

Research paper

Gas phase infrared spectroscopy of the $\text{H}_2\text{C}=\text{NH}_2^+$ methaniminium cation

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HIGHLIGHTS

- $\text{H}_2\text{C}=\text{NH}_2^+$ Ar ions are produced via pulsed discharge in a supersonic expansion.
- The photodissociation spectrum of $\text{H}_2\text{C}=\text{NH}_2^+$ Ar is studied at from 2100 to 4000 cm^{-1} .
- Spectra are predicted with Second Order Vibrational Perturbation Theory (VPT2).
- Two isomers corresponding to different argon attachment sites are characterized.

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ABSTRACT

The methaniminium ion ($\text{H}_2\text{C}=\text{NH}_2^+$) was produced in a pulsed electrical discharge supersonic expansion of argon saturated with ethylenediamine vapor. It was identified and mass selected in a time-of-flight spectrometer. Its infrared spectrum was measured in the region of 2100–4100 cm^{-1} by photodissociation of the argon-tagged complex with a tunable infrared OPO/OPA laser system. The observed infrared spectrum was not described well by scaled harmonic theory, but could be assigned by comparison to second order vibrational perturbation theory computations at the B2PLYP/def2-QZVPP level.

1. Introduction

Small organic cations are seen frequently as fragments from larger precursors in mass spectrometry, and their ion-molecule reactions and thermochemistry have been studied extensively [1,2]. Such ions also feature prominently in the chemistry in interstellar gas clouds, and may lead to the synthesis of more complex organics in space, possibly including biological molecules [3–8]. The spectroscopy of small organic ions has been pursued for many years, but has been limited by the harsh conditions in ion sources and the low densities produced in mass spectrometers [1,2,9]. However, recent progress has been made in producing cold ions and detecting their spectroscopy with more sensitive, mass-selected measurements [10–24]. In the present report, we employ selected-ion photodissociation spectroscopy to obtain the infrared spectrum of the methaniminium cation, $\text{H}_2\text{C}=\text{NH}_2^+$.

Methanimine was detected in the interstellar medium (ISM) in 1973 [25], and is an intermediate in the Strecker synthesis of amino acids [26]. It has been suggested as a precursor to the interstellar synthesis of glycine [27,28]. Methaniminium is the protonated form of methanimine, and would likely also be present in the ISM because of the widespread occurrence of protonation chemistry there [3–8]. This ion is seen frequently in mass spectrometry as a fragment in the ionization of

larger nitrogen-containing organics [29–35]. It is also produced as a major product in the reactions of small organic ions (e.g. CH_3^+) with ammonia [36], providing another possible route to its production in the ISM. The role of resonance stabilization of this ion has been investigated with computational studies of its electronic structure and bonding [29,33–35]. However, there is no previous spectroscopy on this simple cation.

Our group has reported new infrared spectroscopy on a number of small organic ions using the methods of mass selection and infrared laser photodissociation spectroscopy with rare gas atom “tagging” [37–47]. This work was complemented by extensive computational work, exploring the relative energies of different isomeric structures and the role of anharmonic interactions in the vibrational spectroscopy. Coexisting isomeric structures, kinetically trapped by the rapid cooling in the supersonic expansion ion sources, were detected for species such as formaldehyde cation (and its hydroxymethylene HOCH^+ isomer) [46], methanol cation (and its H_2COH_2^+ methylene oxonium isomer) [45], and cyclopropenyl C_3H_3^+ (and its H_2CCCH^+ propargyl cation structure) [41]. In these systems, the co-existing isomers, anharmonic interactions, Fermi resonances (overtone of C–H bends resonant with stretch fundamentals), and the possible isomers resulting from argon attachment sites provided unexpected complexity in spectra otherwise

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expected to be relatively simple. As shown below, methaniminium provides another fascinating example of this kind of rich vibrational structure.

