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ARTICLE

Structures, Energetics, and Infrared Spectra of the Cationic Monomethylamine-Water Clusters†

Shu-kang Jiang[a,b,c,d‡], Dong Yang[b,d‡], Xiang-tao Kong[b‡], Chong Wang[b,d], Xiang-yu Zang[b,d], Hui-jun Zheng[b,d], Gang Li[b], Hua Xie[b], Wei-qing Zhang[b], Xue-ming Yang[a,b,c], Ling Jiang[b*]

a. Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China
b. State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.
c. School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China
d. University of Chinese Academy of Sciences, Beijing 100049, China

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The structures, energetics, and infrared (IR) spectra of the cationic monomethylamine-water clusters, $[(CH_3NH_2)(H_2O)_n]^+$ (n=1−5), have been studied using quantum chemical calculations at the MP2/6-311+G(2d,p) level. The results reveal that the formation of proton-transferred $CH_2NH_3{}^+$ ion core structure is preferred via the intramolecular proton transfer from the methyl group to the nitrogen atom and the water molecules act as the acceptor for the O$\cdots$HN hydrogen bonds with the positively charged $NH_3{}^+$ moiety of $CH_2NH_3{}^+$, whose motif is retained in the larger clusters. The $CH_3NH_2{}^+$ ion core structure is predicted to be less energetically favorable. Vibrational frequencies of CH stretches, hydrogen-bonded and free NH stretches, and hydrogen-bonded OH stretches in the calculated IR spectra of the $CH_2NH_3{}^+$ and $CH_3NH_2{}^+$ type structures are different from each other, which would afford the sensitive probes for fundamental understanding of hydrogen bonding networks generated from the radiation-induced chemical processes in the $[(CH_3NH_2)(H_2O)_n]^+$ complexes.

Key words: Monomethylamine, Water, Structure, Energetics, Infrared spectroscopy

I. INTRODUCTION

The strong hydrogen bonding networks in the water-containing complexes play important roles in the nucleation and growth of atmospheric nanoparticles [1]. The ubiquitous presence of methylamines (monomethylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA)) has been found in the atmosphere [2]. Because of the substitution by one or more organic functional groups, methylamines have stronger basicity than ammonia and often participate in the formation and transformation of atmospheric aerosols [2−4]. For instance, the MMA has been found to be about 25−100 times more effective in enhancing sulfuric acid-water nucleation than ammonia [5]. Microwave spectroscopy of the TMA-water complex revealed the formation of a strong HOH−N$(CH_3)_3$ hydrogen bond, in which the water molecule internally rotates around the symmetry axis of TMA [6]. Theoretical studies of the interaction between the methylamine molecules and one or two water molecules indicated that the water molecules act as the donor for the formation of the OH$\cdots$N hydrogen bonds [7]. A closed ring with four hydrogen-bonded H_2O molecules was observed in the $(TMA)_2(H_2O)_4$ clusters [8].

The study on the hydrogen bonding networks in the cationic complexes generated from the radiation-induced chemical processes is of fundamental importance in many fields, such as interstellar and atmospheric chemistry, and nuclear reactors [9]. Gas-phase cluster studies provide detailed structural, energetic, and spectroscopic information that is difficult to extract from the condense-phase measurement [10−14]. For example, the infrared photodissociation (IRPD) spectroscopy of the $(H_2O)_n{}^+$ clusters has demonstrated that the formation of H_3O^+ ion core is preferred with water and the OH radical is separated from H_3O^+ by at least one water molecule in the $n\geq5$ clusters [15−18]. IRPD spectroscopic and theoretical studies of the cationic $(DMA)_n{}^+$ clusters have revealed that the proton-transferred $(CH_3)_2NH_2{}^+$ ion core is formed via the intermolecular proton transfer from the NH group to the nitrogen atom and the $[(CH_3)_2N]$ radical is separated from the $(CH_3)_2NH_2{}^+$ ion core by one DMA molecule at n=4−6 and by two or more DMA molecules in the larger clusters [19]. For the cationic $(TMA)_n{}^+$ clusters, the formation of the charge-shared (hemibon-

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‡ These authors contributed equally to this work.

* Author to whom correspondence should be addressed. E-mail: ljiang@dicp.ac.cn

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ded) N$\cdots$N type $(TMA)_2{}^+$ ion core was identified [20].

