Ab initio studies on molecular conformation and vibrational spectra of propionamide

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Abstract

The molecular conformation, ground state molecular vibrations and force field of propionamide have been determined at the Hartree–Fock level using the basis sets 6-31 + g* and 6-31 + + g**. The potential energy surface of propionamide was investigated by the ab initio method with full geometry optimization. The *trans* CCCN conformation of propionamide with methyl group in the staggered conformation to the CO group was found to be more stable than all the other conformations. The vibrational spectral analysis has been carried out for *trans* staggered conformer of propionamide and its C- and N-deuterated molecules. The present results are compared with previous studies on the structure and vibrational spectra of propionamide and discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Propionamide; Ab initio; Normal coordinate analysis; Potential energy scan; Vibrational assignment

1. Introduction

Amides are a major functional group in organic chemistry and they also form key linkages in natural macromolecules such as proteins and polypeptides and synthetic macromolecules such as nylons and kevlar [1]. Amides can also coordinate to metal ions and the complexes have potential applications. The structure of 3-mercapto propionamide which is present in captopril, an effective anti hypersensitive drug has recently been investigated [2].

Vibrational spectroscopic studies, which involve both experimental and theoretical work, have received much attention on simple amides such

as formamide and acetamide and their *N*-methyl derivatives [3,4]. However, the higher homologue of acetamide namely propionamide has received only scanty attention. Kuroda et al. [5] have investigated the infrared and Raman spectra of propionamide and its C- and N-deuterated isotopic molecules by classical normal coordinate analysis using the Urey–Bradley force field. Extensive ab initio studies of the vibrational spectra of acetamide have been published [3,4]. We had recently reported the simulation of the infrared spectra of acetamide using the extended molecular mechanics method [6].

Several conformations are possible when one of the hydrogen atoms in the methyl group of acetamide is substituted by a CH₃ group as in propionamide. The possible molecular conformations of propionamide are shown in Fig. 1. The conformation of propionamide can be assigned on the basis of the orientation of the C–C–C–N or C–C–C=O moiety.

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Fig. 1. Conformational isomers of propionamide.

If the orientation of the C–C group is *trans* to C–N, then it is referred as the *trans* conformer, and if the C–C group is *cis* to the C–N group then it is referred as the *cis* conformer. The orientation of the CH₃ group may be eclipsed, gauche or staggered with respect to the CO group. Preliminary studies by microwave spectroscopy coupled with the ab initio calculations using the basis sets such as 6-31g*, 6-311g* and 6-311 + g* at Hartree–Fock level as well as MP2 level have indicated that propionamide has a non-planar geometry [1], the calculated dihedral angle OCCC varied from –6, –7.5, –13.5 to –23°, respectively. However, the authors have suggested from preliminary microwave studies that propionamide has nearly planar heavy atom structure

and that MP2/6-311 + g** computations have over-estimated the OCCC dihedral angle. The X-ray crystal structure analysis has shown that propionamide exists in the *trans* configuration and the heavy atom skeleton is non-planar with a dihedral angle of 172° [7].

Since the intrinsic features of the empirical force field used in normal coordinate analysis lie in their uncertainty, particularly with respect to the interaction force constants, it was felt desirable to carry out the ab initio molecular orbital studies at the HF/6-31 + g* and HF/6-31 + g** to determine the molecular conformation and the force field, then examine the ground state vibrational frequencies and their assignment for

Fig. 2. PES scan for dihedral angle N–C–C–C for the basis set 6-31+g*.

propionamide and its C- and N-deuterated molecules, $\text{CH}_3\text{CH}_2\text{COND}_2$, $\text{CH}_3\text{CD}_2\text{CONH}_2$ and $\text{CH}_3\text{CD}_2\text{COND}_2$. The results are discussed by comparison with the empirical assignments of Kuroda et al. [5] and the previous studies on acetamide [3,4]. The infrared and Raman spectra of propionamide have also been recorded. A discussion of the infrared and Raman band intensities of propionamide at the equilibrium geometry is also presented.

