Threshold photoelectron spectroscopy of unstable N-containing compounds: Resolution of ΔK subbands in HNCO^+ and vibrational resolution in NCO^+

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(Received 30 March 2015; accepted 29 April 2015; published online 13 May 2015)

The threshold photoelectron spectra (TPES) of two unstable nitrogen-containing species, HNCO and NCO, were recorded utilizing vacuum ultraviolet synchrotron radiation. Both are intermediates in combustion processes and play a role in the removal of nitrogen oxides from exhaust gases. The rovibronic structure of the first band in the TPES of HNCO^+ was analyzed within the framework of an orbital ionization model, and the resolved structure of the origin band was assigned to ΔK subbands. An ionization energy of 11.602 ± 0.005 eV was determined and the vibrational structure of the cationic ground state was analyzed by a Franck-Condon fit. Low lying electronically excited states of HNCO^+ were also observed. In a second series of experiments, the NCO radical was generated by flash pyrolysis from chlorine isocyanate. The ionization energy to the $X^+ \ ^3\Sigma^-$ ground state was determined to be 11.76 ± 0.02 eV, while for the $a^+ \ ^1\Delta$ state, a value of 12.93 ± 0.02 eV was obtained. Vibrational structure was observed for both states, and bands were assigned by Franck-Condon simulations. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4920951>]

I. INTRODUCTION

Isocyanic acid HNCO and carbonyl amidogen NCO are both nitrogen-containing molecules that are known to be important intermediates in a number of combustion reactions, especially for bio-fuels.^{1–4} In the RAPRENO_x (rapid reduction of nitrogen oxides) process, HNCO is generated by thermal decomposition of cyanuric acid and is used to remove toxic nitrogen oxides (NO_x) from exhaust gases.⁵ Mechanistic studies have shown that the NCO radical also plays a major role in this process as reaction of HNCO with OH leads to carbonyl amidogen, which reduces NO to N₂O.^{6–8} In addition, HNCO has been observed in the interstellar space,⁹ where NCO is suggested to contribute to its formation.¹⁰ Because of its relevance, isocyanic acid has been investigated extensively. Infrared (IR) and microwave spectra have been recorded,^{11,12} and a number of experiments were aimed at photodissociation processes.^{13–18} Photoionization of isocyanic acid was first investigated by Eland using conventional He(I) photoelectron spectroscopy (PES).¹⁹ He determined the ionization energy (IE) for the formally non-bonding out of plane $a''(\pi_{nb})$ molecular orbital to be 11.60 ± 0.01 eV and observed three

vibrational bands in the ionic ground state, which were assigned to the molecule's three stretching modes. For ionization from the bonding $a'(\pi_b)$ and $a''(\pi_b)$ orbitals, vertical ionization energies of 12.39 ± 0.10 eV and 15.54 ± 0.05 eV were determined. A vibrational progression (565 cm^{-1} and 1113 cm^{-1} , respectively) was observed in both excited states. Cradock *et al.* also investigated HNCO in a similar experiment and reported an ionization energy of 11.62 ± 0.02 eV.²⁰ Further higher excited states corresponding to the ionization of the 4σ and 3σ orbitals were observed at 17.50 ± 0.02 eV and 19.24 ± 0.02 eV, respectively. Computations discussed the assignment of the orbital from which ionization occurs to the second excited state in the cation.²¹ However, Wilsey *et al.* later confirmed the original assignment.²² In addition, the dissociative photoionization (DPI) of HNCO was studied using the photoelectron photoion coincidence (PEPICO) technique. The first fragmentation channel leading to HCO^+ was reported to set in at 15.55 ± 0.03 eV. Appearance energies for 12 ionic fragments were determined, and the dissociation mechanisms were discussed with the help of quantum chemistry. Photoionization mass spectrometry confirmed the ionization energy from the photoelectron spectra,²³ whereas Penning ionization PES yielded a value of 11.55 eV.²⁴

The carbonyl amidogen radical NCO appears as a dissociation product of HNCO.^{13,25} Photoionization of NCO has already been investigated by Dyke *et al.* using He(I) radiation.²³ The ionization energy was determined to be

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11.76 $\pm$ 0.01 eV. Seven photoelectron bands resulting from ionization out of the 2π , 7σ , and 6σ molecular orbitals were observed. However, the PES of NCO was only obtained after subtracting the spectrum of HNCO, which was used as the precursor for the radical generation, and residual gases. To circumvent these issues, Ruscic and Berkowitz employed photoionization mass spectrometry which yielded the same ionization energy.²⁵

Threshold photoelectron spectroscopy using vacuum ultraviolet (VUV) synchrotron radiation has a high resolution and is a versatile tool to investigate photoionization processes. This has been demonstrated in the previous studies focused on other combustion-relevant intermediates.^{26–33} In the present study, it is shown that even rotational ΔK subbands of a small asymmetric-top molecule like isocyanic acid can be resolved and explained within the framework of an orbital ionization model.^{34,35} Partial or full resolution of rotational structure in photoelectron spectra has already been achieved for several polyatomic molecules^{36–40} and anions.^{41,42} In comparison to conventional PES, the imaging photoelectron photoion coincidence (iPEPICO) technique adds the advantage to record mass-selected TPE spectra, i.e., the interference of by-products and/or precursors for the radical generation can be avoided. Here, an undisturbed TPE spectrum of the carbonyl amidogen radical NCO will be presented.

