H_2CN^+ and H_2CNH^+ : New insight into the structure and dynamics from mass-selected threshold photoelectron spectra

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In this paper, we reinvestigate the photoionization of nitrogen containing reactive intermediates of the composition H_2CN and H_2CNH , molecules of importance in astrochemistry and biofuel combustion. In particular, H_2CN is also of considerable interest to theory, because of its complicated potential energy surface. The species were generated by flash pyrolysis, ionized with vacuum ultraviolet synchrotron radiation, and studied by mass-selected threshold photoelectron (TPE) spectroscopy. In the mass-selected TPE-spectrum of $m/z = 28$, contributions of all four isomers of H_2CN were identified. The excitation energy to the triplet cation of the methylene amidogen radical H_2CN was determined to be 12.32 eV. Considerable activity in the C–N mode of the cation is visible. Furthermore, we derived values for excitation into the triplet cations of 11.72 eV for *cis*-HCNH, 12.65 eV for *trans*-HCNH, and 11.21 eV for H_2NC . The latter values are probably accurate to within one vibrational quantum. The spectrum features an additional peak at 10.43 eV that corresponds to excitation into the C_{2v} -symmetric H_2CN^+ . As this structure constitutes a saddle point, the peak is assigned to an activated complex on the singlet potential energy surface of the cation, corresponding to a hydrogen atom migration. For methanimine, H_2CNH , the adiabatic ionization energy IE_{ad} was determined to be 9.99 eV and the vibrational structure of the spectrum was analyzed in detail. The uncertainty of earlier values that simply assigned the signal onset to the IE_{ad} is thus considerably reduced. The spectrum is dominated by the H–N–C bending mode ν_1^+ and the rocking mode ν_3^+ . All experimental data were supported by calculations and Franck-Condon simulations. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4808050>]

I. INTRODUCTION

In this paper, we report threshold photoelectron (TPE) spectra of the nitrogen-containing reactive intermediates H_2CN and H_2CNH obtained by imaging photoelectron-photoion coincidence (iPEPICO) spectroscopy. All four isomers of the composition H_2CN , C_{2v} -symmetric H_2CN , *cis*-HCNH, *trans*-HCNH, and H_2NC were identified in the experiment and excitation energies into the triplet cations were determined.

Small nitrogen-containing molecules play an important role in the combustion chemistry of biofuels, which often leads to undesirable combustion products such as NO_x .¹ The species described in this paper occur especially during combustion of nitramine-containing fuels.^{2,3} Concentrations of intermediates in flames can be monitored online by photoionization using synchrotron radiation,^{4–6} provided that the ionization properties are known. Therefore, selective experiments on the individual species are often crucial to get this information. In addition to their role in combustion, H_2CN ⁷ and H_2CNH ^{8,9} have been discovered in the interstellar medium and are supposed to be involved in the formation of HCN and

the amino acid glycine.^{10–12} Thus, a better understanding of their chemistry and accurate ionization energies are desirable.

The methylene amidogen radical H_2CN and its isomers have been studied extensively by theory due to the unusual potential energy surface with multiple minima and low-lying electronically excited states.^{10,13–17} These studies revealed that the C_{2v} -symmetric radical is the most stable of the four isomers. In the cation, on the other hand, there is only one stable singlet isomer, linear HCNH^+ , while four stable triplet cations with geometries similar to the neutral isomers have been computed. Various spectroscopic techniques have been applied to investigate the physical and chemical properties of methylene amidogen,^{18–23} but the ionization energy (IE) is still not well established. The photoionization of methylene amidogen was investigated before by photoionization mass spectrometry.²⁴ Despite the large geometry change upon ionization, the ionization threshold was tentatively assigned to be 9.4 ± 0.1 eV, a value that was rationalized by autoionization from high-lying Rydberg-states that couple to vibrational excited states of the linear HCNH^+ singlet cation. As the IE was derived from an ion yield curve only, it is hence afflicted with a rather large uncertainty. Therefore, it seems appropriate to reinvestigate the photoionization of the methylene amidogen radical by mass-selected threshold photoelectron spectroscopy (TPES).