2. Materials and methods

2.1. Computational details

The ab initio calculations at the Hartree–Fock level using the basis sets 6-31+g* and 6-31++g** have been performed by employing GAUSSIAN 94 program

[8]. First, the fully optimized geometry of propionamide was obtained by the analytical gradient methods. The Hartree–Fock cartesian force constants, vibrational frequencies and their intensities were obtained for the optimized geometry. The GMAT program of Schachtschneider [9] was employed to obtain the B and G matrices in internal coordinates for the optimized geometry. The atoms in Fig. 1 are numbered to define the optimized bond lengths and bond angles, and to specify the internal coordinates used in the calculation of vibrational spectra. The force constants in cartesian coordinates were transformed to force constants in local coordinates. The force field of propionamide was also obtained in symmetry coordinates through appropriate transformations. The secular equation $|\text{GF} - E\lambda| = 0$ was then solved to obtain the vibrational frequencies and their potential energy distributions for propionamide and its deuterated molecules.

Fig. 3. PES scan for dihedral angle N–C–C–C for the basis set 6-31++g**.

2.2. Spectroscopic measurements

The infrared spectrum of propionamide (Merck chemical) was recorded on a FT infrared Bruker 5 spectrophotometer using Nujol mull technique. The FT Raman spectrum was recorded for the solid sample using Bruker RFS 100/s spectrometer employing Nd³⁺ YAG laser with 30 mW power at the sample, keeping the detector at liquid nitrogen temperature.

3. Results and discussion

The results of the calculations on the molecular conformation of propionamide are discussed first. This is followed by a brief discussion of the assignment of the vibrational frequencies and band intensities.

3.1. Molecular conformation

The potential energy scan for the dihedral angle N–C–C–C of propionamide from 0 to 300° was carried out for both the basis sets 6-31 + g* and 6-31++g** and the potential energy curve is shown in Figs. 2 and 3. The global minima was obtained at a dihedral angle of about 180°. As noted from Figs. 2 and 3, the *trans* configuration is more stable than the *cis* configuration. The *cis* conformation of propionamide with a dihedral angle N–C–C–C of 0° appears at the maxima in the potential energy curve. At the dihedral angle of 180° propionamide possesses C_s symmetry. However, as seen from Figs. 2 and 3, the potential energy curve has a flat region extending from 170 to 190°. In the neighbourhood of the dihedral angle of 180° propionamide possesses C₁ symmetry.

Similar potential energy scans were performed for the CH₃ group orientation with respect to the CO

Fig. 4. PES scan for dihedral angle H–C–C–C for the basis set 6-31++g**.

group by varying the dihedral angle H–C–C–C from 0 to 180° for both the *cis* and *trans* configurations of propionamide using both the basis sets 6-31 + g* and 6-31++g** and the results are shown in Fig. 4 for the basis set 6-31++g**. Fig. 4 exhibits two minima. The first minima is at a dihedral angle of 60° and another

for the dihedral angle of 180°. The orientation of CH₃ group at a dihedral angle 60° refers to gauche orientation and 180° to staggered orientation. The total energy obtained for both gauche and staggered methyl orientation in *trans* conformer is identical for the ab initio calculation using 6-31++g**. However, for the

Table 1

Total energies in hartrees of different conformers of propionamide

Conformers		C_s		C_1	
		6-31 + g*	6-31++g**	6-31 + g*	6-31++g**
<i>trans</i>	Eclipsed	–247.01453	–247.0310513	–247.01895	
	Staggered	–247.0192769	–247.035355	–247.019293	–247.0353598
	Gauche			–247.0192769	–247.0353598
<i>cis</i>	Eclipsed	–247.01734	–247.0331921		
	Staggered	–247.0101296	–247.0262841		
	Gauche			–247.0171348	–247.0331925

