Competitive photodissociation channels in jet-cooled HNCO: Thermochemistry and near-threshold predissociation

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The photoinitiated unimolecular decomposition of jet-cooled HNCO has been studied following $S_1(1A^\pi) \rightarrow S_0(1A')$ excitation near the thresholds of the spin-allowed dissociation channels: (1) $H(\tilde{S}) + NCO(X^2\Pi)$ and (2) $NH(a^1\Delta) + CO(X^1\Sigma^+)$, which are separated by $4470 \text{ cm}^{-1}$. Photofragment yield spectra of NCO($X^2\Pi$) and NH ($a^1\Delta$) were obtained in selected regions in the $260\text{–}220 \text{ nm}$ photolysis range. The NCO($X^2\Pi$) yield rises abruptly at $38\,830 \text{ cm}^{-1}$ and the spectrum exhibits structures as narrow as $0.8 \text{ cm}^{-1}$ near the threshold. The linewidths increase only slowly with photolysis energy. The jet-cooled absorption spectrum near the channel (1) threshold [$D_0(H+NCO)$] was obtained using two-photon excitation via the $S_1$ state, terminating in a fluorescent product. The absorption spectrum is similar to the NCO yield spectrum, and its intensity does not diminish noticeably above $D_0(H+NCO)$, indicating that dissociation near threshold is slow. The NCO product near threshold is cold, as is typical of a barrierless reaction. NH ($a^1\Delta$) products appear first at $42\,840 \text{ cm}^{-1}$, but their yield is initially very small, as evidenced also by the insignificant decrease in the NCO yield in the threshold region of channel (2). The NH ($a^1\Delta$) yield increases faster at higher photolysis energies and the linewidths increase as well. At the channel (2) threshold, the NH ($a^1\Delta$) product is generated only in the lowest rotational level, $J=2$, and rotational excitation increases with photolysis energy. We propose that in the range $260\text{–}230 \text{ nm}$, HNCO ($S_1$) undergoes radiationless decay terminating in $S_0/T_1$ followed by unimolecular reaction. Decompositions via channels (1) and (2) proceed without significant exit channel barriers. At wavelengths shorter than $230 \text{ nm}$, the participation of an additional, direct pathway cannot be ruled out. The jet-cooled photofragment yield spectra allow the determination, with good accuracy, of thermochemical values relevant to HNCO decomposition. The following heats of formation are recommended: $\Delta H^0_f(\text{HNCO}) = -27.8 \pm 0.4 \text{ kcal/mol}$, and $\Delta H^0_f(\text{NCO}) = 30.3 \pm 0.4 \text{ kcal/mol}$. These results are in excellent agreement with recent determinations using different experimental techniques. © 1996 American Institute of Physics. [S0021-9606(96)02941-8]

I. INTRODUCTION

Isocyanic acid, HNCO, is implicated in the removal of NOx products in a process known in combustion as RAPRENOx (rapid reduction of NOx), in energetic materials combustion, and in interstellar space. Therefore, the mechanisms of its decomposition and chemical reactions are of interest. Although much work has been done on the UV photodissociation of HNCO, little is known about the mechanism of its decomposition following excitation to the $S_1(1A^\pi)$ state near the respective thresholds for the two spin-allowed channels:

$$\text{HNCO} \rightarrow H(\tilde{S}) + NCO(X^2\Pi),$$

$$\rightarrow \text{NH}(a^1\Delta) + CO(X^1\Sigma^+).$$

This state of affairs is partly a result of uncertainties regarding the threshold energies for reactions (1) and (2).

Dixon and Kirby have reported that the weak UV absorption of HNCO at $300 \text{ K}$ reaches a plateau around $200 \text{ nm}$ with a tail extending to $280 \text{ nm}$. At the tail, the vibronic bands have a well-defined rotational structure, and the perpendicular nature of the $S_1(1A^\pi) \rightarrow S_0(1A')$ transition, as well as the rotational structure of some of the bands, have been determined. Note that HNCO undergoes substantial bending of the NCO skeleton upon excitation—from $17^\circ$ in the ground state to $120\text{–}130^\circ$ in the excited state. This severe change in geometry accounts for the pronounced Franck–Condon activity in the NCO bend, and in part for the breadth of the absorption band. Dixon and Kirby note that the spectrum becomes progressively more diffuse at shorter wavelengths, and at $<220 \text{ nm}$ vibronic structure can no longer be discerned. These results indicate that the $S_1$ state is bound and that predissociation is likely to be the preferred mechanism following $S_1$ excitation, at least at low excess energies.