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The second nitrogen-containing intermediate investigated in this study is methanimine H_2CNH . It is isoelectronic to formaldehyde and formally a closed-shell molecule, but nevertheless unstable under ambient conditions.²⁵ As the geometry of methanimine also changes significantly during ionization, it is difficult to detect the ionization threshold. Ionization energies for H_2CNH have been determined by conventional photoelectron spectroscopy²⁶ and photoionization mass spectrometry.^{27,28} Bock and Dammel²⁶ reported an adiabatic ionization energy $\text{IE}_{\text{ad}} = 9.97$ eV by simply taking the onset of the photoelectron signal. The partial resolution of the cation's vibrational structure was not analyzed, therefore, the IE_{ad} is associated with a considerable uncertainty. Here, we use TPES to achieve a higher spectral resolution and analyze the vibrational structure in detail to determine the IE_{ad} more precisely.

To study these intermediates, an iPEPICO experiment was conducted,^{29,30} employing synchrotron radiation as the tunable light source. This approach has already yielded TPE spectra for a number of radicals in recent years.^{31–34}

II. EXPERIMENTAL

The nitrogen-containing intermediates were characterized at the VUV beamline X04-DB of the Swiss Light Source (SLS) at the Paul Scherrer Institut in Villigen/CH. As the photoionization experiment is already described in detail elsewhere,^{29,30,35} only a brief overview is given here. Synchrotron radiation is provided by a bending magnet and then collimated onto a silicon grating (600 nm^{-1}) for generating monochromatic radiation. The monochromator's energy resolution is $E/\Delta E \approx 10^4$. A rare gas filter operating with a Kr/Ar/Ne-mixture is used for filtering higher harmonics. In the energy range utilized for this study, the flux is approximately 10^{12} photons s^{-1} . The energy was calibrated on the $11\text{ s}'$ peak of argon, giving a resolution of 5 meV, as measured on the full width at half maximum (fwhm).

The iPEPICO experiments were conducted in a differentially pumped molecular beam apparatus. After photoionization by synchrotron radiation, the cations and electrons were extracted in opposite directions by a vertical electric field of 120 V cm^{-1} . Cations were detected in a time-of-flight (TOF) mass spectrometer, while electrons were focused on the microchannel plates of a position sensitive detector operating with a delay line anode (Roentdek DLD40) to yield a two-dimensional electron image. Collecting cations and electrons in coincidence permits us to record mass-selected threshold photoelectron spectra. Threshold electrons were selected with an energy resolution of 5 meV. The signal was corrected for contributions of background electrons by following a procedure described in the literature and false coincidences were subtracted.³⁶

The reactive intermediates were generated by pyrolysis in an electrically heated SiC-tube³⁷ from the precursor methylhydrazine, $\text{H}_2\text{NNH}(\text{CH}_3)$, which was commercially obtained from Sigma-Aldrich and used without further purification. The liquid compound was seeded in 0.2 bar (absolute) of argon in a bubbler and expanded through a 0.1 mm nozzle into the pyrolysis tube. With a pyrolysis power of 30–50 W almost

complete conversion of the precursor to its pyrolysis products was achieved. All spectra were averaged for 60 s per data point and normalized to the photon flux.³⁵