2. Methods

2.1. Experimental

The $\text{H}_2\text{C}=\text{NH}_2^+$ cation was studied with ion spectroscopy methods described previously [43]. The cation was generated by a pulsed electrical discharge in a pulsed supersonic expansion of argon seeded with ethylenediamine vapor. The argon-tagged methaniminium ion was then mass selected in a reflectron time-of-flight mass spectrometer. Its infrared (IR) spectrum was measured in the region of $2100\text{--}4100\text{ cm}^{-1}$ by photodissociation with a Nd:YAG-pumped infrared OPO/OPA laser system (LaserVision). The obtained IR spectrum corresponds to the photofragmentation yield (loss of argon) with respect to the wave-number of the laser.

2.2. Computational

Geometry optimizations of the ammonium methylene and methaniminium ions were carried out with the modern B2PLYP double-hybrid density functional in combination with the def2-QZVPP quadruple- ζ Karlsruhe basis set. Argon tag isomers of $\text{H}_2\text{C}=\text{NH}_2^+$ were explored and optimized at the same level of theory. To assign the experimental IR transitions, we computed harmonic spectra and scaled the frequencies with a factor of 0.96 and we also computed anharmonic spectra with second order vibrational perturbation theory (VPT2) as implemented in the Gaussian09 electronic structure code [48].

3. Results and discussion

In the course of a study of the protonated ethylenediamine ion and its clusters [49], we employed a pulsed discharge/supersonic expansion containing ethylenediamine vapor. As shown in the mass spectrum in Fig. 1, this discharge produced significant amounts of the $\text{H}_2\text{C}=\text{NH}_2^+$ cation, presumably resulting from the ionization and fragmentation of ethylenediamine. Also shown in the mass spectrum is the argon-complexed ion, which we mass select and study in this experiment.

Computational studies on the $[\text{CNH}_4]^+$ ion identified the most stable $\text{H}_2\text{C}=\text{NH}_2^+$ methaniminium, which has a planar structure, and the much less stable H_3NCH^+ ammonium carbene ($+93.4\text{ kcal mol}^{-1}$) structures for this ion composition, consistent with previous computational work [29,31,33–35]. $\text{H}_2\text{C}=\text{NH}_2^+$ is isoelectronic to ethylene, and the ground state therefore is a closed-shell singlet with C_{2v}

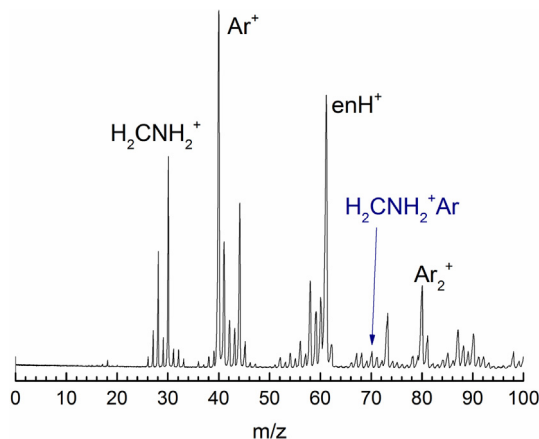


Fig. 1. The mass spectrum of cations produced by the pulsed-discharge supersonic expansion source for ethylenediamine vapor in argon.

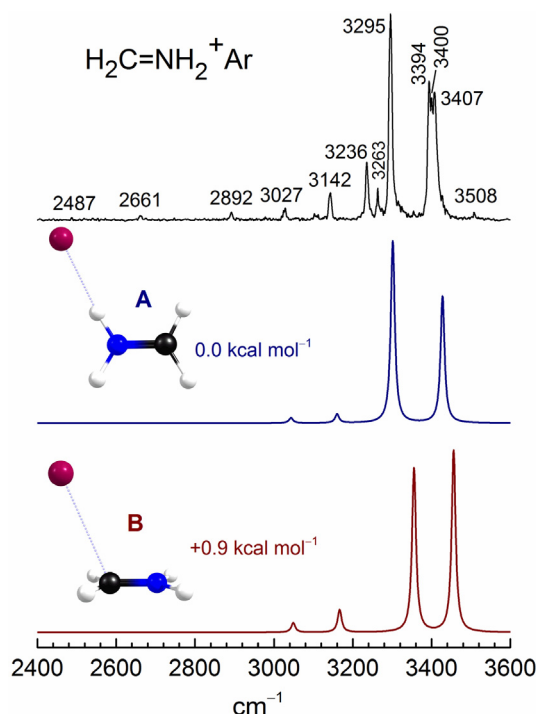


Fig. 2. Comparison of the experimentally observed infrared spectrum of argon-tagged methaniminium cation with harmonic computations for isomers A and B of the methaniminium ion at the B2PLYP/def2-QZVPP level.

