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Vibrational spectra of chloroacetamide and three deuterated analogues in the crystalline state

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Abstract—The IR and Raman Spectra of α-chloroacetamide $CH_2ClCONH_2$ and three deuterated analogues $CH_2ClCOND_2$, $CD_2ClCONH_2$ and $CD_2ClCOND_2$, in the crystalline state have been studied. A complete interpretation of the spectra has been worked out on the basis of spectral comparison and of the normal coordinate analysis of the four analogues.

INTRODUCTION

TO ELUCIDATE relationships between the observed wavenumbers and amide structure, a large number of authors have studied the IR and Raman spectra of acetamide. The IR spectrum of α-chloroacetamide was examined in comparison with those of other related compounds [1–3], and in connection with data of an electron diffraction study [4].

Recently, TROITIÑO *et al.* reported the IR and Raman spectra of α-chloroacetamide together with those of other α-haloacetamides [5]. In these spectra some Raman band positions of α-chloroacetamide were observed to be considerably different from the corresponding IR band positions, suggesting that the molecules form a centrosymmetric structure. In fact, the crystal structure ($P2_1/a$, $Z = 4$) of this amide determined by three-dimensional X-ray data has a center of symmetry and is very complicated [6]; the molecules are connected by one set of hydrogen bonds across centers of symmetry to form dimers. These dimers are further linked by another set of hydrogen-bonds into endless chains.

To establish the band assignments of the complicated spectra through normal coordinate calculations, full spectra data of α-chloroacetamide including those of C-deuterated species are necessary.

In this work, we report the IR and Raman spectra of $CH_2ClCONH_2$, $CH_2ClCOND_2$, $CD_2ClCONH_2$ and $CD_2ClCOND_2$ (MCAA-d_0, -Nd_2, -Cd_2 and -d_4), and the results of normal coordinate calculations for these species.

EXPERIMENTAL

α-Chloroacetamide MCAA-d_0 and C-deuterated species MCAA-Cd_2 were prepared by the reaction of ethyl chloroacetate ($ClCH_2COOCH_2CH_3$ and $ClCD_2COOCH_2CH_3$ [7], respectively) and ammonium hydroxide [8]. The crude products were recrystallized from aqueous solutions. The N-deuterated and the full deuterated compounds MCAA-Nd_2 and -d_4 were prepared from the purified MCAA-d_0 and -Cd_2 by an exchange reaction with heavy water.

The IR spectra were recorded from the samples prepared as KBr disks and Nujol mulls on JASCO DS-701G and Hitachi EPI-G2 IR spectrometers. The Raman spectra were recorded by a capillary sample technique on a SPEX RAMALOG 5M spectrometer with 514.5 nm Ar^+ laser excitation. Calibrated wavenumbers are believed to be accurate to within $\pm 2\,cm^{-1}$ unless the observed bands are weak or broad.

The spectra of MCAA-d_0 were in accordance with those recorded on a Nicolet 60SX FTIR and a Dilor XY Raman (multichannel detector) spectrometer in Universidad Complutense, Madrid.

Table 1. Force constants for chloroacetamide $ClCH_2C(=O)NH_2$

Urey–Bradley type (mdyn Å^{-1})					
K		H		F	
C=O	7.50	H–C–H	0.38	H···H	0.053
C–N	6.10	C–C–Cl	0.15	C···Cl	1.50
C–C	2.50	H–C–Cl	0.06	H···Cl	0.72
C–Cl	1.54	H–C–C	0.19	H···C	0.59
C–H	4.37	H–N–H	0.42	H···H	0.00
N–H	5.67	C–N–H*	0.361	C···H*	0.55
		C–N–H′†	0.361	C···H′†	0.52
		N–C–O	0.30	N···O	1.30
		C–C–N	0.30	C···N	0.52
		C–C–O	0.30	C···O	0.58
Interaction		κ(mdyn Å)	0.077	P(N–H/N–H)	−0.194
Other type (mdyn Å)					
π(C=O) = 0.469		π(NH_2) = 0.112		τ(NH_2) = 0.457	τ(CH_3) = 0.150
Interaction		π(C=O)/π(NH_2) = 0.079		π(C=O)/τ(NH_2) = 0.068	

* For the *trans* O=C–N–H sequence.
† For the *cis* O=C–N–H sequence.

