# Infrared-Vacuum Ultraviolet Spectroscopic and Theoretical Study of Neutral Methylamine Dimer

Published as part of The Journal of Physical Chemistry virtual special issue "W. Lester S. Andrews Festschrift".

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**Supporting Information** 

**ABSTRACT:** The methylamine dimer,  $(CH_3NH_2)_2$ , is a model system to study the  $CH_3$  and  $NH_2$  spectral patterns in the neutral microsolvated systems relevant to chemical biology, atmospheric chemistry, and catalysis. We report infrared-vacuum ultraviolet spectroscopic measurements to probe the neutral  $(CH_3NH_2)_2$ . Quantum chemical calculations and ab initio molecular dynamics simulations were performed to understand the observed spectral features. Experimental and theoretical results indicate the likely coexistence of both cis and trans structures. A salient feature of this work is that the peak widths are not significantly affected by the structural transformation and the fluctuation of hydrogen bond distance, allowing the stretching modes to be clearly resolved.



# 1. INTRODUCTION

Molecular shape, molecular conformation, and molecular charge distribution play crucial roles in the selectivity and function of biomedical, electronics, and materials science. The individual molecules are held together by noncovalent bonds, especially hydrogen bonds (HBs), and the configuration transformation might occur because of flat potential energy surface. The nature of these intermolecular interactions govern the structure, stability, and properties of molecular clusters, and hence, there is enormous interest in the study of these molecules and their bonding properties with water, particularly with relevance to chemical biology, catalysis, and atmospheric chemistry.<sup>1</sup> Well-resolved vibrational spectra are essential to reveal and understand the dynamic nature of these weakly bonded systems. Mass-selected solvated clusters, produced and probed in the gas phase, provide a microscopic model for solutions and are amenable to first-principles theory.

In this work, we report the use of infrared (IR) spectroscopy coupled with single-photon vacuum ultraviolet (VUV) photoionization to probe the neutral methylamine dimer,  $(CH_3NH_2)_2$ . As organic solvents and reagents, amines are ubiquitous in biology and play an important role in enhancing particle nucleation and growth and affecting secondary organic aerosol formation.<sup>2,3</sup> Methylamine is the simplest member of amines and therefore a model molecule with a polar NH<sub>2</sub> group and a nonpolar methyl group, both of which are numerous in biomolecules, with coupled vibrational modes. Methylamine dimer is the simplest case to demonstrate the interaction between two amines and is fundamental to understand the vibrational spectra of biomolecules. It has been the subject of a few theoretical studies,<sup>4–7</sup> but there is limited experimental data on size-selected methylamine clusters.<sup>8–10</sup>

IR-VUV double resonance spectroscopy is suitable to study conformational dynamics in the neutral systems without an ultraviolet chromophore,<sup>11,12</sup> and below we provide a short explanation of the rationale in using this technique. When the

Received:August 14, 2017Revised:September 5, 2017Published:September 11, 2017

solute is an ion, the size can be readily selected by its mass/ charge ratio, while high detection efficiency can also be achieved by measuring the signals of charged particles. Studies on such clusters over the last three decades have shed much insight into the size-dependent microsolvation properties of ions, notably its energetics, <sup>13,14</sup> stability and reactivity, <sup>15,16</sup> and electronic structures.<sup>17,18</sup> The vibrational modes of ionic clusters could be probed by Infrared Multiphoton Dissociation (IRMPD) spectroscopy, providing a wealth of structural information.  $^{19-21}$  In contrast, neutral solvated clusters are more challenging to measure, due to difficulties in both size selection and signal detection. As a result, it is harder to perform experiments relevant to solvation of organic molecules or the solvent-solvent interactions. However, a number of methods have been pioneered to circumvent these difficulties.<sup>11,12,22-25</sup> A particularly interesting method is the IR-VUV spectroscopic technique, which measures the depletion in the VUV ionization signal at a specific cluster size induced by IR vibrational predissociation. Recently, it has been successfully applied to neutral clusters such as protic molecules without an ultraviolet chromophore  $((NH_3)_m, (CH_3OH)_m, \text{ formamide-water})$  and  $C_6F_6-NH_3$  clusters, <sup>11,12,26,27</sup> providing significant insights into the underlying intermolecular interactions.

