

H/D substitution makes difference in photochemical studies: the case of dimethylamine

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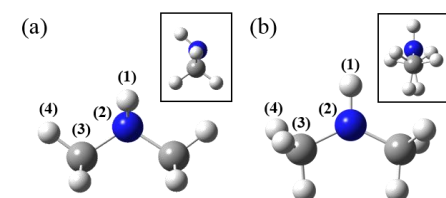
ABSTRACT: When the molecule in the excited state is subject to prompt predissociation, it is quite nontrivial to obtain vibrational structure of the excited state in general. This applies to the case of photochemistry of dimethylamine (DMA:(CH₃)₂NH). When DMA is excited to its first electronically excited state (S₁), the N-H bond dissociation occurs promptly. Therefore, S₁ vibronic bands are homogeneously broadened to give extremely small ionization cross sections and heavily-congested spectral features, making infeasible any reasonable spectral assignment. Here, we demonstrate that the predissociation rate of the excited state could be significantly reduced by the NH/ND substitution to give the much better-resolved S₁ spectral feature, revealing the vibrational structure of the excited state of DMA-d₁ ((CH₃)₂ND) for the first time.

As the simplest primary alkyl amine, methylamine (MA) has been widely studied for many years.¹⁻¹² Recent many theoretical and experimental studies show that the MA photochemistry is very rich in terms of its interesting diverse relaxation pathways and detailed mechanisms involved. Photochemistry of the secondary alkyl amine, however, has not been much studied to date. This is not so surprising though as the size of the molecule becomes large, spectral analysis and associated dynamics get much complicated. The simplest secondary alkyl amine is dimethylamine (DMA). For DMA, to our best knowledge, there has been only one spectroscopic study for the vibronic structure of the first electronically excited state.³ In this study, we extend the spectroscopic investigation on the first excited and cationic states of DMA through the substitution of (CH₃)₂N-H to (CH₃)₂N-D, utilizing the deuterium effect in terms of the longer lifetime resulting from the much reduced tunneling rate along the N-H(D) bond dissociation coordinate.

The experimental setup of Resonance enhanced multiphoton ionization (REMPI) and photoelectron imaging was given in detail previously.^{6,7} One-color two-photon (1+1) ionization scheme was used for both REMPI and photoelectron imaging. Raw photoelectron images taken with a IMACQ acquisition software¹⁴ were reconstructed using the BASEX program.¹⁵ All quantum chemical calculations were performed using the B3LYP/6-311++G** basis set (TD-DFT/B3LYP for excited state calculations) in Gaussian09 programs¹⁶ and Franck-Condon simulations were conducted using the FClab2 program packages.^{17,18}

Predissociative nature of the first excited state of alkyl amine is now quite well understood as the initially bound n-3s transition is coupled to the repulsive potential energy surface along the N-H(D) bond elongation coordinate. Calculated molecular structures and zero-point corrected relative energies for S₀, S₁, and D₀ states of DMA are listed in Table 1. Energetics of DMA-d₁ are shown in parentheses. At the S₀ minimum energy, N-H(D) is bent with respect to the plane of C-N-C. The molecule becomes planar when it is excited at S₁ or ionized to D₀. This structural change has also been observed for methylamine, and it is quite understandable as the nonbonding orbital of the nitrogen atom cannot play a significant role anymore in terms of the electronic structure in S₁ or D₀. It should also be noted that two CH₃ groups are twisted to each other on S₁ and D₀ equilibrium geometries.

Table 1. Calculated molecular structural parameters and minimum energies for the ground (S₀), first excited (S₁), and cationic ground (D₀) states. Geometries for (a) S₀, (b) S₁ and D₀. Insets are corresponds to side view.



	Equilibrium		
	S ₀	S ₁	D ₀
Relative energy (cm ⁻¹)	0 (0)	34 727 (34 804)	65 644 (65 680)
d(H1-N2) (Å)	1.01	1.03	1.02
d(N2-C3) (Å)	1.46	1.43	1.44
γ(C-N-C) (°)	113.43	127.64	125.58
δ(H1-N2-C3-H4) (°)	53.46	45.65	43.23

Figure 1 (a) shows (1+1) REMPI spectrum of DMA in the frequency range of 39,500 ~ 41,500 cm⁻¹. This is consistent with the previously reported result obtained by Taylor and co-workers.³ In contrast to the case of methylamine, the DMA REPI spectrum shows heavy spectral congestion and also severe broadening. Photoelectron images and spectrum obtained by the (1+1) ionization velocity map imaging technique via some internally excited states on S₁ are shown in Figure 1 (b) ~ (e). The literature IP value of DMA is ~ 8.24 eV. As the S₁ vibronic structure of DMA is not resolved, it is nontrivial to