Some mistakes have been found in Table 2 of the previous paper [5]: the IR band at 536 cm^{-1} assigned to the π C=O mode in this paper was not exhibited, and the 1380 m and 1404 s bands must interchange their positions (the 1380 cm^{-1} band appears in the IR solution spectrum and the 1404 cm^{-1} band in the IR solid state spectrum).

NORMAL VIBRATION CALCULATION

The normal coordinate calculations were carried out by assuming a monomeric form with the structural parameters determined by the X-ray structural analysis [6] except for the CH_2Cl– and –NH_2 bond angles, which are assumed to be tetrahedral and 120°, respectively. The Cl–C–C=O dihedral angle is 168.0°, which places the C–Cl bond *cis* to nitrogen.

A modified Urey–Bradley force field [9] was adopted in the calculation. The force constants for amides established by SHIMANOUCHI's group [10] were fundamentally transferred, and were progressively improved by an iterative procedure to get a better fit between the observed and calculated wavenumbers. Finally, some force constants were adjusted by the least-squares method. The final set of the force constants is listed in Table 1.

The computation was carried out by using a program NCTB [11] on a NEAC ACOS 2020 system at the Kobe University Information Center.

RESULTS AND DISCUSSION

The vibrational analysis of MCAAs was carried out on the basis of spectral comparisons among the four isotopic species and with related compounds, and of the results of the normal coordinate calculations. The IR and Raman spectral data of MCAA-d_0 and -Nd_2 are listed in Table 2, and those of MCAA-Cd_2 and -d_4 in Table 3, together with the calculated results of wavenumbers and potential energy distribution (PED).

Generally, in-plane modes give considerable intense Raman bands, while very weak Raman bands are observed for out-of-plane modes (see Fig. 1).

In addition, NH_2-group vibrations give characteristic broad bands, whose intensities are considerably strong in the IR but very weak in the Raman spectrum. Even, in some cases, Raman bands are too weak to be detected. Also, N-deuteration and C-deuteration are of considerable assistance in identifying the $\mathrm{NH_2}$-group bands and the $\mathrm{CH_2}$-group bands, respectively, showing the respective isotope effects on the spectra.

Characteristic bands

The Raman spectrum of MCAA-d_0 exhibits six remarkable strong bands at about 3010, 2960, 1100, 770, 420 and 265 $\mathrm{cm^{-1}}$. In the IR spectrum of MCAA-d_0, bands at about 3380, 3190, 1660, 1620, 1430, 1405, 1270, 1180, 1100, 770, 650, 440 and 265 $\mathrm{cm^{-1}}$ are prominent. On N-deuteration the bands at 3380, 3190, 1620, 1100 and 650 $\mathrm{cm^{-1}}$ change their positions to 2540, 2340, 1170, 920 and 500 $\mathrm{cm^{-1}}$, respectively, and on C-deuteration the bands at 3010, 2960, 1405, 1270 and 1180 $\mathrm{cm^{-1}}$ change their positions to about 2260, 2185, 1060, 1010 and 910 $\mathrm{cm^{-1}}$. Therefore, these bands, which show the isotope effect on N-deuteration, are associated with the $\nu a\mathrm{NH_2}$, $\nu s\mathrm{NH_2}$, $\delta\mathrm{NH_2}$, $\delta r\mathrm{NH_2}$ and $\pi\mathrm{NH_2}$ modes, in the order of decreasing wavenumber, and those showing the

Table 2. Observed and calculated wavenumbers ($\mathrm{cm^{-1}}$) and vibrational assignments for chloroacetamide-d_0 ($\mathrm{CClH_2CONH_2}$) and chloroacetamide-Nd_2 ($\mathrm{CClH_2COND_2}$)