The MMA molecule has one polar NH_2 group and one nonpolar CH_3 group, which affords a model system for studying the hydrogen bonding networks in the radiation-induced chemical processes and the mechanism of proton transfer. So far, much less efforts have been made for the study of the monomethylamine-water complexes, $[(CH_3NH_2)(H_2O)_n]^+$. Herein, we report a theoretical study of the structures, energetics, and infrared spectra of $[(CH_3NH_2)(H_2O)_n]^+$ via a cluster model. It has been found that the formation of proton-transferred $CH_2NH_3{}^+$ ion core structure is preferred via the intramolecular proton transfer from the methyl group to the nitrogen atom and the water molecules act as the acceptor for the O$\cdots$HN hydrogen bonds with the positively charged $NH_3{}^+$ moiety of the $CH_2NH_3{}^+$ ion core. This feature is different from the neutral CH_3NH_2-H_2O clusters [6–8]. The present findings suggest the general trends in the motif of hydrogen bonding networks of the monomethylamine-water complexes.

II. THEORETICAL METHODS

All calculations were carried out using the MP2 method with a basis set of 6-311+G(2d,p) implemented in the Gaussian 09 package [21]. Tight convergence of the optimization and the self-consistent field procedures was imposed, and an ultrafine grid was used. Relative energies, dissociation energies, and energy barriers included the zero-point vibrational energies. Harmonic vibrational frequencies were calculated with analytical second derivatives of energy. A scaled factor of 0.9566 was used for harmonic vibrational frequencies [22]. The resulting stick spectra were convoluted by a Gaussian line shape function with a full width at half-maximum line width of 6 cm^{-1}.

III. RESULTS AND DISCUSSION

A. Optimized structures

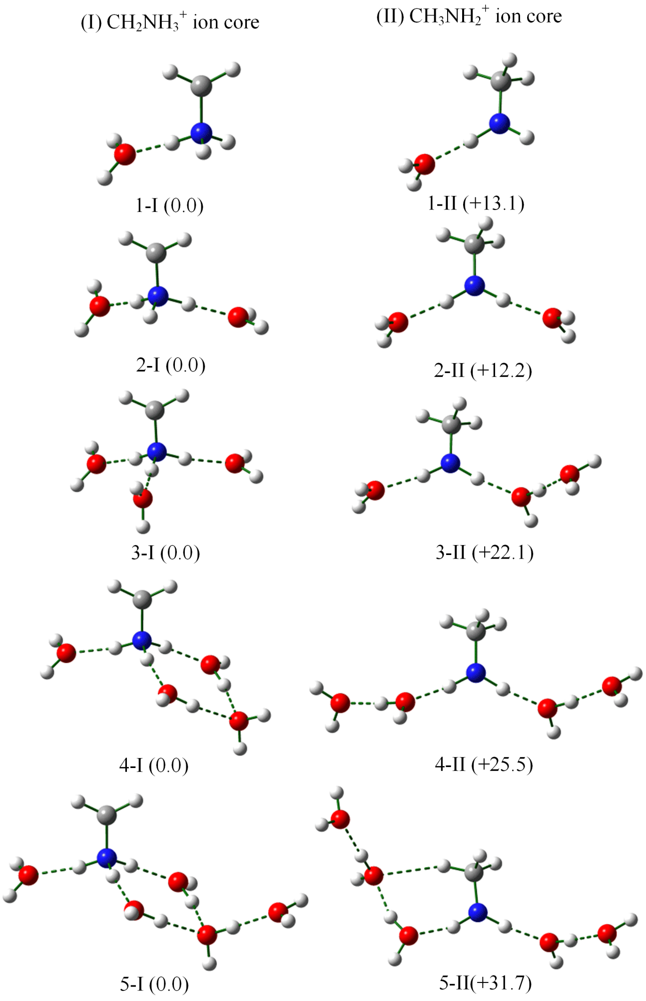

FIG. 1 Optimized structures of $[(CH_3NH_2)(H_2O)_n]^+$ (n=1−5) (C, gray; H, light gray; N, blue; O, red). Relative energies are given in kJ/mol.