The heat of formation of HNCO and its dissociation thresholds via channels (1) and (2) have been the subject of some controversy. A schematic energy diagram is shown in Fig. 1. Recently, Rusic and Berkowitz, and Zhang et al., using different experimental techniques, determined the upper bounds to the dissociation energy of channel (1) as $110.1 \pm 0.3$ and $110.1 \pm 0.5 \text{ kcal/mol}$, respectively. Thus, despite earlier controversy, this value appears now well established. The dissociation threshold of channel (2) remains less certain. The most recent measurements were carried out by Chandler and co-workers who preferred a value of $41 \, 530 \text{ cm}^{-1} (118.7 \text{ kcal/mol})$, although a value of $42 \, 700 \text{ cm}^{-1} (122.0 \text{ kcal/mol})$ can also be deduced from their data (see below). Accurate values of the dissociation thresholds are not only important for establishing the heats of formation of HNCO and the NCO radical, but also for unraveling decomposition mechanisms and their excess energy dependencies.

For near-threshold studies, expansion cooling of the
samples of HNCO. We confirm and improve the accuracy results. In addition, Brown et al. have recently observed a fast and direct dissociation mechanism to explain their results. Brown et al. have recently observed a preference for dissociation via channel (1) relative to channel (2) at a total photolysis energy of 44 400 cm⁻¹ (225 nm) when implanting three quanta of NH stretch excitation in HNCO (S₀), as compared with one-photon dissociation at the same energy. This result is hard to rationalize based solely on unimolecular decomposition on S₀.

II. EXPERIMENT

The experimental arrangement used in these pump-probe experiments was described previously. HNCO was prepared and purified following published procedures by the reaction of KOCN with stearic acid. The reagents were heated under vacuum to 90 °C and reaction products were collected in a liquid nitrogen trap. Impurities, mainly CO₂ and water, were removed by trap-to-trap distillation. HNCO was seeded in He or in 30:70 He:Ne mixtures at a typical pressure of 760 Torr by passing the carrier gas through a bath at 41 °C (−15-Torr HNCO vapor pressure). The rotational temperature of HNCO in the pulsed jet expansion is estimated at ~10 K (see below). The counterpropagating pump and probe laser beams intersected the molecular beam 5–10 mm (10–20 nozzle diameters) from the nozzle orifice. Both beams were collimated to ~2 mm diameter. The delay between the laser pulses was 50 ns unless varied to determine the appearance time of the products. HNCO was photoionized at 260–220 nm using the doubled output of an excimer laser pumped dye laser at typical pulse energies of 1–2 mJ. NCO(X2Π) and NH(a1Δ) products were probed by laser induced fluorescence (LIF) via the A2Σ⁺ − X2Π and the c′1Π − a1Δ transitions, respectively, using a second excimer laser pumped dye laser (pulse energy ~100–150 μJ). NCO fluorescence in the range 440–500 nm was collected through Kopp 3-72 and 5-60 glass filter, while 0-52 and 7-59 glass filters were used to monitor NH fluorescence at 350–460 nm.

The jet-cooled S₁ − S₀ absorption spectrum of HNCO was obtained by sequential two-photon excitation via the S₁ state generating electronically excited products. For these studies, the output of the excitation laser was increased to ~3 mJ and focused at the center of the chamber with a 50-cm focal length lens. Quantum yield studies showed that at total excitation energies (one-photon) of 75 000 cm⁻¹ the main fluorescing species was NCO (A2Σ⁺). The fluorescence was monitored through Kopp 0-56 and 7-59 filters, which transmitted light at 300–460 nm. Sharp absorption features were obtained whenever the excitation wavelength coincided with an absorption feature of the S₁ − S₀ transition, both below and above the threshold of channel (1).

