# VIBRATIONAL AND NMR SPECTRA OF LIGHT AND HEAVY CH₃COSH AND CD₃COSH IN RELATION TO TAUTOMERISM AND HYDROGEN BONDING

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ABSTRACT

The infrared and Raman spectra of CH₃COSH, CH₃COSD, CD₃COSH and CD₃COSD in the liquid and vapor states have been reported and vibrational assignments proposed. The low temperature NMR studies show the presence of hydrogen bonding in this acid. The NMR studies on the neat liquid fail to prove the presence of thion tautomer in thiolacetic acid.

INTRODUCTION

Earlier spectroscopic studies and physical arguments show that thiolacids exist as thiol tautomer (I) with very small or undetectable amounts of thion tautomer (II) [1—8]
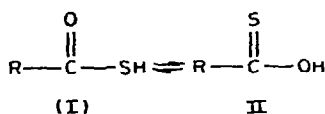
Normal coordinate analysis of thiolacetic acid has recently been carried out employing modified valence force field [9]. The hydrogen bonded dimers in this acid in the solid state and in solution at low temperatures or high solute concentration have also been studied by infrared spectroscopy [10]. Molecular orbital calculations on the intermolecular association through hydrogen bonding has also been reported [5]. The aim of our present study is to verify the physical arguments in connection with thiol—thion tautomerism and also to investigate hydrogen bonding by NMR spectroscopy. In addition, we propose a vibrational assignment for thiolacetic acid which is supported by the extensive infrared and Raman data obtained for CH₃COSD, CD₃COSH and CD₃COSD in the vapor and liquid states.

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## EXPERIMENTAL

Samples of $d_0$- and $d_3$-thiolacetic acids were prepared by the following reaction [11], in which X = H or D

$$CX_3COCl + H_2S \xrightarrow[-15°C]{AlCl_3} CX_3COSH + HCl$$
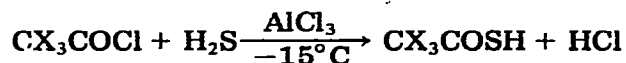
The respective samples were distilled twice and $CH_3COSH$ and $CD_3COSH$ with boiling points at 88°C and 99°C respectively were used in the present investigations. The corresponding heavy acids (i.e. $d_1$ and $d_4$) were obtained by the direct exchange of respective light acids (i.e. $d_0$ and $d_3$) with heavy water.

Infrared spectra of these acids in thin film (using NaCl windows) and the vapor state (using gas cell with NaCl windows) were recorded in the 4000—540 cm$^{-1}$ region on a Perkin—Elmer 421 grating spectrophotometer. The infrared band frequencies (in cm$^{-1}$) along with relative intensities are given in Table 1.

The laser Raman spectra of light and heavy acids in the liquid state were scanned from 0—4000 cm$^{-1}$ on a Cary 82-spectrophotometer. The excitation was by means of the 6328 Å line of a He—Ne laser. The wave numbers along with relative intensities are reported in Table 1. The NMR spectra of $CH_3COSH$ in $CDCl_3$ as well as in $CS_2$ using TMS as reference in the low and high temperature range were recorded on a Varian NV-14 NMR spectrometer.

## DISCUSSION

Assuming that thiolacetic acid belongs to $C_S$ point group, a total of 3N—6 i.e. 18 vibrational modes may be classified as $12a' + 6a''$. All these vibrational modes should be infrared and Raman active. The in-plane $a'$ motions should give rise to polarised Raman lines while $a''$ vibrational modes are associated with out-of-plane depolarised transitions. We have reported only the parallel plane polarized spectra of these acids in Table 1.