II. EXPERIMENTAL SECTION

The TPES of isocyanic acid were recorded at the VUV beamline DESIRS of the synchrotron SOLEIL, France. Only a brief overview of the experiment will be given here, as the beamline and the double imaging photoelectron photoion coincidence (i²PEPICO) endstation DELICIOUS III have already been described in detail elsewhere.^{43–45} VUV synchrotron light emitted from the undulator OPHELIE2 was dispersed with an Eagle off-plane normal-incidence monochromator. A 200 lines mm^{−1} grating with a photon energy resolution of <3 meV was employed. Higher harmonics radiation (>15.5 eV) from the undulator was suppressed by a gas filter filled with Ar for $h\nu < 15.5$ eV.⁴⁶ For experiments with photon energies above 15.5 eV, no gas filter was utilized. A photodiode placed after the photoionization region measured the photon flux to normalize the photon energy scans.

Electrons and ions produced by photoionization were extracted in opposite directions by a constant electric field in DELICIOUS III. Electrons were velocity map imaged (VMI) on a delay-line detector, while a modified Wiley-McLaren time-of-flight (TOF) imaging spectrometer was used to detect the ions. Threshold photoelectrons with a maximum kinetic energy of 2.5–5 meV depending on the scan step size were selected from the center of the 2D electron image while considering the contribution of hot electrons.^{44,47} A coincidence scheme was used to correlate the photoelectrons with a particular mass. The mass-selected TPES were obtained by plotting the threshold electron counts vs. the photon energy.

Isocyanic acid was freshly prepared by heating a mixture of KNCO and stearic acid *in vacuo* to 90 °C and collecting the HNCO in liquid nitrogen. Impurities, mostly CO₂, were then removed by a trap-to-trap distillation between −60 °C

and −120 °C under dynamic vacuum conditions.^{13,48,49} HNCO was seeded in Ne while cooling the sample to −40 °C. The molecular beam was expanded into the SAPHIRS chamber and entered the DELICIOUS III spectrometer after passing a skimmer. The backing pressures in the jet chamber and the spectrometer were 3×10^{-4} and 3×10^{-8} millibars, respectively, with the molecular beam on.

The experiment to investigate the photoionization of the NCO radical was conducted at the X04DB VUV beamline at the Swiss Light Source storage ring using the iPEPICO setup. Experimental details can also be found elsewhere.^{50–52} Here, the VUV synchrotron radiation provided by a bending magnet was dispersed by a 150 lines mm^{−1} grating monochromator, yielding a photon energy resolution of about 8 meV. Higher order radiation was suppressed in a differentially pumped gas filter filled with neon. Coincidence experiments were carried out in a similar way to that at the synchrotron SOLEIL.

The carbonyl amidogen radical NCO was generated by flash pyrolysis of chlorine isocyanate (CINCO). The precursor was seeded in 2.0 bars of Ar, and the chlorine–carbon bond in the precursor was cleaved by passing a SiC tube, which was electrically heated to 700 °C. The pyrolysis temperature was measured using a type C thermocouple. Details on the pyrolysis source can be found elsewhere.⁵³ Chlorine isocyanate was freshly prepared according to the literature⁵⁴ by heating trichloroisocyanuric acid (C₃Cl₃N₃O₃) above 200 °C *in vacuo* and collecting the product in liquid nitrogen. The raw product was further purified by a trap-to-trap distillation between −40 °C and −196 °C under a dynamic vacuum. However, the mass spectra showed that Cl₂ could not be completely removed. During the experiment, the precursor was held at −30 °C as it decomposes above 0 °C and argon was used as carrier gas.

Quantum chemistry was employed to support all the assignments. Density functional theory (DFT) on the B3LYP/6-311G(2d,d,p) level of theory and a complete basis set composite method (CBS-QB3) were performed using the Gaussian09 package.⁵⁵

III. RESULTS AND DISCUSSION

A. Isocyanic acid HNCO

1. Threshold photoelectron spectrum

Figure 1 shows a mass-selected TPES recorded at the SOLEIL synchrotron. The low energy part from 11.5 to 12.0 eV was scanned with a step size of 2 meV and 30 s integration time, 10 meV steps were used from 12.0 to 14.5 eV, while the spectrum above 14.5 eV was scanned in 20 meV steps. For the latter two parts of the spectrum, each data point was averaged for 60 s. Threshold electrons were selected with a resolution of 2.5 meV for the low energy scan, while a resolution of 5 meV was employed for the other scan. All scans overlapped, which enabled us to assemble a complete spectrum.