The optimized structures of the $[(CH_3NH_2)(H_2O)_n]^+$ (n=1−5) clusters are shown in FIG. 1. In the lowest-energy isomer of the n=1 cluster (labeled 1-I), the water molecule acts as an acceptor to form an O$\cdots$HN hydrogen bond with the NH_3 moiety of $CH_2NH_3{}^+$, in which the $CH_2NH_3{}^+$ ion core is formed via the intramolecular proton transfer from the methyl group to the nitrogen atom. In the 1-I isomer, the Mulliken charge on the C atom, H_2O, CH_2, and NH_3 moiety are −0.12, 0.01, 0.25, and 0.74, respectively, indicating that the NH_3 moiety is the most positively charged. The bond distance of C−N and O$\cdots$HN hydrogen bonds are 1.46 and 1.66 Å, respectively. Isomer 1-II consists of a $CH_3NH_2{}^+$ ion core, in which the CH_3NH_2 and water molecules are held together by an O$\cdots$HN hydrogen bond. Isomer 1-II lies 13.1 kJ/mol higher in energy than isomer 1-I. In the 1-II isomer, the Mulliken charge on the C atom, H_2O, CH_3, and NH_2 moiety is −0.26, 0.01, 0.32, and 0.67, respectively. The bond distance of C−N and O$\cdots$HN hydrogen bonds in isomer 1-II is 1.43 and 1.62 Å, respectively.

In the lowest-energy isomer for $[(CH_3NH_2)(H_2O)_2]^+$, labeled 2-I in FIG. 1, each water molecule forms an O$\cdots$HN hydrogen bond with the proton-transferred $CH_2NH_3{}^+$ ion core. In the isomer 2-II (+12.2 kJ/mol), the two water molecules fill the $NH_2{}^+$ moiety of the $CH_3NH_2{}^+$ ion core. In the lowest-energy structure for $[(CH_3NH_2)(H_2O)_3]^+$ (3-I), the three water molecules fill the $NH_3{}^+$ moiety of the $CH_2NH_3{}^+$ ion core. In the isomer 3-II (+22.1 kJ/mol), the third water molecule does not directly bond to the $CH_3NH_2{}^+$ ion core but rather to one other water molecule, thus forming a water-water hydrogen bond.

In the lowest-energy structure for $[(CH_3NH_2)(H_2O)_4]^+$ (4-I), the fourth water molecule bonds to the

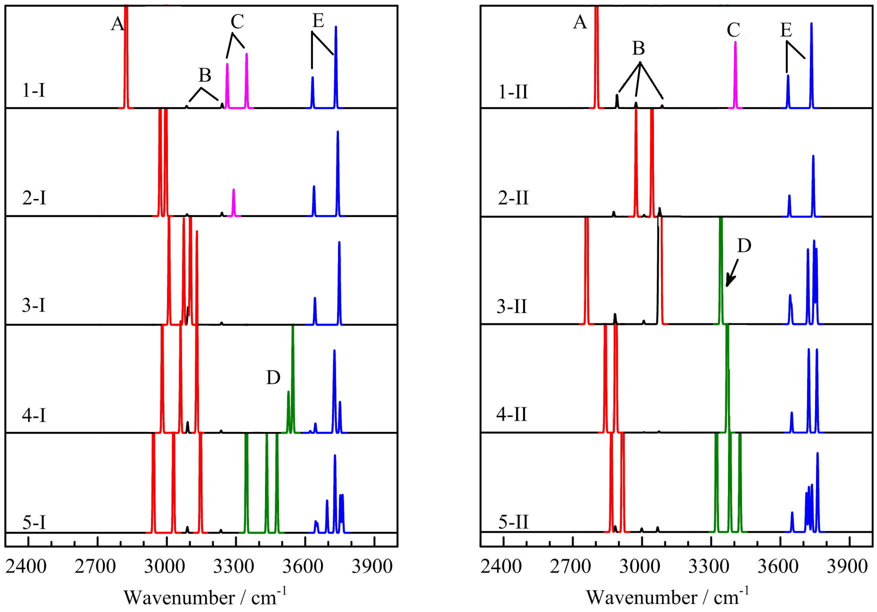

FIG. 2 Simulated IR spectra of the two lowest-lying isomers of $[(CH_3NH_2)(H_2O)_n]^+$ (n=1−5). The assignment is: A, H-bonded NH stretch (red); B, CH stretch (black); C, free NH stretch (magenta); D, H-bonded OH stretch (green); E, free OH stretch (blue).

two other water molecules, forming a four-membered hydrogen bonding network with the $CH_2NH_3^+$ ion core. In the isomer 4-II (+25.5 kJ/mol), the position of the fourth water molecule is symmetry-equivalent to that of the third water molecule. In the 5-I structure for $[(CH_3NH_2)(H_2O)_5]^+$, the fifth water molecule extends the water-water hydrogen bonding network with the four-membered ring and forms a second solvation layer. The isomer 5-II (+31.7 kJ/mol) consists of a four-membered hydrogen bonding network, in which the oxygen atoms of the two water molecules act as the hydrogen bond donors to the hydrogen atoms of the NH_2 and CH_3 groups of the $CH_3NH_2^+$ ion core.