$\mathrm{CClH_2CONH_2}$ (MCAA-d_0)			$\mathrm{CClH_2COND_2}$ (MCAA-Nd_2)			Assignment
IR	Raman	νcalc.	IR	Raman	νcalc.	PED %
3385 vs	3378 m	3401	[3372 wm	3368 vw]		$\nu a\mathrm{NH_2}$ 100
3292 m						
3188 sb	3153 wmb	3198	[3226 wb]			$\nu s\mathrm{NH_2}$ 99
3014 ssh	3012 s	3039	3014 s	3012 s	3039	$\nu a\mathrm{CH_2}$ 100
2960 ssh	2958 vs	2987	2961 s	2961 vs	2987	$\nu s\mathrm{CH_2}$ 100
			2540 vs	2536 ms	2520	$\nu a\mathrm{ND_2}$ 100
			2494 ssh	2496 vw		$\nu\mathrm{NHD}$
			2391 s			
			2341 s	2323 ms	2311	$\nu s\mathrm{ND_2}$ 98
1645 vsb	1675 wm	1669				$\nu\mathrm{C{=}O}$ 34, $\nu\mathrm{C{-}N}$ 31, $\delta\mathrm{NH_2}$ 25
			1627 vs	1613 ms	1645	$\nu\mathrm{C{=}O}$ 61, $\nu\mathrm{C{-}N}$ 36
1620 sb	1589 wmb	1605				$\delta\mathrm{NH_2}$ 65, $\nu\mathrm{C{=}O}$ 26
1430 vsb	1447 wm	1432				$\nu\mathrm{C{-}N}$ 34, $\nu\mathrm{C{-}C}$ 20, $\delta r\mathrm{NH_2}$ 15
			1442 vs	1451 ms	1434	$\nu\mathrm{C{-}N}$ 36, $\nu\mathrm{C{-}C}$ 22, $\delta\mathrm{NCO}$ 15
1415 msh			1414 vs			
		1403			1403	$\delta\mathrm{CH_2}$ 92
1403 vs	1406 ms		1404 vs	1407 m		
1266 vs	1265 wm	1277	1267 vs	1268 w	1281	$\delta w\mathrm{CH_2}$ 100
			1180 s	1201 wm	1177	$\delta\mathrm{ND_2}$ 46, $\delta t\mathrm{CH_2}$ 33, $\nu\mathrm{C{-}C}$ 12
1178 s	1185 m	1182				$\delta t\mathrm{CH_2}$ 85
			1173 s	1183 m	1185	$\delta t\mathrm{CH_2}$ 62, $\delta\mathrm{ND_2}$ 26
1100 vs	1105 s	1102				$\delta r\mathrm{NH_2}$ 61, $\nu\mathrm{C{=}O}$ 23
931 w	936 vw	930	937 vs	935 m	929	$\delta r\mathrm{CH_2}$ 86
			921 s	920 ms	944	$\delta r\mathrm{ND_2}$ 35, $\nu\mathrm{C{=}O}$ 19
892 vw	891 m	895	836 m	838 ms	833	$\nu\mathrm{C{-}C}$ 59, $\delta\mathrm{ND_2}$ 25
809 m		813				$\delta t\mathrm{NH_2}$ 89
768 vs	772 vs	772	766 vs	769 vs	767	$\nu\mathrm{C{-}Cl}$ 78, $\delta\mathrm{CCCl}$ 15
645 sb	635 vwb	636				$\pi w\mathrm{NH_2}$ 100
			637 m	611 vw	635	$\delta t\mathrm{ND_2}$ 48, $\pi\mathrm{C{=}O}$ 37
585 s	578 w	587	[580 wb]			$\delta\mathrm{NCO}$ 51, $\delta\mathrm{CCCl}$ 20
			528 s	520 vw	533	$\delta\mathrm{NCO}$ 40, $\delta\mathrm{CCCl}$ 23
			510 msh	492 vw	495	$\pi w\mathrm{ND_2}$ 79, $\pi\mathrm{C{=}O}$ 17
536 m	539 w	526				$\pi\mathrm{C{=}O}$ 83, $\pi t\mathrm{NH_2}$ 10
530 wsh						
			478 m	470 w	478	$\pi\mathrm{C{=}O}$ 34, $\pi t\mathrm{ND_2}$ 25
439 vs	426 vs	430	429 s	419 vs	426	$\delta\mathrm{CCN}$ 25, $\delta\mathrm{CCCl}$ 25
268 vs	266 s	251	258 vs	254 s	235	$\delta\mathrm{CCCl}$ 48, $\delta\mathrm{CCN}$ 47
		126			122	$\tau\mathrm{CH_2}$ 92

Abbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad; ν, stretching; δ, scissoring; δw, wagging; δt, twisting; δr, rocking; π, out-of-plane bending; τ, torsion; *as*, antisymmetric; *s*, symmetric.