#### 2. EXPERIMENTAL METHOD

Experiments were performed using the Dalian IR-VUV apparatus, which consists of a pulsed supersonic cluster source and a reflectron time-of-flight (TOF) mass spectrometer. A schematic diagram of the experimental apparatus is depicted in Figure 1, which is similar to those used previously in the



Figure 1. Schematic diagram of the experimental apparatus consisting of a pulsed supersonic cluster source and a reflectron TOF mass spectrometer.

literature.<sup>11,12</sup> The VUV light at 118 nm used in this study was generated by third harmonic generation (355 nm) of a Nd:YAG laser (Nimma-600) via Xe/Ar gas mixture at 1:10 relative concentration for 200 torr total pressure. A beam of neutral complexes was generated from supersonic expansions of 5% CH<sub>3</sub>NH<sub>2</sub> seeded in Ar using a pulsed valve (General Valve, Series 9) at 5 atm backing pressure and passed through a 4 mm diameter skimmer and an aperture with 3 mm opening. The cations were produced from the 118 nm one-photon ionization process in the center of the extraction region of a reflectron TOF mass spectrometer, and the signal intensity of the particular mass channel was monitored. Here, the tunable IR light pulse was introduced at ~30 ns prior to the VUV laser pulse in a crossed manner. When the resonant vibrational transition with the IR light caused vibrational predissociation,

the dissociation induced depopulation of the neutral cluster. The depopulation can be monitored as a reduction of the ion signal intensity in the cluster mass channel. An IR spectrum of the size-selected neutral species was obtained as a depletion spectrum of the monitored ion signal intensity by scanning the IR wavelength. The VUV laser was operated at 20 Hz, and IR laser was operated at 10 Hz. IR spectra were recorded in the difference mode of operation.

The tunable IR laser beam was generated by a KTP/KTA optical parametric oscillator/amplifier system (OPO/OPA, LaserVision) pumped by an injection-seeded Nd:YAG laser (Continuum Surelite EX). This system is tunable from 700 to 7000 cm<sup>-1</sup> with a line width of 1 cm<sup>-1</sup>. The wavelength of the OPO laser output was calibrated using a commercial wavelength meter (Bristol, 821 Pulse Laser Wavelength Meter). IR spectrum was determined from the relative depletion of the mass spectrometric ion signal ( $I_0$  and  $I(\nu)$ ) and the frequency-dependent laser power  $P(\nu)$  using  $\sigma = -\ln[I(\nu)/I_0]/P(\nu)$ . The normalization with the IR laser pulse energy accounted for its variations over the tuning range.

## 3. THEORETICAL METHOD

Quantum chemical calculations were performed using the Gaussian 09 package.<sup>28</sup> The M06-2X, BLYP, and MP2 methods with 6-311+G(d,p) basis set were employed. Relative energies and binding energies included zero-point vibrational energies. A scaled factor of 0.950 was use M06-2X/6-311+G(d,p) harmonic vibrational frequencies and 0.942 for MP2/6-311+G(d,p) harmonic vibrational frequencies, to account for anharmonicities and for the method-dependent systematic errors on the calculated harmonic force constants. The resulting stick spectra were convoluted by a Gaussian line shape function with a width of 4 cm<sup>-1</sup> (full width at half-maximum (fwhm)).

The dynamic motion of the clusters was simulated by the Ab Initio Molecular Dynamics (AIMD) method, in which the atoms were treated as classical particles and the potential energy and forces on the atoms were calculated within the framework of density functional theory (DFT) at each time step, as implemented in the CP2K package.<sup>29</sup> The wave functions were expanded in a double- $\zeta$  Gaussian basis set, while the electron density was expanded in Gaussians and auxiliary plane waves (GPW) with an energy cutoff at 280 Ry for the electron density. The atomic cores were modeled by the Goedecker-Teter-Hutter (GTH) type of pseudopotentials. The exchange and correlation energies were calculated by the BLYP functional, with additional Grimme's dispersion corrections at the D3 level. A cluster ion was put at the center of a periodic cubic box, and the effects of the periodic charge density images were corrected by the decoupling technique developed by Martyna and Tuckerman.<sup>30</sup> The box length was 16 Å. The convergence criterion for the self-consistent field (SCF) electronic procedure was set to be  $1 \times 10^{-7}$  a.u. at each time step. For molecular dynamics, the temperature was controlled by a Nose-Hoover thermostat, with a time step of 0.5 fs. An equilibration period of up to 10 ps was performed first, with the temperature scaled to an interval of 10 K around the intended value. A data collection run was then followed in the microcanonical ensemble. At 20 K, when the structure was basically frozen around the equilibrium geometry, a short run of 20 ps was performed. At 50 and 100 K, the duration of a trajectory was more than 40 ps. Each trajectory was then cut into 20 ps interval for Fourier transformation and then added

# The Journal of Physical Chemistry A

up to produce the dipole time-correlation function (DTCF) spectrum for a specific temperature.