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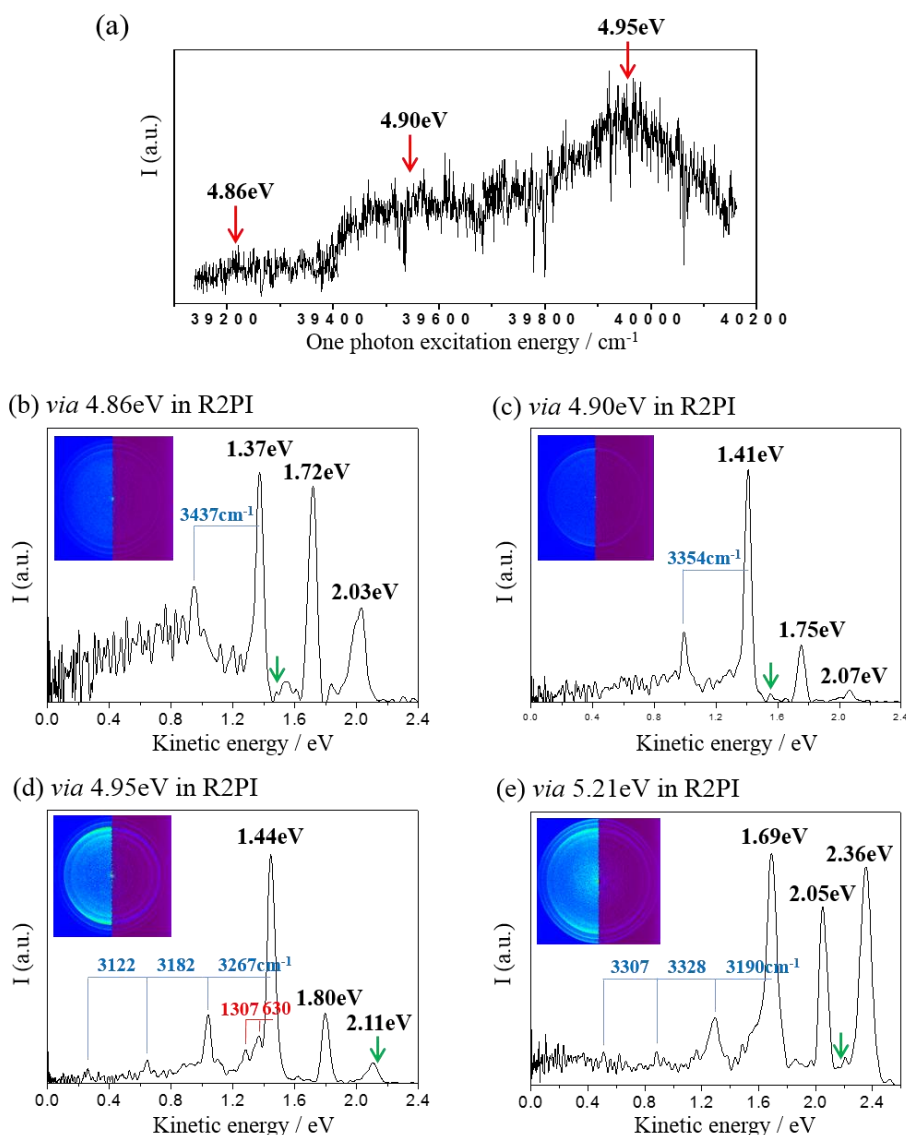


Figure 1. $S_1 \leftarrow S_0$ R2PI spectrum of jet cooled DMA(a) and (1+1) Photoelectron image (inset, the left is raw images and the right is reconstructed images.) and spectra taken via 4.86 eV(b), 4.90 eV(c), 4.95 eV(d), and 5.21 eV (e) correspond to internally excited region of S_1 state. Green vertical arrow indicates maximum kinetic energies.

accurately assign photoelectron signals with appropriate cationic vibrational modes. Strong peaks observed at 1.37, 1.41, 1.44, or 1.69 eV in photoelectron spectra taken by two-photon absorption at 4.86, 4.90, 4.95, or 5.21 eV are most likely to be associated with cationic states of the largest Franck-Condon overlap. Simple energetics suggests that the photoelectron signal associated with the cationic origin is expected to be located at ~ 1.48 eV in the (1+1) imaging spectrum taken at the photon energy of 4.86 eV, Figure 1 (b). A peak of 1.37 eV in Figure 1 (b) could then be ascribed to the photoelectron signal combined with the vibrationally hot cationic states with the maximum energy of 887 cm^{-1} ($1.48 - 1.37 = 0.11$ eV). This in turn means that the $S_1 \leftarrow S_0$ origin is $\sim 887 \text{ cm}^{-1}$ below 4.86 eV. However, this value cannot be taken seriously as there are many uncertain values involved in this rough estimation. One interesting observation is that there is a progression band of the mode with a

frequency of $\sim 3200 \text{ cm}^{-1}$ in all photoelectron spectra. This is most likely associated with the N-H stretching mode, meaning that the S_1 potential is quite dissociative in nature along the N-H elongation coordinate. Several distinct photoelectron signals with kinetic energies above IP of DMA may be attributed to those coming from trimethylamine which is present in the jet as an impurity.