III. RESULTS

A. H(2S)+NCO(X2Π) channel

A portion of the two-photon S₁ − S₀ absorption spectrum of jet-cooled HNCO is shown in Fig. 2(a), while the NCO photofragment yield spectrum near the channel (1) threshold, D₀(H−NCO), is shown in Fig. 2(b). The Q₁1 bandhead of the NCO (A2Σ⁺ − X2Π) transition (low J’s) was monitored. The NCO yield rises abruptly at 38 380 cm⁻¹ and the spectrum remains highly structured. Notice that there are no significant changes in the intensities and
widths of the spectral features in the absorption spectrum obtained by sequential two-photon absorption via $S_1$ when the dissociation threshold is crossed [Fig. 2(a)]. The complete jet-cooled absorption spectrum from the origin of the $S_1$ state ($\sim 35000 \text{ cm}^{-1}$) has been obtained in this manner; assignments are in progress and will be reported separately. No one-photon LIF from HNCO could be detected. The spectral features below $D_0$(H–NCO), and some above, exhibit rotational structure within our resolution ($0.2 \text{ cm}^{-1}$). The rotational line spacings are consistent with a small change in the $B$ rotational constant in $S_1$ compared to $S_0$, in accordance with Dixon and Kirby. Simulated rotational contours of C-type bands give a rotational temperature of $\sim 10 \text{ K}$. The small shoulder to the red of the first main peak in the NCO yield spectrum [Fig. 2(b)] results from photolysis of parent molecules with some rotational excitation.

The NCO($X^2\Pi$) product obtained near $D_0$ is cold and the number of populated rotational levels increases with excitation energy. Yet, dissociation at the peak of the first NCO spectral feature ($38387 \text{ cm}^{-1}$) generates NCO with rotational levels up to $J=6.5$, corresponding to a maximum of $20 \text{ cm}^{-1}$ in rotational energy. The rotational excitation may derive partly from rotationally excited HNCO in the $\sim 10 \text{ K}$ expansion; however, it is more likely due to the fact that no absorption feature exists at the exact dissociation threshold, as can be seen by comparing Figs. 2(a) and 2(b). Taking the rotational excitation of NCO into account we place the dissociation threshold at $38370 \pm 30 \text{ cm}^{-1}$.

Since spectral features separated by $0.8 \text{ cm}^{-1}$ could be resolved even above $D_0$(H–NCO), the near-threshold lifetimes of the $S_1$ state are estimated at $\geq 6 \text{ ps}$. This is only a lower bound on the lifetime, since saturation and spectral overlap can broaden the peaks. However, some spectral feature are broader than $\sim 1 \text{ cm}^{-1}$; for example, in Fig. 3 we display an absorption band obtained following photolysis at $60 \text{ cm}^{-1}$ above $D_0$(H–NCO) which does not reveal rotational structure, while in the spectrum obtained at $315 \text{ cm}^{-1}$ above $D_0$(H–NCO) rotational structure can be discerned. Near-threshold time resolved measurements of NCO($X^2\Pi$) indicate appearance times $<10 \text{ ns}$, limited by the time resolution of our measurement.

**B. NH($a^1\Delta$)+CO($X^1\Sigma^+$) channel**

The NH($a^1\Delta$) (hereafter referred to as $^1\text{NH}$) yield spectrum is shown in Fig. 4(a). The spectrum was obtained by monitoring the $Q(2)$ line (arising from the lowest rotational level of the $a^1\Delta$ state). The overall decrease observed in the yield spectrum above $44500 \text{ cm}^{-1}$ does not signify a drop in the $^1\text{NH}$ quantum yield, but is due to a decrease in the fractional population of $^1\text{NH} J=2$ with excitation energy. From the average envelope of the yield spectrum and the rotational distributions shown in Fig. 4(b), we estimate an eightfold increase in $^1\text{NH}$ yield between $43320$ and $44500 \text{ cm}^{-1}$. Notice that the yield increases only slowly initially, but then rises more steeply with photolysis energy. The structure in the spectrum is reproducible and includes fairly narrow features even at the highest photolysis energies.

