Vibrational structures of methylamine isotopomers in the predissociative \( \tilde{A} \) states: \( {\text{CH}}_3{\text{NHD, CD}}_3{\text{NH}}_2, {\text{CD}}_3{\text{NHD, and CD}}_3{\text{ND}}_2 \)

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Mass-resolved two-photon (1 + 1) resonance-enhanced multiphoton ionization spectra of the \( \tilde{A} \)-\( X \) transitions of various methylamine isotopomers (\( {\text{CH}}_3{\text{NHD, CD}}_3{\text{NH}}_2, {\text{CD}}_3{\text{NHD, and CD}}_3{\text{ND}}_2 \)) cooled in the supersonic jet expansion have been measured and analyzed. The band analysis using the Hamiltonian for the internal and overall rotational motions provides the accurate vibrational band positions, allowing for unambiguous assignments for all observed vibrational bands of methylamine isotopomers in the \( \tilde{A} \) states. Amino wagging (\( \nu_9 \)) and methyl rocking (\( \nu_8 \)) modes are found to be Franck-Condon active, and associated anharmonicity constants are precisely determined to give the detailed shape of the potential energy surface in the vicinity of the minimum electronic molecular structure. The barrier height for the nearly free internal rotation about the C–N bond in the \( \tilde{A} \) state is calculated to be strongly dependent on the excitation of the other higher-frequency vibrational modes, and it is found that the trend is consistent with the experiment. Experimentally measured spectroscopic constants are compared with \textit{ab initio} calculations, confirming all vibronic assignments. Experimental and theoretical results on all possible H/D isotopomers of methylamine in this work, with the earlier report on \( {\text{CH}}_3{\text{NH}}_2 \) and \( {\text{CH}}_3{\text{ND}}_2 \) Baek \textit{et al.}, \textit{J. Chem. Phys.} \textbf{118}, 11026 (2003), provide the complete spectroscopic characterization of the \( \tilde{A} \) state of methylamine. © 2006 American Institute of Physics. [DOI: 10.1063/1.2338322]

I. INTRODUCTION

Methylamine (\( {\text{CH}}_3{\text{NH}}_2 \)) is the simplest primary amine which constitutes amino acids and a variety of heterocyclic compounds. The structure and chemical reactivity of methylamine exposed to various external conditions are therefore quite essential for the understanding of many organic and/or biological reactions involving primary amines as reactants or products. Photochemistry of methylamine has long been investigated for unraveling the structure of the excited state and various reaction channels.\(^1\)\textendash\(^{15}\) Even though many previous spectroscopic and dynamic works on methylamine had been reported in the mid-1990s\(^9\)\textendash\(^{14}\) the proper spectroscopic characterization of the excited methylamine has only recently been established.\(^{16}\)\textendash\(^{18}\) In our earlier report, rovibrational structures of \( {\text{CH}}_3{\text{NH}}_2 \) and \( {\text{CH}}_3{\text{ND}}_2 \) in the excited \( \tilde{A} \) state have been investigated by using the resonance-enhanced (1 + 1) two-photon ionization (R2PI) spectroscopic method.\(^{16}\)\textendash\(^{18}\) Due to the relatively long lifetimes of the excited states of \( {\text{CH}}_3{\text{ND}}_2 \) rotational fine structures could be well resolved for the first few vibronic bands to provide accurate spectroscopic constants associated with rovibrational motion of the excited \( {\text{CH}}_3{\text{ND}}_2 \) molecule.\(^{16}\)\textendash\(^{18}\) The rather broad vibronic bands of the excited \( {\text{CH}}_3{\text{NH}}_2 \) have also been very successfully analyzed based on the internal/overall-rotational Hamiltonian used for the analysis of \( {\text{CH}}_3{\text{ND}}_2 \). According to the structural change from the NH\(_2\) bent to NH\(_2\) planar with respect to the C–N axis upon the electronic transition, NH\(_2\) wagging and CH\(_3\) rocking modes are found to be mostly active in the \( \tilde{A} \)-\( X \) transition, and their vibrational term values has been accurately determined. Vibronic band broadening is found to be due to the fast N–H(D) bond dissociation in the predissociative \( \tilde{A} \) state.\(^ {16}\)\textendash\(^{18}\)

