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# High-resolution far-infrared synchrotron FTIR spectrum of the $\nu_{12}$ band of formamide-$d_1$ ($DCONH_2$)

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ABSTRACT

The spectrum of the $\nu_{12}$ band of formamide-$d_1$ ($DCONH_2$) was recorded using a synchrotron Fourier transform infrared (FTIR) spectrometer coupled to the Australian Synchrotron THz/Far-IR beamline, with an unapodized resolution of 0.00096 $cm^{-1}$ in the 350–210 $cm^{-1}$ region. For the first time, rovibrational constants up to five quartic and two sextic terms were derived for the $\nu_{12} = 1$ state through the fitting of a total of 2072 far-infrared transitions using Watson's *A*-reduced Hamiltonian in the $I^r$ representation with a root-mean-square (rms) deviation of 0.000073 $cm^{-1}$. The band centre of the $\nu_{12}$ band of $DCONH_2$ was found to be 289.3327553(47) $cm^{-1}$ although the experimental uncertainty was limited to ±0.0002 $cm^{-1}$. Ground state rovibrational constants of $DCONH_2$ up to five quartic and two sextic constants were derived from a fit of 847 ground state combination differences (GSCDs) obtained from the infrared transitions of the $\nu_{12}$ band, together with 6 previously reported microwave transitions, with a rms deviation of 0.000108 $cm^{-1}$. The ground state rotational constants (*A*, *B*, and *C*) of $DCONH_2$ were improved while the ground state centrifugal distortion constants were accurately obtained for the first time. The uncertainty of the measured infrared lines was estimated to be ±0.0002 $cm^{-1}$. From the ground state rotational constants, the inertial defect of $DCONH_2$ was calculated to be 0.0169412(11) uÅ$^2$.



## 1. Introduction

Formamide ($HCONH_2$) is an important molecule to study mainly because it contains the simplest amide with a peptide bond ($NH_2$-CO). This peptide bond has been long established to be the building block of proteins and polypeptides of amino acids [1,2]. Furthermore, the formamide molecule has been detected in the interstellar medium in 1971 [3], and it is considered to be the potential precursor of acetamide [4] which also carries a peptide bond. Molecular studies on these two peptide-carriers are useful for the understanding of interstellar prebiotic chemistry [5].

Infrared spectroscopic studies on the formamide molecule were carried out as early as 1960 when Suzuki [6] measured the vibrational spectra of formamide ($HCONH_2$) and its deuterated species ($HCOND_2$, $DCONH_2$, and $DCOND_2$) in their liquid phases. In his work, the band centers of 9 fundamental bands of each of the 4 molecules were obtained. In 1960, Costain and Dowling [7] were among the first to study the microwave spectrum and molecular structure of formamide and some of its isotopologues. They suggested a non-planar, pyramidal structure for the molecule based on the inertial defects and other evidence through various isotologues. In 1974, Hirota et al. [8] concluded the formamide molecule to be planar, based upon microwave spectroscopy and low resolution far-infrared data for $^{13}C$ and $^{18}O$ species of $NH_2CHO$ and $ND_2CHO$. Later in 1983, Sugawara et al. [9] recorded the Fourier transform infrared (FTIR) spectra of $HCONH_2$ and $DCONH_2$ in the vapour phase in the 4000–400 $cm^{-1}$ region with a resolution of 0.24 $cm^{-1}$. They identified the band centers of most of the fundamental bands of both formamide molecules and derived the rotational constants (*A* and *B*) of the $\nu_{12} = 2$, and $\nu_{12} = 3$ states of $HCONH_2$ for the first time. Furthermore, high-resolution infrared spectra of $HCONH_2$ and $DCONH_2$ were recorded by Brummel et al. [10] in 1994 using molecular-beam optothermal spectroscopy in the 3456–3426 $cm^{-1}$ region of the symmetric NH stretching mode (the $\nu_2$ band). In their work, the rotational constants (*A*, *B*, and *C*) of the ground state and excited state of $HCONH_2$ and $DCONH_2$ were derived with a rms deviation of 0.0026 $cm^{-1}$ and 0.0048 $cm^{-1}$, respectively.

