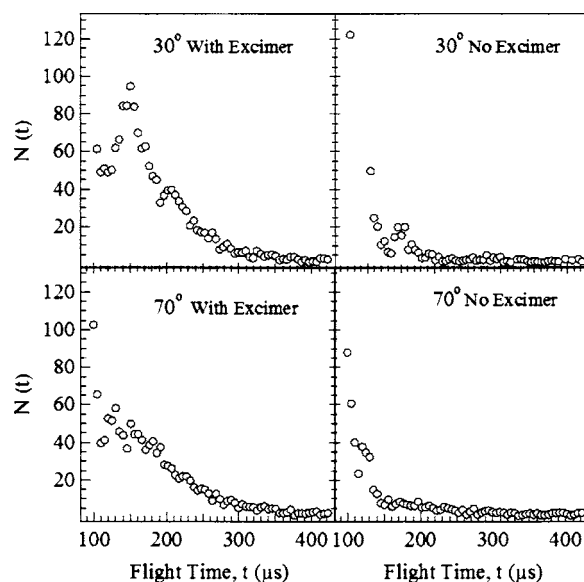

FIG. 1. Time-of-flight spectra at indicated laboratory angles relative to CN beam at $E_{coll}=3.1$ kcal/mol. Left panels: raw TOF spectra at two angles with C$_2$N$_2$ photolysis laser unblocked. Right panels: raw TOF spectra at the same angles with a photolysis laser blocked.

set, the rotational temperature of the CN beam was approximately 55 K for $J=0-7$. The fits were obtained using a forward convolution program which takes as input a center of mass translational energy $[P(E)]$ and angular distribution $[T(\theta)]$ and averages over the known experimental parameters to generate simulated TOF data. The trial translational energy and angular distributions were iteratively improved until the simulations matched the experimental TOF data, as well as the integrated laboratory angular distribution.

The TOF and angular distributions were best fitted with a center of mass (c.m.) angular distribution that is forward-backward symmetric with a $P(E)$ that is energetically broad. Both the $P(E)$ and $T(\theta)$ are shown in Fig. 3. In Fig. 4, the
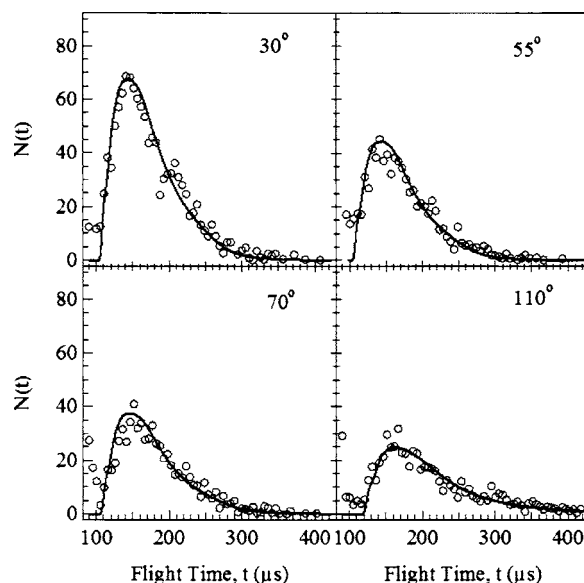

FIG. 2. Subtracted TOF spectra at indicated laboratory angles relative to CN beam along with fit (solid line) for CN beam with $T_{rot}=55$ K and $E_{coll}=3.1$ kcal/mol.
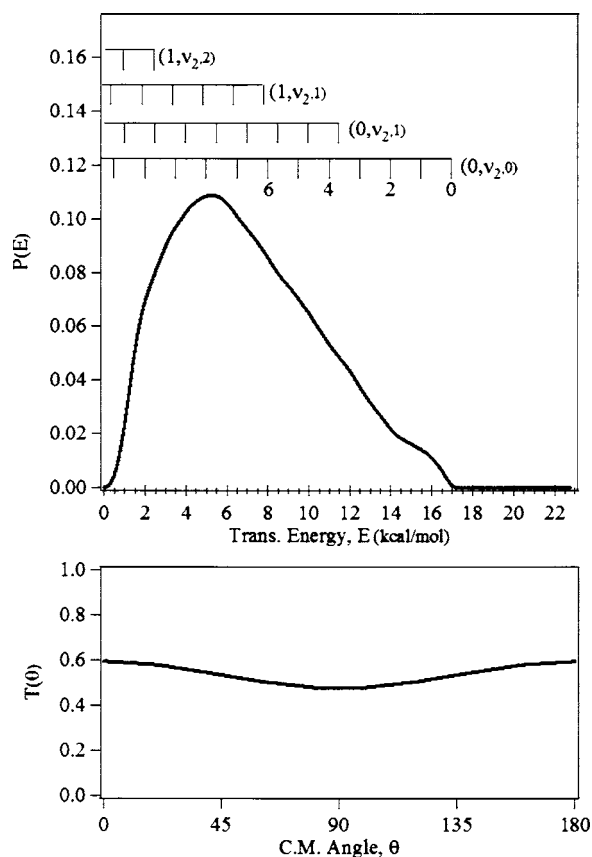
FIG. 3. Top panel: O atom center of mass translational energy distributions for $O(^3P_2)$. Maximum available energy using ΔH_0 from Ref. 13 and collision energy of 3.1 kcal/mol. The combs indicate the energies of various bending levels for given (v_1, v_3) combinations. Bottom panel: center of mass angular distribution, $T(\theta)$.