Table 3. Observed and calculated wavenumbers ($\mathrm{cm^{-1}}$) and vibrational assignments for chloroacetamide-Cd_2 ($\mathrm{CClD_2CONH_2}$) and chloroacetamide-d_4 ($\mathrm{CClD_2COND_2}$)

$\mathrm{CClD_2CONH_2}$ (MCAA-Cd_2)			$\mathrm{CClD_2COND_2}$ (MCAA-d_4)			Assignment
IR	Raman	νcalc.	IR	Raman	νcalc.	PED %
3385 vs	3378 m	3401	[3372 w	3370 vw]		$\nu a\mathrm{NH_2}$ 100
3300 m						
3186 sb	3154 wmb	3198	[3229 vwb]			$\nu s\mathrm{NH_2}$ 99
			2540 vs	2536 ms	2520	$\nu a\mathrm{ND_2}$ 100
			2496 sh	2498 vw		νNHD
			2387 s			
			2342 s	2326 ms	2311	$\nu s\mathrm{ND_2}$ 97
2264 w	2262 s	2241	2263 m	2264 vs	2241	$\nu a\mathrm{CD_2}$ 100
2190 w	2189 vs	2164	2188 m	2183 vs	2164	$\nu s\mathrm{CD_2}$ 100
1650 vs	1675 wm	1667				νC=O 35, νC–N 32, $\delta\mathrm{NH_2}$ 27
			1620 vsb	1611 s	1642	νC=O 60, νC–N 32
1613 vs	1590 wmb	1605				$\delta\mathrm{NH_2}$ 64, νC=O 27
1423 vs	1451 wm	1420				νC–N 43, νC–C 31, $\delta r\mathrm{NH_2}$ 17
			1440 vsb	1452 s	1425	νC–N 44, νC–C 31, δNCO 16
			1170 m	1208 wmb	1182	$\delta\mathrm{ND_2}$ 75, νC–C 15
1100 sb	1105 ms	1103				$\delta r\mathrm{NH_2}$ 61, νC=O 23
1062 m	1058 w	1058	1060 s	1057 wm	1052	$\delta\mathrm{CD_2}$ 63, $\delta w\mathrm{CD_2}$ 25
1011 s	1019 m	986	1012 vs	1018 ms	991	$\delta w\mathrm{CD_2}$ 65, $\delta\mathrm{CD_2}$ 22, νC–C 12
			920 vs	923 s	934	$\delta r\mathrm{ND_2}$ 40, νC=O 14, $\delta w\mathrm{CD_2}$ 14
916 vw	916 w	887	906 wsh	913 m	881	$\delta t\mathrm{CD_2}$ 67, $\delta r\mathrm{CD_2}$ 15, πC=O 14
825 m	822 s	849	[823 w	822 vs]		νC–C 41, νC–N 13, $\delta w\mathrm{CD_2}$ 10
			784 s	787 ms	792	νC–C 42, $\delta r\mathrm{ND_2}$ 20, νC–N 11
806 m		804				$\pi t\mathrm{NH_2}$ 84, $\delta t\mathrm{CD_2}$ 10
774 w	780 m	757	772 s	773 s	756	$\delta r\mathrm{CD_2}$ 60, $\delta t\mathrm{CD_2}$ 26, πC=O 11
728 vs	733 vs	735	728 s	732 vs	731	νC–Cl 82, δCCCl 13
640 sb	634 vwb	634				$\pi w\mathrm{NH_2}$ 100
			614 mb		618	$\pi t\mathrm{ND_2}$ 60, πC=O 19
568 m	570 wm	571	[562 w]	[582 vw]		δNCO 48, δCCCl 20
			515 vs	511 w	523	δNCO 40, δCCCl 24, $\delta r\mathrm{ND_2}$ 17
			490 sb	477 vw	493	$\delta w\mathrm{ND_2}$ 85, πC=O 10
475 m	482 wm	490				πC=O 75, $\delta r\mathrm{CD_2}$ 14
			453 s	452 wm	455	πC=O 43, $\pi t\mathrm{ND_2}$ 25
			440 msh			
429 s	421 vs	425	421 vs	414 vs	420	δCCN 23, δCCCl 20, δNCO 15
265 sb	264 s	250	256 s	254 s	233	δCCCl 45, δCCN 43
		119			115	$\tau\mathrm{CD_2}$ 93