Table 2
Geometrical parameters of C_1 conformer of propionamide

Parameters ^{a,b}	X-ray Ref. [7]	6-31 + g [*]	6-31 + +g ^{**}
C–N	1.327	1.3571	1.3568
C=O	1.254	1.2003	1.2005
C–C	1.476	1.5191	1.5187
C–C(me)	1.502	1.5245	1.5239
N–H ^c	1.066	0.9958	0.9939
C–H ^e	0.948	1.0868	1.0884
C(me)–H ^h	1.070	1.0822	1.0838
C(me)–H ^k	0.909	1.0839	1.0824
C(me)–H ^l	1.170	1.0839	1.0854
N–C=O	121.7	121.8	121.78
N–C–C	117.1	115.07	115.07
C–C–C	115.7	113.1	113.18
H ^c –N–C	118.0	118.4	118.43
H ^f –N–C	113.4	122.31	122.38
H ^g –C–C	103.6	109.0	107.16
H ^h –C–C		107.12	108.73
H ^k –C(me)–C	111.1	110.98	111.06
H ^l –C(me)–C	119.2	111.1	110.9
H ^m –C(me)–C		110.03	110.0
N–C–C–C(me)	171.8	165.6	169.09
O=C–C–C(me)	– 10.3	14.79	– 11.54
H–C(me)–C–C	179.4	– 178.6	178.5

^a Bond lengths are in angstroms and bond angles and dihedral angles in degrees.

^{c,f,g,h,k,l,m} Denote the atoms defined in Fig. 1.

basis set, 6-31 + g^{*}, the staggered methyl orientation represents the global minima. Hence in the present calculations, the *trans* conformer of staggered methyl orientation of propionamide is considered. In the *cis* conformer, gauche conformer possess C_1 symmetry and has higher energy than eclipsed methyl orientation. Most molecules possessing a CH₃–CH₂– group have barriers to internal rotation of the methyl group generally in the range of 12–14 kJ mol^{–1}. The barrier height was calculated to be 11.3 kJ mol^{–1} by the ab initio method using the basis set 6-31 + +g^{**} for *trans* propionamide.

The geometry optimization for propionamide was carried out for all the conformations shown in Fig. 1. The total energies for each of the conformations are given in Table 1. From the total energy, in both the basis sets, it was found that *trans* conformation of propionamide with staggered orientation of the CH₃ group with respect to CO group represents the global minima.

The optimized geometry obtained by the ab initio

method for both the basis sets 6-31 + g^{*} and 6-31 + +g^{**} is compared with that reported from X-ray diffraction studies for the solid at 123 K in Table 2 [7]. There is good agreement between the calculated and experimental values of the geometrical parameters. The calculated dihedral angle of C–C–C–N of 169° from the ab initio studies using 6-31 + +g^{**} basis set is in very good agreement with the experimental value of 172° as reported from the X-ray diffraction method [7]. On closer examination, the geometrical parameters obtained from the basis set 6-31 + +g^{**} appear to give slightly better agreement with the experimental values than those obtained using any other basis set.

The geometrical parameters of propionamide also resemble its lower amide namely of acetamide for the amide group. The X-ray and neutron diffraction studies of acetamide have shown that it possesses planar symmetry [10]. In propionamide, the amide group –CONH₂ is also planar as noted by the present work.

3.2. Vibrational spectra

The vibrational spectra of propionamide is discussed in relation to the empirical assignments of Kuroda et al. [5] for propionamide and the assignments of acetamide. More detailed assignments have been made for acetamide from the ab initio and molecular mechanics methods, including the simulation of infrared spectra [3,4,6]. The calculated and observed vibrational frequencies and their relative intensities of propionamide and their assignments based on the calculated potential energy distributions for the stablest *trans* conformation, with staggered methyl group orientation possessing the C_1 symmetry obtained using the basis set 6-31 + +g^{**} are given in Table 3.

All the conformations of propionamide possessing C_s symmetry yielded one imaginary vibrational frequency corresponding to an energy maximum while the conformations with non-planar C_1 symmetry produced all positive vibrational frequencies supporting non-planar symmetry for structure of propionamide. Kuroda et al. [5] had assumed *trans* configuration for propionamide with C_s symmetry.