**FIG. 4.** (a) NH($a^1\Delta$) photofragment yield spectrum obtained by monitoring the $Q(2)$ line of the $c^1\Pi\rightarrow a^1\Delta$ transition. The spectrum is not normalized to the fractional yield of NH in the $J=2$ state. Arrows with numbers indicate excitation energies at which NH rotational distributions were taken. (b) NH ($c^1\Pi\rightarrow a^1\Delta$) LIF spectra recorded at photolysis energies: (1) $42900 \text{ cm}^{-1}$; (2) $43160 \text{ cm}^{-1}$; (3) $43320 \text{ cm}^{-1}$; (4) $43600 \text{ cm}^{-1}$; (5) $44500 \text{ cm}^{-1}$.

The first spectra peak that can be confidently assigned to one-photon dissociation via channel (2) is at $\approx 42900 \text{ cm}^{-1}$, where only $J=2$ of $^1\text{NH}$ is populated. The rotational excitation increases rather monotonically with photolysis energy.
yields of channels
spectra are not normalized to reflect the relative quantum
~ does not drop significantly with the opening of channel
2
low the 42 900-cm
!

in the threshold region, where very small peaks
~

in the photofragment recoil, supporting relatively slow dis-
tion is nearly constant over this narrow excitation energy
range, is monitored.18 The peak heights within each spectrum
reflect the correct relative intensities, but the NCO and 1 NH
yield spectra are not normalized to each other to reflect their
relative quantum yields.

Thermochemical implications

The jet-cooled product yield spectra and state distributions
allow us to determine or verify thermochemical data with
good accuracy. After correction for rotational excitation
in the NCO photofragment, we obtain D0(H–NCO)
=38.370±30 cm
−1 (109.7±0.1 kcal/mol). This value is
slightly lower than, but in excellent agreement with, the
values of ≤110.1±0.5 kcal/mol obtained by Zhang et al.,4 and
≤110.1±0.3 kcal/mol by Russic et al.,9 as well as with the
recent results of Brown et al. (38.320±140 cm
−1 ; 109.6±0.4
kcal/mol).15 The heat of formation of HNCO calculated
using ΔH
f(H)=51.63 kcal/mol (Ref. 20) and
ΔH
f(NCO)=30.4±1.0 kcal/mol (Ref. 21) is −27.7±1.0
kcal/mol, limited mainly by the accuracy of the NCO value.

The appearance threshold of channel (2) has been more
controversial. We place the threshold at 42 840±0.4
60 cm
−1 , (122.5±0.03 kcal/mol) with no or a very small barrier. The
upper limit is determined by the uncertainty in wavelength
calibration and the possibility of excitation of hot rotational
bands. The lower limit is determined by the fact that no 1 NH
signal is observed at 42 800 cm
−1 , while a peak appears in
the NCO yield spectrum at this location (Fig. 5). The value
of 114 kcal/mol calculated from Okabe’s UV absorption
data22 was increased by Spiglanin et al. to 118.7 kcal/mol
(41 530 cm
−1 ).13 This value was obtained from their 1 NH
yield spectra recorded at 300 K after correction for thermal
excitation. However, these authors also noted that the average
1 NH rotational excitation decreased linearly with photolysis
energy in the region from 53 000 cm
−1 to ~43 000
cm
−1 , but then leveled off. A straight line extrapolation of
their data to zero average 1 NH rotational energy (Fig. 4 of
Ref. 2) yields a threshold of 42 700±200 cm
−1 , in good
agreement with our measurements. We believe that this latter
method of estimating dissociation thresholds from 300 K
data is superior. The recent value obtained by Brown et al.
with 300-K samples,15 42 710±100 cm
−1 , also supports the
new value. Note that our value is also in excellent agreement
with the threshold calculated using ΔH
f(HNCO)
=−27.7±1.0 kcal/mol, ΔH
f(NH)=85.6±0.3 kcal/mol,23
ΔH
f(CO)=−27.20±0.04 kcal/mol, and NH singlet–
triplet separation of 36.28 kcal/mol,15 which gives 122.4
±1.0 kcal/mol.