The maximum of the first peak in the TPES lies at 11.60 eV. This peak can be assigned to the adiabatic ionization transition from the neutral ground state to the HNCO⁺ X⁺ ²A'' ground state and is in good agreement with the previous PES

FIG. 1. Mass-selected TPES of isocyanic acid. The peaks can be assigned to the $\text{HNCO}^+ X^+ 2\tilde{A}''$ ground state and the first two excited states. The symmetry of the second excited states cannot be unambiguously assigned as computations predict two states to be very close.

studies.^{19,20,22} It is followed by several pronounced, but significantly less intense bands below 12 eV. A single vibrational progression between 12 and 13 eV with a spacing of 590 cm^{-1} can be identified in the TPES and be assigned to the $A^+ 2\tilde{A}''$ excited state. At 15.50 eV, the spectrum features another band that corresponds to higher electronic states of the cation.

2. Rotational structure and photoionization selection rules

Upon zooming into the most intense band at 11.60 eV, it becomes apparent that this band features additional structure, which can be assigned to ΔK_a subbands (see Figure 2). HNCO is *per se* an asymmetric top molecule with C_s symmetry as all three rotational constants are different. However, experiments¹¹ show that in the neutral ground state, the rotational constants B'' and C'' are almost identical ($B'' = 0.369\text{ cm}^{-1}$ and $C'' = 0.364\text{ cm}^{-1}$) and about two orders of magnitude lower than constant $A'' = 30.645\text{ cm}^{-1}$. Therefore, the molecule can be regarded in good approximation as a prolate symmetric top ($\kappa = -0.9996$). Hence, in the following, although we are keeping the asymmetric top representation, several approximations will be made. First, for such near prolate symmetric top molecules, the rotational energy of an asymmetric top level (J, K_a, K_c) is well approximated, neglecting centrifugal distortion terms, by

$$E(J, K_a, K_c) = \frac{1}{2}(B + C)J(J + 1) + \left(A - \frac{1}{2}(B + C)\right)K_a^2. \quad (1)$$

In this approximation, the non-diagonal matrix elements of the rotational Hamiltonian coupling the two (J, K) and ($J, K \pm 2$) vectors of the prolate symmetric top base, on which the (J, K_a, K_c) states are expanded, are neglected.

From expression (1), it becomes obvious that the K_a -stacks are well separated in a near prolate symmetric top molecule, and thus, this structure is likely to be resolved in the TPES.

FIG. 2. Expanded view of the first band in the threshold photoelectron spectrum. The high photon energy resolution allows observing ΔK_a subbands. The photoionization selection rules favor transitions with $\Delta K_a = \pm 1$. The assignment of the ΔK_a subbands is based on a simulation (blue sticks and red line: convolution with Gaussian fwhm = 3 meV; see text for details). An ionization energy of $11.602 \pm 0.005\text{ eV}$ can be extracted.

In order to simulate rotational structure in a photoelectron spectrum, knowledge on the rovibronic photoionization selection rules for the investigated species is necessary. During photoionization, the neutral molecule interacts with a photon, and a cation and an electron are generated,

$$\langle \Psi_{\text{ion}} \Psi_{\text{electron}} | \mu | \Psi_{\text{neutral}} \rangle. \quad (2)$$

Conservation of parity and nuclear spin symmetry leads to a general symmetry selection rule for rovibronic photoionization,⁵⁶

$$\Gamma_{e-} \otimes \Gamma_{rve}^+ \otimes \Gamma_{rve}'' \supset \Gamma^*. \quad (3)$$

Here, Γ_{e-} stands for symmetry of the outgoing electron. Γ_{rve}^+ and Γ_{rve}'' represent the cation and neutral rovibronic states irreducible representation, respectively, and Γ^* denotes the antisymmetric representation of the molecular symmetry group. The electron's representation is dependent on l , the orbital angular momentum quantum number of its partial wave. If l is even, the photoelectron wavefunction will transform as the totally symmetric representation and, if l is odd, as the antisymmetric representation. Using this relation in Eq. (3) leads to the single-photon rovibronic selection rules, which define the allowed changes of the rovibronic symmetry Γ_{rve} between neutral and ionic states.⁵⁶ The angular momentum quantum number l of the photoelectron can be predicted using the orbital ionization model.^{34,35,57} The HOMO (a'') orbital of HNCO lies perpendicular to the molecular plane and has two nodal planes—one in the molecular plane and one perpendicular to it. Therefore, it can be considered in first approximation as a d_{xz} atomic orbital with an l'' -value of 2, and a l'' -value of ± 1 (l'' being the projection of l'' on the molecular a -axis). The $\Delta l = \pm 1$ selection rule leads to the result that l can be either 1 or 3, i.e., the photoelectron is emitted into the p - or f -continuum. Hence, according to the single-photon selection rules for odd l -values discussed above, a rotational transition from the neutral molecule to the cation will in first order be allowed if both states have the same