Therefore, it is now well known that methylamine, in its excited state, undergoes the N–H bond dissociation through the vibronic coupling of the optically bright \( n-3s \) Rydberg state to the dissociative valence electronic state. At the zero-point energy level the N–H dissociation proceeds via tunneling through a reaction barrier, showing the huge H/D isotope effect in the reaction rate.\(^ {16}\)\textendash\(^{18}\) Internal rotation of methylamine around the C–N axis becomes nearly free in the first electronically excited state, and the barrier height of 5 cm\(^{-1}\) at the zero-point energy level of the excited \( {\text{CH}}_3{\text{ND}}_2 \) has been accurately estimated from the spectroscopic analysis. Although our earlier report on methylamines in the \( \tilde{A} \) state has provided these essential spectroscopic and dynamic features,\(^ {17}\)\textendash\(^{18}\) the exploration of other isotopomers are necessary for the complete spectroscopic characterization of methylamines in the electronically excited state. In this work, we investigate all other possible isotopomers of methyl-
II. EXPERIMENT

Various methylamine isotopomers were prepared by keeping the 1:1 mixture of CH$_3$NH$_2$ (Aldrich, 98%) and CD$_3$ND$_2$ (Cambridge Isotopes, 98%) gases in a lecture bottle for several days. The resultant sample mixture contained all possible methylamine isotopomers: CH$_3$NH$_2$, CH$_3$NHD, CH$_3$ND$_2$, CD$_3$NH$_2$, CD$_3$NHD, and CD$_3$ND$_2$ by the H/D exchange reactions. Methylamine isotopomers were introduced into a gas cylinder to be mixed with Ne with a concentration of ~1%. The gas mixture was then expanded into vacuum through a nozzle orifice (General Valve 9 Series) with a backing pressure of ~3.5 atm and a repetition rate of 10 Hz. The 355 nm output of a Nd:YAG (yttrium aluminum garnet) laser (Continuum, Precision II 8010) was used to pump a dye laser (Lumonics, HD500) to generate laser pulses in the 440–480 nm range. The absolute laser wavelength was calibrated within ±0.1 cm$^{-1}$ by the use of a wavemeter (Coherent, 33-2619). The output of the dye laser was frequency doubled in a beta barium borate (BBO) crystal placed on a homemade autotracking system to generate the tunable laser pulse in the 220–240 nm range. The UV laser pulse was then overlapped with the molecular beam spatially and temporally to ionize methylamines by the (1+1) R2PI process. The ions were extracted, accelerated, drifted along the field-free region, and detected by microchannel plates (MCPs) (Jordan). The signal was digitized by an oscilloscope (LeCroy, LT584) and stored in a personal computer. Ab initio calculations were carried out by using the GAUSSIAN 03 program package using a personal computer. The excited state geometry and fundamental vibrational frequencies were calculated using the complete active space self-consistent field (CASSCF(6,6)) method with a 6-31++G(d,p) basis set.

III. RESULTS AND DISCUSSION

The $\tilde{A}$-X excitation spectra of all six different methylamine isotopomers (CH$_3$NH$_2$, CH$_3$NHD, CH$_3$ND$_2$, CD$_3$NH$_2$, CD$_3$NHD, and CD$_3$ND$_2$) taken in the 41 600–45 550 cm$^{-1}$ region are shown with appropriate assignments in Fig. 1. The major structural change of methylamine induced by the electronic transition (3$s$-n) is that the bent amino group becomes planar in the excited state. Accordingly, the NH$_2$ wagging mode ($v_9$) is most active in the excitation spectrum giving a quite long progression. Another active mode is found to be the CH$_3$ rocking mode ($v_7$), and the corresponding progression and combination modes are identified in all of excitation spectra in Fig. 1. It is found that the rotational structure of the origin and first $v_6$ band is well resolved for CD$_3$ND$_2$ and CH$_3$ND$_2$, while it is not resolved for CH$_3$NHD, CD$_3$NHD, CH$_3$NH$_2$, and CD$_3$NH$_2$. This experimental finding confirms that the broadening of the vibrionic bands of the $\tilde{A}$ state methylamine is originated from the ultrafast N–H bond predissociation, as has been reported.
A. Spectral analysis for the excitation spectrum of CD3ND2 (Å)