As the predissociation of N-H or N-D occurs via tunneling through a barrier, the NH/ND isotope substitution influence is expected to be quite substantial.⁴⁻¹² Indeed, the much more resolved R2PI spectrum could be obtained for DMA-d₁, Figure 2(a). And yet, the spectrum is overall quite broad and individual peaks are Lorentzian shaped, indicating that the excited state, in spite of NH/ND substitution, decays very fast. Franck-Condon simulated spectrum using the FClab2 program is shown in Figure 2(b), where scaled harmonic frequencies of the ground and first excited states are used in the

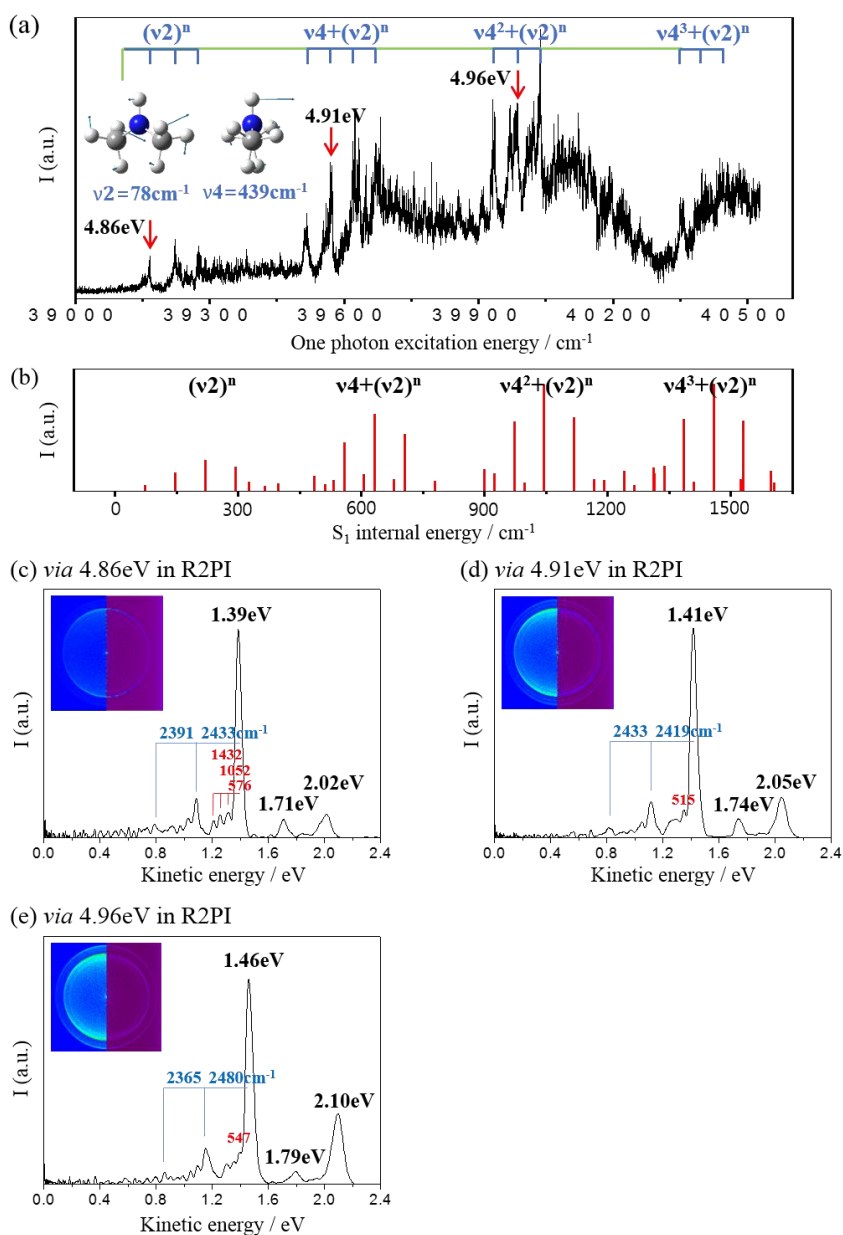


Figure 2. $S_1 \leftarrow S_0$ R2PI spectrum of jet cooled DMA- d_1 (a) and Franck-Condon simulations between S_0 and S_1 (b). (1+1) Photoelectron image (inset, the left is raw images and the right is reconstructed images.) and spectra taken via 4.86eV (c), 4.91eV (d), and 4.96eV (e) correspond to internally excited region of S_1 state.

