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The $5\nu_{\mathrm{NH}}$ and $5\nu_{\mathrm{ND}}$ vibrational bands of partially deuterated ammonia species

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Abstract

Absorption spectra of gaseous samples containing NH_2D and NHD_2 have been measured in the 11580–11880 and 15280–15610 cm^{-1} regions, corresponding to the $5\nu_{\mathrm{ND}}$ and $5\nu_{\mathrm{NH}}$ vibrational bands, respectively. Photoacoustic spectroscopy has been utilized for the measurement. The molecular constants of NH_2D in the $5\nu_{\mathrm{ND}}$ state and NHD_2 in the $5\nu_{\mathrm{NH}}$ state have been determined from the analysis of the obtained absorption spectrum. From the comparison of the constants with those of the vibrational ground states, structural changes caused by the stretching excitations have been elucidated. The HND bond angles are decreased by these excitations. The dependence of the molecular constants on the stretching quantum number has also been derived by simple Birge-Sponer and Dunham analyses.

Keywords: Ammonia; Deuterated species; Vibrational excitation; Fourth overtone state; Photoacoustic spectroscopy

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1. Introduction

Rigorous assignment of overtone spectra is often demanded in the study of the vibrationally mediated photodissociation (VMP), which is a challenging approach to understand bond-selective photodissociation. After the pioneering work by Crim's and Rosenwaks' groups for the HOD molecule [1,2], we recently investigated VMP of NH_3 [3], NH_2D, and NHD_2 [4]. In comparison with HOD and NH_3, the spectroscopic information was quite limited for NH_2D and NHD_2. In particular, no data are available for the fourth ND-stretching overtone state ($5\nu_{\mathrm{ND}}$) of NH_2D and the fourth NH-stretching overtone state ($5\nu_{\mathrm{NH}}$) of NHD_2. Thus, we started a study for assigning these overtone spectra to identify the intermediate states used in our recent study of VMP [4]. Furthermore, molecular constants of these overtone states determined in the spectroscopic analysis would provide new information on the intermediate structures. Consequently, additional information on the dynamics of VMP might be revealed in terms of the initial geometry of the dissociating wave packet in the upper electronic state.

The molecular structures of NH_2D and NHD_2 are asymmetric tops with the C_s symmetry. These molecules have two low-lying vibrational states arising from the tunneling in the well-known double minima in the symmetric bending mode, that is, inversion motion. Therefore, the rovibrational lines in the overtone spectra must be assigned by including the parity of this doubling, i.e., "*s* level" for the symmetric wave function against the inversion and "*a* level" for the anti-symmetric wavefunction. The molecular constants are available for the $\upsilon = 0$ state of NH_2D [5–9] and $\upsilon = 0$ [5–7,9,10] and $\upsilon = 1$ states [11] of NHD_2, where υ stands for the

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quantum number of the stretching modes of D-NH_2 and H-ND_2. For the other stretching states, no studies have been made to determine the molecular constants as far as we know. In the $\upsilon = 5$ region, the $5\nu_{NH}$ or $5\nu_{ND}$ band would be brighter than any other combination bands for one-photon transition as a result of the local-mode like character of the NH and ND stretching.

2. Experimental details

In practice, it is difficult to prepare a gaseous sample of pure NH_2D or NHD_2 in a cell, because an H/D exchange reaction takes place probably on the wall of the cell. Thus, we used mixtures of NH_3 and ND_3 with various mixing ratio to prepare equilibrated mixtures with different compositions of NH_2D and NHD_2, which were determined by the initial mixing ratio. Three types of gas mixtures containing NH_2D and NHD_2 were prepared by mixing NH_3 (Nippon-Sanso 99.999%) and ND_3 (Isotec 99.38 atom%) at the ratios of 3:1, 1:1, and 1:3 (hereafter cited as 25, 50, and 75% deuterated samples, respectively). These gas mixtures were kept for more than one week to make the H/D exchange reaction equilibrated. Absorption spectra were measured by utilizing photoacoustic (PA) spectroscopy [12,13] for five samples with different compositions: pure NH_3, pure ND_3, and the three gas mixtures.