The band positions are precisely located by comparing the rotationally resolved peaks with the simulated ones based on the overall/internal rotor Hamiltonian with a small barrier along the torsional angle around the C–N axis. The detailed spectral analysis for CH3NH2 and CH3ND2 was already given previously in Ref. 17. Here, we will show the analysis for the rotationally resolved vibronic bands of the excited CD3ND2. Analyses of vibronic bands of CD3NH2, CH3NHD, and CD3NHD have been carried out in the similar way. As the rovibrational levels in Å state are predissociative, the Lorentzian function convoluted with the proper Gaussian-shaped instrumental function is used for the vibronic band simulation. The full description of the simulation procedure had been given in our earlier report. Briefly, the Hamiltonian for the overall/internal rotation is given as follows:

\[ H = H_{rot} + F(p - P)^2 + V(\phi). \] (1)

Here, \( H_{rot} \) is the rigid-rotor Hamiltonian based on the symmetric-top approximation reflecting the overall rotation of the excited methylamine. \( F \) is the effective rotational constant for the internal rotation of the top (CH3) with respect to the frame (NH2). \( V \) is the sixfold torsional potential with a form of \( V(\phi) = V_b/2 \left[ 1 - \cos(6\phi) \right] \) where \( V_b \) is the barrier height along the torsional angle \( \phi \). The \((p - P)\) term is the relative angular momentum of the top and frame. The 100 × 100 Hamiltonian matrix is constructed with a free rotor basis set, \(|m\rangle = (2\pi)^{-1/2} \exp(-im\phi)\) to give nonvanishing matrix elements as follows:

\[
\langle m|H|m\rangle = (A^T + A^F)m^2 + BJ(J + 1) + (A^F - B)K^2 - 2A^F mK' + (V_b/2),
\] (2)

\[
\langle m|H|m \pm 6\rangle = -(V_b/4),
\] (3)

where \( A^T \) and \( A^F \) are rotational constants of the top and frame, respectively, while \( B \) is the overall rotational constant and \( K' \) is the angular momentum of methylamine in the excited state. The resultant Hamiltonian matrix is diagonalized to give energies and associated eigenstates.

In Fig. 2, the origin band of CD3ND2 is shown with the simulation with a \( T_{rot} = 3.5 \) K. Two sets of peaks denoted by dotted lines in Fig. 2 are very sensitive to the value of the torsional barrier height, giving \( V_b = 5.5 \pm 1.0 \text{ cm}^{-1} \) for the zero-point level of the Å state CD3ND2. This is quite similar to the torsional barrier height of 5.0 cm\(^{-1}\) which was found for CH3ND2 at the zero point level in Ref. 17. The torsional barrier of CD3ND2(Å) is found to be 19 cm\(^{-1}\) when one quantum of the \( \nu_9 \) mode is excited (Table I). The increase of the torsional barrier height with the \( \nu_9 \) mode excitation has also been observed for CH3ND2. The predissociation lifetime of the zero-point energy level of CD3ND2, extracted from the homogeneous linewidth of the spectrum is \(~11\) ps, and this is slightly larger than the lifetime of \(~9\) ps found for CH3ND2. Thus except for rotational constants which are naturally changed by the H to D substitution, the underlying dynamics in terms of torsional motions and predissociation seem to remain nearly same even when the methyl group of CH3ND2 is totally deuterated to CD3ND2. Other vibronic bands are analyzed by the same procedure, and associated spectroscopic constants are listed in Table I. In this way, the positions of all the observed vibrational levels in the Å state of CD3ND2 could be quite accurately determined within the

\[
\begin{array}{cccc}
\mathrm{0}^0_v & \nu_9 & \nu_7 & 2\nu_9 \\
A^T & 4.95 \pm 0.1 & 4.56 \pm 0.1 & (4.3) & (4.2) \\
A^F & 2.50 \pm 0.1 & 2.47 \pm 0.1 & (2.2) & (2.1) \\
B' & 0.59 \pm 0.07 & 0.55 \pm 0.07 & (0.5) & (0.5) \\
\text{FWHM} & 0.50 \pm 0.03 & 0.50 \pm 0.03 & (1.0) & (3.0) \\
\tau (\text{ps}) & 10.6 \pm 0.6 & 10.6 \pm 0.6 & (5.3) & (1.8) \\
\nu_6 & 5.5 \pm 1.0 & 19 \pm 2 & \cdots & \cdots \\
E_{\text{vib}} & 0 & 456 \pm 1 & 799 \pm 1 & 932 \pm 1 \\
\end{array}
\]
The overall shapes of the excitation spectrum of CH3ND2 to give the more accurate term values of two different modes. The frequencies of the amino-wagging mode are found to be larger when the amino moiety is deuterated compared with that caused by the methyl group H/D substitution. This observation indicates that the N–H stretching is more sensitive to the H → D substitution than the C–H stretching is. Time dependent density-functional theory (TD-DFT) calculation [B3LYP/6-31+ +G(d,p)] assuming the \( \tilde{A} \) state geometry optimized by CASSCF [6-31 + +G(d,p)] gives \( T_o=41.598 \) cm\(^{-1}\). Using this theoretical term value of \( T_o \) and vibrational frequencies calculated by CASSCF, \( T_o \) of each isotopomer is calculated to be compared with the experiment (Table II). Though absolute values are not exactly matched, the trend with the H/D substitution is quite consistent with the experiment. The anharmonicity especially along the predissociative N–H axis should be largely responsible for any mismatch between theory and experiment.