See footnote to Table 2 for explanation of abbreviations.

isotopic effect on C-deuteration, with the $\nu a\mathrm{CH_2}$, $\nu s\mathrm{CH_2}$, $\delta\mathrm{CH_2}$, $\delta w\mathrm{CH_2}$ and $\delta t\mathrm{CH_2}$ modes. The bands at 1660, 1430, 420 and 265 $\mathrm{cm^{-1}}$ keeping their positions on both N-deuteration and C-deuteration are assigned to the νC=O, νC–N, δCCN and δCCCl modes in the order of decreasing wavenumber.

An IR band is distinctly observed between the $\nu a\mathrm{NH_2}$ and $\nu s\mathrm{NH_2}$ bands of MCAA-d_0 and -Cd_2, but the corresponding Raman band is too weak to be detected. A few IR bands are also observed between the $\nu a\mathrm{ND_2}$ and $\nu s\mathrm{ND_2}$ bands of MCAA-Nd_2 and -d_4, but the corresponding Raman bands do not appear clearly in the Raman spectra of MCAA-Nd_2 and -d_4. Therefore, the bands, which appear clearly in the Raman spectra, are assigned to the νN–H fundamentals. The IR band at 3300 $\mathrm{cm^{-1}}$ must be associated with the combination tone of the νC=O vibration at 1675 $\mathrm{cm^{-1}}$ (in-phase, Ag species on the dimeric structure) and the νC=O vibration at 1645 $\mathrm{cm^{-1}}$ (out-of-phase, Bu species). A few IR bands observed between the $\nu a\mathrm{ND_2}$ and $\nu s\mathrm{ND_2}$ bands of MCAA-Nd_2 and -d_4 must be associated with the νN–D modes of the –NDH group (*cis* and *trans* to the C=O group) produced by imperfect N-deuteration [12].

On N-deuteration of MCAA-d_0 and -Cd_2, the intensities of Raman bands at 1675 and 1450 $\mathrm{cm^{-1}}$ (νC=O and νC–N bands) are enhanced. According to the results of calculation, the 1675 $\mathrm{cm^{-1}}$ band of MCAA-d_0 and -Cd_2 arises from a mixed vibration with main

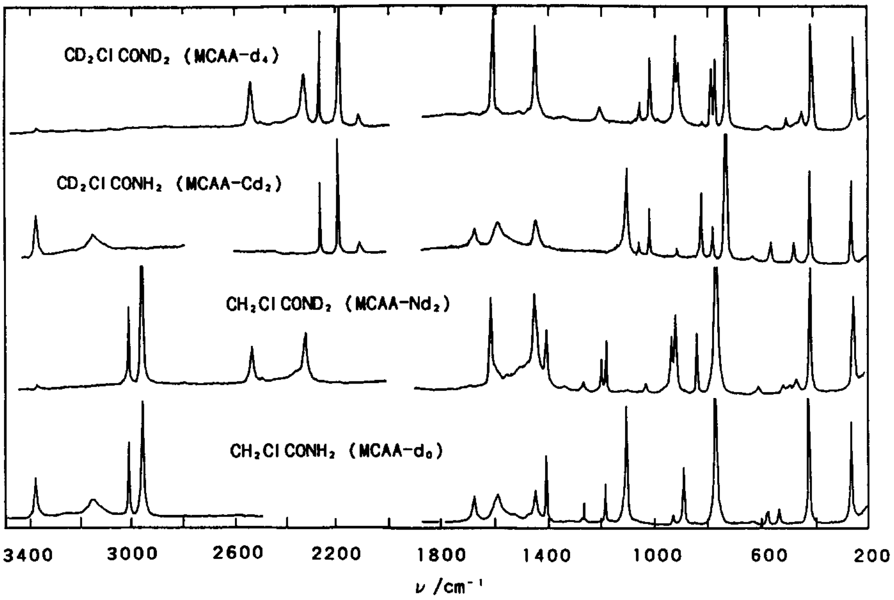

Fig. 1. Raman spectra of chloroacetamide MCAA-d_0, MCAA-Nd_2, MCAA-Cd_2 and MCAA-d_4 in the crystalline state at room temperature.