To validate the experimental data, quantum chemical computations were performed. Several methods were applied, second-order Møller-Plesset perturbation theory (MP2) with a cc-pVTZ basis, density functional theory (DFT) employing the B3LYP functional and a 6-311++G** basis set, the composite methods CBS-QB3 and G4, and coupled-cluster theory (CCSD(T)) with the aug-cc-pVTZ basis set. All computations were carried out with the GAUSSIAN 09 program.³⁸ For calculating excitation and ionization energies, the geometries of both neutral molecule and cation were optimized, absolute energies determined and harmonic vibrational frequencies calculated. Details of the computational results are given in the supplementary material.³⁹ The electronic energies were corrected by the corresponding vibrational zero-point energies. Excitation and ionization energies were then obtained by subtracting the neutral molecule's energy from the cation's one. Based on these computations, Franck-Condon (FC) simulations were performed to simulate the photoelectron spectra, employing either DFT or MP2 geometries and frequencies. Two different programs, FCFit, version 2.8.8⁴⁰ and ezSpectrum,⁴¹ were used. Note that all vibrational wavenumbers given below are unscaled. Transition states for estimating isomerization barriers were calculated with the GAUSSIAN 09 option QST2,^{42,43} which employs a quadratic synchronous transit approach to locate the transition state and then performs an optimization.

III. RESULTS AND DISCUSSION

A. Mass spectra

As mentioned above, nitrogen-containing reactive intermediates were generated by flash pyrolysis of methylhydrazine. Figure 1 shows both the mass spectra of the precursor (upper trace) and of its pyrolysis products (lower trace) at

FIG. 1. Photoionization mass spectra of methylhydrazine (upper trace) and its pyrolysis products (lower trace) at 11.0 eV photon energy.

a photon energy of 11.0 eV. Dissociative photoionization of methylhydrazine ($m/z = 46$) is already observed at this energy, as can be seen in the upper trace. The peak at $m/z = 45$ corresponds to a loss of atomic hydrogen, whereas the peak at $m/z = 31$ can be assigned to the loss of methyl. Since the dissociative photoionization of methylhydrazine has already been described in detail elsewhere⁴⁴ and appearance energies of 9.85 ± 0.05 eV and 10.25 ± 0.05 eV have been reported for the fragments of $m/z = 45$ and 31, respectively, it will therefore not be discussed further.

The precursor signal almost completely disappears when the pyrolysis is turned on, as well as the signal of the fragment at $m/z = 45$. Because of the almost complete conversion, only little perturbation by ion signals from dissociative photoionization of the precursor is expected while investigating the pyrolysis products. As Figure 1 illustrates, pyrolysis is rather unselective and multiple pyrolysis products are observed. There are intense peaks at $m/z = 15$, 17, and 31, which can be assigned to the methyl radical CH_3 ,⁴⁵ ammonia NH_3 ,⁴⁶ and methylamine CH_3NH_2 ,⁴⁷ respectively, based on the threshold photoelectron spectra. Again, the photoionization of these species is well investigated. The signal at $m/z = 30$ can be assigned to CH_2NH_2^+ , which originates from dissociative photoionization of methylamine. We only obtained an approximate appearance energy of 10.2 eV from the breakdown diagram due to a low signal/noise ratio, which nevertheless is in good accordance with the literature value ($\text{AE}_{0\text{K}} = 10.228$ eV).⁴⁸ Therefore, only the mass-selected threshold photoelectron spectra of the signals at $m/z = 28$, methylene amidogen and its isomers, and $m/z = 29$, methanimine, will be discussed in detail. The number of reactive species present in the mass spectra indicates that a considerable amount of bimolecular chemistry occurs in the pyrolysis.

B. Threshold photoelectron spectra of $m/z = 28$

When turning on the pyrolysis, a distinct peak at $m/z = 28$ appears that can be assigned to isomers of the composition H_2CN . As discussed in the literature,^{13–16} there are four stable isomers of this composition: H_2CN , *cis*-HCNH, *trans*-HCNH, and H_2NC . An energy diagram is displayed in Figure 2, showing the relative energies of these isomers and the corresponding transition states. While a local minimum can be found on the triplet potential energy surface of the cation for all four isomers, there is only one stable minimum on the singlet surface, corresponding to linear HCNH^+ . In contrast, on the potential energy surface of the neutral ground state linear HCNH is not a minimum energy structure. Therefore, the transition to linear HCNH^+ is not likely to be observed in a photoionization experiment due to unfavorable FC-factors. The C_{2v} -symmetric isomer H_2CN^+ on the other hand is supposed to represent a first order saddle point on the singlet potential energy surface of the cation.^{10,17} For aiding in the interpretation of the experimental data, excitation energies into the triplet cations were computed for all H_2CN -isomers by MP2. The results, presented in Figure 2, are in accordance with earlier computational work.^{10,13–16} Transition states for isomerization reactions between the isomers were calculated to determine barrier heights. As visible, the energy difference between the radicals H_2CN , *cis*-HCNH, and *trans*-HCNH is small and in particular the barrier between *cis*-HCNH and *trans*-HCNH is low. Note that details on all calculations are given in the supplementary material.³⁹