Term values for vibrational levels of each isotopomer in the \( \tilde{A} \) state are obtained by subtracting the transition frequency of the origin band from the measured frequencies of vibronic bands. The measured vibrational term values of all isotopomers, which are given with respect to the zero-point level, are summarized in Table III with appropriate assignments. The isotopic substitution provides the most conclusive clue to the proper mode assignment as the fundamental frequency of a particular mode shows a systematic shift upon isotopic substitution depending on the extent of involvement of the substituted nuclear motion in the corresponding normal mode. The frequencies of the amino-wagging mode are 636.4 cm\(^{-1}\) for CH3NH2, 546.5 cm\(^{-1}\) for CH3NHD, and 482.6 cm\(^{-1}\) for CH3ND2. The fundamental frequencies and their isotopic shifts are in excellent agreement with the \( \tilde{X} \) state.

B. Vibrational term values and anharmonicity fitting

From the spectral analysis, the band origins of CH3NH2, CH3NHD, CH3ND2, CD3NH2, CD3NHD, and CD3ND2 are accurately located to be 41 664, 41 844, 42 035, 41 793, 41 948, and 42 139 cm\(^{-1}\), respectively (Fig. I). Thus it is quite secure to state that the long time confusion about the location of the origin band of the \( \tilde{A} \)-\( \tilde{X} \) transition for any methyamine isotopomer is now completely settled.\(^{10-15}\) Band origins (\( T_o \)) of various isotopomers are listed in Table II. It should be noted that \( T_o \) is blueshifted with the H → D substitution. Very interestingly, the amount of \( T_o \) shift is found to be larger when the amino moiety is deuterated compared with that caused by the methyl group H/D substitution.

\[ T_o = T_e + ZPE(\tilde{A}) \]

\[ T_e = T_e + ZPE(\tilde{X}) \]

Uncertainties in the assignment of each band to the appropriate isotopomer are possible due to vibronic couplings to optically dark states (see the text).

![FIG. 3. (a) The R2PI spectrum of CD3ND2 for the \( \nu_7 \) (CH3 rock) and 2\( \nu_9 \) (ND3 wag) vibronic bands with (b) the simulation based on parameters listed in Table I. The normal mode description for \( \nu_7 \) and \( \nu_9 \) is given. The relatively poor simulation to the experiment in the high internal energy range is possibly due to vibronic couplings to optically dark states (see the text).](image-url)

| TABLE II. Experimental and theoretical band origins of various methylamine isotopomers (cm\(^{-1}\)). |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( T_o \) \(^\dagger\)           | 41 598          | 41 844          | 42 035          | 41 793          | 41 948          | 42 139          |
| ZPE (X)                         | 15 000          | 14 220          | 13 430          | 12 761          | 11 977          | 11 184          |
| ZPE (\( \tilde{A} \))\(^b\)     | 13 893          | 13 207          | 12 519          | 11 685          | 11 017          | 10 338          |
| \( T_e \) (Calc.)               | 40 490          | 40 584          | 40 686          | 40 521          | 40 637          | 40 752          |
| \( T_e \) (Expt.)               | 41 664          | 41 844          | 42 035          | 41 793          | 41 948          | 42 139          |

\(^\dagger\)TD-DFT result calculated by the B3LYP method with a basis set of 6-31+ +G(d,p). \( T_o = T_e + ZPE(\tilde{A}) \)

\(^b\)ZPE for the torsional mode is not included since it is almost zero in the \( \tilde{A} \) state.
Vibrational good agreement with the respective experimental values of $\nu_{6}$ (see the text for details).

$\nu_{7}$ has been given in Ref. 17.