The latest reported high-resolution FTIR studies of the formamide vapour have been on the $HCONH_2$ molecule. In 1999, McNaughton et al. [11] recorded the far-IR spectrum of $HCONH_2$

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with a resolution of 0.0035 $cm^{-1}$ in the 650–100 $cm^{-1}$ region. They derived the rovibrational constants of the ground state, $v_{12} = 1$, $v_{12} = 2$, $v_{11} = 1$, and $v_9 = 1$ states up to 4 sextic constants with high accuracy. The band centers and resonance parameters of the 3 perturbing bands ($v_9$, $v_{11}$ and $2v_{12}$) were also accurately obtained. Moreover, they identified the band centers of the 12 fundamental bands and the various combination bands of $HCONH_2$ using a low-resolution spectrum in the 4000–200 $cm^{-1}$ region. In 2009, the band centers and rovibrational constants of the 4 bands ($v_9$, $v_{11}$, $v_{12}$ and $2v_{12}$) of $HCONH_2$ were largely improved by Sztraka and Horneman [12] in their FTIR study using a resolution of 0.00125 $cm^{-1}$ in the 1060–90 $cm^{-1}$ region. Furthermore, in 2009, new measurements of the microwave spectrum (340–49 GHz) of $HCONH_2$ have been reported by Kryvda et al. [13]. A detailed analysis (including that of Coriolis interaction couplings) of the rotational spectra of $v_9$, $v_{11}$, $v_{12}$ and $2v_{12}$ excited vibrational states of the main isotopic species ($HCONH_2$) as well as of the ground states of the $^{13}C$, $^{15}N$, and $^{18}O$ substituted species were carried out.

High-resolution FTIR spectroscopic studies on $DCONH_2$ remain very limited. A literature search showed that rovibrational constants of the ground state and all excited states of $DCONH_2$ have not been reported so far. In this work, we report the first rovibrational analysis of the unperturbed $v_{12}$ band of $DCONH_2$ measured at a resolution of 0.00096 $cm^{-1}$ using synchrotron FTIR spectroscopy in the 350–210 $cm^{-1}$ region. Rovibrational constants up to two sextic terms are accurately obtained for the $v_{12} = 1$ state of $DCONH_2$ for the first time. Moreover, the rotational constants ($A$, $B$, and $C$) of the ground state were improved and for the first time, its rovibrational constants were accurately obtained from a simultaneous fit of the ground state combination-differences (GSCDs) which were derived from the IR transitions of the $v_{12}$ band, and the 6 microwave transitions previously reported [7].

## 2. Experimental details

Liquid formamide-$d_1$ ($DCONH_2$) of 98% atomic purity in deuterium (D) was obtained from Sigma-Aldrich Corporation. $DCONH_2$ samples in the vapour phase were obtained by using direct low-pressure vaporization from the liquid at the ambient temperature of 296 K. The FTIR spectra of the vapour-phase $DCONH_2$ were measured in the 350–210 $cm^{-1}$ region at a resolution of 0.00096 $cm^{-1}$ using Bruker IFS 125HR Fourier transform spectrophotometer located at the THz/far-infrared beamline (beam current of about 200 mA) of the Australian Synchrotron. A liquid helium-cooled Si bolometer and 6 μm Mylar beamsplitter were used in spectral collection, which was carried out at an ambient temperature of about 296 K. The absorption cell with a 0.55 m base path length was adjusted for 44 passes to obtain a total optical path length of 24.2 m. The spectra of $DCONH_2$ were recorded at a vapour pressure of 0.475 mbar (mb) (measured by a capacitance pressure gauge) to ensure non-saturation of strong absorption lines. The final spectrum for the sample was produced by co-adding 130 scans with a total scanning time of about 13 h. The interferogram of the spectrum was apodized with the four-point function using a zero-filling factor of 8.

The IR absorption lines of the $v_{12}$ band of $DCONH_2$ were calibrated using a total of 27 $H_2O$ absorption lines present in the spectrum in the 500–80 $cm^{-1}$ region. The observed $H_2O$ wavenumber values were fitted against standard values taken from HITRAN (2012) [14] with a relative precision of 0.00016 $cm^{-1}$. The average full width at half maximum (FWHM) of the lines was found to be 0.0014 $cm^{-1}$. The absolute uncertainty of the measured $DCONH_2$ lines is estimated to be about one-tenth of the linewidth, that is approximately ±0.0002 $cm^{-1}$ for all absorption lines in the spectrum.