In Figure 3, the TPE-signal in the $m/z = 28$ channel is plotted as a function of photon energy. The depicted spectrum was assembled of different scans that overlapped in a small energy region. In all scans, the step size was 5 meV and each data point was averaged over 60 s. The mass-selected

FIG. 2. Calculated energies of the neutral and cationic H_2CN isomers. Energies are referenced to the absolute energy of the most stable neutral isomer, H_2CN .

FIG. 3. Mass selected threshold photoelectron spectrum (black line) and calculated Franck-Condon factors (stick spectra, blue lines) of the mass channel $m/z = 28$. Traces (a)–(d) correspond to the simulated photoelectron spectra of the isomers H_2CN , *cis*-HCNH, *trans*-HCNH, and H_2NC . Trace (e) depicts the sum spectrum of those four simulations. The peak at 10.43 eV could not be simulated, but is assigned to an activated complex on the singlet potential energy surface of the cation, $[\text{H}_2\text{CN}^+]^\ddagger$.

TPE-spectrum shows a number of different features. The signal rises above noise level at around 10 eV, at an energy significantly higher than the 9.4 eV reported before.²⁴ However, this onset should not be mistaken as a measure of the IE as will be discussed below. At 10.43 eV, a single intense peak is observed, followed by a series of minor broad peaks beginning at 11.20 eV. Finally, a pronounced progression with sharp, intense, and equidistant peaks is visible above 12.32 eV. Since it is not possible to explain the complete spectrum by transitions originating from one carrier only, it suggests that more than one isomer of the composition H_2CN is formed during pyrolysis. Below we will discuss the contributions of various isomers separately. The assignments are based on the computed ionization energies and on Franck-Condon simulations of the vibrational structure.

The most prominent structure is the intense progression beginning at 12.32 eV with four peaks separated by 0.16 eV (1290 cm^{-1}). By comparing with theory, the first peak at 12.32 eV can be assigned to the excitation from the $X\ ^2\text{B}_2$ electronic ground state of neutral H_2CN to the $^3\text{A}_2$ triplet state of H_2CN^+ . MP2 computations yield a value of 12.24 eV and predict a significant elongation of the CN-bond by more than 10 pm. Thus, Franck-Condon factors for the transition from the vibrational ground state of the neutral to ionic states with excitation in the CN-stretching mode ν_3^+ are expected to be large. Calculations yield a wavenumber of 1299 cm^{-1} for this mode, which is in excellent agreement with the observed progression. For further confirmation, the mass-selected TPE-

FIG. 4. Isomerization of linear HCNH^+ via the C_{2v} -symmetric transition state.

spectrum was fitted by a Franck-Condon simulation including a geometry optimization of the cation to match the experimental spectrum as good as possible. The result is shown in trace (a) of Figure 3. Furthermore, this Franck-Condon-fit revealed that not only the CN-stretching mode, but also the HCH-bending mode ν_4^+ (1495 cm^{-1}) and combination bands of both modes contribute to the observed structure. Note that the peak around 12.8 eV is still underestimated in the fit. A possible explanation will be given below.