Considering anharmonic couplings associated with $\nu_{7}$ and $\nu_{9}$ modes, it is then possible to extract at least three anharmonicity constants from the fit using the following equation: \[ G_{0}(\nu_{7}, \nu_{9}) = \omega_{\nu_{7}}^{0} \nu_{7} + \omega_{\nu_{9}}^{0} \nu_{9} + \lambda_{\nu_{7} \nu_{9}}^{0} (\nu_{7})^{2} + \lambda_{\nu_{9} \nu_{9}}^{0} (\nu_{9})^{2} + \lambda_{\nu_{7} \nu_{9}}^{0} (\nu_{7}) (\nu_{9}), \] where $\nu_{7}$ and $\nu_{9}$ are the vibrational quantum numbers for $\nu_{7}$ and $\nu_{9}$, respectively, and $G_{0}$ represents the term values of

<table>
<thead>
<tr>
<th>Vibrational levels</th>
<th>CH$_3$NH$_2$</th>
<th>CH$_3$NHD</th>
<th>CH$_3$ND$_2$</th>
<th>CD$_3$NH$_2$</th>
<th>CD$_3$NHD</th>
<th>CD$_3$ND$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0^0_0 [T_{00}^1]$</td>
<td>0 [41664±1]</td>
<td>0 [41844±1]</td>
<td>0 [42035±1]</td>
<td>0 [41793±4]</td>
<td>0 [41948±2]</td>
<td>0 [42139±1]</td>
</tr>
<tr>
<td>$\nu_{9}$</td>
<td>634(+2.4)</td>
<td>552(5.4)</td>
<td>480(0.7)</td>
<td>549(11.3)</td>
<td>518(1.7)</td>
<td>456(-3.1)</td>
</tr>
<tr>
<td>$\nu_{7}$</td>
<td>1000(10.9)</td>
<td>...</td>
<td>1000(9.9)</td>
<td>819(-11.0)</td>
<td>825(6.3)</td>
<td>799(-4.1)</td>
</tr>
<tr>
<td>$2\nu_{9}$</td>
<td>1275(2.1)</td>
<td>1122(6.4)</td>
<td>970(1.14)</td>
<td>1139(11.4)</td>
<td>1038(-2.7)</td>
<td>932(4.8)</td>
</tr>
<tr>
<td>$\nu_{7} + \nu_{9}$</td>
<td>1603(-31.0)</td>
<td>1587(-16.5)</td>
<td>1491(-9.7)</td>
<td>1404(7.0)</td>
<td>1349(0.7)</td>
<td>1276(6.5)</td>
</tr>
<tr>
<td>$3\nu_{9}$</td>
<td>1938(28.6)</td>
<td>...</td>
<td>1476(7.3)</td>
<td>1694(-8.1)</td>
<td>1577(3.6)</td>
<td>1402(-2.4)</td>
</tr>
<tr>
<td>$2\nu_{7}$</td>
<td>2002(8.3)</td>
<td>2123(9.1)</td>
<td>1997(-0.3)</td>
<td>1661(-8.8)</td>
<td>1635(-1.2)</td>
<td>1592(0.6)</td>
</tr>
<tr>
<td>$\nu_{7} + 2\nu_{9}$</td>
<td>2262(-16.9)</td>
<td>2156(6.4)</td>
<td>2017(-4.6)</td>
<td>1989(17.9)</td>
<td>1887(10.9)</td>
<td>1741(-3.8)</td>
</tr>
<tr>
<td>$4\nu_{9}$</td>
<td>2520(-25.8)</td>
<td>...</td>
<td>1975(-3.9)</td>
<td>2267(-16.6)</td>
<td>2112(-2.1)</td>
<td>1890(-0.4)</td>
</tr>
<tr>
<td>$2\nu_{7} + \nu_{9}$</td>
<td>2656(9.0)</td>
<td>...</td>
<td>...</td>
<td>2171(-8.2)</td>
<td>2067(2.0)</td>
<td>...</td>
</tr>
<tr>
<td>$\nu_{7} + 3\nu_{9}$</td>
<td>2956(32.1)</td>
<td>...</td>
<td>...</td>
<td>2552(0.3)</td>
<td>2433(0.9)</td>
<td>2229(-0.2)</td>
</tr>
<tr>
<td>$3\nu_{7}$</td>
<td>3012(-1.8)</td>
<td>3099(-3.0)</td>
<td>3020(-1.5)</td>
<td>2528(8.6)</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$2\nu_{7} + 2\nu_{9}$</td>
<td>3288(-12.4)</td>
<td>3096(4.7)</td>
<td>...</td>
<td>2731(0.6)</td>
<td>2544(-3.6)</td>
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</tr>
<tr>
<td>$5\nu_{9}$</td>
<td>...</td>
<td>...</td>
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<td>...</td>
</tr>
<tr>
<td>$3\nu_{7} + \nu_{9}$</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>3012(2.9)</td>
</tr>
<tr>
<td>$\nu_{7} + 4\nu_{9}$</td>
<td>...</td>
<td>3310(0.9)</td>
<td>...</td>
<td>3130(-10.5)</td>
<td>...</td>
<td>2724(1.4)</td>
</tr>
<tr>
<td>$2\nu_{7} + 3\nu_{9}$</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>3040(0.9)</td>
</tr>
<tr>
<td>$\nu_{7} + 5\nu_{9}$</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>3225(0.2)</td>
</tr>
<tr>
<td>$4\nu_{7}$</td>
<td>...</td>
<td>...</td>
<td>3376(-2.8)</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