irreducible representation. Therefore, as the symmetry of the asymmetric top rotational wavefunctions in the C_s symmetry is a' (a'') for even (odd) K_c values and the symmetries of the vibronic (ve) ground state wavefunctions are a' for $\text{HNCO}(X^1A')$ and a'' for $\text{HNCO}^+(X^+2A'')$, the transitions are allowed only between levels for which the parity of K_c'' and K_c^+ is different.

In the framework of the orbital ionization model, intensities of rovibronic photoionization transitions depend on l'' and λ'' . With these quantum numbers, it is possible to compute the total ionization cross section σ_{tot} according to Eq. (7) in Ref. 35 at the energy E of a certain rotational transition, $(N^+, K_a^+, K_c^+) \leftarrow (N'', K_a'', K_c'')$, between two asymmetric top rotational states of HNCO and HNCO^+ in the photoelectron. The orbital ionization model further restricts the selection rules,

$$|\Delta N| = |N^+ - N''| \leq l'', \quad (4)$$

$$\Delta K = K^+ - K'' = \lambda''. \quad (5)$$

For HNCO , $l'' = 2$ and $\lambda'' = \pm 1$; so, the rovibronic photoionization selection rules are defined as $\Delta N = 0, \pm 1$, or ± 2 and $\Delta K = \pm 1$. As HNCO and HNCO^+ are near symmetric top molecules, the last rule reduces essentially to $\Delta K_a = \pm 1$ here.

The rovibronic transitions from the neutral HNCO ground state to the cationic electronic and vibrational HNCO^+ ground state were simulated. For the neutral molecule, the experimentally determined rotational constants of Yamada given at the beginning of this section were used.¹¹ B3LYP/6-311G(2d,d,p) computations predict a slightly smaller A constant for the cation compared to the computed constant for the neutral, while the B and C constants ($B^+ = 0.364 \text{ cm}^{-1}$ and $C^+ = 0.359 \text{ cm}^{-1}$) remain more or less unchanged. As will be discussed later, the computations of the cation are not sufficiently accurate. Therefore, the A constant, which has the greatest effect on the rovibrational levels' energies, was varied systematically. Choosing $A^+ = 27.50 \text{ cm}^{-1}$, based on the Franck-Condon (FC)-fit described below, results in a good fit of the experimental spectrum, and the simulation depicted in Figure 2 was obtained. As shown, the overall shape of the band can be described by transitions following the selection rule $\Delta K_a = \pm 1$. A temperature of 170 K was assumed for the simulation. At this temperature, the rotational levels up to $K_a'' = 3$ are populated. At 11.575 eV, the transition $K_a^+ = 3 \leftarrow K_a'' = 4$ also might be visible but is not represented in the simulation. However, we believe that the signal is mainly caused by the vibrational sequence bands of $1(a')$ and $2(a')$. From the fit to the rotational band structure, we determined the ionization energy of $11.602 \pm 0.005 \text{ eV}$. Note that this energy does not correspond to the peak maximum. Moreover, the rotational $J_{K_aK_c} 0_{00}-0_{00}$ transition $\text{HNCO}^+(X^+2A'') \leftarrow \text{HNCO}(X^1A')$, which would occur at this precise energy is—in the framework of the orbital ionization model—not allowed. We computed the ionization energy of isocyanic acid using the CBS-QB3 composite method^{58,59} to be $\text{IE} = 11.506 \text{ eV}$, which matches our experimental result reasonably well. Note that the orbital ionization model uses assumptions summarized as the frozen-core Hartree-Fock approximation, i.e., the electronic transition moment is reduced to a one-electron integral which

FIG. 3. Threshold photoelectron spectrum of HNCO . All bands can be assigned to the fundamentals of normal modes or to combination bands (dashed arrows) in HNCO^+ . The Franck-Condon fit based on B3LYP/6-311G(2d,d,p) computations confirms this assignment. However, the $4(a')^+$ mode (HNC in plane bending) shows an unexpectedly high wavenumber deviation due to a disturbed potential energy surface along the HNC angle coordinate. Dashed arrows represent combination bands. Note that the step size increases at 12.0 eV, as the spectrum is assembled from two overlapping scans.

describes the molecular orbital from which ionization occurs and the photoelectron continuum.^{34,35}

3. Vibrational bands in the TPE spectrum

As our sample did not contain any contamination and no dissociative photoionization is expected below 15.5 eV,²⁵ no mass-selectivity was employed for recording the low energy part of the threshold photoelectron spectrum shown in Figure 3.