simulation. The R2PI spectrum clearly shows long progressions and combinations of ν_4 (N-D wagging) and ν_2 (CH_3 torsion with N-D wagging). All of the major spectral features below $40,500 \text{ cm}^{-1}$ represent excitation of these two vibronic modes. This is quite consistent with the structural change of DMA upon the $S_1 \leftarrow S_0$ ($3s \leftarrow n$) electronic transition, Table 1. Photoelectron images and associated spectra of DMA- d_1 taken via some internally excited states on S_1 are shown in Figure 2 (c) ~ (e). The similar pattern of progressions compared to DMA, is observed in the photoelectron spectrum of DMA- d_1 , yet this time with a much reduced spectral gap of $2400 \text{ cm}^{-1}/500 \text{ cm}^{-1}$. These large frequency shift results from the NH/ND substitution, strongly indicate that these progressions arise

from N-H(D) stretching and N-H(D) wagging modes where associated normal modes are described in Figure 3.

Anisotropy parameters (β_2) of the strongest photoelectron signal (peak a in Table 2) and red-shifted photoelectron signal combined with the N-H(D) stretching mode (peak b in Table 2) in photoelectron images of DMA and DMA- d_1 taken at several excitation energies are listed in Table 2. The value of β_2 remains positive for all excitation energies representing the p -partial wavelike character of the outgoing photoelectron from the $3s$ Rydberg state. Intriguingly, however, the anisotropy parameter of 1.0 ± 0.1 (0.9 ± 0.1) of the strong photoelectron signal (peak a) of DMA (DMA- d_1) is decreased to $\sim 0.4 \pm 0.1$ for the photoelectron peak (peak b)

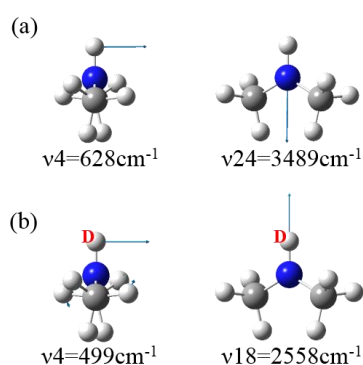
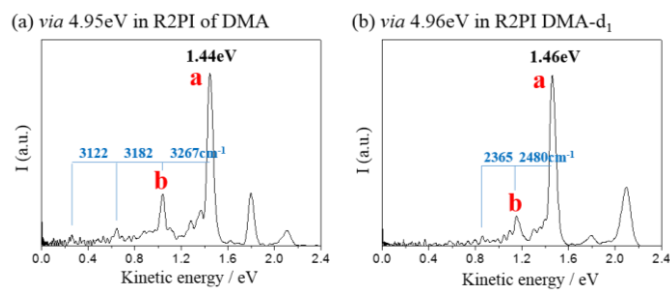


Figure 3. Calculated cationic normal modes and eigenvectors of the C-H(D) wagging (ν_4), and C-H(D) stretching (ν_{24} (ν_{18} in DMA- d_1)) for DMA(a) and DMA- d_1 (b)

Table 2. Anisotropy parameters of the peak a and b specified on the photoelectron kinetic energy spectrum for DMA(a) and DMA- d_1 (b) according to excitation energies. (errors in ± 0.1)



DMA	a	b
via 4.86 eV	-	1.04
via 4.90 eV	0.43	1.13
via 4.95 eV	0.44	1.04
via 5.21 eV	0.43	1.04
via 5.29 eV	-	1.01
DMA- d_1	a	b
via 4.86 eV	0.45	0.92
via 4.91 eV	0.42	0.92
via 4.96 eV	0.46	0.93

combined with the single quantum of the N-H(D) stretching mode for both isotope analogs. The decreased value of β_2 of the 'peak b' reflects dilution of the 3s Rydberg character of the electronic configuration as the molecule is coupled more strongly to the repulsive potential surface at the molecular structure relaxed along the N-H(D) stretching coordinate. In our previous work of methylamine, a similar decrease in β_2 with the vibrational excitation along the reaction coordinate has been observed.⁷

In summary, resonance-enhanced multiphoton ionization spectroscopy and photoelectron imaging experiments have been carried out for DMA and DMA- d_1 . By the successful H/D substitution, it becomes possible to get the resolved vibronic structure of DMA for the first time. Active excitation of N-H(D) wagging and CH₃ torsion modes upon the $S_1 \leftarrow S_0$ transition is well understood by the bent-to-planar structural change of the NH moiety with respect to the rest of the molecule. Photoelectron spectra give the valuable information about the potential energy surface along the reaction coordinate especially regarding the electronic configurations related the structural change of the molecule undergoing the ultrafast

predissociation. Further more accurate and precise experiments will be definitely needed for better understanding of the secondary amine photochemistry.

KEYWORDS: Dimethylamine, REMPI, photoelectron imaging, predissociation

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