We can also use the improved thermochemical data ob-
tained in this work to determine more accurately the heat of
formation of NCO. From D0(1 NH–CO) and the 1 NH and
CO heats of formation given above, we determine
ΔH
f(NCO)=−27.8±0.4 kcal/mol. This value and
D0(H–NCO)=109.7±0.1 kcal/mol are then used to deter-
mine ΔH
f(NCO)=30.3±0.4 kcal/mol, in excellent agree-
ment with the value obtained by Cyr et al. using a different
method.21

Near-threshold decomposition mechanism

The reported jet-cooled absorption and yield spectra, as
well as the product state distributions, strongly suggest that
HNCO predissociated via channels (1) and (2) without sig-
significant barriers following radiationless decay to a bound electronic state, most likely $S_0$. From the widths of the absorption features above $D_0$ (H–NCO), we infer that the $S_1$ lifetime near $D_0$ is longer than $\sim 6$ ps (but shorter than 10 ns, as obtained from the NCO appearance time). The widths increase only slowly with excitation energy; in fact, the lines remain rather narrow even $>1000$ cm$^{-1}$ above $D_0$. Another signature of the slowness of the near-threshold dissociation is obtained from the two-photon absorption spectrum [Fig. 2(a)]. The spectral intensity does not diminish noticeably above $D_0$ (H–NCO), indicating that second photon absorption easily competes with dissociation. This mechanism suggests that the linewidths near threshold reflect the coupling strengths in the radiationless decay step, which are expected to vary only slowly with energy.\textsuperscript{24} Had predissociation occurred on $S_1$ (whose well depth is $<4000$ cm$^{-1}$), its rate would have increased much faster, and large state-to-state fluctuations in the widths [as seen for example in the photodissociation of HCO (Ref. 25) and CH$_3$O (Ref. 26)] might also be expected. We do observe some state specificity in the linewidths above $D_0$ (H–NCO). For example, in Fig. 3 the linewidths obtained at excess energy $\sim 60$ cm$^{-1}$ above $D_0$ (H–NCO) are broader than those obtained at 315 cm$^{-1}$. This state specificity most probably originates in the radiationless decay step and is not associated with the dissociation rate on $S_0$.\textsuperscript{24}

Rate calculation of the decomposition using the Rice–Ramsperger–Kassel–Marcus (RRKM) theory support dissociation on $S_0$ rather than on $S_1$. Assuming a loose transition state and no barrier to channel (1), we find dissociation rates between $D_0$ and $D_0 + 1000$ cm$^{-1}$ that range from $\sim 10^9$ s$^{-1}$ to $\sim 5 \times 10^{11}$ s$^{-1}$. At comparable excess energies, decomposition on $S_1$ would result in rates faster than $10^{12}$ s$^{-1}$ (corresponding to linewidths $>5$ cm$^{-1}$) that increase rapidly with excess energy, which is in contradiction with the experimental observations.

Dissociation via channel (1) is favored to proceed on $S_0$ rather than on $T_1$, since recent calculations reveal a substantial barrier to channel (1) on the latter surface.\textsuperscript{28} Even at energies above that barrier, dissociation on $S_0$ is likely to dominate since dissociation on $T_1$ would be difficult to reconcile with a significant yield of H+NCO when the energetically lowest pathway, NH(X $^3\Sigma^-$) + CO, is already open (see Fig. 1).

The $S_1/S_0$ coupling matrix elements must be small; using the observed linewidth $\Gamma \approx 1$ cm$^{-1}$ and $\rho \approx 10^7$ cm$^{-1}$ (as a rough estimate of the density of states on $S_0$) in Fermi’s golden rule $\Gamma = 2 \pi \rho^2 \rho$, we obtain that the average coupling matrix element is $\nu \approx 10^2$ cm$^{-1}$.\textsuperscript{24} Another experimental observation supporting weak coupling is the absence of clumps, extra lines, or other manifestations of strong couplings in the $S_1$–$S_0$ spectrum near the $S_1$ origin.\textsuperscript{17,29} Nevertheless, the absence of detectable fluorescence following $S_1$ excitation suggests that nonradiative decay of the bright $S_1$ vibronic states competes favorably with fluorescence. The absence of fluorescence is not surprising, since the $S_1$–$S_0$ transition is weak (it is equivalent to the forbidden $A_2^+ \Sigma^+_u \rightarrow X^1\Sigma^+_g$ transition in the isoelectronic CO$_2$, and thus allowed only in $C_s$ symmetry).\textsuperscript{9,22} and its radiative lifetime is expected to be long. Consequently, radiationless decay must be efficient, and a barrier to dissociation via channel (1) on $S_1$ must exist.