B. IR spectra

FIG. 2 shows the calculated IR spectra of the $[(CH_3NH_2)(H_2O)_n]^+$ (n=1−5) clusters in the spectra range of 2400−3900 cm^{-1}. Vibrational frequencies of isomers n-I and n-II and band assignments are listed in Table I.

The calculated IR spectrum of isomer 1-I shows four main absorption features labeled A, B, C, and E in FIG. 2. The peak at 2824 cm^{-1} (labeled A, highlighted in red in FIG. 2) is due to the hydrogen-bonded NH stretch of the $CH_2NH_3^+$ ion core (Table I). The peaks at 3086 and 3240 cm^{-1} (labeled B, shown in black in FIG. 2) are attributed to the CH symmetric and antisymmetric stretches of the CH_2 group of the $CH_2NH_3^+$ ion core. The peaks at 3262 and 3346 cm^{-1} (labeled C, highlighted in magenta in FIG. 2) are attributed to the free NH symmetric and antisymmetric stretches of the NH_3 group in the $CH_2NH_3^+$ ion core. The peaks at 3632 and 3733 cm^{-1} (labeled E, highlighted in blue in FIG. 2) are attributed to the free OH symmetric and antisymmetric stretches of the water molecule. In the calculated IR spectrum of isomer 1-II, band A is predicted at 2802 cm^{-1}, showing a redshift of 22 cm^{-1} as compared to isomer 1-I; band B shows a triplet splitting at 2892, 2974, and 3087 cm^{-1} for the CH symmetric and antisymmetric stretches of the CH_3 group in the $CH_3NH_2^+$ ion core; band C appears as a single peak at 3405 cm^{-1} for the free NH stretch of the $CH_3NH_2^+$ ion core; band E is calculated at 3633 and 3735 cm^{-1}.

In the calculated IR spectrum of isomer 2-I, band A shows a doublet splitting at 2971 and 2996 cm^{-1} for the hydrogen-bonded NH stretches of the $CH_2NH_3^+$ ion core; the CH symmetric and antisymmetric stretches of the CH_2 group are calculated at 3088 and 3239 cm^{-1}, respectively, which are very similar to the positions in isomer 1-I (3086 and 3240 cm^{-1}); one free NH stretch appears at 3290 cm^{-1}; the two free OH symmetric and antisymmetric stretches of the water molecules are predicted at 3638 and 3742 cm^{-1}, respectively. In the calculated IR spectrum of isomer 2-II, the positions of bands A and E are similar to those of isomer 2-I; the free NH stretch disappears because of the full solvation of the NH_2^+ moiety by the water molecules, showing obvious difference from the calculated IR spectrum of isomer 2-I.

In the calculated IR spectrum of isomer 3-I, band A shows a triplet splitting at 3010, 3074, and 3102 cm^{-1} for the hydrogen-bonded NH stretches of the $CH_2NH_3^+$ ion core; the CH symmetric and anti-

TABLE I Calculated scaled harmonic frequencies (in cm^{-1}) at MP2/6-311+G(2d,p) level and band assignments for $[(CH_3NH_2)(H_2O)_n]^+$ (n=1−5) clusters.

Isomer	Band A	Band B	Band C	Band D	Band E
1-I	2824	3086, 3240	3262, 3346		3632, 3733
1-II	2802	2892, 2974, 3087	3405		3633, 3735
2-I	2971, 2996	3088, 3239	3290		3638, 3742
2-II	2974, 3043	2877, 3009, 3077			3639, 3742
3-I	3010, 3074, 3102	3092, 3237			3643, 3748
3-II	2760, 3081	2883, 3008, 3072		3342	3642, 3648, 3719, 3746, 3756
4-I	2980, 3060, 3130	3090, 3235		3528, 3546	3622, 3644, 3723, 3727, 3730, 3751
4-II	2841, 2887	3009, 3073		3370	3649, 3723, 3758
5-I	2942, 3029, 3146	3089, 3234		3345, 3433, 3478	3645, 3653, 3695, 3729, 3731, 3752, 3762
5-II	2867, 2916	2884, 2999, 3068		3323, 3381, 3425	3650, 3652, 3713, 3724, 3737, 3760, 3762
Assign.	Hydrogen-bonded NH stretch	CH stretch	Free NH stretch	Hydrogen-bonded OH stretch	Free OH stretch