structure. Examination of the vibrational structure for the ammonium carbene ion showed three strong bands with roughly equal intensities in the $3100\text{--}3300\text{ cm}^{-1}$ region, with no resemblance to the observed spectrum. We therefore eliminated this ion structure from any further consideration. Computational studies also identified two isomers of $\text{H}_2\text{C}=\text{NH}_2^+\text{Ar}$ differing only in the binding site of the argon tag atom. In the most stable isomer A, the argon attaches in an $\text{NH}\cdots\text{Ar}$ configuration in the plane of the molecule, whereas isomer B has the argon in a site above the plane of the molecule and over the carbon atom lying only 0.9 kcal mol^{-1} higher in energy. The argon binding energies for these two isomers are 670 and 340 cm^{-1} , respectively.

Fig. 2 shows the spectrum measured for the $\text{H}_2\text{C}=\text{NH}_2^+\text{Ar}$ ion, where it is compared to the spectra predicted for these two argon-isomers using harmonic theory and scaling for the frequencies. The experiment has a most-intense band at 3295 cm^{-1} and a closely-spaced triplet with somewhat lower intensity at 3394 , 3400 and 3407 cm^{-1} . Weaker bands are also seen at 2487 , 2661 , 2892 , 3027 , 3142 , 3236 , 3263 and 3508 cm^{-1} . The predicted spectra for both isomers have four bands each corresponding to the symmetric and antisymmetric stretches of the CH_2 and NH_2 groups. As expected, the N-H stretches lie at higher frequency and are more intense than the C-H stretches. Although the N-H stretches for both isomers fall in the approximate region of the more intense experimental bands, and the C-H stretches fall in the region of some of the weaker bands, neither of the predicted spectra for the two isomers provide a compelling match with the experimental spectrum. In particular, no bands are predicted for either isomer in the lower frequency range, and no bands are predicted near the 3236 and 3263 cm^{-1} experimental features.

To better understand the spectrum, we performed VPT2 computations of the relevant isomers at the B2PLYP/def2-QZVPP level of theory. The comparison of the computed anharmonic spectra for the two argon-tag isomers to the experimental spectrum is presented in Fig. 3. The vibrational band positions from experiment and theory are given in Table 1. As shown in the figure, it is again true that neither isomer alone matches all the bands in the experimental spectrum. However, the two isomers taken together do provide a reasonable explanation for