The subsequent dissociation on $S_0$ proceeds with no significant barrier as suggested by the low rotational excitation of the NCO fragment. With 38 387-cm$^{-1}$ photolysis (the first peak in the NCO yield spectrum), the average rotational energy in the NCO product is only $\sim 10$ cm$^{-1}$, and the next absorption feature to the red of this peak is $\sim 35$ cm$^{-1}$ away.

Establishing the dissociation mechanism at wavelengths where both channels (1) and (2) are open is less straightforward. The rotational distributions of the $^1$NH fragment [Fig. 4(b)] show that only the lowest rotational level, $J = 2$, is populated when exciting in the 42 900-cm$^{-1}$ threshold band. Higher rotational levels are populated in turn as the excess energy increases. Again, this behavior is typical of dissociation without a significant barrier. Indeed, quenching experiments of $^1$NH by CO indicate that no barrier exists in the approach of the two fragments,\textsuperscript{30} and recent electronic structure calculations show no barrier on $S_0$, but barriers on $S_1$ and $T_1$.\textsuperscript{31} The absence of barrier on $S_0$ has been rationalized by a change in hybridization as CO approaches $^1$NH. By analogy with the isoelectronic HN$_3$, barriers on $S_1$ and $T_1$ are due to electron–electron repulsion between the in-plane $\pi$ nonbonding orbital of NH and the $\sigma$ nonbonding orbital of CO.\textsuperscript{32} The electronic configuration of $S_0$ is more complicated, and in HN$_3$ is best described at long range as excitation of the 10$^a$ orbital whose energy increases as CO and $^1$NH approach. At closer separation, there is rehybridization to a 2a$^\sigma$ orbital which is attractive. In HN$_3$ this leads to a barrier on $S_0$; however, in HNCO the $S_0$ well is much deeper and the barrier is apparently eliminated.\textsuperscript{31,32}

The relative quantum yield of $^1$NH is initially very small; NCO yield spectra taken at the $^1$NH threshold region show no significant decrease when channel (2) opens (Fig. 5), and Brown et al. have very recently estimated that following excitation of 300 K HNCO at 43 480 cm$^{-1}$ the relative $^1$NH quantum yield $\Phi_{^1\text{NH}}(230 \text{ nm}) \approx 0.03$.\textsuperscript{12} At higher excess energies, the $^1$NH relative yield increases. Assuming that for jet-cooled HNCO $\Phi_{^1\text{NH}}(230 \text{ nm}) = 0.03$ as well and ignoring the increase in the average absorption cross section between 230 and 225 nm, we obtain $\Phi_{^1\text{NH}}(225 \text{ nm}) \approx 0.3$. Since the branching ratio between channels (1) and (2) depends sensitively on the characteristics of the respective transition states and their dependence on excess energy, it is hard to predict without detailed knowledge of the potential energy surfaces. Nevertheless, assuming that dissociation via both channels proceeds only on $S_0$, representative RRKM calculations are capable of simulating the observed trends in the branching ratios with physically reasonable parameters for the (rather loose) transition states.\textsuperscript{27} Had dissociation to $^1$NH occurred on $S_1$ from its onset, the increase in $^1$NH relative yield and linewidth would have been much faster. Notice that there is no abrupt change in the widths of the spectral features near the threshold for channel (2) mitigating, again, against $S_1$ participation. At higher excitation energies, the lines progressively broaden and an underlying continuum appears [Fig. 4(a)]. Obviously, this continuum derives partly
from increased spectral congestion, but the participation of a direct channel cannot be ruled out.