symmetric stretches of the CH_2 group are calculated at 3092 and 3237 cm^{-1}, respectively; the free NH stretch disappears due to the full solvation of the $NH_3{}^+$ moiety by the water molecules; the two free OH symmetric and antisymmetric stretches of the water molecules are predicted at 3643 and 3748 cm^{-1}, respectively. In the calculated IR spectrum of isomer 3-II, band A appears at 2760 and 3081 cm^{-1}; the positions of bands B and E are similar to those of isomer 2-II; a new feature is observed at 3342 cm^{-1} (labeled D, highlighted in green in FIG. 2), which is attributed to the hydrogen-bonded OH stretch of the water molecule.

As compared to the calculated IR spectrum of isomer 3-I, the hydrogen-bonded OH stretching vibraitonal mode starts to appear in isomer 4-I (band D, 3528 and 3546 cm^{-1}) because of the formation of water-water hydrogen bond. The calculated IR spectrum of isomer 4-II is very similar to that of isomer 3-II, except that the separation of the two peaks of band A (46 cm^{-1}) is much smaller than that in isomer 3-II (321 cm^{-1}). As shown in FIG. 1, the number of the hydrogen-bonded O−H bonds in 5-I and 5-II is three, resulting in three vibrational peaks for band D (FIG. 2).

C. General trend

Two types of structure are obtained for each cationic monomethylamine-water cluster (FIG. 1). The first type is the proton-transferred $CH_2NH_3{}^+$ ion core type structure (labeled n-I), which is the most stable motif in the $[(CH_3NH_2)(H_2O)_n]^+$ clusters studied here. The next energetically higher motif consists of the $CH_3NH_2{}^+$ ion core type structure (labeled n-II). The isomerization barrier from 1-II to 1-I and from 2-II to 2-I is calculated to be 154.1 and 155.8 kJ/mol at the MP2/6-311+G(2d,p) level, respectively. These results suggest the formation of proton-transferred $CH_2NH_3{}^+$ ion core structure is preferred via the intramolecular proton transfer from the methyl group to the nitrogen atom and the water molecules act as the acceptor to form the O$\cdots$HN hydrogen bonds with the positively charged $NH_3{}^+$ moiety of $CH_2NH_3{}^+$. Note that the barrier for the isomerization from the $CH_3NH_2{}^+$ type structure to the $CH_2NH_3{}^+$ type one is not low, the $CH_3NH_2{}^+$ type structure could be kinetically trapped prior to its rearrangement to the lower energy species. High energy isomers have been observed experimentally in several cluster systems [23, 24]. In contrast, the water molecules act as the donor for the formation of OH$\cdots$N hydrogen bonds with the NH_2 group of CH_3NH_2 in the neutral CH_3NH_2-H_2O clusters [7], which is different from the hydrogen bonding network in the cationic CH_3NH_2-H_2O clusters.

The lowest dissociation energy for the loss of one water molecule for isomer n-I of $[(CH_3NH_2)(H_2O)_n]^+$ (n=1−5) is calculated to be 94.2, 66.5, 58.0, 48.5, and 44.6 kJ/mol at the MP2/6-311+G(d,p) level (Table II), respectively. While the internally cold $[(CH_3NH_2)(H_2O)_n]^+$ species is formed, the absorption of at least 3, 2, 2, 2, and 2 photons at 3000 cm^{-1} is required to overcome the dissociation limit for n=1−5 (Table II), respectively. Considering that the CH stretch, the free/hydrogen-bonded NH stretch, and the free/hydrogen-bonded OH stretch have been measured in the IRPD spectra of methylamine, ammonia, water, and protonated trimethylamine-water clusters [19, 20, 25–27], the predicted IR spectra for the $[(CH_3NH_2)(H_2O)_n]^+$ (n=1−5) clusters could be measured by the IRPD technique using optical parametric oscillator/optical parametric amplifier (OPO/OPA) table-top laser system or infrared free electron laser (IR-FEL) source.