As noted from Table 3, the amide I and II bands (CO stretching and NH₂ bending modes, respectively) are

Table 3

Observed and calculated frequencies and their intensities and assignments of C_1 conformer of propionamide

Observed (cm^{-1})		Calculated			
IR	Raman	Freq. (cm^{-1})	IR intensity ^a	Raman intensity ^b	PED ^c
3360vs	3351mw	3987	61.1	38.3	NH ₂ as(59), NH ₂ s(41)
3192vs	3173m	3843	58.9	102.2	NH ₂ s(59), NH ₂ as(41)
2990vs	2979ms	3285	31.0	39.0	CH ₃ as(51), CH ₃ as(45)
2990vs	2979ms	3260	37.7	64.3	CH ₃ as(53), CH ₃ as(43)
2943vs	2942vs	3214	18.3	83.2	CH ₂ as(94)
2920ms	2912vs	3196	29.1	185.9	CH ₃ s(89)
2820sh		3180	32.2	32.2	CH ₂ s(92)
1695vs	1677vs	1945	447.9	8.3	COs(78)
1630vs	1591s	1776	137.3	2.4	NH ₂ b(89)
1463m	1451sh	1622	11.9	4.1	CH ₃ ab(80)
1463m	1451sh	1613	5.8	10.8	CH ₃ ab(91)
1419m	1423ms	1595	4.8	11.3	CH ₂ b(89)
1419m	1423ms	1559	23.1	10.5	CH ₃ sb(40), CH ₂ w(23)
1377m		1536	56.1	1.0	CH ₃ sb(50), CH ₂ w(22)
1261w	1261w	1398	1.9	6.0	CH ₂ r(73), CH ₃ r(16)
1296ms	1302w	1390	161.9	1.6	CNs(33), CH ₂ w(27)
1143ms	1148ms	1221	1.89	8.2	NH ₂ r(31), CH ₃ r(25)
1087m	1085wsh	1204	0.6	1.0	CH ₃ r(33), CH ₂ t(27), CH ₂ r(18)
1060m	1071w	1149	9.5	0.4	NH ₂ r(25), CCH ₃ s(23), CNs(21), CH ₃ r(20)
1004vw	1010w	1076	2.7	4.4	CC(me)s(43), CH ₃ r(22), CH ₂ w(16)
823ms	823s	884	9.5	0.7	CH ₃ r(36), CH ₂ t(26), Π_{CO} (19)
823ms	823s	856	0.9	11.9	CCs(49)
648ms	622vw	680	10.0	1.1	Π_{CO} (28), τ_{NH_2} (21), CH ₂ t(20)
568vw	568vw	644	15.4	1.4	COb(47), τ_{NH_2} (17)
477ms	470ms	537	3.3	0.5	τ_{NH_2} (45), Π_{CO} (29), CH ₂ t(15)
	413ms	475	4.4	1.9	NCCb(57)
284w	284w	273	0.2	10.7	CCCb(57), NCCb(28)
		230	0.1	0.1	τ_{CH_3} (93)
175w		162	268.0	0.2	τ_{CN} (65), τ_{NH_2} (19)
	96vs	20	0.6	0.3	τ_{CC} (55), CH ₂ t(18)

^a km/mole.^b a⁴/mole.^c s = symmetric stretching, as = asymmetric stretching, b = bending, ab = asymmetric bending, t = twisting, r = rocking, τ = torsion, Π = out of plane bend, w = wag.

localized. They were obtained as coupled modes by Kuroda et al. [5]. The present assignment of CN stretching for propionamide is in agreement with that in acetamide assigned at 1319 cm^{-1} . The results show that the CN stretching mode (amide III band) is highly coupled and it could be assigned at 1296 cm^{-1} in agreement with the observed and calculated infrared and Raman intensities while Kuroda et al. [5] have assigned it at 1418 cm^{-1} . However, the assignment of the CC stretching modes of propionamide agrees with Kuroda et al. [5].