### $CX_3$ stretching vibrations

The complete vibrational spectra of the four isotopic species of thiolacetic acid provide a sound basis for the assignment of the three C—X stretching vibrations of each $CX_3$ (X = H or D) group. The intensity of these motions in the infrared spectra (Table 1) is generally weak or medium [12]. The symmetric stretching mode occurs as an intense Raman band in $CH_3COSH$ (Table 1) and is in accordance with observations reported earlier in acetic acid and its deuterated derivative [13]. The $CD_3$—C motions behave similarly in $CD_3COSH$. Therefore the Raman lines centred at 2108 cm$^{-1}$, 2135 cm$^{-1}$ and 2258 cm$^{-1}$ have been assigned to the $a'$-symmetric, $a'$-asymmetric and $a''$-asymmetric stretching modes on the basis of their relative intensities. Our assignment of these lines to the $CD_3$ stretching modes finds support from the work of Weltner [13] on acetic acid and its deuterated derivatives. The additional Raman lines centred at 1870 cm$^{-1}$, 2052 cm$^{-1}$ and 2228 cm$^{-1}$

## TABLE 1

Infrared and Raman band frequencies (in cm⁻¹) for $CH_3COSH$, $CH_3COSD$, $CD_3COSH$ and $CD_3COSD$[a]

| $CH_3COSH$ | | | $CH_3COSD$ | | | $CD_3COSH$ | | | $CD_3COSD$ | | | Assignment and Species |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (A) | (B) | (C) | (A) | (B) | (C) | (A) | (B) | (C) | (A) | (B) | (C) | |
| 3380m | 3380m | — | 3380m | 3380m | — | 3380m | 3380m | — | 3380m | 3380m | — | $2 \times 1700$ |
| 3020m | 3000m | 3010(1) | 3020m | 3000m | 3008(0.5) | 2260bw | 2250bm | 2258(2) | 2260bw | 2250bm | 2258(2) | $CX_3$ asym str $a''$ |
| — | — | — | — | — | — | — | — | 2135(7) | — | — | 2135(7) | $CX_3$ asym str $a'$ |
| 2940m | 2920m | 2928(38) | 2940m | 2920m | 2928(22.8) | — | 2095m | 2108(31.5) | — | 2095m | 2108(31.5) | $CX_3$ sym str $a'$ |
| 2585vvw | 2585m | 2578(27) | 1890vw | 1865m | 1870(41.5) | 2585vw | 2565m | 2578(13) | 1890vw | 1865m | 1870(45.8) | SX str $a'$ |
| — | — | — | — | — | — | — | — | 2228(2) | — | — | 2228(2.5) | overtone |
| — | — | — | — | — | — | — | — | 2052(2.8) | — | — | 2052(3) | overtone |
| — | — | — | — | — | — | — | 1920m | — | — | — | — | |
| — | — | — | — | — | — | 1880w | 1860m | 1870(6.5) | — | — | — | overtone |
| 1735vst | 1700vst | 1685(8) | 1735vst | 1700vst | 1683(9) | 1735vst | 1700vst | 1688(7.7) | 1735vst | 1700vst | 1685(12) | $C=O$ str $a'$ |
| 1425m | 1420m | 1428(3.2) | 1425m | 1420m | 1425(3.2) | 1035w | — | 1035(3) | — | 1030sh | 1035(1.5) | $CX_3$ asym bend $a'$, $a''$ |
| 1365st | 1352st | 1360(1.4) | 1365st | 1355st | 1360(1.4) | 990st | 980st | 990(7) | 970st | 975st | 990(5.5) | $CX_3$ sym bend $a'$ |
| 1287m | 1287m | — | 1287m | 1295m | — | 1300w | 1295m | — | — | 1285m | — | Impurity band |
| 1225w | 1215m | — | — | — | — | 1220vw | — | — | — | — | — | ? |
| 1128vst | 1125st | 1135(7.2) | 1128vst | 1125st | 1130(6.3) | 900m | 900m | 905(10) | — | 900m | — | $CX_3$ rock + C—C str $a'$ |
| 1072w | — | — | — | — | — | — | — | — | — | — | — | ? |
| 1000st | 990st | 1065(0.8) | 1000st | 960st | 1060(1) | — | 765st | 775(14) | — | 765(w) | 775(2) | $CX_3$ rock $a''$ |
| 860w | — | 998(7.2) | 860w | — | 970(9) | 1140st | 1140st | — | 1140st | 1140st | — | C—C str + $CX_3$ rock $a'$ |
| — | — | — | — | — | — | 855w | — | — | — | — | — | 451 + 438 |
| 830m | 830m | 835(9) | — | — | 658(16) | 845m | 845m | 830(4.5) | — | — | 645(7) | CSX bend $a'$ |
| — | — | 732(2.6) | — | — | 730(5.8) | — | 820m | 805(1) | — | 820m | 805(0) | ? |
| — | — | — | — | — | — | — | — | — | — | — | — | Impurity band |
| — | — | 628(96) | — | — | 628(79.5) | — | — | 575(82) | — | — | 575(63) | C—S str $a'$ |
| — | — | — | — | — | 560(3) | — | — | — | — | — | — | ? |
| — | — | 525(1) | — | — | 525(1) | — | — | — | — | — | — | 835—330 |
| — | — | 451(68.5) | — | — | 289(3.5) | — | — | 442(44) | — | — | — | CSX bend $a''$ |
| — | — | 438(32) | — | — | 438(92) | — | — | 430(32) | — | — | 429(49) | OCS bend $a'$ |
| — | — | 352(2) | — | — | 348(3.2) | — | — | 325(2) | — | — | — | $C=O$ wag $a''$ |
| — | — | 330(6.5) | — | — | 325(2.6) | — | — | 303(5) | — | — | 308(7) | CCS bend $a'$ |