Solvated clusters are bound by HBs, which are relatively weak and therefore fairly flexible at finite temperature. Dynamic simulations are essential for sampling the solvation structures and for examining the thermal stability of a particular structure. More importantly, the fluctuations of HBs have strong effects on the vibrations that can be captured by AIMD simulations. A vibrational spectrum can be directly simulated by the Fourier transform of the DTCF

$$\alpha(\omega) = \frac{2\pi\beta\omega^2}{3n(\omega)cV} \int_{-\infty}^{+\infty} dt \langle \overrightarrow{M}(t) \bullet \overrightarrow{M}(0) \rangle \exp(i\omega t)$$

where  $\beta = 1/kT$ ,  $n(\omega)$  is the refractive index, *c* is the speed of

light in a vacuum, V is the volume, and M is the total dipole moment of the system, calculated by the polarization including both ionic and electronic contributions.

# 4. RESULTS AND DISCUSSION

**a. Experimental Results.** Figure 2 shows a typical mass spectrum of the cations produced by the 118 nm one-photon



Figure 2. TOF mass spectrum of the cations produced from the 118 nm one-photon ionization process in a pulsed supersonic expansion of 5% CH<sub>3</sub>NH<sub>2</sub> seeded in Ar.

ionization of methylamine clusters. Two series of methylamine cluster cations are observed, one unprotonated  $((CH_3NH_2)_n^+)$  and the other protonated  $(H^+(CH_3NH_2)_n)$ . Protonated cations are often produced when clusters of alcohol or amine are ionized. For the IR-VUV measurement, it has been addressed by previous studies, for example, in the cases of methanol<sup>27</sup> and ammonia.<sup>31</sup> With a proton affinity of ~930 kJ/mol,<sup>32</sup> CH<sub>3</sub>NH<sub>2</sub> could also easily pick up a proton. It is known that the reaction

$$CH_3NH_2^+ + CH_3NH_2 \rightarrow H^+(CH_3NH_2) + CH_3NH_2$$

is exothermic by 30.9 kJ/mol,<sup>33</sup> and upon photoionization, methylamine clusters initially exist as  $CH_3NH\cdots$   $H^+(CH_3NH_2)_{n-1}$ .

Structural relaxation after ionization, which takes place around the CH<sub>3</sub>NH···H<sup>+</sup>(CH<sub>3</sub>NH<sub>2</sub>) ion core, could lead to further fragmentation via two possible channels. One channel is the loss of CH<sub>3</sub>NH radical, which produces the protonated  $H^+(CH_3NH_2)_{n-1}$  as the daughter ions observed in experiment. The other channel is the loss of CH<sub>3</sub>NH<sub>2</sub>, but it is more difficult. Near the ion core, the hydrogen bond between  $H^+(CH_3NH_2)$  and CH<sub>3</sub>NH<sub>2</sub> is known to be strong, with a binding energy above 90 kJ/mol.<sup>34</sup> Away from the ion core, there should not be much structural relaxation upon ionization. The unprotonated signals of  $(CH_3NH_2)_n^+$  detected in our experiment should be due to undissociated  $CH_3NH\cdots$  $H^+(CH_3NH_2)_{n=1}$ .

During our experiment, source conditions were optimized by carefully adjusting the buffer spring and shims of General Valve (Series 9) so that the VUV ionization of a supersonic jet of 5% CH<sub>3</sub>NH<sub>2</sub>/Ar mixture produced a mass spectrum with very small signal intensities for unprotonated and protonated trimer and larger clusters (Figure 2). It can be seen from Figure 2 that the signal intensity of  $(CH_3NH_2)_2^+$  is ~19 times larger than that of  $(CH_3NH_2)_3^+$ , suggesting a very small presence of larger clusters. When the tunable IR laser pulse was introduced at ~30 ns prior to the VUV pulse, the depletion spectrum obtained by monitoring the intensity of the  $(CH_3NH_2)_2^+$  mass channel and scanning the IR frequency in the 2500–3600 cm<sup>-1</sup> region (Figure 3) was mainly attributed to the vibrational predis-