Table III. Measured electronic origins and term values (cm$^{-1}$) for the vibrational levels of six methylamine isotopomers in the $\tilde{A}$ state. The numbers in parentheses are the differences between the measured values and fitted ones ($\nu_{obs} - \nu_{th}$) (see the text for details).

Table IV. Ab initio vibrational frequencies (cm$^{-1}$) of methylamines in the $\tilde{A}$ states. The torsional mode ($\nu_{12}$) was not included. The symmetry species (A',A'') is classified according to the MS group of Cs where the molecular plane containing a C=H bond bisects the HNH angle. The symmetry consideration for the torsional mode in the CNPI group of $\Gamma_{12}$ has been given in Ref. 17.
various quantum states with respect to the zero-point level. Measured experimental values are fitted to Eq. (4) to give the harmonic frequencies and anharmonicity constants associated with \( \nu_7 \) and \( \nu_9 \) modes. The fitted values are summarized in Table V, while the differences between the experiment and calculation are listed in Table III. There are large uncertainties for harmonic frequencies and anharmonic constants of \( \text{CH}_3\text{NH}_2 \) and \( \text{CH}_3\text{NHD} \), and this should be attributed to less accurately measured band positions due to both the intrinsic broad linewidth and severe overlaps of corresponding vibrionic bands.\(^{17,18}\) On the other hand, both harmonic frequencies and anharmonic constants are quite precisely determined for some isotopomers such as \( \text{CD}_3\text{ND}_2 \) and \( \text{CD}_3\text{NHD} \). The mode dependence of the effective torsional barrier height based on the following equation, introduced by Johnson and Sears:\(^{22}\)

\[
V(\phi) = E_{el}(\phi) + \sum_n \hbar \omega_n(\phi)(v_n + 1/2).
\]

Here \( E_{el}(\phi) \) is the electronic energy as a function of torsional angle, while \( \omega_n(\phi) \) and \( v_n \) are the vibrational frequency and number of quanta of the \( n \)th mode, respectively. The sum is over all vibrational modes except the torsional mode. For the \( \text{CH}_3\text{CH}_2 \) radical, it was reported in Ref. 22 that the torsional barrier is 17.6 \( \text{cm}^{-1} \) in the zero level and 10.9 \( \text{cm}^{-1} \) for the \( \nu=1 \) level of the \( \text{CH}_2 \) rocking mode. This calculation was carried out by using the B3LYP method with the basis set of 6-311++G(2df,2pd), and it reproduces the experimental result well.\(^{22}\) Here, we calculate the barrier height of \( \text{CH}_3\text{NH}_2(\tilde{A}) \) by the same way using Eq. (5) using the configuration interaction singles (CIS) method with the 6-311++G(2df,2pd) basis set. In Fig. 4, the calculated torsional barriers at the zero-point level, with one quantum of the \( \text{NH}_2 \) wag \( (\nu_9) \), and the level with one quantum of the \( \text{CH}_3 \) rock \( (\nu_7) \) are plotted as a function of the torsional angle. In the calculation, all degrees of freedom are relaxed except the torsional barrier of \( \text{CH}_3\text{CH}_2(\tilde{X}) \) and \( \text{CH}_3\text{NH}_2(\tilde{A}) \) should originate from the difference in the vibrational energy changes of two molecules with the change of the torsional angle.