FIG. 5. Product flux contour map of $O(^3P_2)$ velocities in the c.m. frame. The maximum O atom velocity is about 2300 m/s.

$T_{rot}=20$ K by using a high pressure expansion and mix of H_2/N_2 carrier gas. No observable change was seen in the $P(E)$ using this rotationally colder beam.

There has been a considerable discussion about a possible correlation between initial CN rotational excitation and the product NCO bending (v_2) excitation.[13,18,19,22] Since our $P(E)$ lacks structure to distinguish the three vibrational modes of NCO, we are not able to examine any relationship that may exist between the v_2 distribution and CN rotational energy. It is notable, however, that with a rotational temperature of 20 K, our $P(E)$ peaked at 5 kcal/mol. Since the maximum available energy is ~17 kcal/mol, this corresponds to a most probable NCO internal energy of ~12 kcal/mol. For simple O–O bond fission in a long-lived NCOO complex with at most a small potential energy barrier above D_0(NCO–O), one would expect a substantial fraction of the available energy to appear as NCO vibrational energy, as inferred from our measurement and from the previous gas cell experiments.[18–20] In the experiments of Liu and co-workers,[21,22] carried out in crossed beams, the NCO was found to be formed with very little bending excitation. In those experiments, the rotational temperature of the CN reactant was extremely low, with most CN in N=0.[22] We did attempt to achieve such extremely cold CN rotational temperatures using the conditions described in Ref. 22. However, because the CN produced from photodissociation of cyanogen is rotationally hot,[32,33] this is quite difficult. Although we were not able to get our CN beam as cold as that reported by Liu and co-workers, we did not observe any change in the $P(E)$ derived from our data upon cooling the beam from 55 to 20 K.

A forward-backward symmetric angular distribution in a crossed molecular beam experiment usually is taken as evidence that the reaction involves intermediate complexes having lifetimes comparable to or longer than their rotational periods. Indeed, this is the criterion which is often used to distinguish between "direct" and "complex" reaction dynamics.[13] Because both reactants are radicals, the potential energy surface for $CN+O_2$ is highly attractive and all previous works indicate that NCOO is bound relative to reactants and products. We see no evidence for any anisotropic contribution (i.e., either forward or backward scattered O atom products) that might be attributable to a direct abstraction mechanism.

The shape of the c.m. angular distribution can be understood by applying statistical complex theory to the reacting system, as developed by Miller et al.[39] and later updated by Jarvis and Grice.[40] In this treatment, intermediate complexes

simulated laboratory angular distribution is compared to the one obtained by integrating the experimental TOF spectra. By combining our best-fit $P(E)$ with its associated $T(\theta)$, we generated the product flux contour map in the center of mass velocity space shown in Fig. 5.

For the experiments where the CN rotational temperature was 55 K, we have obtained a full set of data at both 3.1 and 4.1 kcal/mol collision energies. The difference in collision energy was not found to affect the center of mass angular distribution and affects the translational energy release only by shifting the $P(E)$ to slightly higher energy at the higher collision energy. In addition, we have run the experiment at $E_{coll}=3.1$ kcal/mol while cooling the CN to
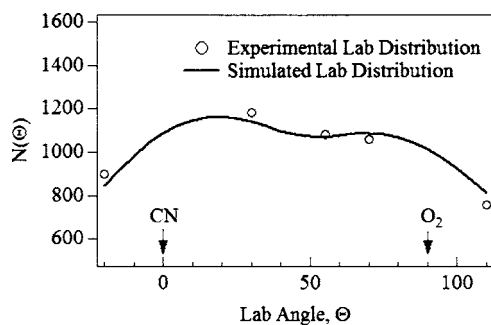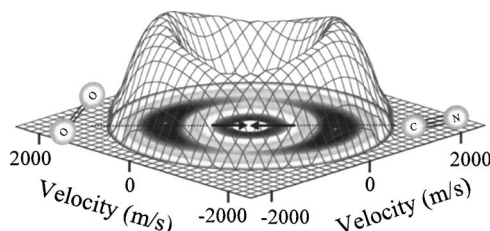

FIG. 4. Simulated and experimental laboratory angular distributions.

that are best described as prolate tops, where two moments of inertia are approximately equal and much greater than the unique one, give rise to angular distributions that are peaked at the poles, while an oblate top will result in sideways peaking. Doublet NCOO is best represented as a prolate top with moments of inertia equal to 31.2, 321.8, and 353.0 amu Å². Quantitative modeling of NCOO dissociation using these moments of inertia is entirely consistent with our broad c.m. angular distribution peaking at 0° and 180°.