Figure 3. IR laser power dependence for infrared spectra of neutral  $(CH_3NH_2)_2$ . The best resolution was achieved at an average energy of IR laser pulse of 5 mJ/mm<sup>2</sup>, showing that both features A and B are doublets and better resolved peaks for feature D as well. When the IR laser pulse energy was increased to 10 mJ/mm<sup>2</sup>, the resolution was somewhat degraded, while a new peak, labeled by an asterisk, was observed at 2803 cm<sup>-1</sup>.

sociation of the neutral dimer  $(CH_3NH_2)_2$ . IR laser power dependence was performed to check the saturation effect as shown in Figure 3. As demonstrated before for the first overtone of the antisymmetric O-H stretching in the IRMPD spectra of  $[MgNO_3(H_2O)_n]^+$   $(n = 1-3)^{35}$  the intensity of a higher-order excitation is more sensitive to the IR laser power. As illustrated in Figure 3, the peak labeled with an asterisk (2803 cm<sup>-1</sup>) fits such a behavior very well, with its disappearance at low IR laser power, and is assigned to an overtone or combination band. The best resolution was achieved at low IR laser power of 5 mJ/mm<sup>2</sup>, implying that the four intense bands (labeled A–D) were due to fundamental vibrational excitations. The present infrared spectrum at the IR laser pulse of 5 mJ/mm<sup>2</sup> shows nice signal/noise ratio and resolution without congested bands, which also indicates the measured infrared spectrum is mainly due to  $(CH_3NH_2)_2$ . Experimental frequencies of bands A-D are listed in Table 1. Above 3200 cm<sup>-1</sup>, features A and B are due to the N-H stretching ( $\nu_{\rm N-H}$ ). Below 3000 cm<sup>-1</sup>, features C and D are due to the C–H stretching ( $\nu_{C-H}$ ).

**b.** Flat Potential Energy Surface. Quantum chemical calculations and molecular dynamics simulations were performed to interpret the experimental IR spectra and structural dynamics of  $(CH_3NH_2)_2$ . Optimized stable and transition structures are shown in Figure 4, and harmonic

Table 1. Experimental IR-VUV Band Positions (in cm<sup>-1</sup>), Calculated Scaled Harmonic Frequencies, and Band Assignments for Neutral  $(CH_3NH_2)_2$ 

label	IR-VUV	M06-2X		MP2		
		cis	trans	cis	trans	assignment
Α	3403	3446	3444	3427	3424	$\nu_{\rm a(N-H)}$
	3393	3432	3436	3410	3410	
В	3319	3319	3344	3295	3294	$\nu_{\rm s(N-H)}$
	3299					
С	2975	2971	2987	2995	2998	$\nu_{\rm a(C-H)}$
	2953	2966	2962	2979	2979	
		2941	2953	2958	2962	
		2932	2925	2939	2939	
D	2927	2876	2871	2875	2876	$\nu_{\rm s(C-H)}$
	2913	2859	2850	2854	2853	
	2897					
	2877					



**Figure 4.** Minimum-energy (cis and trans) and transition-state (TS1– TS4) structures of neutral  $(CH_3NH_2)_2$ . M06-2X/6-311+G(d,p) relative energies (in kJ/mol) are listed inside round brackets.

vibrational spectra are in Figure 5 (more results are also shown in Supporting Information). The potential energy surface of methylamine dimer has been mapped previously by ab initio calculations.<sup>6</sup> The dimer is held together by a single hydrogen bond, with the two methyl groups being either cis or trans to each other (Figures 4 and S1). The cis dimer is slightly more stable, but the energy difference is very small, less than 0.5 kJ/ mol, depending on the computational method. Furthermore, two types of transformations are possible. In the first type, the cis and trans dimers are transformed into each other, by maintaining the HB and twisting the CN…NC torsion, through the two transition structures TS1 and TS2. In the second type, the transformation is either cis to cis or trans to trans, both involving HB flipping through TS3 and TS4. The energy barrier calculated depends on the method employed, but overall it is less than 4 kJ/mol. The potential energy surface is flat, and the transformation between the two isomers is facile. In addition, a methylamine molecule is also known to go through two types of internal motion: the rotation of the methyl group around the C-N bond, with a barrier of 8.1 kJ/mol, and the inversion around the NH<sub>2</sub> group, with a barrier of 22.6 kJ/



**Figure 5.** Comparison of the experimental IR-VUV spectrum (bottom) of neutral  $(CH_3NH_2)_2$  to the M06-2X/6-311+G(d,p) calculated harmonic vibrational spectra of the cis and trans isomers. The average energy of IR laser pulse was 5 mJ/mm<sup>2</sup>. The best agreement is obtained when assuming a 1:1 mixture of cis and trans (trace labeled Mix).

mol.<sup>33,34</sup> For methylamine dimer, these two channels are less accessible than the configuration changes described earlier.