We will now turn our attention to the distinct feature at 10.43 eV that cannot be assigned to any of the four isomers. A comparison with the calculated ionization energies shows that the observed transition is very close to the energy of 10.24 eV computed for the transition to the C_{2v} -symmetric saddle point on the singlet cation potential energy surface, i.e., a transition state (cf. Figure 2). This is reminiscent of the work by Neumark and co-workers^{49,50} who have shown in photodetachment experiments that activated complexes (transition states) of neutral reactions can be observed by photoelectron spectroscopy starting from the anion and that considerable information on the reaction dynamics can be extracted. They succeeded to investigate neutral transition states such as IHI ,⁵¹ FH_2 ,⁵¹ and H_3O .⁵² Here, we observe an activated complex in the cation by photoelectron spectroscopy, starting from a neutral molecule. Considering that there is only one stable isomer on the singlet potential energy surface, linear HCNH^+ , the saddle point constitutes the transition state of an isomerization reaction that leads to an exchange of the two hydrogen atoms in linear HCNH^+ , a possible reaction being sketched in Figure 4. The imaginary frequency in the H_2CN^+ transition state is the HCH in-plane rocking mode, in which both hydrogen atoms move alternately towards the nitrogen atom. From a chemist's point of view, this imaginary frequency represents the motion over the transition state for an exchange of the hydrogen atoms. In principle, the peak width gives information on the lifetime of the activated complex, which is determined by the imaginary frequency, but the fwhm of 40 meV is probably determined by photon energy resolution and thermal excitation in the neutral.

The geometry optimization of the C_{2v} singlet H_2CN^+ cation converges to a saddle point with about the same geometry as the neutral molecule. Therefore, little vibrational structure is expected to appear. This is in agreement with our experimental spectrum which shows only one intense peak at 10.43 eV. In addition, a band with an intensity only barely above noise level appears at a photon energy of 10.30 eV, which might be assigned to a hot- or sequence band transition from a thermally excited radical to the activated complex. We also suggest that the onset of the signal around 10 eV marks the energy at which the region of the cationic activated complex becomes accessible for vibrationally excited radicals. Interestingly, a resonance at 10.43 eV has also been

observed in previous photoion yield spectra, but was assigned to an autoionizing resonance of H_2CN .²⁴ In the TPE-spectrum in Figure 3, some further minor features are visible in this energy region, e.g., weak bands at 10.51, 10.57, and 10.67 eV. These very weak bands can be explained by a small amount of ethylene,⁵³ which possesses the same m/z value as the H_2CN -isomers and is generated during pyrolysis as a side product due to recombination of two methyl radicals and subsequent hydrogen loss.

For analyzing the remaining spectral features in Figure 3, other isomers of H_2CN were taken into account. As discussed above, the mass spectra already indicate the occurrence of bimolecular chemistry in the pyrolysis reactor, so the formation of other isomers of similar energy is not surprising. On the neutral potential energy surface, the second most stable isomer is *cis*-HCNH, which is only 0.1 eV higher in energy. MP2 computations predict an excitation energy into the triplet cation of 11.72 eV, while other methods predict 11.88 eV (B3LYP), 11.85 eV (CBS-QB3), and 11.84 eV (G4). In the TPE-spectrum, a small peak is observed at 11.72 eV, followed by a progression of broad peaks separated by roughly 1260 cm^{-1} . We therefore assign this progression to the photoelectron spectrum of *cis*-HCNH, i.e., to the $^3\text{A}' \leftarrow ^2\text{A}'$ transition. As the calculations predict a reduction of both the HCN- and the CNH-bonding angle by about 10° , an excitation of the corresponding cationic bending modes is expected. A Franck-Condon simulation (see trace (b)) in Figure 3) based on the MP2 geometries provides once again a good agreement with a part of the spectrum and confirms the considerations above. With the help of the FC simulation, the excitation energy of *cis*-HCNH to the triplet cation is therefore determined to be 11.72 eV, in good agreement with the *ab initio* values. Due to the contributions of several isomers to the spectrum and a correspondingly low signal/noise ratio, we cannot rule out that the assignment is off by one vibrational quantum. Despite the good agreement with theory, the value has thus to be considered with care.