Besides the 0-0 transition at 11.60 eV, the spectrum features four pronounced bands below 12 eV. They can be assigned to transitions into the fundamentals of vibrational modes in the X^+2A'' of HNCO^+ . ΔK subband structure is also covertly visible in some of them. The relative energy of most of these bands with respect to the 0-0 transition shows little deviation from the values obtained in B3LYP/6-311G(2d,d,p) computations (see Table I). In the previous He(I) PES experiments,^{19,20,22} the $4(a')^+$ HNC and $5(a')^+$ NCO stretching modes have not been observed. The position of the NH-stretching mode band at ca. 12 eV cannot be determined as accurately as for the other modes in our spectrum, as it overlaps with structure resulting from the first electronically excited state. In addition, the first overtone of the $4(a')^+$ mode and several combination bands can be assigned.

It is noteworthy that the HNC in plane bending mode wavenumber $4(a')^+$ is computed to be 70 cm^{-1} lower than the band observed in the TPE spectrum, an unusually large deviation. Scanning the $\text{HNCO}^+ X^+2A''$ potential energy surface along the HNC angle reveals that the potential is highly perturbed at the near-linear geometry. The vertical excitation energy to the first excited $\text{HNCO}^+ A^+2A'$ electronic state lies at 12.34 eV (B3LYP/6-311G(2d,d,p)), which corresponds to removal of an electron from the non-bonding in plane π_{nb} orbital, while for the ground state, the ionization occurs from

TABLE I. Comparison of experimentally observed vibrational bands in TPE spectrum with B3LYP/G-311G(2d,d,p) computations (scaled by 0.967).⁶⁰

		Experiment	B3LYP/6-311G(2d,d,p)
1(a') ⁺	$\nu(\text{NH})$	3210 cm ⁻¹	3276 cm ⁻¹
2(a') ⁺	$\nu(\text{CO})$	2030 cm ⁻¹	1992 cm ⁻¹
3(a') ⁺	$\nu(\text{CN})$	1170 cm ⁻¹	1181 cm ⁻¹
4(a') ⁺	$\delta(\text{HNC})_{\text{in plane}}$	790 cm ⁻¹	720 cm ⁻¹
5(a') ⁺	$\delta(\text{NCO})_{\text{in plane}}$	495 cm ⁻¹	502 cm ⁻¹
1(a'') ⁺	$\delta(\text{NCO})_{\text{out of plane}}$	...	462 cm ⁻¹

the also non-bonding out of plane π_{nb} orbital. The A^+ state is thus only less than 1 eV above the cationic ground state. At a linear geometry, both states are degenerate. Therefore, the two states, $X^+ {}^2A''$ and $A^+ {}^2A'$, can be regarded as the two Renner-Teller components of a degenerate state. This conical intersection between ground and first excited states has already been discussed in the literature.²² Due to the breakdown of the Born-Oppenheimer approximation, DFT computations do not converge to a minimum for the $A^+ {}^2A'$ state. The $X^+ {}^2A''/A^+ {}^2A'$ conical intersection at a 180° HNC bonding angle also perturbs the energy levels of the corresponding bending mode. Hence, a large anharmonicity is expected for the HNC bending mode especially for small quantum numbers. DFT, which computes frequencies in a harmonic approximation and uses only single-reference wavefunctions, will fail in describing the potential curves correctly in such a situation. In contrast, the wavenumbers of the other observed modes are predicted accurately. As both neutral isocyanic acid and its cation are planar, an excitation of the NCO out of plane bending mode 1(a'')⁺ is neither expected nor observed. To confirm the assignment above, a Franck-Condon simulation based on B3LYP/6-311G(2d,d,p) computations was performed by using the program FCFit v2.8.20⁶¹ which includes Duschinsky rotation. As expected, the relative peak positions were reproduced, but the intensities of both the 5(a')⁺ and the 4(a')⁺ bands were significantly underestimated when the *ab initio* geometries were employed. All combination bands involving the HNC-in plane bending mode also display a significant deviation. The simulated intensities of the stretching modes showed by contrast a good agreement with the experiment. Therefore, we performed a Franck-Condon fit of the cation geometry by displacing molecular coordinates until the experimentally observed intensities are obtained. This is possible, because the neutral molecule's geometry is very well known from the previous experiments¹¹ and high-level computations.⁶² The result of the fit is shown in Figure 3 and Table II. Note that only the intensities of the peaks are recalculated and not the vibrational frequencies. While all bonding distances remain more or less the same, the two bonding angles are affected by the fit. Our fit suggests that the HNC bonding angle is computed too big and the NCO bonding angle too small. By comparing the fitted cation geometry to the neutral molecule's one, it becomes apparent that in particular the NCO bonding angle decreases upon ionization. Therefore, the cation's moment of inertia along the *a* molecule axis is greater than the neutral's one resulting in a smaller rotational constant A^+ for the cation. The FC fit yields an even larger

decrease of the NCO angle and thus results in a smaller rotational constant A^+ . The *B* and *C* constants on the other hand should not be significantly affected by the change of geometry.

