

## PUBLISHED VERSION

Hoops, Alexandra A.; Ryan, R. T.; Gascooke, Jason Robert; Neumark, D. M.  
State-resolved translation energy distributions for NCO photodissociation, *Journal of Chemical Physics*, 2001; 114 (20):9020-9027.

© 2001 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.

The following article appeared in *J. Chem. Phys.* **114**, 9020 (2001) and may be found at <http://link.aip.org/link/doi/10.1063/1.1369132>

### PERMISSIONS

[http://www.aip.org/pubservs/web\\_posting\\_guidelines.html](http://www.aip.org/pubservs/web_posting_guidelines.html)

The American Institute of Physics (AIP) grants to the author(s) of papers submitted to or published in one of the AIP journals or AIP Conference Proceedings the right to post and update the article on the Internet with the following specifications.

On the authors' and employers' webpages:

- There are no format restrictions; files prepared and/or formatted by AIP or its vendors (e.g., the PDF, PostScript, or HTML article files published in the online journals and proceedings) may be used for this purpose. If a fee is charged for any use, AIP permission must be obtained.
- An appropriate copyright notice must be included along with the full citation for the published paper and a Web link to AIP's official online version of the abstract.

31<sup>st</sup> March 2011

<http://hdl.handle.net/2440/34961>

# State-resolved translation energy distributions for NCO photodissociation

Alexandra A. Hoops, Ryan T. Bise,<sup>a)</sup> Jason R. Gascooke, and Daniel M. Neumark<sup>b)</sup>

*Department of Chemistry, University of California, Berkeley, California, 94720*

*and Chemical Sciences Division, Lawrence Berkeley National Laboratories, Berkeley, California 94720*

(Received 30 January 2001; accepted 12 March 2001)

The photodissociation dynamics of NCO have been examined using fast beam photofragment translational spectroscopy. Excitation of the  $1_0^2$ ,  $3_0^1$ , and  $1_0^2 3_0^2$  transitions of the  $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$  band produces  $N(^4S) + CO$  photofragments exclusively, while excitation of the  $1_0^3 3_0^3$  transition yields primarily  $N(^2D) + CO$  photoproducts. The translational energy [ $P(E_T)$ ] distributions yield  $D_0(N-CO) = 2.34 \pm 0.03$  eV, and  $\Delta H_{f,0}^0(NCO) = 1.36 \pm 0.03$  eV. The  $P(E_T)$  distributions exhibit vibrationally resolved structure reflecting the vibrational and rotational distributions of the CO product. The  $N(^2D) + CO$  distribution can be fit by phase space theory (PST), while the higher degree of CO rotational excitation for  $N(^4S) + CO$  products implies that NCO passes through a bent geometry upon dissociation. The  $P(E_T)$  distributions suggest that when the  $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$  band is excited, NCO undergoes internal conversion to its ground electronic state prior to dissociation. Excitation of NCO at 193 nm clearly leads to the production of  $N(^2D) + CO$  fragments. While conclusive evidence for the higher energy  $O(^3P) + CN(X^2\Sigma^+)$  channel was not observed, the presence of this dissociation pathway could not be excluded. © 2001 American Institute of Physics. [DOI: 10.1063/1.1369132]

## I. INTRODUCTION

The reaction dynamics of combustion intermediates have been investigated in many studies. Among the species examined, the NCO free radical has received considerable attention for its role as an intermediate in the combustion of nitrogenous fuels in air, whereby  $NO_x$  pollutants are released into the atmosphere. NCO has also been proposed as a key intermediate in the RAPRENO<sub>x</sub> (rapid reduction of  $NO_x$ ) process, which serves to reduce the amount of  $NO_x$  from combustion exhausts.<sup>1,2</sup> This has stimulated much interest in the thermochemistry, spectroscopy, and photodissociation dynamics of NCO. In this work, we present results on the photodissociation of NCO that address these areas of interest.

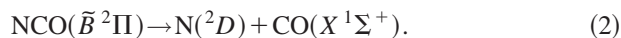
Historically there has been some controversy over the value of the heat of formation of this free radical. Early determinations of  $\Delta H_{f,0}^0(NCO)$  clustered around 1.6 eV.<sup>3-5</sup> A more direct measurement from the fast radical beam photodissociation experiments by Cyr *et al.*<sup>6</sup> yielded  $\Delta H_{f,0}^0(NCO) = 1.32 \pm 0.04$  eV. Corroboration of this lower value has come from subsequent theoretical<sup>7</sup> and experimental<sup>8-10</sup> investigations. However, a recent VUV photolysis study<sup>11</sup> has raised the issue again.

The spectroscopy of the ground and first two excited states of NCO has been studied by a variety of methods yielding vibrationally and rotationally resolved spectra. The first observation of the  $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$  and  $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$  transitions came in 1958 (Ref. 12) with analysis by Dixon in

1960.<sup>13,14</sup> Subsequently, there have been several investigations using absorption,<sup>15,16</sup> stimulated emission pumping,<sup>17-19</sup> and laser-induced fluorescence (LIF).<sup>20-27</sup> Additionally, the spectroscopy of the  $\tilde{B}^2\Pi$  state was examined in the photodissociation experiments by Cyr *et al.*<sup>6</sup>

Several of these studies have also provided insight into the dynamical processes that NCO undergoes upon dissociation. Figure 1 illustrates the energy level diagram for NCO and its lowest energy fragmentation channels. In 1989, Liu and Coombe<sup>5</sup> investigated the photodissociation of NCO at 193 nm and observed  $O(^3P) + CN(X^2\Sigma^+)$  products. Attempts to detect the  $N(^2D)$  photofragment were unsuccessful, leading the authors to conclude that photolysis of NCO at 193 nm did not yield  $N(^2D)$  as a major photoproduct. They observed a bimodal rotational distribution of the  $CN(X^2\Sigma^+)$  photofragments; this distribution was interpreted as resulting from a bent excited dissociative state, yielding highly rotationally excited CN, and a linear bound excited state, generating CN products with little rotational excitation.