νC=O, νC–N and δNH_2 contributions. The N-deuteration makes the νC=O contribution increased at the expense of the δNH_2 contribution (25~27%). Similarly, the 1450 cm^{-1} band with main νC–N, νC–C and δrNH_2 contributions, on the N-deuteration, loses the δrNH_2 contribution (15~17%) and, at the same time, obtains the δNCO contribution to enhance the band intensity.

Neither IR bands nor Raman bands except for the νC=O, δNH_2 and νC–N bands are observed in the 1700–1150 cm^{-1} region of MCAA-Cd_2, and only the νC=O and νC–N bands are observed in this region of the MCAA-d_4 spectrum. Therefore, the three bands appearing in the 1420–1150 cm^{-1} region of the Raman spectra of MCAA-d_0 and -Nd_2 are associated with CH_2 vibrations; the δCH_2 (1406 and 1407 cm^{-1}), δwCH_2 (1265 and 1268 cm^{-1}) and δtCH_2 (1185 and 1183 cm^{-1}) modes. In the Raman spectra of MCAA-Cd_2 (-d_4), the δCD_2, δwCD_2 and δtCD_2 bands are observed at 1058 (1057), 1019 (1018) and 916 (913) cm^{-1}, respectively. The δrCH_2 band is observed at 936 (935) cm^{-1} and δrCD_2 band at 780 (773) cm^{-1} in the corresponding Raman spectra. It is noted that only the δwCH_2 mode of the four methylene deformations of MCAA-d_0 appears at a higher wavenumber than those of *n*-alkyl chloroacetates [7, 13].

The νC–C mode appears as a Raman band with a considerable intensity whose wavenumber decreases characteristically with deuterium substitution; 891 cm^{-1} (MCAA-d_0), 838 cm^{-1} (-Nd_2), 822 cm^{-1} (-Cd_2) and 787 cm^{-1} (-d_4).

Apart from the strong νC–Cl band already assigned, four fundamental bands, the πtNH_2, πwNH_2 and πC=O (out-of-plane), and δNCO (in-plane) mode, are expected to appear in the 830–430 cm^{-1} region. The IR bands at 809 (806) and 645 (640) cm^{-1} of MCAA-d_0 (-Cd_2) and those at 637 (614) and 510 (490) cm^{-1} of MCAA-Nd_2 (-d_4) are characteristically broad, and the corresponding Raman bands are very weak. They are assignable to the $NH_2(ND_2)$ out-of-plane modes. Of the two C=O deformations the in-plane δNCO band appears at a higher wavenumber than the out-of-plane πC=O band.

Centrosymmetric cyclic dimers

Although the bands in the spectra of MCAAs have been assigned as above, eight bands, at least, exhibit apparently different wavenumbers between the IR and Raman spectra, suggesting the formation of a centrosymmetric dimer [6], as has been described

Table 4. Bond stretching (cm^{-1}) and bond length (Å)

		MCAA		DCAA		TCAA	r(standard)
		This study		[5]		[5]	[17]
νC=O	IR	1645	<	1680	<	1695	
	Raman	1675		1700		1693	
rC=O		1.234 [6]		—		1.230 [15]	1.18 Å
νC–N	IR	1430	>	1415	>	1386 · 1354	
	Raman	1447		1428		1399 · 1363	
rC–N		1.313 [6]		—		1.328 [15]	1.47 Å
νC–C	IR	892	<	910	<	930	
	Raman	891		913		934	
rC–C		1.504 [6]		—		1.550 [15]	1.54 Å

previously [5]. In such a dimer the out-of-phase (antisymmetric) mode of the respective vibrations of the two molecules is active only in the IR spectrum, while the in-phase (totally symmetric) mode is active only in the Raman spectrum. Therefore, the two bands, arising from the same vibrational origin, can appear at different wavenumbers. For examples, the Raman band assigned to the νC–N mode appears at a higher wavenumber than that of the corresponding IR band while the Raman $\nu s\mathrm{NH_2}(\nu s\mathrm{ND_2})$ band is observed at a lower wavenumber than that of the IR one. Infrared and Raman wavenumbers of νC–N vibrations show the same behavior in all four isotopic species. In fact, the bands stated above exhibit the same tendency among the four isotopic species. This is not the case for the νC=O and $\delta\mathrm{NH_2}$ bands since the change in the PED mentioned above occurs on N-deuteration.