Since the torsional motion is much slower compared to the other vibrational motions, it is reasonable to calculate the effective torsional barrier height based on the following equation, introduced by Johnson and Sears:\(^{22}\)

\[
V(\phi) = E_{el}(\phi) + \sum_n \hbar \omega_n(\phi)(v_n + 1/2).
\]

C. The torsional barrier height depending on the vibrational excitation

One of the interesting experimental findings is that the torsional barrier height increases when the amino wagging mode \( (\nu_9) \) is excited. That is, the torsional barrier height, which is 5 or 5.5 \( \text{cm}^{-1} \) at the zero-point energy level, increases to 19 \( \text{cm}^{-1} \) with \( \nu_9 \) mode excitation for \( \text{CH}_3\text{ND}_2 \) (Refs. 17 and 18) or \( \text{CD}_3\text{ND}_2 \). The mode dependence of the torsional barrier height of methyamine is especially intriguing when this is compared with that found for the \( \text{CH}_3\text{CH}_2 \) radical in the ground state. Sears et al.\(^{23}\) and Johnson and Sears\(^{22}\) found that the torsional barrier of \( \text{CH}_3\text{CH}_2(\tilde{X}) \) in the zero level is 17 \( \text{cm}^{-1} \) and it decreases to 10 \( \text{cm}^{-1} \) when one quantum of the \( \text{CH}_2 \) rocking mode is excited, which is the opposite trend to the case of \( \text{CH}_3\text{NH}_2(\tilde{A}) \). The \( \text{CH}_3\text{CH}_2(\tilde{X}) \) radical is isoelectronic to the \( \text{CH}_3\text{NH}_2 \) cation: the electronic structure of those two species should be similar. Accordingly, the electronic energy associated with the torsional motion is expected to be quite similar for \( \text{CH}_3\text{CH}_2(\tilde{X}) \) and \( \text{CH}_3\text{NH}_2(\tilde{A}) \). However, as pointed out earlier by Sears et al.\(^{21}\) and Johnson and Sears,\(^{22}\) when the torsional barrier height is small the change of the vibrational energy as a function of the torsional angle becomes the dominant factor in determining the effective torsional barrier height. Therefore, the explanation for the different mode dependence of

<table>
<thead>
<tr>
<th>( \omega_n )</th>
<th>( \omega_n^\prime )</th>
<th>( \lambda_n )</th>
<th>( \lambda_n^\prime )</th>
<th>( \chi_n )</th>
<th>( \chi_n^\prime )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{NH}_2 )</td>
<td>( \text{CH}_3\text{NHD} )</td>
<td>( \text{CH}_3\text{ND}_2 )</td>
<td>( \text{CD}_3\text{NH}_2 )</td>
<td>( \text{CD}_3\text{NHD} )</td>
<td>( \text{CD}_3\text{ND}_2 )</td>
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<td>981.4±22.3</td>
<td>1102.8±16.7</td>
<td>981.6±7.0</td>
<td>825.1±9.4</td>
<td>819.2±3.5</td>
<td>810.6±3.9</td>
</tr>
<tr>
<td>636.4±15.7</td>
<td>535.3±7.6</td>
<td>474.1±5.1</td>
<td>556.7±6.5</td>
<td>512.2±2.9</td>
<td>454.6±1.5</td>
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<tr>
<td>7.7±8.5</td>
<td>−22.9±6.2</td>
<td>8.5±2.7</td>
<td>4.9±2.8</td>
<td>−0.6±1.3</td>
<td>−7.4±2.0</td>
</tr>
<tr>
<td>0.006±4.5</td>
<td>11.2±2.7</td>
<td>5.1±1.5</td>
<td>3.5±1.5</td>
<td>4.1±0.9</td>
<td>4.5±0.4</td>
</tr>
<tr>
<td>8.5±7.2</td>
<td>−22.9±6.6</td>
<td>31.3±2.5</td>
<td>6.7±3.8</td>
<td>13.3±1.4</td>
<td>7.2±0.8</td>
</tr>
</tbody>
</table>