Most likely *trans*-HCNH is also generated during pyrolysis because both conformers do not differ much in absolute energy and the barrier for isomerization is low (0.25 eV = 53 kJ/mol). MP2 computations yield an IE of 12.55 eV. B3LYP provides a value of 12.60 eV, the CBS-QB3 and G4 value of 12.71 eV is only slightly higher. Since these values are close to the transition to the $^3\text{A}_2$ state of H_2CN^+ , possible transitions from *trans*-HCNH are expected to be hidden under the intense signal of H_2CN^+ in this energy region. The assignments to the $^3\text{A}''$ state of *trans*-HCNH⁺ is therefore only tentative. When the adiabatic IE was set to 12.65 eV, the FC simulation (trace (c)) in Figure 3) seems to add intensity to the bands at 12.65 eV and 12.83 eV, respectively. In particular, the latter is underestimated in the simulation of triplet H_2CN^+ (trace (a) in Figure 3), so a contribution from *trans*-HCNH⁺ might provide the missing intensity for a good fit. According to the quantum chemical calculations, the CN-bonding distance in *trans*-HCNH is stretched by 12 pm during ionization and a progression of the corresponding CN-stretching mode (1479 cm^{-1}) is expected in the FC simulation.

The only part of the mass-selected TPE-spectrum that is left unexplained so far is the small, broad signal onset

TABLE I. Excitation energies for transitions into the cationic triplet states of the H_2CN isomers, computed on different levels of theory and derived in the present work.

	MP2/cc- pVTZ	B3LYP/6- 311++G**	CBS-QB3	G4	This experiment
$\text{H}_2\text{CN}(\text{sing})$	10.24	...	10.48	10.45	10.43 ^a
$\text{H}_2\text{CN}(\text{trip})$	12.24	12.47	12.63	12.59	12.32
<i>cis</i> -HCNH	11.72	11.88	11.85	11.84	11.72
<i>trans</i> -HCNH	12.55	12.60	12.71	12.71	12.65
H_2NC	10.69	10.99	10.87	10.82	11.21

^aEarlier experimental work arrived at an IE of 9.4 eV and assigned it to the transition from H_2CN to HCNH^+ .²⁴

at 11.21 eV followed by two further bands separated by 1750 cm^{-1} . H_2NC is the energetically highest lying isomer in the neutral ground state. Although considerable rearrangement is required for its formation, the barriers for H-atom shift might be sufficiently low. The MP2-calculations predict an excitation energy for the $\text{H}_2\text{NC}^+ (^3\text{A}'') \leftarrow \text{H}_2\text{NC} (^2\text{A}'')$ transition of 10.69 eV, while B3LYP, CBS-QB3, and G4 yield values of 10.99 eV, 10.87 eV, and 10.82 eV, respectively. As the computations predict an enlargement of the HNH-bonding angle and a contraction of the CN-bonding distance during ionization for H_2NC , the spectral structure can be explained with the excitation of the corresponding vibrations in the cation. A FC simulation leads to reasonable assignment of this part of the TPE-spectrum to H_2NC . However, the onset of 11.21 eV seen in the spectrum deviates somewhat from the calculated values. Since the bands are of low intensity and rather broad, an accurate assignment is difficult for this transition and the onset might again be off by one vibrational quantum in the N–C stretching mode ν_3^+ .

A figure showing a simulation of the complete spectrum, i.e., the sum of all contributions, is given in trace (e) of Figure 3. The excitation energies derived in the present work are summarized in Table I. Although some of the excitation energies are tentative, the individual isomers can be distinguished in the iPEPICO spectra. Note that this is not easily achieved in conventional photoelectron or photoion yield spectra of H_2CN .^{24,54}

C. Methanimine

Another nitrogen-containing intermediate generated in the pyrolysis of methylhydrazine is the closed-shell molecule methanimine, H_2CNH . For the mass-selected threshold photoelectron spectrum, four scans from 9.8 to 11.0 eV and one scan from 10.0 to 11.2 eV were recorded with a step size of 5 meV and an average of 60 s per data point. The best intensity of the $m/z = 29$ signal was achieved at relatively high pyrolysis temperatures. The resulting mass-selected TPE-spectrum is shown in Figure 5.