A comparison of the assignments for the amide

bands of propionamide and acetamide is shown in Table 4. It is satisfying to note that there is very good agreement in the assignment of bands for this two primary amide molecules. The assignments for acetamide are taken from ab initio results of Sugawara et al. [3]. The in plane and out of plane CO bending vibrations have been assigned by Kuroda et al. [5] at 640 and 570 cm^{-1} for amide IV and VI bands, respectively. Interestingly, the present studies favour a reverse assignment. The present assignments find support from the ab initio study of acetamide of Sugawara et al. [3] as noted from Table 4.

Table 4

Comparison of the amide bands of propionamide and acetamide

Acetamide	Propionamide	Assignments ^a	
Observed (cm ⁻¹) Ref. [3]	Observed (cm ⁻¹)	Acetamide Sugawara [3]	Propionamide Present work
1733	1695	COs(79)	COs(78)
1600	1630	NH ₂ b(93)	NH ₂ b(90)
1319	1296	CNs(48), COb(21)	CNs(33), CH ₂ w(23)
548	568	COb(75)	COb(48), τ_{NH_2} (20)
608	651	Π_{CO} (63), CH ₃ r(26)	Π_{CO} (30), τ_{NH_2} (20)
507	477	τ_{NH_2} (88), Π_{CO} (20)	τ_{NH_2} (43), Π_{CO} (29)

^a Refer Table 3.

Table 5

Calculated and observed frequencies of CH₃CH₂COND₂

Observed Ref. [5]		Calculated			
Raman (cm ⁻¹)	IR (cm ⁻¹)	Freq. (cm ⁻¹)	Raman scattering ^a	IR intensity ^a	PED ^a
2978m	2980m	3285	39.1	30.9	CH ₃ as(51), CH ₃ as(45)
2978m	2980m	3260	64.3	37.7	CH ₃ as(53), CH ₃ as(43)
2912vs	2920w	3214	83.4	18.2	CH ₂ as(94)
2884w	2927vw	3196	185.7	29.1	CH ₃ s(89)
2825vw	2820vw	3180	67.6	31.9	CH ₂ s(92)
2525s	2530vs	2955	20.1	37.9	ND ₂ as(55), ND ₂ s(44)
2350s	2370vs	2777	49.6	60.5	ND ₂ s(55), ND ₂ as(43)
1610vs	1630vs	1938	8.2	426.7	COs(81)
1462sh	1466m	1623	3.9	17.4	CH ₃ ab(78)
		1612	10.9	5.9	CH ₃ ab(91)
1435vs	1425vs	1596	11.8	7.2	CH ₂ b(88)
		1565	1.2	93.0	CH ₂ w(26), CH ₃ sb(18), CNs(15)
1380vw	1382m	1542	0.6	73.0	CH ₃ sb(71)
1327vw	1318vs	1436	0.6	164.0	CH ₂ w(34), CNs(28), ND ₂ b(24)
1260vw		1398	6.2	0.6	CH ₂ r(75), CH ₃ r(17)
1180w	1165m	1250	2.3	20.7	ND ₂ b(56), COb(14)
1078vs	1078s	1204	0.6	1.3	CH ₃ r(35), CH ₂ t(29), CH ₂ r(20)
	1078s	1188	7.2	9.8	CH ₃ r(43), CCH ₃ s(24)
1009m	1006w	1077	3.3	1.8	CCH ₃ s(56)
945vs	942s	1000	5.0	1.9	ND ₂ r(37), CNs(19)
806vw	808m	882	0.5	11.4	CH ₃ r(37), CH ₂ t(28), Π_{CO} (19)
769s	765w	802	8.4	0.2	CCs(51), ND ₂ r(22)
	625sh	648	2.1	9.8	Π_{CO} (37), CH ₂ t(21)
570vw	580sh	606	1.7	12.7	COb(37), Π_{CO} (19)
470vw	475m	436	1.2	5.9	NCCb(44), ND ₂ r(22)
438m	443m	409	0.1	5.4	τ_{ND_2} (82)
282vw	281m	268	0.2	9.1	CCCb(53), NCCb(33)
	170w	229	0.1	0.3	τ_{CH_3} (91)
	117w	123	0.2	143.0	τ_{CN} (66), τ_{ND_2} (19)
	70vw	20	0.2	0.5	τ_{CC} (55), CH ₂ t(18)

^a Refer Table 3.