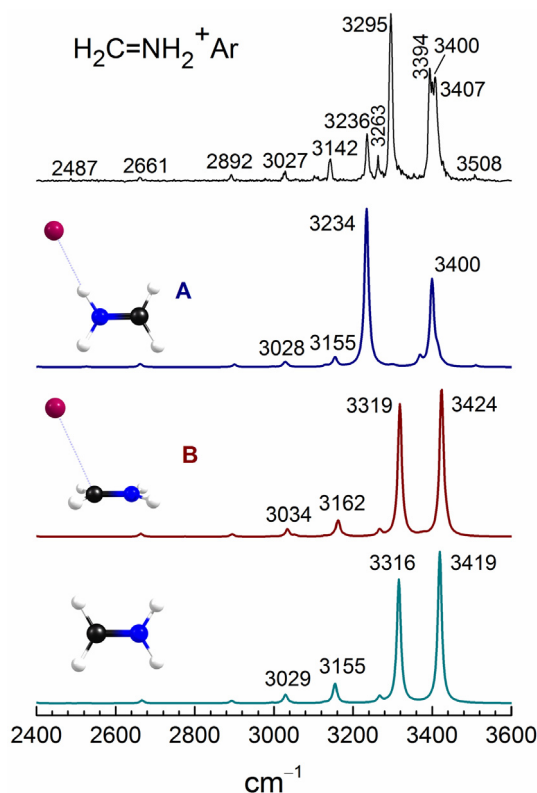


Fig. 3. Comparison of the experimentally observed infrared spectrum of argon tagged methaniminium cation with VPT2 anharmonic computations for the argon-tag isomers A and B and the tag-free structure of the methaniminium ion at the B2PLYP/def2-QZVPP level.

Table 1

Experimentally observed infrared bands (cm^{-1}) compared to the computed anharmonic frequencies and intensities (km mol^{-1}) for the argon-tag isomers A and B of the methaniminium ion at the B2PLYP/def2-QZVPP level of theory.

Obs.	Isomer	ν (i)	Description
3508	A	3511 (3)	asym. $\nu_{\text{NH}_2} + \delta_{\text{NH}-\text{Ar}}$ (o.o.p.)
3407	B	3425 (161)	asym. ν_{NH_2}
3400	A	3415 (23)	$\nu_{\text{C}=\text{N}} + \delta_{\text{NH}_2, \text{CH}_2}$ (i.p. and o.o.p.) [*]
3394	A	3400 (174)	asym. ν_{NH_2}
3295	B	3320 (144)	sym. ν_{NH_2}
3263	B	3268 (7)	$\nu_{\text{C}=\text{N}}$, sym. $\delta_{\text{NH}_2, \text{CH}_2} + \nu_{\text{C}=\text{N}}$, asym. $\delta_{\text{NH}_2, \text{CH}_2}$
3236	A	3235(320)	sym. ν_{NH_2}
3142	A, B	3156 (19), 3163 (17)	asym. ν_{CH_2}
3107	A	3132 (3)	$\nu_{\text{C}=\text{N}} + \text{asym. } \delta_{\text{NH}_2, \text{CH}_2}$ (i.p. and o.o.p.) [*]
3027	A, B	3028 (8), 3035 (8)	sym. ν_{CH_2}
2892	A, B	2902 (6), 2896 (3)	$\nu_{\text{C}=\text{N}}$, asym. $\delta_{\text{NH}_2, \text{CH}_2} + \text{asym. } \delta_{\text{HNC}}$, asym. δ_{HCN}
2661	A	2664 (7)	$\nu_{\text{C}=\text{N}}$, sym. $\delta_{\text{NH}_2, \text{CH}_2} + \text{sym. } \delta_{\text{HNC}}$, sym. δ_{HCN}
2487	A	2527 (1)	$\nu_{\text{C}=\text{N}}$, asym. $\delta_{\text{NH}_2, \text{CH}_2} + \text{sym. } \delta_{\text{HNC}}$, sym. δ_{HCN}

* Bands with mixed vibrational character.

most of the experimental bands. The two strong N–H stretches for isomer A both shift to the red when anharmonicity is included, and their relative intensities are reversed compared to the harmonic theory. A red shift was already observed in these vibrations compared to those predicted for the tag-free molecule, arising from the attachment of the argon. Apparently the harmonic theory underestimates this shift. In the anharmonic theory, the two most intense bands of isomer A are now in good alignment with the features at 3236 and 3394 cm^{-1} in the

experimental spectrum. The N–H stretches for isomer B also shift to the red when anharmonicity is included. These two bands line up well with the experimental features at 3295 and 3407 cm^{-1} . The C–H stretches for both isomers lie at roughly the same positions, which makes sense because the argon attachment does not involve these hydrogens. Likewise, there is also no strong anharmonic effect on these frequencies. They explain the experimental bands at 3027 and 3142 cm^{-1} . The very weak features at 2487, 2661 and 2892 cm^{-1} are also matched by weak bands in the spectra predicted for both isomers.