The work by Cyr *et al.*<sup>6</sup> in 1992 provided further insight into the dynamics of the dissociation of NCO. All vibrational levels of the  $\tilde{B}^2\Pi$  state were found to predissociate to the following photoproducts:



The photofragment time-of-flight (TOF) distributions for both channels were fit using a vibrational distribution of the CO photofragments. Heats of reaction for the spin-forbidden channel (1) and the spin-allowed channel (2) were found to be  $2.38 \pm 0.04$  and  $4.76 \pm 0.04$  eV, respectively. Below the

<sup>a)</sup>Current address: Lucent Technologies, Room 7C-227, 600-700 Mountain Ave., Murray Hill, New Jersey 07974.

<sup>b)</sup>Author to whom correspondence should be addressed. Electronic mail: dan@radon.cchem.berkeley.edu



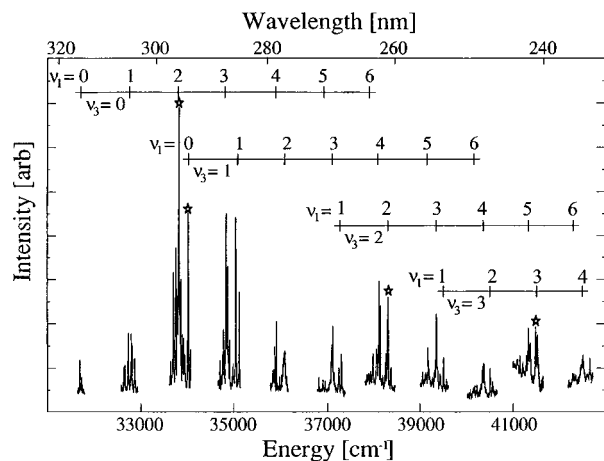


FIG. 3. NCO  $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$  photodissociation cross section from Ref. 6. Asterisks (\*) indicate dissociation wavelengths at which  $P(E_T)$  distributions were obtained.

locity vector and the electric vector of the polarized dissociation laser. The photofragment mass resolution is  $m/\Delta m \approx 10$ , while the translational energy resolution is  $\Delta E_T/E_T = 2.2\%$ .

The presence of a beam block across the center of the TPS detector reduces the acceptance of the detector for those fragments that are of low translational energy or have values of  $\theta$  close to  $0^\circ$  or  $180^\circ$ , while fragments of high translational energy with  $\theta$  close to  $90^\circ$  miss the detector entirely. These effects are accounted for by normalizing the raw translational energy distributions with a detector acceptance function (DAF),<sup>28</sup> and all data presented here have been corrected with the DAF.

### III. RESULTS

#### A. Translational energy distributions, $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$ transitions

The PFY spectrum for the  $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$  band of NCO is shown in Fig. 3. Peaks marked with an asterisk indicate the transitions at which  $P(E_T)$  distributions were obtained. Photofragment coincidence experiments with the TPS detector were performed at photon energies of 4.20, 4.22, 4.76, and 5.15 eV, which correspond to the  $1_0^2$ ,  $3_0^1$ ,  $1_0^2 3_0^2$ , and  $1_0^3 3_0^3$  transitions, respectively. The entire band in Fig. 3 lies below the threshold for dissociation to O+CN, 5.71 eV, as calculated with the use of the value of  $\Delta H_{f,0}^0(\text{NCO})$  determined in this work (see Sec. IV).<sup>36,37</sup> Thus, N+CO is the only mass channel that needs to be considered. At each of the four transition energies, angle-independent translational energy distributions,  $P(E_T)$ , and energy-dependent anisotropy parameters,  $\beta(E_T)$ , were determined.<sup>28</sup>

$P(E_T)$  distributions for the  $1_0^2$ ,  $3_0^1$ , and  $1_0^2 3_0^2$  transitions are shown in Fig. 4. All of these measurements were taken with the TPS detector at a distance of 1 m from the photodissociation volume and with the laser polarization parallel to the radical beam axis. Only the spin-forbidden products,  $\text{N}(^4S) + \text{CO}$ , are accessible when these transitions are excited. The vertical dashed lines indicate the maximum trans-