4. Excited states

The second band system in the TPE spectrum of HNCO shown in Figure 3 features a distinct vibrational progression. Like stated above, the vertical excitation energy to the first excited electronic state of the HNCO⁺ cation is computed to be 12.34 eV. Thus, the observed structure can be assigned to the $A^+ {}^2A'$ state of isocyanic acid. A pronounced excitation of the HNC bending mode is expected to appear, because the HNC bonding angle changes significantly from about 124° to 180°. The components of the observed progression are almost equally spaced by 590 cm⁻¹ and relatively broad, as higher combination bands from the ground state might be underlying. The spacing is close to the wavenumber observed for the HNC bending mode in the ground state of HNCO and also matches the wavenumbers of 565 cm⁻¹ and 610 cm⁻¹ determined in the previous studies.^{19,20} Ruscic and Berkowitz, by contrast, explain the structure in this part of the spectrum by autoionizing Rydberg state series.²⁵ No confirmation for the latter assignment can be found in the photoion yield curve that has also been recorded in our experiment. As the spacing between the various components in our spectrum is regular and FC-factors to low-lying levels are expected to be small, we assume that the energy levels lie considerably above the conical intersection. Hence, the first component at 12.00 eV is tentatively assigned to the third overtone of the HNC bending mode 4(a')⁺. This was estimated from an extrapolation of the computed $A^+ {}^2A'$ potential energy surface to a harmonic potential with a minimum at about 11.74 eV. The vibrational

TABLE II. Molecular geometry of neutral and cationic HNCO computed on B3LYP/6-311G(2d,d,p) level of theory. The third column contains the result of the Franck-Condon fit.

	HNCO X ¹ A' (Ref. 11)	HNCO ⁺ X ⁺ ² A'' B3LYP/6-311G(2d,d,p)	Fit
r(NH)/Å	0.995	1.033	1.034
r(NC)/Å	1.214	1.260	1.268
r(CO)/Å	1.166	1.139	1.141
<(HNC)/°	123.9	124.5	122
<(NCO)/°	172.6	170.9	167

levels were then assigned in a simple harmonic approximation assuming a frequency of 590 cm^{-1} . Note that the observed peak at 12.0 eV also contains significant contribution of the $1(a')^+$ excitation in the HNCO^+ ground state, but is underestimated in the Franck-Condon fit. Our assignment therefore explains this deviation. The ostensible splitting of some of the bands visible in Figure 3 might also originate from contributions of transitions into the X^+ state.

At 15.50 eV the TPE spectrum features a third band with one sharp peak (see Figure 1) followed by a smaller peak at $+490\text{ cm}^{-1}$. Computations show that the second and third excited states are nearly degenerate with an energy difference of less than 50 meV .²² Therefore, a definitive assignment of this band to either the $2^+ {}^2A'$ state or the $2^+ {}^2A''$ state is not possible. As the geometries of the two states are also similar, an assignment based on the vibration, which TD-DFT computations for both possible states identify as a HNC in plane bending mode with a frequency of 490 cm^{-1} , is not possible. Beyond the vibrational band at 15.56 eV , the mass-selected TPE signal for HNCO ($m/z = 43$) disappears because dissociative photoionization to the HCO^+ ($m/z = 29$) ion sets in. Therefore, we assign the observed vibronic peak position as a lower limit for the appearance energy, $\text{AE}_{0K}(\text{HNCO}, \text{HCO}^+) \geq 15.56\text{ eV}$. In a previous study, a similar value of $15.55 \pm 0.03\text{ eV}$ was reported for the onset of the $\text{HCO}^+ + \text{N}$ fragmentation channel.²² Further dissociative photoionization channels to NCO^+ ($m/z = 42$) and NH^+ ($m/z = 15$) have also been observed at higher photon energies. The onsets of the respective fragment ion signal agree well with the literature values for the appearance energies $\text{AE}_{0K}(\text{NCO}^+) = 16.46 \pm 0.03\text{ eV}$ and $\text{AE}_{0K}(\text{NH}^+) = 17.20 \pm 0.05\text{ eV}$.²²

B. NCO radical

Pyrolysis of chlorine isocyanate (CINCO) yields a distinct peak in the mass spectrum at $m/z = 42$ that can be assigned to the carbonyl amidogen radical NCO . Figure 4 shows the mass-selected photoelectron spectrum of $m/z = 42$, which was recorded with a 10 meV step size and an integration time of 9 min per data point at the Swiss Light Source storage ring up to a photon energy of 13.5 eV . Threshold photoelectrons with up to 5 meV kinetic energy were analyzed.