Table 6

Calculated and observed frequencies of $\text{CH}_3\text{CD}_2\text{CONH}_2$

Observed Ref. [5]		Calculated			
Raman (cm^{-1})	IR (cm^{-1})	Freq. (cm^{-1})	Raman scattering ^a	IR intensity ^a	PED ^a
3350s	3350vs	3987	38.3	61.0	NH ₂ as(59), NH ₂ s(41)
3172vs	3190vs	3843	101.9	59.0	NH ₂ (59), NH ₂ as(41)
2978vs	2970m	3283	54.8	23.8	CH ₃ as(54), CH ₃ as(44)
2940vs	2970m	3260	71.8	34.3	CH ₃ as(56), CH ₃ as(41)
2880s	2935w	3196	36.9	143.0	CH ₃ s(95)
2190vs	2180vw	2384	34.8	13.4	CD ₂ as(98)
2130vs	2120w	2318	52.5	11.8	CD ₂ s(97)
1674vs	1665vs	1944	8.0	456.0	COs(79)
1585vs	1625vs	1776	2.4	137.2	NH ₂ b(89)
1457s	1462w	1618	7.5	5.6	CH ₃ ab(90)
1457s	1462w	1611	9.9	5.7	CH ₃ ab(92)
1416vs	1409vs	1549	0.6	1.4	CH ₃ sb(90)
1372w	1378sh	1486	2.2	198.0	CNs(34), CCs(24), NH ₂ b(17)
1179m	1174m	1288	0.5	43.0	CD ₂ w(31), CCH ₃ s(17), CH ₃ r(17)
1143vs	1136s	1234	8.0	1.1	CD ₂ b(32), CH ₃ r(23)
1143vs	1136s	1232	0.1	2.0	CH ₃ r(72)
1095w	1093sh	1180	3.5	1.8	NH ₂ r(38), CD ₂ b(34), CNs(15)
1020m	1016s	1113	3.1	10.5	CD ₂ b(36), CH ₃ r(23), CCH ₃ s(16)
	918w	1030	2.1	4.3	CD ₂ r(47), Π_{CO} (34), CD ₂ t(16)
850s	850w	908	5.3	4.1	CD ₂ w(49), CCH ₃ s(30), CH ₃ r(16)
807vs	803m	831	9.4	2.4	CCs(50), NH ₂ r(15)
780sh		771	1.1	7.4	CD ₂ r(39), CH ₃ r(24), Π_{CO} (18)
	670sh	651	1.7	11.0	COb(47)
618m	625vs	625	0.4	14.1	τ_{NH_2} (61)
492vw	495vw	495	0.9	2.1	Π_{CO} (29), CD ₂ t(27), τ_{NH_2} (20)
440w	442vw	462	1.6	3.0	NCCb(45), CD ₂ t(10)
280s	288m	272	0.2	10.5	CCCb(57), NCCb(29)
		228	0.13	0.07	τ_{CH_3} (94)
	175w	162	0.2	268.0	τ_{CN} (65), τ_{NH_2} (19)
	70vw	19	0.3	1.4	τ_{CC} (55), CD ₂ t(18)

^a As in Table 3.