## 3. Rovibrational analysis

The formamide-$d_1$ ($DCONH_2$) molecule is a near prolate asymmetric top with a symmetry parameter κ of approximately −0.914 and has been established to be essentially planar [10,11]. $DCONH_2$ belongs to the $C_s$ point group (the molecular structure is shown in Fig. 1) and gives rise to 12 fundamental modes of vibration that are all infrared active. The $v_{12}$ band of lowest frequency is assigned to the out-of-plane $NH_2$ inversion mode, having $A''$ symmetry.

The spectrum of the $v_{12}$ band of $DCONH_2$ (Fig. 2) shows a profile characteristic of a $C$-type band. An intense central $Q$ branch of the band, made up mostly of transitions belonging to $^PQ_1$ and $^RQ_0$, is located at about 289.2 $cm^{-1}$. The other absorption lines of $\Delta J = J' - J'' = 0$ are situated in the $P$ and $R$ branches, with distinct $Q$ clusters observed for $K_a' \geq 4$ located at regular wavenumber intervals of approximately $2A - (B + C) \approx 3$ $cm^{-1}$. Besides the $Q$ clusters, the $P$ and $R$ branches are made up of overlapping series located about $2A$ (≈3.6 $cm^{-1}$) apart and each series of transitions shares the same $K_a'$ but differs in quantum number $J$. Within each series, absorption lines of unresolved asymmetry doublets are well-separated by about $B + C$ (≈0.7 $cm^{-1}$). As with a $C$-type band (e.g. $v_{12}$ band of $HCONH_2$), asymmetric splitting begins at a higher $J$ value as $K_a$ increases. The assignments of upper state $J$-series of $^PP_1$ to $^PP_5$ in the $P$ branch and $^RR_2$ to $^RR_6$ and the $^RQ_8$ cluster in the $R$ branch are shown in Fig. 3(a) and Fig. 4(a) respectively.

In the preliminary analysis of the spectrum, the ground state rotational constants ($A''$, $B''$ and $C''$) of $DCONH_2$ in Refs. [7,10] were used for both the ground and the $v_{12} = 1$ state as initial values, together with the centrifugal distortion constants reported of $HCONH_2$ [11,12]. The band center of the $v_{12}$ band of $DCONH_2$ was first estimated to be 289.2 $cm^{-1}$ from the intense $Q$ branch region of the spectrum (Fig. 2).

### 3.1. Upper state ($v_{12} = 1$) analysis

The approximate line positions calculated from the preliminary rovibrational constants of the ground state and $v_{12} = 1$ state of $DCONH_2$, and the profile of the $C$-type $v_{12}$ band of $HCONH_2$ [11,12] were used as a guide in the analysis of the $v_{12}$ band of $DCONH_2$. The assignment began with strong absorption lines belonging to transitions of low $J'$ values of $K_a' = 4$ to 7 in the $P$ and $R$ branches. The ground state rovibrational constants from Refs. [7,10,12] were taken in a fitting program developed by Maki

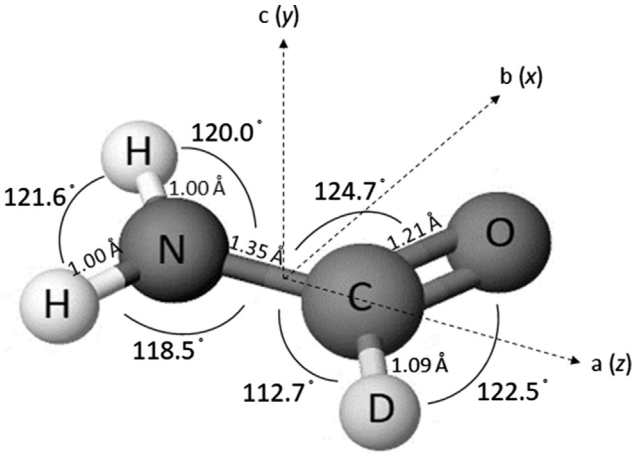


**Fig. 1.** The molecular structure of formamide-$d_1$ ($DCONH_2$) ($I^r$ representation). Note: The bond angle and bond length (Å) are taken from Ref. [8], based on the structure of formamide and its isotopologues.