V. CONCLUSIONS

The jet-cooled studies presented in this paper enable us to deduce improved thermochemical values relevant to HNCO decomposition. The dissociation thresholds of channels (1) and (2) are 38 370±30 cm⁻¹ (109.7±0.1 kcal/mol) and 42 840±60 cm⁻¹ (122.5±0.17 kcal/mol), respectively. From these values, we derive improved heats of formation: \( \Delta H^0_\text{f}(\text{HNCO}) = -27.8±0.4 \) kcal/mol, and \( \Delta H^0_\text{f}(\text{NCO}) = 30.3±0.4 \) kcal/mol. We believe that the thermochemistry of HNCO is now well established.

From the jet-cooled absorption and photofragment yield spectra, as well as the near-threshold NCO(\(^{\text{2}}\)\(3\text{P}\)) and NH(\(^{\text{2}}\)\(\text{A}_\text{u}\)) rotational distributions, we infer the photodissociation mechanism following \( S_1 \rightarrow S_0 \) excitation. At least up to \( \sim 5000 \) cm⁻¹ above \( D_0(H\text{-NCO}) \), radiationless decay accesses high vibrational levels of \( S_0 \) from which HNCO predissociates via channels (1) and (2) without significant barriers. This mechanism implies that significant barriers to dissociation must exist on \( S_1 \).

Previous product rotational and translational energy distributions following photolysis of 300 K HNCO in the range 41 000–53 000 cm⁻¹ were interpreted by assuming an impulsive dissociation mechanism on \( S_1 \). However, the values for the bond dissociation energies used in the data analyses were incorrect, and in light of the improved thermochemical values now available a reinterpretation of the previous results is recommended. Note also that at 225 nm, Brown et al. observe state-specific effects in the vibrationally mediated photodissociation of HNCO, a result that is hard to explain with dissociation proceeding solely on \( S_0 \). Thus, at high photolysis energies the mechanism may change. Experiments are currently in progress to compare the product state distributions with statistical theories, and to explore decomposition mechanism(s) at higher photolysis energies.

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23 B. Ruscic (private communication). The recommendation to use the above value of \( \Delta H^0_\text{f}(\text{NH}) = 85.6±0.3 \) kcal/mol is based on the combination of the appearance potentials of \( \text{NH}_2/\text{NH} \) and \( \text{NH}_2/\text{NH}^+ \), which are 15.768±0.004 eV and 17.440±0.005 eV, respectively, and \( \text{IP}(\text{NH}_2) = 11.140±0.010 \) eV and \( \text{IP}(\text{NH}) = 13.476±0.002 \) eV, along with \( \Delta H^0_\text{f}(\text{NH}_2) = 9.31±0.008 \) kcal/mol. A slightly different value, \( \Delta H^0_\text{f}(\text{NH}) = 85.3±0.2 \) kcal/mol, was recommended by Anderson [W. R. Anderson, J. Phys. Chem. 93, 530 (1989)].
24 E. S. Medvedev and V. I. Osherov, Radiationless Transitions of Polyatomic Molecules (Springer-Verlag, Berlin, 1995).
27 In these simulations the H–NCO transition state frequencies were assumed to include those of free NCO, i.e., 1290, 2338, 680 cm⁻¹ (C–N and C–O stretches and NCO bend, respectively), and two nearly free rotors corresponding to the H-atom motion perpendicular to the reaction coordinate and the angular momentum associated with the nearly degenerate bend of the NCO skeleton (20 cm⁻¹ for both). The H–NCO transition state frequencies included the N–H and C–O frequencies (3186 and 2214 cm⁻¹, respectively), while three other degrees of freedom (N–C and H–N–C bends and H–N–C relative rotation) were assumed to be rather loose (50, 20, and 20 cm⁻¹). The harmonic density of states of HNCO(\( S_0 \)) near the opening of channel (2) used in the calculations is \( \sim 600 \) per cm⁻¹, surely a gross underestimate. However, under the assumption of complete Intramolecular Vibrational Redistribution (IVR) this parameter does not affect the NH/NCO channel ratio, as derived from the RRKM theory.
29 The weak coupling may be a result of the large energy gap between \( S_0 \) and \( S_1 \) which gives rise to unfavorable Franck–Condon overlap factors.