FIG. 4. The calculated torsional potential energy curves in the zero-point energy level, with the amino wagging mode \( (\nu_9) \) excitation, or with \( \text{CH}_3 \) rocking mode \( (\nu_7) \) excitation plotted vs the torsional angle around the \( \text{C}–\text{N} \) axis. The calculation was carried out by using the CIS method with the 6-311++G(2df,2pd) basis set.
fixed torsional angle to give the minimum energy and associated vibrational frequencies. The barrier height from the calculation is then found to be 9.2 cm$^{-1}$ for the zero-point level, while it is 29.8 cm$^{-1}$ for the level with one quantum of NH$_2$ wag ($\nu_9$) (Fig. 4). Even though the theoretical value does not reproduce the experiment perfectly in terms of the absolute value, the calculation still seems to be in good agreement with the experiment. Moreover, it is quite remarkable that the experimental trend of the torsional barrier with $\nu_9$ excitation is so well explained by the calculation. The other interesting theoretical finding is that the torsional barrier height is calculated to be 33.9 cm$^{-1}$ and the minimum energy structure is changed to the eclipsed form when the CH$_3$ rocking mode ($\nu_7$) is excited by one quantum (Fig. 4). This torsional potential for the $\nu_7$ ($v = 1$) level which is upsidedown compared to the that at the zero point or $\nu_9$ ($v = 1$) level could be responsible for the shape of the $\nu_7$ rovibrational band which is quite different from that of $\nu_9$, as clearly shown in Figs. 1 and 3. The dramatic change of the torsional potential upon vibrational excitation indicates that the torsional barrier height, especially when it is small, may be truly dominated by the vibrational energy of modes which are perpendicular to the torsional angle. At high internal energies where mode couplings are expected to be active, a more complicated expression for the barrier potential would be needed.

We have also carried out the same calculations for the cationic and ground neutral states of CH$_3$NH$_2$ (Table VI). In the cationic ground state of CH$_3$NH$_2$, the torsional barrier height is found to be 9.0, 19.5, and $-11.5$ cm$^{-1}$ for the zero level, $v = 1$ of the $\nu_7^c$ mode, and $u = 1$ level of the $\nu_9^c$ mode, respectively, when it is calculated by using the B3LYP method using the 6-311+G(2df,2pd) basis set. The negative sign of the torsional barrier height indicates that the torsional potential becomes upsidedown at the level with the $\nu_7^c$ mode excited, as in the case of CH$_3$NH$_2$(A). This calculation is consistent with the experimental observation that the torsional barrier becomes higher when one quantum of the NH$_2$ wagging mode is combined with the torsional mode.$^{1,12}$ Meanwhile, the torsional barrier for CH$_3$NH$_2$ in the ground electronic state is calculated to be quite high, giving the value of $V_6 = 688.0$ cm$^{-1}$. Amazingly, this is in excellent agreement with the experimental value of 690 cm$^{-1}$ for CH$_3$NH$_2$(X).$^{23}$ For ground state CH$_3$NH$_2$, the torsional barrier is quite high, the effect of vibrational energy on the barrier height is found to be less significant, giving $V_6 = 652$ or 684 cm$^{-1}$ for the level with the $\nu_9$ or $\nu_7$ mode excitation, respectively (Table VI). It is interesting to note that the NH$_2$ wagging mode excitation in CH$_3$NH$_2$(X) lowers the torsional barrier; this is in the opposite trend to the case of the excited or cationic state.

### IV. CONCLUSIONS

Here, the spectroscopic characterization of six methylamine isotopomers (CH$_3$NH$_2$, CH$_3$NHD, CH$_3$ND$_2$, CD$_3$NH$_2$, CD$_3$NHD, and CD$_3$ND$_2$) in the first electronically excited state has been carried out. The internal/overall rotation Hamiltonian is used for the spectral analyses for all observed rovibronic bands to give accurate vibrational band positions, associated rotational constants, rotational temperature, and predissociation lifetimes. Vibrational frequencies and anharmonicity constants associated with amino wagging ($\nu_9$) and methylrocking ($\nu_7$) modes are precisely determined to give the detailed shape of the potential energy surface along the corresponding nuclear motions. The torsional barrier height is found to be strongly dependent on vibrational excitation, and its increase with $\nu_9$ excitation is theoretically well explained for CH$_3$NH$_2$(A). In fact, the torsional barrier height seems to originate from vibrational energy as a function of torsional angle when the electronic origin for the torsional barrier is less important. In conclusion, the longtime confusion about the origin positions, vibrational assignments, and rotational structures of various methylamine isotopomers in the A state is completely resolved. Dynamical studies of methylamines based on this firm spectroscopic framework will be investigated in the near future.

### ACKNOWLEDGMENT

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