For band A, the number of the hydrogen-bonded NH stretching vibrational peaks is three in the n-I isomers (n=3−5), whereas it is two in the n-II isomers (n=3−5)

TABLE II The lowest dissociation energies ($E_{\rm diss}$) for the loss of one water molecule for isomer n-I of $[(CH_3NH_2)(H_2O)_n]^+$ (n=1−5) and the number of IR photon N required to overcome the dissociation limit at 3000 cm^{-1}.

isomer	$E_{\rm diss}$/(kJ/mol (cm^{-1}))	N
1-I	94.2 (7877)	3
2-I	66.5 (5557)	2
3-I	58.0 (4844)	2
4-I	48.5 (4054)	2
5-I	44.6 (3732)	2

(FIG. 2 and Table I). For band B, two peaks of the CH stretches are observed in the n-I structures ($CH_2NH_3^+$ ion core type), whereas three peaks are obtained in the n-II structures ($CH_3NH_2^+$ ion core type). The number of the free NH stretching vibrational peaks (band C) is two and one for the 1-I and 1-II isomers, respectively; the 2-I isomer yields one peak for band C, whereas the 2-II isomer and the larger clusters do not show the feature of the free NH stretch. Band D firstly appears in the 3-II isomer. Band E is similar in the n-I and n-II isomers. Thus, the features of band A−D in the calculated IR spectra of the $CH_2NH_3^+$ and $CH_3NH_2^+$ type structures for $[(CH_3NH_2)(H_2O)_n]^+$ are different from each other, which would afford the sensitive probes for the structural identification by comparing the calculated IR spectra with the experimental IRPD spectra. These findings would have important implications for molecular-level understanding of the hydrogen bonding networks in the $[(CH_3NH_2)(H_2O)_n]^+$ complexes.

IV. CONCLUSION

The trends in the stepsize formation of hydrogen bonding networks in the cationic monomethylamine-water clusters, $[(CH_3NH_2)(H_2O)_n]^+$, were studied using quantum chemical calculations. The results indicate that the most stable structures of the nominal $[(CH_3NH_2)(H_2O)_n]^+$ clusters could be regarded as the proton-transferred $CH_2NH_3{}^+$-$(H_2O)_n$ motifs, which involve the intramolecular proton transfer from the methyl group to the nitrogen atom. The $CH_3NH_2^+$ ion core structures are predicted to be less energetically favorable. Calculated infrared spectra suggest that the CH stretching, hydrogen-bonded and free NH stretching, and hydrogen-bonded OH stretching vibrational modes would afford the sensitive probes for the structural identification. IR spectra for the $[(CH_3NH_2)(H_2O)_n]^+$ clusters could be measured by the infrared photodissociation spectroscopic technique and thus provide a fundamental understanding of the early stage of hydrogen bonding networks in the $[(CH_3NH_2)(H_2O)_n]^+$ clusters.

V. ACKNOWLEDGEMENTS

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[1] R. Zhang, A. Khalizov, L. Wang, M. Hu, and W. Xu, Chem. Rev. **112**, 1957 (2012).

[2] C. Qiu and R. Zhang, Phys. Chem. Chem. Phys. **15**, 5738 (2013).

[3] L. Yao, O. Garmash, F. Bianchi, J. Zheng, C. Yan, J. Kontkanen, H. Junninen, S. B. Mazon, M. Ehn, P. Paasonen, M. Sipila, M. Wang, X. Wang, S. Xiao, H. Chen, Y. Lu, B. Zhang, D. Wang, Q. Fu, F. Geng, L. Li, H. Wang, L. Qiao, X. Yang, J. Chen, V. M. Kerminen, T. Petaja, D. R. Worsnop, M. Kulmala, and L. Wang, Science **361**, 278 (2018).

[4] M. Kulmala, J. Kontkanen, H. Junninen, K. Lehtipalo, H. E. Manninen, T. Nieminen, T. Petaja, M. Sipila, S. Schobesberger, P. Rantala, A. Franchin, T. Jokinen, E. Jarvinen, M. Aijala, J. Kangasluoma, J. Hakala, P. P. Aalto, P. Paasonen, J. Mikkila, J. Vanhanen, J. Aalto, H. Hakola, U. Makkonen, T. Ruuskanen, R. L. Mauldin III, J. Duplissy, H. Vehkamaki, J. Back, A. Kortelainen, I. Riipinen, T. Kurten, M. V. Johnston, J. N. Smith, M. Ehn, T. F. Mentel, K. E. J. Lehtinen, A. Laaksonen, V. M. Kerminen, and D. R. Worsnop, Science **339**, 943 (2013).