The recorded spectrum features two different band structures between 11.5 and 13.5 eV . At 11.76 eV , the TPE signal starts to rise and is followed by a pronounced progression with peaks at 11.87 , 11.99 , 12.13 , 12.24 , and 12.36 eV . In between those, significantly less intense peaks are visible 11.80 , 11.92 , 12.08 , and 12.18 eV . The first peak maximum at $11.76 \pm 0.02\text{ eV}$ can be assigned to the ionization energy of the NCO radical $\text{NCO}^+ X^+ {}^3\Sigma^- \leftarrow \text{NCO } X {}^2\Pi$. This value validates the ionization energy of 11.76 eV determined by Dyke *et al.* in a He(I) photoelectron study, in which the NCO spectrum was perturbed by bands of side-products from the radical generation and residual gases, which were subtracted.²³ Computations on CBS-QB3 level of theory agree also very well with this value, predicting an ionization energy of 11.78 eV . In the PES of Dyke *et al.*, a progression with a spacing of $1000 \pm 30\text{ cm}^{-1}$

FIG. 4. Mass-selected threshold photoelectron spectrum of the NCO radical and Franck-Condon simulation (blue sticks and red lines) including hot and sequence bands. The ionization energy of the cationic ground state $X^+ {}^3\Sigma^-$ was determined to be $11.76 \pm 0.02\text{ eV}$. The transition energy into the $a^+ {}^1\Delta$ state can be assigned to be $12.93 \pm 0.02\text{ eV}$. Both states feature excitation of the $\text{CO } 1(\sigma^+)^+$ and $\text{CN } 1(\sigma^+)^+$ stretching modes. The less intense bands which are not predicted in the simulation, but seem to belong to a progression of 415 cm^{-1} , and the intensity deviations can be explained by autoionization resonances from an excited neutral state with bent geometry.

(125 meV) was observed, whose overall envelope is very similar to the band structure of the present TPES study. The computations reveal a $C_{\infty v}$ symmetry for both neutral molecule and cation. Therefore, only transitions to the vibrationally excited cationic states of the CN stretching mode $2(\sigma^+)^+$ and CO stretching mode $1(\sigma^+)^+$ are expected. These transitions explain the pronounced progression in the TPES. By assigning this progression, experimental values for $2(\sigma^+)^+ = 970\text{ cm}^{-1}$ and $1(\sigma^+)^+ = 2015\text{ cm}^{-1}$ can be determined, which are in good agreement with the computed B3LYP/6-311G(2d,d,p) values (949 and 1996 cm^{-1} , unscaled). A Franck-Condon simulation, also shown in Figure 4, predicts the peak positions of this progression correctly. For the simulation, the program ezSpectrum was employed.⁶³ Note that hot and sequence bands are taken into account in the simulation. However, there is a disagreement in the intensities, and, in addition, the less intense peaks in between the pronounced progressions are missing in the simulation. An underlying progression with a spacing of about 415 cm^{-1} is derived, which matches the NCO bending mode wavenumber computed at 414 cm^{-1} (B3LYP/6-311G(2d,d,p)). Since NCO is linear in both the neutral and the cationic ground states, a bending mode progression is forbidden by symmetry. Alternatively, these features might be explained by autoionization of a superexcited state with bent geometry, as is observed, for example, in the TPE spectrum of CO_2 .^{64–66} This would explain the additional peaks and intensity deviations in the spectrum compared to the Franck-Condon simulation. Small steps are visible in the photoionization efficiency curve at the expected photon energies, which supports this interpretation.

At 12.93 eV , a second band system is visible with an intense peak followed by two smaller peaks at 13.07 and 13.20 eV . This spectral feature can be assigned to the ionization into the $a^+ {}^1\Delta$ first excited state of the cation NCO^+ , although CBS-

QB3 computations predict a slightly higher value of 13.24 eV. The assigned ionization energy and vibrational structure of the TPES agree well with the literature reporting an IE of 12.92 eV.²³ The smaller bands are again due to the excitation of the CO- and CN-stretching modes $2(\sigma^+)^+ = 1120\text{ cm}^{-1}$ and $1(\sigma^+)^+ = 2175\text{ cm}^{-1}$ (B3LYP/6-311G(2d,d,p): 1105 cm^{-1} and 1951 cm^{-1}). This part of the spectrum could also be reproduced in a Franck-Condon simulation, as shown in Figure 4. As the excited cation possesses also a linear geometry, an excitation of the NCO bending mode is neither observed nor expected.