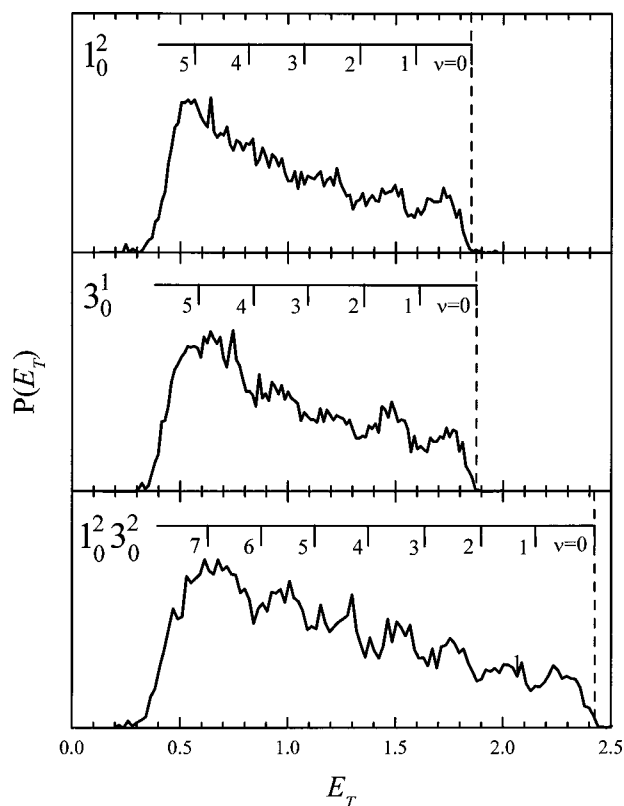


FIG. 4.  $P(E_T)$  distributions for the N+CO channel resulting from  $1_0^2$ ,  $3_0^1$ , and  $1_0^2 3_0^2$  transitions of the  $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$  band. The vertical dashed lines indicate  $E_T^{\text{max}}$  for  $\text{N}(^4S) + \text{CO}$  products.

lational energy ( $E_T^{\text{max}}$ ) for  $\text{N}(^4S) + \text{CO}$  at each excitation energy as determined by the analysis in Sec. IV. All three distributions extend to, but not beyond, this limit. The resolved structure apparent in these translational energy distributions consists of peaks spaced by approximately 270 meV, which corresponds to the frequency of the CO stretch. On average, the full width at half maximum (FWHM) of the resolved features is 220 meV with no significant variation in width with respect to either vibrational level or photon energy. However, there is more resolved structure at low  $E_T$  for the higher energy transitions. The vibrational and rotational distributions corresponding to these transitions are presented in Sec. IV.

At a photon energy of 5.15 eV ( $1_0^3 3_0^3$  transition), dissociation to  $\text{N}(^2D) + \text{CO}$  is possible. Figure 5 illustrates the  $P(E_T)$  distribution at this photon energy taken at a 2 m flight length with the laser polarization parallel to the radical beam. At this flight length, the detector has a greater sensitivity to low translational energy fragments. Although this transition lies only 0.39 eV higher than the  $1_0^2 3_0^2$  transition, the  $P(E_T)$  distribution is very different. Virtually no signal is seen beyond  $E_T = 0.43$  eV, which corresponds to  $E_T^{\text{max}}$  for  $\text{N}(^2D) + \text{CO}$ . Hence, the spin-allowed channel dominates once it becomes accessible, in agreement with the previous work by Cyr *et al.*<sup>6</sup> The  $P(E_T)$  distribution exhibits two peaks separated by 270 meV, again corresponding to the CO stretch. The FWHM of these peaks is approximately 90 meV, substantially narrower than the peaks in Fig. 4. TPS data could

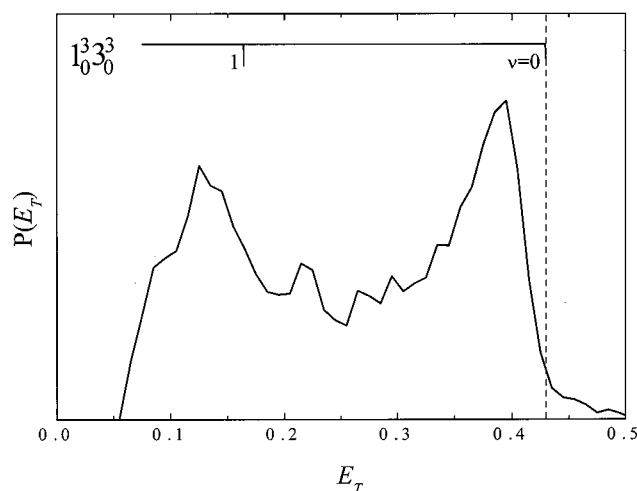


FIG. 5.  $P(E_T)$  distributions for the N+CO channel resulting from the  $1_0^3 3_0^3$  transition of the  $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$  band. The vertical dashed lines indicate  $E_T^{\max}$  for the  $N(^2D)+CO$  fragments.

not be obtained for higher energy transitions of the  $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$  band due to low signal intensity.

Previously, Cyr *et al.*<sup>6</sup> found the spin-forbidden channel to have an anisotropy parameter of  $\beta = +0.1$ , with  $\beta = +0.2$  for the spin-allowed channel. This is consistent with the current results. For both dissociation channels, the distributions were found to be nearly isotropic.

### B. Translational energy distributions at 193 nm

$P(E_T)$  distributions for the photodissociation of NCO at 193 nm (6.42 eV) are shown in Fig. 6. The distributions displayed in Figs. 6(a) and 6(b) were taken at flight lengths of 1 and 2 m, respectively, with a detachment energy of 3.66 eV. In Fig. 6(c) the flight length was 2 m and the detachment energy was 4.03 eV, the latter resulting in some  $\nu_3 = 1$  population of the NCO radicals (see Sec. II). The vertical dashed and dotted lines in Fig. 6 indicate  $E_T^{\max}$  for the  $N(^2D)+CO$  and  $O(^3P)+CN(X^1\Sigma^+)$  channels at 1.70 and 0.71 eV, respectively, assuming NCO is in its vibrational ground state.