The present ab initio study favours the assignment of NH₂ torsion to a band at 477 cm^{-1} in agreement with that of acetamide at 507 cm^{-1} . However, it differs from Kuroda et al. [5], who have assigned it at a rather higher frequency, at 820 cm^{-1} . The calculated infrared and Raman intensities for methyl torsion are negligibly small and hence the band due to methyl torsion is possibly not observed. The weak band at 175 cm^{-1} assigned by Kuroda et al. [5] to methyl torsion could be reassigned to CN torsion according to the present ab initio study. The assignment of CN torsion at 175 cm^{-1} is consistent with that of *N*-methylacetamide where it has been assigned at 170 cm^{-1} [11]. There is large deviation between the observed and calculated frequencies for the lowest

fundamental. These may be attributed to the neglect of zero point correction [12].

There is no report on the quantitative measurement of infrared and Raman band intensities for propionamide. However, qualitative band intensities of the observed infrared and Raman spectra are compared with the calculated values in Table 3. It is satisfying to note that there is general agreement between the observed and calculated intensities. The calculated intensity of CO stretching is the highest in the infrared as expected. However, the intensities of some of the hydrogen involving bending vibrations are not correctly reproduced.

The calculated and observed frequencies for the deuterated molecules, $\text{CH}_3\text{CH}_2\text{COND}_2$, $\text{CH}_3\text{CD}_2\text{CONH}_2$ and $\text{CH}_3\text{CD}_2\text{COND}_2$ are summarized in Tables 5–7.

Table 7

Calculated and observed frequencies of $\text{CH}_3\text{CD}_2\text{COND}_2$

Observed Ref. [5]		Calculated			
Raman (cm^{-1})	IR (cm^{-1})	Freq. (cm^{-1})	Raman ^a scattering	IR ^a intensity	PED ^a
2974s	2970m	3283	54.8	23.8	$\text{CH}_3\text{as}(54)$, $\text{CH}_3\text{as}(44)$
2940s	2935w	3260	71.7	34.2	$\text{CH}_3\text{as}(56)$, $\text{CH}_3\text{as}(41)$
2877s	2870w	3196	142.6	32.7	$\text{CH}_3\text{s}(95)$
2525vs	2520vs	2955	20.1	37.9	$\text{ND}_2\text{as}(55)$, $\text{ND}_2\text{s}(44)$
2335vs	2360vs	2777	50.1	60.1	$\text{ND}_2\text{s}(55)$, $\text{ND}_2\text{as}(43)$
2190vs	2180vw	2384	34.8	13.3	$\text{CD}_2\text{as}(98)$
2130vs	2120w	2318	12.3	52.5	$\text{CD}_2\text{s}(97)$
1605vs	1630vs	1936	7.9	434.5	$\text{COs}(81)$
1460sh	1462w	1618	7.5	6.5	$\text{CH}_3\text{ab}(90)$
1460sh	1462w	1611	9.9	5.8	$\text{CH}_3\text{ab}(92)$
1428vs	1425vs	1549	0.7	1.9	$\text{CH}_3\text{sb}(88)$
1376w	1377vw	1520	1.0	315.0	$\text{CNs}(44)$, $\text{CCs}(18)$
1224w		1339	2.2	14.5	$\text{ND}_2\text{b}(35)$, $\text{CD}_2\text{w}(24)$
1138vw	1120w	1232	1.9	0.04	$\text{CH}_3\text{r}(73)$
1095m	1096vw	1227	3.9	7.6	$\text{CH}_3\text{r}(35)$, $\text{CD}_2\text{b}(26)$
1073w	1070w	1215	3.7	20.0	$\text{CD}_2\text{b}(27)$, $\text{ND}_2\text{b}(21)$, $\text{CCH}_3\text{s}(20)$
1018m	1014s	1116	6.0	11.0	$\text{CD}_2\text{b}(47)$, $\text{CH}_3\text{r}(18)$
960vs	956s	1032	2.2	5.2	$\text{CD}_2\text{r}(43)$, $\Pi_{\text{CO}}(30)$, $\text{CD}_2\text{t}(15)$
960vs	956s	1011	2.5	1.3	$\text{ND}_2\text{r}(34)$, $\text{CNs}(20)$
850s	845w	905	5.8	3.8	$\text{CD}_2\text{w}(48)$, $\text{CCH}_3\text{s}(27)$, $\text{CH}_3\text{r}(17)$
750m	740sh	779	4.0	4.9	$\text{CCs}(26)$, $\text{CD}_2\text{r}(21)$
	700vw	761	3.9	4.3	$\text{CCs}(21)$, $\text{CD}_2\text{r}(21)$, $\text{CH}_3\text{r}(15)$
600w	575sh	624	2.7	10.9	$\text{COb}(47)$, $\text{CCCb}(10)$
	525sh	551	0.6	11.5	$\text{CD}_2\text{t}(40)$, $\Pi_{\text{CO}}(29)$
480w	470s	430	1.1	5.5	$\text{NCCb}(42)$, $\text{CD}_2\text{r}(20)$
420w	420sh	398	0.2	3.2	$\tau_{\text{ND}_2}(68)$, $\Pi_{\text{CO}}(14)$
280s	280w	266	0.2	8.9	$\text{CCCb}(53)$, $\text{NCCb}(34)$
		227	0.1	0.2	$\tau_{\text{CH}_3}(92)$
	170w	123	0.2	143.0	$\tau_{\text{CN}}(66)$, $\tau_{\text{ND}_2}(19)$
	70vw	18	0.3	0.1	$\tau_{\text{CC}}(54)$, $\text{CD}_2\text{t}(18)$