A number of theoretical studies have addressed the temperature dependence of the CN+O₂ reaction rate constant. Klippenstein and Kim's calculations focused only on the CN+O₂ association step.[25] They found that variational statistical calculations employing a realistic CN+O₂ potential energy surface which fully incorporates the short-range CN+O₂ interactions were in quantitative agreement with the experimental data for temperatures ranging from 50 to 3000 K. The calculations by Vallance *et al.* addressed the dissociation of NCOO to NCO+O over a tight transition state as well as decay back to CN+O₂ via a loose transition state.[10] In order to gain some insight into the lifetimes of the NCOO complexes, we have used the calculated geometries[10] to carry out simple Ria-Ramsperger-Kassel-Marcus (RRKM) calculations using a standard program[41] to calculate the decay rate of a NCOO complex for various well depths.[42] The program takes as input the moments of inertia and vibrational frequencies of the NCOO intermediate state and NCOO transition state, total available energy (E_T), and barrier height and calculates the unimolecular rate constant (k_{uni}) for passage over the barrier. For our calculations, we assumed that the position of the transition state corresponds to a NCO–O bond length of 1.72 Å, compared to 1.3 Å for the intermediate complex.[10] Assuming also that the NC–O–O bond angle is 112° for both the NCOO intermediate and transition states (we assume that dissociation only involves lengthening of the O–O bond),[26] we used Gaussian to calculate the moments of inertia and vibrational frequencies of both the complex and transition states. We ran the RRKM program a number of times assuming a tight transition state lying 2 kcal/mol above NCO+O, while varying the NCOO well depth. Using Do(NC–OO)=38 kcal/mol, we found $\tau \approx 1.0$ ps; decreasing Do(NC–OO) to 34 kcal/mol led to $\tau \approx 0.5$ ps. While the exact rotational time scale for NCOO depends strongly on the rotational level, which in turn depends on the impact parameter, binding energies of 38 kcal/mol (or higher) appear to be consistent with our experimental results, but only if the transition state for O–O bond fission is assumed to be tight.

A tight transition state for NCO+O production appears to lend some support to the novel mechanism for the NO+CO channel postulated by Mohammad *et al.* involving a secondary collision between the departing O atom and the N within NCOO.[16] The NCO+O is produced with a relatively small translational energy release. The $P(E)$ shown in Fig. 3 peaks at ~5 kcal/mol, with the contribution dropping sharply to near zero at ≲1 kcal/mol. For a mechanism involving decomposition of long-lived NCOO complexes, the absence of NCO+O products with $E_{trans} ≲ 1$ kcal/mol could be attributable to the existence of a small potential energy

barrier for O atom elimination. Alternatively, it is possible that the low-energy O atom products are consumed by reaction within the complex to form NO+CO. Mohammad *et al.* have shown in detail that this mechanism is plausible, particularly because the transition vector for the formation of NCO+O corresponds to a bending motion in NCOO.[16] Thus, any repulsive forces in the exit channel will be preferentially channeled into NCO rotation, increasing the probability for a secondary encounter between the O atom and the N in NCO. For $J=16$, NCO executes one-quarter of a rotation in 0.21 ps.[16] At a relative NCO+O translational energy of 0.5 kcal/mol, corresponding to a relative velocity of 600 m/s, the products have separated only 1.5 Å after 0.84 ps, facilitating capture of the O atom producing NO+CO. The NCO+O reaction is known to proceed readily with the products though to be NO+CO.[43] Indeed, Rim and Hershberger have found that the quantum yield for CO+NO production from CN+O₂ is 0.22±0.02 at 296 K; they suggested that this channel actually becomes the dominant channel at low temperatures.[3] The tight transition state for the NCO+O channel implied by our RRKM calculations thus restricts the rate constant for O–O bond fission, effectively facilitating a kinetic competition with the CO+NO channel. Dagdigian and co-workers were unsuccessful in observing NO ($v=0,1$) production in their room temperature experiments.[19] Owing to the large available energy for the NO+CO channel, NO is likely to be produced primarily in $v>0$,[19] making studies of the NO+CO channel using quantum state resolved detection experimentally challenging.

IV. CONCLUSIONS

A study of the CN+O₂ reaction in crossed molecular beams has provided the first measurement of the nascent O atom angular and velocity distributions. The angular distributions were found to be forward-backward symmetric and the translational energy release was broad. This suggests the involvement of NCOO collision complexes with lifetimes comparable to or longer than their rotational periods. This is consistent with the RRKM calculations using NC–OO binding energies of ≥38 kcal/mol, assuming that NCO+O is formed via a tight transition state.

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[27] The calculations in Ref. 26 yielded a reaction exothermicity of 19.8 kcal/mol, which is considerably larger than the experimental value of 13.1 kcal/mol. Using the calculated value for D_o (NC–OO), it was concluded that NCOO is only bound by 12.2 kcal/mol relative to NCO +O.

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