The distributions in Fig. 6 were obtained assuming a 14:28 mass ratio, which corresponds to the N+CO mass channel. Measured mass distributions above and below the threshold for the O+CN mass channel do not exhibit any appreciable differences. Although the mass resolution of these experiments hinders the separation of the two mass channels, in previous studies of NCN and CNN we observed the presence of a  $N_2+C$  mass channel that was energetically overlapped with a  $CN+N$  mass channel.<sup>38,39</sup> A broadening and shifting of the peaks in the mass spectrum from those of a single channel marked the presence of both channels. A similar trend was not observed in the mass spectrum of the products of NCO photodissociation, indicating that the contribution from the O+CN mass channel is not substantially greater than the contribution from the N+CO mass channel in the region of  $E_T \leq 0.71$  eV.

All of the signal at translational energies greater than 0.71 eV must be from N+CO, and the abrupt fall-off in

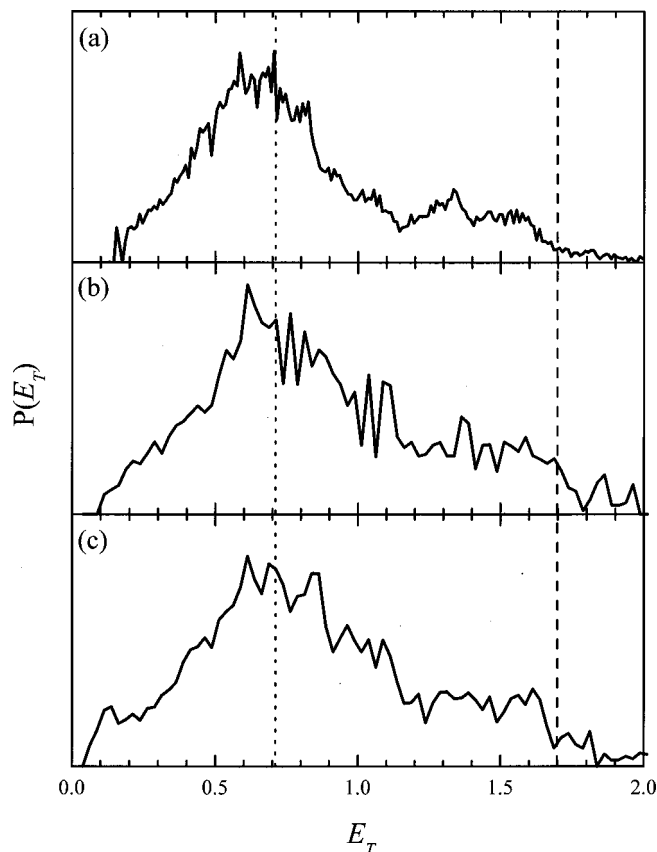


FIG. 6.  $P(E_T)$  distributions for the dissociation of NCO at 193 nm. The flight lengths and photodetachment energies for these distributions are as follows: (a) 1 m, 3.66 eV; (b) 2 m, 3.66 eV; (c) 2 m, 4.03 eV. The vertical dashed and dotted lines indicate  $E_T^{\max}$  for the  $N(^2D)+CO$  and  $O(^3P)+CN$  photoproducts, respectively.

signal above 1.70 eV indicates this to be  $N(^2D)+CO$ . A progression of peaks spaced by 270 meV with a FWHM of 220 meV is seen at high  $E_T$  in Fig. 6(a) and is assigned to the stretching vibration of the CO photofragment, since the O+CN channel is inaccessible in this translational energy range.

Although there is increased intensity in the region near the energetic threshold for  $O(^3P)+CN(X^1\Sigma^+)$  products, there is no clear feature that develops at the threshold that confirms the production of these photofragments. Extension of the flight length to 2 m to increase the sensitivity of the detector toward low translational energy fragments does not result in any changes in the product mass spectrum or  $P(E_T)$  distribution [Fig. 6(b)]. Comparison of Figs. 6(b) and 6(c) shows that populating the  $\nu_3 = 1$  level of  $NCO(\tilde{X}^2\Pi)$  causes only minor differences in the  $P(E_T)$  distribution, the most significant being a slight enhancement of signal below  $E_T = 0.20$  eV in Fig. 6(c).

## IV. ANALYSIS

### A. Translational energy distributions, $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$ transitions

Conservation of energy dictates that the photodissociation of NCO to N+CO mass fragments is described by



$$h\nu + E_{\text{int}}(\text{NCO}) = D_0(\text{N-CO}) + E_T + E_V(\text{CO}) + E_R(\text{CO}) + E_{\text{elec}}(\text{N}), \quad (3)$$

where  $h\nu$  is the photon energy and  $E_{\text{int}}(\text{NCO})$  is the average rotational energy of the parent radical.  $D_0(\text{N-CO})$  is the bond dissociation energy,  $E_T$  is the measured center-of-mass translational energy,  $E_V(\text{CO})$  is the vibrational energy of the CO fragment,  $E_R(\text{CO})$  is the rotational energy of the CO fragment, and  $E_{\text{elec}}(\text{N})$  is the atomic state energy of the nitrogen fragment. An equivalent equation can be written for the O+CN mass channel.