^a As in Table 3.

The frequencies have been calculated using the force constants transferred from the ab initio calculations carried out at 6-31++g^{**}. The present results generally support the assignments of Kuroda et al. [5] for these three isotopic molecules. However, the present work suggests some revisions in one or two bands for each of the molecules.

For $\text{CH}_3\text{CH}_2\text{COND}_2$ molecule, Kuroda et al. [5] have assigned a weak band (shoulder) at 580 cm^{-1} to in plane CO bending as well as to ND_2 torsion. The present calculation partly supports the former assignment and favours the assignment of ND_2 torsion to a new medium intensity infrared band at 443 cm^{-1} which is not present in the parent compound. The bending mode of CCN assigned

443 cm^{-1} by Kuroda et al. [5] could be reassigned at 475 cm^{-1} .

Regarding the isotopic molecule $\text{CH}_3\text{CD}_2\text{CONH}_2$, the calculations suggest that two vibrations could be assigned at 1136 cm^{-1} which is a strong band both in the infrared and Raman corresponding to the calculated frequencies 1234 and 1232 cm^{-1} . The calculations also do not favour the assignment of 1070 cm^{-1} band which is a shoulder both in the infrared and Raman to CH_3 rocking mode. The calculation favours the assignment of 1093 cm^{-1} band to a coupled vibration of NH_2 rocking and CD_2 bending. In the low frequency region, the present studies favour the assignment of 780 cm^{-1} band (observed in the Raman) as a shoulder to a highly coupled vibration of CD_2 rocking instead of a band

at 710 cm^{-1} . Kuroda et al. [5] have assigned both C–C stretching and out of plane NH_2 torsion to an infrared band at 803 cm^{-1} . The present study favours the assignment of NH_2 torsion at 625 cm^{-1} .

Regarding the isotopic molecule $\text{CH}_3\text{CD}_2\text{COND}_2$, the present studies support the assignment of two vibrations around 956 cm^{-1} which is an intense band both in the infrared and in the Raman spectra. Kuroda et al. [5] have assigned to CD_2 twisting a band at 918 cm^{-1} which they have not listed among the observed infrared and Raman bands. The present calculations also do not support the assignment of two vibrations to a band at 575 cm^{-1} which is observed as a shoulder in the infrared spectrum. The present studies support the assignment of ND_2 torsion at 420 cm^{-1} consistent with that at 440 cm^{-1} in $\text{CH}_3\text{CH}_2\text{COND}_2$. The present work supports the assignment of in plane CO bending at 575 cm^{-1} but the coupled out of plane mode is observed at 525 cm^{-1} .

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