The highest molecular orbital of NCO $X^2\Pi$ is a degenerate and formally non-bonding π -orbital with three electrons. Therefore, one would expect the general shape of the spectrum and the relative band intensities to resemble those observed for the isoelectronic N_3 radical.⁶⁷ In N_3 , the adiabatic and vertical IEs were found to coincide, and the relative intensities of the first three transitions were found to be 3:2:1. While for the $a^+1\Delta$ state the adiabatic and vertical ionization energy coincide, a geometry change upon ionization is evident for the $X^+3\Sigma^-$ ionic ground state. B3LYP/6-311G(2d,d,p) computations predict that the NC bond increases by 10 pm upon ionization and the CO bond decreases by 5 pm. Hence, the NC bonding is significantly reduced upon ionization. Furthermore, the relative intensity of the first two bands seems to deviate from the simple 3:2 ratio expected from the statistical weight. The electronic structure of NCO is thus more complicated than the one of N_3 . A thorough theoretical description of the $X^+3\Sigma^-$ ionic ground state probably requires a multireference approach.

IV. SUMMARY AND CONCLUSION

In this study, the photoionization of two important nitrogen containing unstable molecules, isocyanic acid HNCO and carbonyl amidogen NCO, was investigated in detail by threshold photoelectron spectroscopy. Isocyanic acid was freshly prepared from its potassium salt and stearic acid and ionized with tunable VUV synchrotron radiation at SOLEIL. ΔK transitions are visible in the TPES. The rotational structure of the $\text{HNCO}^+ X^+2A'' \leftarrow \text{HNCO } X^1A'$ band was analyzed in the framework of the orbital ionization model, and transitions following the $\Delta K_a = \pm 1$ photoionization selection rule were identified in the spectrum. The molecule's rotational temperature was $T_{\text{rot}} = 170\text{ K}$. This analysis enabled us to determine an accurate value for the ionization energy of isocyanic acid of $\text{IE} = 11.602 \pm 0.005\text{ eV}$. Vibrational structure of the $\text{HNCO}^+ X^+2A''$ ground state was observed, including the HNC- and NCO- in plane bending modes not visible in the previous spectra. A Franck-Condon fit yielded a good approximation for the cation's geometry, which differs slightly from DFT computations in the HNC and NCO bonding angles. The cationic ground state potential along the bending coordinate is perturbed due to a conical intersection with the first excited A^+2A' state at a linear NCO bonding angle. Therefore, single-determinant methods fail in computing this angle correctly. In addition, vibrational structure of the A^+2A' first excited state was observed and assigned to the HNC in plane bending mode, and the transition energy into the second excited state of HNCO^+ was determined

to be $15.50 \pm 0.03\text{ eV}$. From the disappearance of the mass-selected threshold photoelectron signal due to dissociative photoionization, a lower limit for the appearance energy for the HCO^+ fragment of $\text{AE}_{0\text{K}}(\text{HCO}^+) \geq 15.56\text{ eV}$ was determined.

The carbonyl amidogen radical NCO was studied in an iPEPICO experiment at the Swiss Light Source. Pyrolysis of chlorine isocyanate generates the desired radical and a mass-selected threshold photoelectron spectrum was obtained. The ionization energy of the $X^+3\Sigma^-$ state was determined to be $\text{IE} = 11.76 \pm 0.02\text{ eV}$. Besides the vibrational structure of the CN- and CO-stretching mode, a progression matching the NCO bending mode frequency is detected. As both neutral and cationic NCOs are linear, this excitation cannot arise from direct ionization but is explained by autoionization from a superexcited neutral state with bent geometry. The first excited electronic state of NCO^+ was observed, and the ionization energy for this state was determined to be $\text{IE}(a^+1\Delta) = 12.93 \pm 0.02\text{ eV}$. All results are supported by quantum chemical computations.

ACKNOWLEDGMENTS

The experiments on HNCO were performed on the DESIRS beamline at SOLEIL Synchrotron, Saint-Aubin, France. We are grateful to Dr. G. Garcia and Dr. L. Nahon for their assistance in the experiments and to the SOLEIL staff for smoothly running the facility and providing beamtime under Project No. 20130715. The NCO radical was investigated on the VUV X04DB beamline of the Swiss Light Source, Paul Scherrer Institut (PSI), Villigen, Switzerland. All computations were performed at the Linux-Cluster of the Leibniz-Rechenzentrum der Bayerischen Akademie der Wissenschaften (LRZ). We would like to thank Christopher Schwarz for helping with the HNCO synthesis and Christof Walter and Kilian Hader for useful advices concerning quantum chemistry and programming issues. This work was supported by the Deutsche Forschungsgemeinschaft (DFG), Contract No. FI575/7-3, the RTRA "Triangle de la Physique" (project "RADICAUX"), and the Swiss Federal Office for Energy (BFE Contract No. 101969/152433). Travel subsidies were provided by SOLEIL through the European Commission program "Transnational access to research infrastructures."

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