The spectrum features a pronounced vibrational progression with a weak onset below 10 eV and a band maximum at 10.72 eV. The intensity of the various peaks separated each by roughly 550 cm^{-1} is increasing with the photon energy, indicating a large geometry change upon ionization. Above 10.80 eV, the spectrum becomes less structured and the signal

FIG. 5. Mass-selected threshold photoelectron spectrum of $m/z = 29$ (black line) and Franck-Condon simulation blue sticks; convolution with Gaussian function (fwhm = 25 meV): red bold line.

drops suddenly at a photon energy of 11.13 eV, possibly due to dissociative photoionization. Our B3LYP/6-311++G** computations indicate that the C–N–H bonding angle increases by about 40° from 111° to 152° upon ionization,³⁹ so significant activity in the HNC-bending mode ν_1^+ can be expected. Due to the low photoelectron count rate in the onset region, the IE_{ad} of methanimine can only be determined in a Franck-Condon simulation. However, methanimine possesses a double minimum potential energy curve with respect to the C–N–H bonding angle. While the barrier is 1.18 eV in the neutral ground state, a significant decrease can be expected for the cation and the harmonic approximation is expected to break down for low-lying vibrational states of the cation. In fact, CCSD(T)/aug-cc-pVTZ computations provide a barrier height of 50 meV (4.8 kJ/mol) for the inversion on the cationic potential energy surface, i.e., on the order of vibrational energy. We therefore calculated the eigenenergies of the low-lying vibrational states, solving the time-dependent Schrödinger equation by imaginary time propagation.⁵⁵ Figure 6 shows the potential energy curve and the energetic positions of the five lowest lying vibrational states. As visible, the vibrational spacing of the first states is highly irregular and deviates strongly from the harmonic value of 577 cm^{-1} computed by DFT. In particular, the $\nu_1^+ = 0$ and $\nu_1^+ = 1$ levels are close together. While the vibrational ground state is still below the barrier for isomerization, the $\nu_1^+ = 1$ is already above the barrier.

A simulation of the spectrum (Figure 5) and a determination of the ionization energy are thus not possible without taking accurate vibrational energies explicitly into account. The FC simulations (Figure 5) were carried out with the program ezSpectrum, computing the FC factors within a harmonic approximation.⁴¹ The simulation is based on DFT geometries and vibrational frequencies, which are again listed in the supplementary material.³⁹ To account for the inverse anharmonicity, we assigned one band to the transition into the $\nu_1^+ = 3$ state and tried to match the position of the first three bands (transitions to $\nu_1^+ = 0, 1$, and 2 of the H–N–C-

FIG. 6. Potential energy curve of cationic methanimine along the HNC-bonding angle, depicting the vibrational states of the HNC-bending mode ν_1^+ .

bending mode ν_1^+) to the energies shown in Figure 6. This procedure was carried out for two different assignments of $\nu_1^+ = 3$. For transitions into higher ν_1^+ states ($\nu_1^+ \geq 4$), we assumed harmonic behavior. As visible, the threshold region in Figure 5 is described rather well, but the transitions into $\nu_1^+ = 0$ and $\nu_1^+ = 1$ are not distinguishable in the spectrum. Without the explicit computation of the vibrational eigenstates, a reliable assignment of the IE is therefore not possible. In addition to the HNC-bending mode ν_1^+ , the cationic in plane-rocking mode ν_3^+ with a computed wavenumber of 983 cm^{-1} is active and appears with several overtones. As a consequence, several 1^n3^m combination bands appear in the spectrum too. From the FC simulation, an IE_{ad} of 9.99 eV is determined. The small signal below this energy is assigned to hot and sequence band transition. For comparison, the quantum chemical calculations performed on the CBS-QB3 level yielded an ionization energy of 9.93 eV and are therefore in very good agreement with the experimentally derived ionization energy. The earlier experimental value of 9.97 eV obtained from a conventional photoelectron spectrum was based on the onset of the electron signal and did not include an analysis of the vibrational structure.²⁶ Although the values are rather close, the uncertainty of the IE is significantly reduced by assigning individual vibrational bands as performed in this work.