With such a flat potential energy surface, the presence of more than one isomer structure needs to be considered, as recently demonstrated in our studies on  $H_2PO_4^{-}(H_2O)_n$  (n = 1-12).<sup>36,37</sup> Furthermore, the fluctuation in the HB distance might shift and broaden the peaks of related vibrational modes. Dynamic simulations are required to understand such effects, and the vibrational spectra obtained by the Fourier transform of the dipole moment time correlation function should capture the vibrational features better than harmonic analysis or anharmonic corrections.

Our AIMD simulations indeed show that the dimer exists as a mixture of cis and trans configurations. At a temperature of 20 K, the two configurations transform into each other during the simulation, by twisting the CN···NC torsion while maintaining the HB. At 50 K, HB flipping through TS3 and TS4 is observed as shown in Figure 6b. As the HB length fluctuates between 2.0 and 2.5 Å, the  $\nu_{\rm N-H}$  peaks are not significantly broadened in the AIMD spectra (Figure 6a). With an equilibrium distance of ~2.2 Å, the HB holding the methylamine dimer together is not very strong, and its fluctuation does not induce the kind of broadening in X–H stretching observed in some hydrated ionic clusters.<sup>36–38</sup> Raising the temperature further to 100 K, the HB in this dimer could be broken.

c. Splitting of C–H and N–H Symmetric Stretching Modes. While these calculation results present an overall picture of the structural transformation in a methylamine dimer, it is however a challenge to reproduce quantitatively the fine splittings that are resolved in this experiment. This is especially the case for feature D, which is due to the symmetric C–H stretching ( $\nu_{s(C-H)}$ ). A stable structure should have only two peaks, one for each methyl group, while four peaks (2877, 2897, 2913, and 2927 cm<sup>-1</sup>) are resolved in our experiment. Considering the AIMD results and the flat potential energy surface, one should tentatively take the splitting of band D as the proof for the presence of both isomer structures.

However, the harmonic  $\nu_{s(C-H)}$  values calculated by MP2/6-311+G(d,p) are almost the same for the cis and trans dimers, with only a difference of 1 cm<sup>-1</sup> shown in Figure S2 and Table



**Figure 6.** (a) Comparison of the experimental IR-VUV spectrum (bottom) of neutral  $(CH_3NH_2)_2$  to DTCF spectra from the AIMD simulations of the cis and trans isomers at 20 and 50 K. (b) Fluctuation in the N–H distances during AIMD simulation at 50 K in the cis and trans isomers. The average energy of IR laser pulse was 5 mJ/mm<sup>2</sup>.

1, and also by BLYP/6-311+G(d,p) (Figure S3). Similar results are obtained in our AIMD simulation (Figure 6a), which is not surprising, since the BLYP functional is also employed in AIMD simulations. According to these results, there would be only two  $\nu_{s(C-H)}$  peaks, even when the sample is a mixture of the cis and trans dimers. Only when the M062X functional is employed, there is a significant gap for the  $\nu_{s(C-H)}$  peaks between the cis and trans dimers to produce four  $\nu_{s(C-H)}$  peaks for a 1:1 mixture of the two isomers (Figure 5). Note that the result of anharmonic calculation (Figure S4) is not as good as harmonic analysis.

It is expected that reproducing the very small difference in  $\nu_{\rm s(C-H)}$  (band D), ~20 cm<sup>-1</sup>, between the cis and trans dimers will be challenging, even for high-level ab initio or DFT calculation. But all the harmonic analysis agree on one point: all the  $\nu_{\rm (C-H)}$  and  $\nu_{\rm (N-H)}$  modes are localized, with little coupling between functional groups, since both methylamine dimer structures are low in symmetry. The well-resolved four peaks contained in feature D could only be due to the fundamental  $\nu_{\rm s(C-H)}$  and should be taken as an indication for the coexistence of the cis and trans dimers.

For  $\nu_{a(C-H)}$ , each methyl group contributes two peaks, and there are a total number of eight peaks for the two isomers with significant overlaps, coalescing into two strong peaks (feature C). By mixing the M06-2X harmonic spectra of the two configurations, as shown in Figure 5, the basic outline for features D and C are well-reproduced. Further evidence for the coexistence of both cis and trans dimers is seen in feature B  $(\nu_{s(N-H)})$ . It contains two peaks, which are well-resolved when the IR laser pulse energy is at ~5 mJ/mm<sup>2</sup>.