Based on a previous determination of the rotational temperature of NCO in the fast beam photofragment translational spectrometer,<sup>6</sup> a parent rotational temperature of 50 K was assumed in these experiments, corresponding to  $E_{\text{int}}(\text{NCO}) = 0.004$  eV. Consequently,  $D_0$  can be determined by finding the maximum translational energy,  $E_T^{\text{max}}$ , of the photoproducts from the  $P(E_T)$  distributions, at which point  $E_V(\text{CO}) = E_R(\text{CO}) = 0$ ,

$$D_0(\text{N-CO}) = E_{h\nu} + 0.004 \text{ eV} - E_T^{\text{max}} - E_{\text{elec}}(\text{N}). \quad (4)$$

Each distribution in Figs. 4 and 5 shows an abrupt onset of the dissociation signal so that the determination of  $E_T^{\text{max}}$ , indicated by the dashed vertical lines, is relatively straightforward. The corresponding values for  $D_0(\text{N-CO})$  agree within the experimental resolution of 30 meV, and the average of the values is  $D_0 = 2.34 \pm 0.03$  eV. This represents a refinement of the dissociation energy previously determined by Cyr *et al.*,<sup>6</sup>  $2.38 \pm 0.04$  eV, and is the value used in drawing the vertical dashed lines in Figs. 4–6.

The heat of formation of NCO can be calculated from this dissociation energy. Using the literature values of the heats of formation of atomic nitrogen and carbon monoxide,<sup>36</sup>  $\Delta H_{f,0}^0(\text{NCO})$  was determined to be  $1.36 \pm 0.03$  eV. This is within the error bars of the previous determination of  $\Delta H_{f,0}^0(\text{NCO}) = 1.32 \pm 0.04$  eV by Cyr *et al.*,<sup>6</sup> and agrees with several other theoretical<sup>7</sup> and experimental<sup>8,40</sup> investigations. However, in a recent paper by Schönnenbeck and Stuhl,<sup>11</sup> in which VUV photolysis of NCO was monitored by emission from electronically excited CN products, evidence was presented for a lower limit of  $\Delta H_{f,0}^0(\text{NCO}) \geq 1.72$  eV. The radicals in their experiment were produced by the F+HNCO reaction and were at room temperature or higher, which probably accounts for the discrepancy with our value as discussed previously.<sup>6</sup>

The translational energy distributions in Fig. 4 do not extend past  $E_T^{\text{max}}$  for  $\text{N}(^4S) + \text{CO}$ . However, the  $P(E_T)$  distribution for the  $1_0^3 3_0^3$  transition shows a small number of products beyond  $E_T^{\text{max}} = 0.43$  eV for  $\text{N}(^2D) + \text{CO}$ . Such fragments are likely due to the spin-forbidden pathway. Consequently, an upper limit on the branching ratio between the spin-allowed and spin-forbidden channels was obtained by assigning signal above and below 0.43 eV to  $\text{N}(^2D) + \text{CO}$  and  $\text{N}(^4S)$  photoproducts, respectively, yielding a branching ratio  $\text{N}(^2D) : \text{N}(^4S) \leq 96:4$  for the  $1_0^3 3_0^3$  transition.

The  $P(E_T)$  distributions show resolved structure attributable to the vibration of the CO fragment. In order to determine the relative populations of the vibrational levels, each of the  $P(E_T)$  distributions was fit to a series of distribution

TABLE I. CO fragment vibrational distribution for transitions of the  $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$  band from a fit of the  $P(E_T)$  distributions.

Transition	$\nu=0$ (%)	$\nu=1$ (%)	$\nu=2$ (%)	$\nu=3$ (%)	$\nu=4$ (%)	$\nu=5$ (%)
$1_0^2$	13	11	15			
$3_0^1$	11	11	13	15		
$1_0^2 3_0^2$	10	8	12	12	14	18
$1_0^3 3_0^3$	64	36				

functions composed of Gaussians convoluted with a Boltzmann distribution. The details of this procedure have been described previously.<sup>38</sup> The resulting vibrational distributions are presented in Table I. Although vibrational levels beyond  $\nu=2$  for the  $1_0^2$  transition and  $\nu=3$  for the  $3_0^1$  transition are populated, the features were not of sufficient resolution to permit acceptable modeling by this method; Table I shows populations only for those vibrational levels that can be resolved. For the three  $P(E_T)$  distributions in Fig. 4, all of the vibrational levels contribute between 10%–20% of the total distribution, with no apparent trends in vibrational population with excitation energy. The  $1_0^3 3_0^3$  transition yields  $\text{N}(^2D) + \text{CO}$  products in which approximately twice as many of the CO fragments are in the  $\nu=0$  vibrational level as in the  $\nu=1$  level.

The contours of the vibrational features reflect the rotational excitation of the CO photofragment. Thus, each vibrational feature can be evaluated in order to determine the rotational quantum number,  $N_{\text{peak}}$ , corresponding to the most populated CO rotational level. As shown in Table II, the values of  $N_{\text{peak}}$  for  $\text{N}(^4S) + \text{CO}$  fall in a narrow range, between 25 and 29, and appear to be independent of excitation energy and CO vibrational level. The blurring of resolved features at low  $E_T$  in Figs. 4(a) and 4(b) must reflect greater rotational excitation for the highly vibrationally excited CO products, but we cannot quantify this effect reliably. On the other hand, the  $1_0^3 3_0^3$  transition leading to  $\text{N}(^2D) + \text{CO}$  photoproducts resulted in CO fragments with considerably less rotational excitation ( $N_{\text{peak}} = 13$ ) in the two populated CO vibrational levels.

The measured  $P(E_T)$  distributions were then compared to the translational energy distributions obtained from phase space theory (PST).<sup>41</sup> In this statistical theory, all product states allowed by conservation of energy and angular momentum are assumed to be equally probable. The details of determining translational energy distributions using PST have been described in detail previously.<sup>42–44</sup> Our application of PST assumes a long-range potential  $V(r) = -C_0/r^6$ , that the vibrational levels are described by the

TABLE II. Values of  $N_{\text{peak}}$  for the CO fragment vibrational features for transitions of the  $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$  band.