As Figure 5 shows, our approach describes the experimental spectrum well up to around 10.5 eV, i.e., $\nu_1^+ = 9$. At higher energies, the simulation starts to deviate significantly from the experiment. This effect can often be observed for Franck-Condon simulations containing transitions to high quantum states, because the quality of the calculated wave functions for highly excited vibrational states is lower and the harmonic approximation becomes worse. Therefore, the computed Franck-Condon-factors deviate from the experiment for high lying ν_1^+ -states. Note also that the simulation is based on the *ab initio* geometries and no fit was attempted.

IV. SUMMARY AND CONCLUSION

We investigated the photoionization of several nitrogen-containing intermediates of the composition H_2CN and

H_2CNH generated by flash pyrolysis of methylhydrazine. Excitation energies into the triplet cations of all H_2CN isomers were determined by mass-selected threshold photoelectron spectroscopy. As the precursor's mass signal is very low with active pyrolysis, contributions from dissociative photoionization were ignored. The signal in the mass spectrum at $m/z = 28$ was assigned to four isomers, H_2CN , *cis*- HCNH , *trans*- HCNH , and H_2NC that are formed in the pyrolysis by efficient bimolecular reactions. The only minimum on the singlet potential energy surface of the cation corresponds to the linear isomer HCNH^+ , which was not observed in our experiment due to small Franck-Condon factors for the transition. The TPE-spectrum is dominated by one single peak at 10.43 eV and an intense progression at 12.32 eV. The latter is assigned to the transition of C_{2v} -symmetric H_2CN to the $a^+{}^3\text{A}_2$ triplet state of H_2CN^+ . Quantum chemical calculations indicate a significant change in geometry during ionization, which explains the observed progression in the CN-stretching mode ν_3^+ . The single peak at 10.43 eV is assigned to a transition to C_{2v} -symmetric H_2CN^+ , which corresponds to a first order saddle point on the singlet potential energy surface. The corresponding chemical reaction is presumably an isomerization of linear HCNH^+ that leads to an exchange of hydrogen atoms. While activated complexes in the neutral have been studied before in photodetachment, our work constitutes the first observation in the cation. With the help of computations, the remaining parts of the spectrum were assigned to the other three isomers. Consequently, excitation energies of other H_2CN isomers for transitions into their triplet cations could be determined from the experiment. For H_2CN , we found an energy of 12.32 eV. For the other three isomers, we found 11.72 eV (*cis*- HCNH), 12.65 eV (*trans*- HCNH), and 11.21 eV (H_2NC). The transition to the only stable singlet cation, linear HCNH^+ cannot be observed due to negligible FC factors, therefore the interpretation of previous photoion yield spectra that reported an ionization energy of 9.4 eV for H_2CN is revised. The values for *cis*- and *trans*- HCNH and H_2NC might be uncertain to within one vibrational quantum. The computed energies are in very good agreement with the experimental values, with the exception of H_2NC . We have thus shown that the iPEPICO technique is a suitable tool to disentangle the isomeric composition of a reaction, even if four different species of the same mass are present.

In addition, the closed-shell reactive intermediate methanimine, H_2CNH ($m/z = 29$), was generated in the pyrolysis. The adiabatic ionization energy of this species was determined to be $\text{IE}_{\text{ad}} = 9.99$ eV, in good agreement with the value of 9.93 eV computed by CBS-QB3. The H–N–C bond angle increases from 111° to 152° upon ionization and the barrier of the double minimum potential decreases to 4.8 kJ mol^{-1} . Franck-Condon simulations revealed significant activity in the H–N–C bending mode ν_1^+ and the rocking mode ν_3^+ as well as in combination bands of these two modes.

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