[5] J. H. Zollner, W. A. Glasoe, B. Panta, K. K. Carlson, P. H. McMurry, and D. R. Hanson, Atmos. Chem. Phys. **12**, 4399 (2012).

[6] M. J. Tubergen and R. L. Kuczkowski, J. Am. Chem. Soc. **115**, 9263 (1993).

[7] B. T. Mmereki and D. J. Donaldson, J. Phys. Chem. A **106**, 3185 (2002).

[8] M. Rozenberg, A. Loewenschuss, and C. J. Nielsen, J. Phys. Chem. A **116**, 4089 (2012).

[9] B. C. Garrett, D. A. Dixon, D. M. Camaioni, D. M. Chipman, M. A. Johnson, C. D. Jonah, G. A. Kimmel, J. H. Miller, T. N. Rescigno, P. J. Rossky, S. S. Xantheas, S. D. Colson, A. H. Laufer, D. Ray, P. F. Barbara, D. M. Bartels, K. H. Becker, H. Bowen, S. E. Bradforth, I. Carmichael, J. V. Coe, L. R. Corrales, J. P. Cowin, M. Dupuis, K. B. Eisenthal, J. A. Franz, M. S. Gutowski, K. D. Jordan, B. D. Kay, J. A. LaVerne, S. V. Lymar, T. E. Madey, C. W. McCurdy, D. Meisel, S. Mukamel, A. R. Nilsson, T. M. Orlando, N. G. Petrik, S. M. Pimblott, J. R. Rustad, G. K. Schenter, S. J. Singer, A. Tokmakoff, L. S. Wang, C. Wittig, and T. S. Zwier, Chem. Rev. **105**, 355 (2005).

[10] A. Fujii and K. Mizuse, Int. Rev. Phys. Chem. **32**, 266 (2013).

[11] N. Heine and K. R. Asmis, Int. Rev. Phys. Chem. **34**, 1 (2015).

DOI:10.1063/1674-0068/cjcp1905103

[12] A. B. Wolk, C. M. Leavitt, E. Garand, and M. A. Johnson, Acc. Chem. Res. **47**, 202 (2014).

[13] L. S. Wang, Int. Rev. Phys. Chem. **35**, 69 (2016).

[14] Z. Luo, A. W. Castleman Jr., and S. N. Khanna, Chem. Rev. **116**, 14456 (2016).

[15] K. Mizuse, J. L. Kuo, and A. Fujii, Chem. Sci. **2**, 868 (2011).

[16] K. Mizuse and A. Fujii, J. Phys. Chem. A **117**, 929 (2013).

[17] J. D. Herr, J. Talbot, and R. P. Steele, J. Phys. Chem. A **119**, 752 (2015).

[18] J. D. Herr and R. P. Steele, J. Phys. Chem. A **120**, 7225 (2016).

[19] X. Lei, X. Kong, Z. Zhao, B. Zhang, D. Dai, X. Yang, and L. Jiang, Phys. Chem. Chem. Phys. **20**, 30125 (2018).

[20] X. Lei, X. Kong, Z. Zhao, B. Zhang, D. Dai, X. Yang, and L. Jiang, Phys. Chem. Chem. Phys. **20**, 25583 (2018).

[21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision D.01*, Wallingford CT: Gaussian Inc., (2013).

[22] J. P. Merrick, D. Moran, and L. Radom, J. Phys. Chem. A **111**, 11683 (2007).

[23] G. E. Douberly, R. E. Miller, and S. S. Xantheas, J. Am. Chem. Soc. **139**, 4152 (2017).

[24] D. J. Goebbert, T. Wende, L. Jiang, G. Meijer, A. Sanov, and K. R. Asmis, J. Phys. Chem. Lett. **1**, 2465 (2010).

[25] R. Shishido, Y. C. Li, C. W. Tsai, D. Bing, A. Fujii, and J. L. Kuo, Phys. Chem. Chem. Phys. **17**, 25863 (2015).

[26] R. Shishido, J. L. Kuo, and A. Fujii, J. Phys. Chem. A **116**, 6740 (2012).

[27] M. Hachiya, Y. Matsuda, K. I. Suhara, N. Mikami, and A. Fujii, J. Chem. Phys. **129**, 094306 (2008).

DOI:10.1063/1674-0068/cjcp1905103