Transition	$\nu=0$	$\nu=1$	$\nu=2$	$\nu=3$	$\nu=4$	$\nu=5$
$1_0^2$	29	27	27			
$3_0^1$	25	25	27	27		
$1_0^2 3_0^2$	29	28	27	28	29	28
$1_0^3 3_0^3$	13	13				

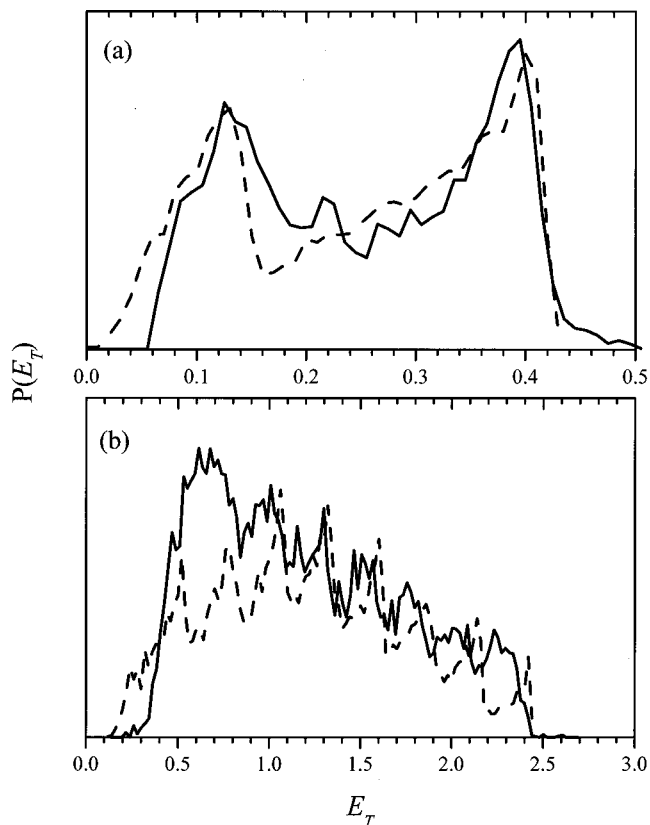


FIG. 7. Translational energy distributions for the (a)  $1_0^3 3_0^3$  transition and (b)  $1_0^2 3_0^2$  transition of the  $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$  band as measured experimentally (solid) and calculated from phase space theory (dashed).

harmonic oscillator approximation, and an initial parent temperature of 50 K. Finally, the calculated PST distributions have been convoluted with a Monte Carlo simulation program in order to account for the apparatus parameters.<sup>28</sup>

The translational energy distributions determined from PST are expected to agree with the measured  $P(E_T)$  distributions if the dissociation process is barrierless and statistical. Furthermore, it is anticipated that the PST translational energy distributions for NCO will resemble those determined by Bonnet and Rayez<sup>45</sup> for the dissociation of the CCO radical as both radicals yield atoms of similar masses plus CO. As shown in Fig. 7(a), the  $P(E_T)$  distribution for  $N(^2D) + CO$  resulting from the  $1_0^3 3_0^3$  transition agrees well with the PST calculation. In contrast, there is a clear disparity between the PST calculation and the  $N(^4S) + CO$  distributions, as shown in Fig. 7(b) for the  $1_0^2 3_0^2$  transition. The vibrational features in the experimental distribution show considerably more rotational excitation than in the PST calculation. These comparisons are discussed further in Sec. V.

### B. Translational energy distributions, 193 nm dissociation

The  $P(E_T)$  distributions at  $h\nu = 6.42$  eV do not lend themselves to as thorough of an evaluation as those discussed above for the  $\tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$  band. The vertical dotted line at 0.71 eV denotes the expected  $E_T^{\max}$  for the  $O(^3P) + CN(X^1\Sigma^+)$  photoproducts. Due to the energetic overlap of the two mass channels and the lack of sufficient mass

resolution, the  $O+CN$  mass channel could not be distinguished from the  $N+CO$  mass channel. An upper limit on the branching ratio between the  $O+CN$  and  $N+CO$  mass channels was determined by assigning intensity greater than 0.71 eV to  $N+CO$  and the remaining signal to  $O+CN$ . This yields  $(O+CN):(N+CO) \leq 47:53$ . However, the discussion in the following section suggests that the  $O+CN$  yield is considerably less than this upper limit.

Determination of the relative vibrational populations was hindered by poorer resolution of discrete features in the  $P(E_T)$  distributions. We were able to assign values of  $N_{\text{peak}}$  for  $\nu = 0-2$  of the  $N(^2D) + CO$  channel, finding  $N_{\text{peak}} = 28-30$ . The amount of rotational excitation of the  $N(^2D) + CO$  products resulting from 193 nm excitation was greater than that of the same products from the  $1_0^3 3_0^3$  transition and could not be suitably modeled by PST, indicating that the dissociation pathway for the two transitions is different.

### V. DISCUSSION

The results from this experiment provide new insight into the dissociation mechanisms of NCO. The vibrationally resolved photofragment translational energy distributions reveal the extent of rotational excitation in the CO photoproducts. The products of the  $N(^2D) + CO$  channel have substantially lower rotational excitation than those of the  $N(^4S) + CO$  channel and the  $P(E_T)$  distribution for the spin-allowed channel agrees with PST calculations. In contrast, the CO fragments associated with the  $N(^4S) + CO$  channel exhibit greater rotational excitation, and the photofragment translational energy distributions for this channel cannot be suitably modeled by PST.