The lower theory trace in Fig. 3 is the spectrum predicted for the methaniminium ion without any argon tag. As shown, the spectrum is essentially the same as that predicted for isomer B. Each of the bands in the tag-free spectrum is actually 3–7 cm^{-1} to lower frequency compared to the bands predicted for isomer B. Considering that the experimental bands for isomer B are lower in frequency than those predicted, the bands for the tag-free ion would also likely be found at slightly frequencies than those predicted here.

With the alignment of these bands between experiment and theory, it is then possible to assign the vibrations in the experiment, as summarized in Table 1. The most intense bands in the higher frequency region are from the symmetric and antisymmetric stretches of the NH_2 groups on the two isomers, with the antisymmetric vibration having the higher frequency for each pair. The bands at 3295/3407 cm^{-1} are those for isomer B and the bands at 3236/3394 cm^{-1} are those for isomer A. The antisymmetric NH_2 stretches seen here at 3394 and 3407 cm^{-1} can be compared to that of the neutral methanimine at about 3372 cm^{-1} [50]. The methaniminium cation apparently has a higher frequency than its corresponding neutral, but the neutral was studied in an argon matrix, perhaps explaining some of the difference. The bands at 3027 and 3142 cm^{-1} are the overlapping symmetric and asymmetric stretches of the CH_2 group on the A and B isomers. These frequencies are much lower than the corresponding frequencies of ethylene at 3185 and 3217 cm^{-1} , although the motions on ethylene involve all four hydrogens and not just a single CH_2 group. The weak bands at 2487, 2661 and 2892 cm^{-1} not found in the harmonic theory are all combinations involving the C=N stretch with HCN or HNC bending motions. Similar combinations of the C=N stretch with both in-phase and out-of-phase CH_2 and NH_2 bends can tentatively be assigned to the weak band at 3400 cm^{-1} . The 3508 band is a combination of the NH_2 asymmetric stretch and an out-of-plane argon bend for isomer A.

The anharmonic theory described here is therefore quite successful in explaining this spectrum. It accounts for all of the major features, predicting frequencies within a few cm^{-1} of their observed values. Surprisingly, the experiment can only be assigned if we conclude that both of the two argon isomers A and B are present with roughly equal abundances. It is somewhat surprising the two isomers would be frozen in and not interconvert, when they apparently lie so close in energy. However, we found similar argon isomers in the C–H stretching bands of the C_3H_3^+ spectrum [44,46]. As seen in previous systems, when the argon tag atom binds to a hydrogen, that stretching vibration is shifted significantly to lower frequency. This explains why the NH_2 vibrations of isomer A are at lower frequencies than those of isomer B. The CH_2 vibrations do not involve the tag atoms and are at essentially the same frequencies for both isomers. Isomer B has the argon attached above the plane of the molecule where it does not interfere with the CH_2 or NH_2 stretch vibrations. As shown in Fig. 3, its predicted frequencies are within 3–7 cm^{-1} of the predictions for the tag-free ion, and therefore its spectrum is essentially that of the isolated cation. The strong NH_2 bands (e.g., the 3295 and 3407 cm^{-1} features) would be recommended targets for future absorption experiments at higher resolution or for possible interstellar identification.

4. Conclusion and outlook

The $\text{H}_2\text{C}=\text{NH}_2^+$ methaniminium cation has been produced in a pulsed discharge of ethylenediamine in argon. Its infrared spectrum was

measured with selected-ion infrared spectroscopy in the 2100–3600 cm^{-1} region. The spectrum exhibits poor agreement with that predicted by harmonic computations, but much better agreement with that predicted by anharmonic theory. The spectrum is consistent with a planar ion structure having two argon-attachment isomers in roughly equal abundance. The isomer with argon attached above the plane of the molecule has a spectrum most like that of the tag-free cation. Because this ion is produced in the fragmentation of many nitrogen-containing organics, it should be possible to produce it in high enough abundance for high resolution direct absorption spectroscopy measurements in other labs, thus perhaps enabling its future detection in space.

Conflict of interest

The authors declared that there is no conflict of interest.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cplett.2019.04.032>.

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