Bond stretchings, bond lengths and force constants

The νC=O wavenumbers of MCAAs are lower than those of the corresponding esters: ~1750 cm^{-1} in *n*-alkyl chloroacetates [7, 13]. The νC–N wavenumbers are extraordinarily higher than those of primary amines [14]. The lower νC=O wavenumbers and the higher νC–N wavenumbers are ascribed to resonance effects in the amide bonds, naturally reflecting their bond lengths.

Here, let us examine relationships between bond-stretching wavenumbers and bond lengths of α-chlorinated acetamides. The crystal structural data of MCAA [6] and trichloroacetamide TCAA [15], and force constants evaluated for TCAA [16] are available (see Table 4).

As expected from the resonance of amide forms, the C=O bond is longer and the C–N bond is much shorter than the corresponding standard bonds [17]. The C=O bond lengths (rC=O) in MCAA and TCAA are almost the same, thus, the difference in wavenumber is considered to be dependent on the value of force constant K(C=O). Since MCAA gives the lowest νC=O wavenumber of three α-chloroacetamides, the value of force constant K(C=O) must be the smallest of the three. In fact, the value of K(C=O) in 7.5 (mdyne Å^{-1}) for MCAA, which is much smaller than the value 8.0 for TCAA [16] and the value 8.7–8.8 given by SCHIMANOUCHI for amides [10].

The C–N bond length of MCAA is similar to that of TCAA. Of the extraordinarily high νC–N wavenumbers of acetamides, MCAA gives the highest νC–N wavenumber, and the force constant K(C–N) = 6.1 for MCAA is higher than the value 5.8 for TCAA and Shimanouchi's values are 5.5–6.35.

The C–C bond length in MCAA is smaller than that in TCAA, and the νC–C wavenumber of MCAA is lower than that of TCAA. The wavenumber difference occurs mainly from the difference in bond length. Thus, the force constant K(C–C) 2.50 is in the limited range 2.0–2.6 of Shimanouchi.

REFERENCES

[1] M. A. Herman and P. De Bièvre, *Bull. Soc. Chim. Belg.* **68**, 558 (1959).
[2] Y. Mido, *Bull. Chem. Soc. Jpn* **46**, 782 (1973).
[3] F. M. Abid, J. M. Al-Katti and M. F. El-Bermani, *J. Molec. Struct.* **67**, 169 (1980).
[4] S. Samdal and R. Seip, *J. Molec. Struct.* **52**, 195 (1979).
[5] D. Troitiño, E. Sánchez de Blanca and M. V. García, *Spectrochim. Acta* **46A**, 1281 (1990).
[6] B. Kalyanaraman, L. D. Kispert and J. L. Atwood, *J. Cryst. Molec. Struct.* **8**, 175 (1978).
[7] Y. Mido, N. Kakizawa, H. Matsuura, M. A. Raso, M. V. García and J. Morcillo, *J. Molec. Struct.* **220**, 169 (1990).
[8] W. A. Jacobs and M. Heidelberger, *Org. Synth.* **1**, 153 (1955).
[9] T. Shimanouchi, in *Physical Chemistry, An Advanced Treatise*, Vol. IV, (Edited by H. Eyring, D. Henderson and W. Jost), Chap. 6. Academic Press, New York (1970).
[10] T. Shimanouchi, *Pure Appl. Chem.* **7**, 131 (1963).
[11] T. Shimanouchi, *Computer Programs for Normal Coordinate Treatment of Polyatomic Molecules*. University of Tokyo (1968).
[12] T. Uno, K. Machida and Y. Saito, *Bull. Chem. Soc. Jpn* **42**, 897 (1969).
[13] Y. Mido, T. Shono and H. Matsuura, *J. Molec. Struct.* **265**, 75 (1992).
[14] L. J. Bellamy, *Infrared Spectra of Complex Molecules*, 3rd Edn, Vol. 1, Chap. 14, p. 277. Chapman and Hall, London (1975).
[15] M. Hashimoto, K. Hamada and K. Mano, *Bull. Chem. Soc. Jpn* **60**, 1924 (1987).
[16] Y. Mido, in preparation.
[17] L. Pauling, *The Nature of the Chemical Bond*, Chaps 7 and 8. Cornell University Press, Ithaca, New York (1960).