Whether the dimer is cis or trans, there are two symmetric  $\nu_{\rm s(N-H)}$  modes for NH<sub>2</sub> groups, one for the HB donor group and the other for the HB acceptor group, which are fairly localized according to harmonic analysis. MP2 and DFT calculations all indicate that the intensity of  $\nu_{s(N-H)}$  for the HB acceptor NH<sub>2</sub> is less than 1% of that for the HB donor NH<sub>2</sub>, so there is only one  $\nu_{s(N-H)}$  peak for each of the cis or the trans dimer. The two resolved peaks serve as another indication for the coexistence of the cis and trans dimers, consistent with the analysis on  $\nu_{\rm s(C-H)}$  peaks contained in feature D. As listed in Table 1, the frequency gap between the cis and trans dimers is underestimated by MP2 to be only 1 cm<sup>-1</sup>. On the one hand, the coincidental overlap of these two  $\nu_{\rm s(N-H)}$  frequencies would predict only one peak for feature B, in contradiction to experiment. On the other hand, M06-2X does predict a gap of 25 cm<sup>-1</sup>, which compares favorably with the experimental gap of 20 cm<sup>-1</sup>.

Feature A is also a doublet as shown in Figure 5, which is due to the N–H asymmetric stretching,  $\nu_{a(N-H)}$ . Regarding this mode, there is overall agreement among the results of harmonic analysis by various methods. For each of the cis and trans dimers, there are two  $\nu_{a(N-H)}$  peaks, one for the HB donor and the other for the acceptor at a slightly higher frequency 10–15 cm<sup>-1</sup>, as listed in Table 1. There is again little coupling between the two NH<sub>2</sub> groups, but the intensity of the acceptor  $\nu_{a(N-H)}$  is ~15% of that of the donor  $\nu_{a(N-H)}$ . The gap between the corresponding  $\nu_{a(N-H)}$  peaks of cis and trans dimers is no more than 3 cm<sup>-1</sup>. Therefore, the doublet in feature A with a splitting of ~10 cm<sup>-1</sup> is probably due to the difference between the acceptor and donor  $\nu_{a(N-H)}$  peaks.

# 5. CONCLUSION

The approach of IR-VUV spectroscopy combined with quantum chemical calculation and molecular dynamics simulation was employed to study the CH<sub>3</sub> and NH<sub>2</sub> vibrational spectral patterns of neutral (CH<sub>3</sub>NH<sub>2</sub>)<sub>2</sub>. The coexistence of the cis and trans structures is likely for  $(CH_3NH_2)_2$ , which is consistent with the small predicted energy difference between the two configurations separated by low barriers. This is expected for solvated clusters bound by HBs, which dynamic nature is elucidated by the present wellresolved vibrational spectra. It is well-known that CH<sub>3</sub> and NH<sub>2</sub> groups in organic and biomolecules are often coupled and complicated by high-order excitations. But here we demonstrate for methylamine dimer, which is one of the simplest models for amine solutions, the stretching region can be resolved and assigned. The ability to decipher such isomers, where very subtle forces and energies are at play, suggests that the present method could be applied to larger complexes and clusters, which are directly relevant to the fields of chemical biology, atmospheric chemistry, and catalysis.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b08096.

Minimum-energy and transition-state structures of neutral  $(CH_3NH_2)_2$  calculated at the MP2/6-311+G-(d,p) level; comparison of the experimental IR-VUV spectrum of neutral  $(CH_3NH_2)_2$  to the MP2/6-311+G-

(d,p) simulated harmonic vibrational spectra of the two lowest-energy isomers; comparison of the experimental IR-VUV spectrum of neutral  $(CH_3NH_2)_2$  to the BLYP/ 6-311+G(d,p) simulated harmonic vibrational spectra of the two lowest-energy isomers; comparison of the experimental IR-VUV spectrum of neutral  $(CH_3NH_2)_2$ to the M062X/6-311+G(d,p) calculated harmonic and anharmonic vibrational spectra of the two lowest-energy isomers (PDF)

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## Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21327901, 21473151, 21503222, and 21673231), the Key Research Program (Grant No. KGZD-EW-T05), and the Strategic Priority Research Program (Grant No. XDB17010000) of the Chinese Academy of Science. We greatly appreciate advice from Prof. A. Fujii on the design of experimental apparatus and valuable disscussions from Prof. M. Ahmed.

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