Since the experimental procedure is similar to the previous one [3], the experimental apparatus and procedure are described briefly. A homemade PA cell was filled with each gas sample at the pressure of 20–100 Torr, and the laser beam for the overtone excitation was introduced into the PA cell. A dye laser (Lambda Physik FL3002) pumped by a XeCl excimer laser (Lambda Physik EMG 201MSC) was used for the excitation. This laser system produced 10-mJ/pulse wavelength-tunable light with a linewidth of ca. 0.2 cm^{-1}. The acoustic signal induced by the photoabsorption was detected with a condenser microphone (Rion UC-53AH) installed in the PA cell. During the PA spectrum measurements, the laser intensity was monitored with a photodiode (Hamamatsu S1336-5BQ) and used to normalize the PA signal. The wavenumbers of absorption peaks in the 11 580–11 880 cm^{-1} region were calibrated by using the absorption lines in the $2\nu_1 + \nu_2 + \nu_3$ band of H_2O [14], whereas the absorption lines in the $5\nu_{NH}$ band of NH_3 were used as wavenumber standards in the 15 280–15 610 cm^{-1} region [15]. All measurements were performed at room temperature.

3. Analysis of the spectra

For rotational assignments of the absorption peaks and determination of the molecular constants, we repeated the following three-step procedure: 1. Computer simulation performed with a set of trial/improved molecular constants; 2. Tentative assignment of some rotational peaks comparing the simulated spectrum with the measured one; and 3. Optimization of the molecular constants by a non-linear least-squares fitting of the transition wavenumbers with respect to the assigned peaks. This procedure was repeated until almost all of the peaks were assigned, and also the standard deviation went down below the laser linewidth of ca. 0.2 cm^{-1}.

For the vibrationally excited states of NH_2D and NHD_2, an ordinary rigid rotor Hamiltonian for asymmetric top molecules was used [16]:

$$^{p}H_{\upsilon} = {}^{p}T_{\upsilon} + {}^{p}A_{\upsilon}J_a^2 + {}^{p}B_{\upsilon}J_b^2 + {}^{p}C_{\upsilon}J_c^2. \quad (1)$$

The superscript p is the parity for the inversion motion of the ammonia molecules. For each parity state of NH_2D ($5\nu_{ND}$) and NHD_2 ($5\nu_{NH}$), the molecular constants of $^{p}T_{\upsilon}$, $^{p}A_{\upsilon}$, $^{p}B_{\upsilon}$, and $^{p}C_{\upsilon}$ were determined by the present analysis.

For the vibrational ground states of NH_2D [5–9] and NHD_2 [5–7,9,10], the molecular constants including the centrifugal distortion constants and the vibration–rotation interaction constants have been determined by several groups. We found that all mentioned sets of the ground-state molecular constants gave the same molecular constants of the overtone states within experimental uncertainty. In the present analysis, the full sets of the ground-state molecular constants reported by Kartha and co-workers [8,10] were used for both isotopomers.

4. Results

4.1. The $5\nu_{ND}$ band region (11 580–11 880 cm^{-1})

Absorption spectra of the five samples in the 11 580–11 880 cm^{-1} region were measured with a sample pressure of 100 Torr (1.3×10^4 Pa). The obtained spectra are shown in Fig. 1.

For pure NH_3, absorption peaks are observed in the energy region below 11 750 cm^{-1}, as shown in Fig. 1A. No absorption peaks have been reported in this region. These peaks are located at the high energy end in the $3\nu_1 + \nu_4$ vibrational band (3 quanta in the symmetric stretching and 1 quantum in the anti-symmetric bending) of NH_3 [17].

For pure ND_3, many peaks were observed in the energy region below 11 730 cm^{-1}, as shown in Fig. 1E. These peaks are assigned to the rovibrational transitions from the ground state to the $5\nu_1$ (5 quanta in the symmetric stretching) and/or $4\nu_1 + \nu_3$ states (4 quanta in the symmetric stretching and 1 quantum in the anti-symmetric stretching) of ND_3, because the band origins are estimated, respectively, to be 11 647 and 11 655 cm^{-1} by a model calculation utilizing the simplified model reported by Kauppi and Halonen [18].