Agreement between the measured  $P(E_T)$  distribution for the  $N(^2D) + CO$  channel and that predicted by PST implies the absence of an exit barrier. The lack of such a barrier is also supported by the dominance of this channel as low as 0.1 eV above its energetic threshold.<sup>6</sup> These observations can be interpreted with reference to Fig. 1, which shows an adiabatic correlation diagram between NCO and various  $N+CO$  product channels for  $C_{\infty v}$  (dashed lines) and  $C_s$  (dotted lines) symmetries.<sup>5,46</sup> For linear dissociation, the  $\tilde{X}^2\Pi$  state of NCO correlates to  $N(^2D) + CO$  products, whereas the  $\tilde{A}^2\Sigma^+$  and  $\tilde{B}^2\Pi$  states correlate to higher energy  $N(^2P) + CO$  products. Although the  $\tilde{A}^2\Sigma^+$  and  $\tilde{B}^2\Pi$  states correlate to  $N(^2D) + CO$  in bent geometries, these dissociation pathways are likely to involve avoided crossings from higher lying NCO states, resulting in barriers with respect to  $N(^2D) + CO$  products. Hence, linear dissociation from the  $\tilde{X}^2\Pi$  state appears to be the most plausible barrierless path to  $N(^2D) + CO$  products. Thus, we propose that these products are formed by internal conversion (IC) of NCO( $\tilde{B}^2\Pi$ ) to the  $\tilde{X}^2\Pi$  state followed by dissociation.

We next consider the mechanism for  $N(^4S) + CO$  production. Figure 1 shows that dissociation to these products can occur, in principle, by intersystem crossing (ISC) from the  $\tilde{X}$ ,  $\tilde{A}$ , or  $\tilde{B}$  states of NCO to the  $^4\Sigma^- (^4A'')$  surface. However, the experimental observation that the spin-forbidden channel disappears as soon as the  $N(^2D) + CO$





with a dissociation mechanism that passes through a bent NCO geometry. An increase of the excitation energy to 5.15 eV resulted in the  $N(^2D)+CO(X^1\Sigma^+)$  channel becoming the dominant pathway of dissociation. The degree of CO rotational excitation in these products was less than that of the spin-forbidden channel and could be modeled by phase space theory. These findings are consistent with a dissociation mechanism involving rapid IC from the  $\tilde{B}$  to the  $\tilde{X}$  state, followed by either (a) ISC to the  $^4\Sigma^-(^4A'')$  surface and dissociation to  $N(^4S)+CO$  products or (b) linear dissociation to  $N(^2D)+CO$  products along a barrierless pathway. From the measured  $P(E_T)$  distributions, the value of  $D_0(N-CO)$  was directly determined to be  $2.34 \pm 0.03$  eV, and  $\Delta H_{f,0}^0(NCO) = 1.36 \pm 0.03$  eV.

Photodissociation of NCO at 193 nm was also studied. The photofragment mass and  $P(E_T)$  distributions show that  $N(^2D)+CO$  is the dominant product channel at this wavelength;  $O+CN$  production appears to be at most a minor channel. It would clearly be of interest to perform experiments on NCO photodissociation at 193 nm and higher wavelengths using other product detection schemes such as laser-induced fluorescence or multiphoton ionization in order to corroborate the results reported here. In addition, the calculation of the potential energy surfaces and dissociation pathways for NCO should be a theoretically tractable problem, and we hope our work encourages efforts along these lines in order to provide a deeper understanding into the rich dynamics of this species.

## ACKNOWLEDGMENTS

This research is supported by the Director, Office of Energy and Research, Office of Basic Energy Science, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76F00098. We would also like to thank Dr. H. Choi for valuable advice on phase space theory, and Professor R. Coombe for discussions of his earlier work on NCO photodissociation.

<sup>1</sup>R. A. Perry and D. L. Siebers, *Nature (London)* **324**, 657 (1986).

<sup>2</sup>J. A. Miller and C. T. Bowman, *Int. J. Chem. Kinet.* **23**, 289 (1991).

<sup>3</sup>H. Okabe, *J. Chem. Phys.* **53**, 3507 (1970).

<sup>4</sup>B. J. Sullivan, G. P. Smith, and D. R. Crosley, *Chem. Phys. Lett.* **96**, 307 (1983).

<sup>5</sup>X. Liu and R. D. Coombe, *J. Chem. Phys.* **91**, 7543 (1989).

<sup>6</sup>D. R. Cyr, R. E. Continetti, R. B. Metz, D. L. Osborn, and D. M. Neumark, *J. Chem. Phys.* **97**, 4937 (1992).

<sup>7</sup>A. L. L. East and W. D. Allen, *J. Chem. Phys.* **99**, 4638 (1993).

<sup>8</sup>B. Ruscic and J. Berkowitz, *J. Chem. Phys.* **100**, 4498 (1994).

<sup>9</sup>S. S. Brown, H. L. Berghout, and F. F. Crim, *J. Chem. Phys.* **105**, 8103 (1996).

<sup>10</sup>M. Zyryanov, T. Drozgeorget, A. Sanov, and H. Reisler, *J. Chem. Phys.* **105**, 8111 (1996).

<sup>11</sup>G. Schönnenbeck and F. Stuhl, *Chem. Phys. Lett.* **264**, 199 (1997).

<sup>12</sup>R. Holland, D. W. G. Style, R. N. Dixon, and D. A. Ramsay, *Nature (London)* **182**, 337 (1958).

<sup>13</sup>R. N. Dixon, *Can. J. Phys.* **38**, 10 (1960).

<sup>14</sup>R. N. Dixon, *Philos. Trans. R. Soc. London, Ser. A* **252**, 165 (1960).

<sup>15</sup>D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **47**, 5157 (1967).

<sup>16</sup>P. S. H. Bolman, J. M. Brown, A. Carrington, I. Kopp, and D. A. Ramsay, *Proc. R. Soc. London, Ser. A* **343**, 17 (1975).

<sup>17</sup>F. J. Northrup, M. Wu, and T. J. Sears, *J. Chem. Phys.* **96**, 7218 (1992).

<sup>18</sup>M. Wu, F. J. Northrup, and T. J. Sears, *J. Chem. Phys.* **97**, 4583 (1992).

<sup>19</sup>M. Wu and T. J. Sears, *Mol. Phys.* **82**, 503 (1994).

<sup>20</sup>V. E. Bondybey and J. H. English, *J. Chem. Phys.* **67**, 2868 (1977).

<sup>21</sup>T. R. Charlton, T. Okamura, and B. A. Thrush, *Chem. Phys. Lett.* **89**, 98 (1982).

<sup>22</sup>K. N. Wong, W. R. Anderson, A. J. Kotlar, and J. A. Vanderhoff, *J. Chem. Phys.* **81**, 2970 (1984).

<sup>23</sup>R. A. Copeland and D. R. Crosley, *Can. J. Phys.* **62**, 1488 (1984).

<sup>24</sup>D. R. Woodward, D. A. Fletcher, and J. M. Brown, *Mol. Phys.* **62**, 517 (1987).

<sup>25</sup>D. Patel-Misra, D. G. Sauder, and P. J. Dagdigian, *J. Chem. Phys.* **93**, 5448 (1990).

<sup>26</sup>S. A. Wright and P. J. Dagdigian, *J. Chem. Phys.* **104**, 8279 (1996).

<sup>27</sup>J. L. Yao, J. A. Fernandez, and E. R. Bernstein, *J. Chem. Phys.* **107**, 8813 (1997).

<sup>28</sup>R. E. Continetti, D. R. Cyr, D. L. Osborn, D. J. Leahy, and D. M. Neumark, *J. Chem. Phys.* **99**, 2616 (1993).

<sup>29</sup>D. J. Leahy, D. L. Osborn, D. R. Cyr, and D. M. Neumark, *J. Chem. Phys.* **103**, 2495 (1995).

<sup>30</sup>D. L. Osborn, H. Choi, D. H. Mordaunt, R. T. Bise, D. M. Neumark, and C. M. Rohlfing, *J. Chem. Phys.* **106**, 3049 (1997).

<sup>31</sup>D. L. Osborn, D. J. Leahy, D. R. Cyr, and D. M. Neumark, *J. Chem. Phys.* **104**, 5026 (1996).

<sup>32</sup>J. M. B. Bakker, *J. Phys. E* **7**, 364 (1974).

<sup>33</sup>J. M. B. Bakker, *J. Phys. E* **6**, 785 (1973).

<sup>34</sup>S. E. Bradforth, E. H. Kim, D. W. Arnold, and D. M. Neumark, *J. Chem. Phys.* **98**, 800 (1993).

<sup>35</sup>D. P. de Bruijn and J. Los, *Rev. Sci. Instrum.* **53**, 1020 (1982).

<sup>36</sup>M. W. Chase and National Institute of Standards and Technology (U.S.), *NIST-IANAF Thermochemical Tables*, 4th ed. (American Chemical Society, American Institute of Physics for the National Institute of Standards and Technology, Washington, D.C., 1998).

<sup>37</sup>Y. H. Huang, S. A. Barts, and J. B. Halpern, *J. Phys. Chem.* **96**, 425 (1992).

<sup>38</sup>R. T. Bise, H. Choi, and D. M. Neumark, *J. Chem. Phys.* **111**, 4923 (1999).

<sup>39</sup>R. T. Bise, A. A. Hoops, H. Choi, and D. M. Neumark, *J. Chem. Phys.* **113**, 4179 (2000).

<sup>40</sup>M. Zyryanov, T. H. Drozgeorget, and H. Reisler, *J. Chem. Phys.* **106**, 7454 (1997).

<sup>41</sup>P. Pechukas and J. C. Light, *J. Chem. Phys.* **42**, 3281 (1965).

<sup>42</sup>P. Pechukas, J. C. Light, and C. Rankin, *J. Chem. Phys.* **44**, 794 (1966).

<sup>43</sup>P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley-Interscience, New York, 1972).

<sup>44</sup>H. Choi, R. T. Bise, A. A. Hoops, D. H. Mordaunt, and D. M. Neumark, *J. Phys. Chem. A* **104**, 2025 (2000).

<sup>45</sup>L. Bonnet and J. C. Rayez, *Chem. Phys. Lett.* **296**, 19 (1998).

<sup>46</sup>M. H. Alexander and H.-J. Werner (private communication).

<sup>47</sup>G. Busch and K. Wilson, *J. Chem. Phys.* **56**, 3626 (1972).

<sup>48</sup>H. Levene and J. Valentini, *J. Chem. Phys.* **87**, 2594 (1987).

<sup>49</sup>R. Schinke, *J. Chem. Phys.* **85**, 5049 (1986).