[a] Abbreviations: (A) gaseous infrared; (B) film infrared; (C) Raman; w, weak; st, strong; vst, very strong; bw, broad weak; m, medium;

(Table 1) may be due to the overtones of $CD_3$ bending modes in Fermi resonance with specific $CD_3$ stretching vibrations.

### $CX_3$ bending vibrations

Of the molecules containing $CD_3$ groups for which assignments have been reported, $CD_3COOH$ is structurally the closest to $d_3$-thiolacetic acid. Thus using the assignments for $CD_3COOH$ [13] as a guide, we prefer to assign the bands at 1035 cm$^{-1}$ and 990 cm$^{-1}$ (Table 1) to the asymmetric $a'$, $a''$ and symmetric $a'$ bending motions of $CD_3$. Their counterparts in $CH_3COSH$ are at 1425 cm$^{-1}$ and 1365 cm$^{-1}$ respectively.

### C—C stretching and $CX_3$ rocking vibrations

Earlier workers [1, 2, 9] have assigned the bands at 1128 cm$^{-1}$ and 1065 cm$^{-1}$ to the $CH_3$ in-plane and out-of-plane rocking motions respectively. However the assignment of the $CD_3$ rocking modes is more difficult than for other internal modes. The 1065 cm$^{-1}$ band in $d_0$- and $d_1$ species (Table 1) has a counterpart at 765 cm$^{-1}$ in $d_3$- and $d_4$-species and may be assigned to the $CD_3$ out of plane rocking mode. Our assignment to this mode finds support from the work of Weltner [13] on $CD_3COOH$.

The assignment of the strong band at 1140 cm$^{-1}$ in the infrared absorption spectra of $d_3$- and $d_4$-species (Table 1) is of particular interest. We prefer to assign the band at 1140 cm$^{-1}$ to the C—C stretching mode in $d_3$- and $d_4$-species while its counterpart in $d_0$- and $d_1$-species is at 1000 cm$^{-1}$ (Table 1). The band at 900 cm$^{-1}$ which is seen in both the infrared as well as Raman spectra of $d_3$- and $d_4$-species (Table 2) is assigned to the $CD_3$ in-plane rocking vibration. The two vibrations C—C stretch and $CX_3$ rock seem to be highly mixed. This is in accordance with potential energy distribution calculated by Crowder et al. [9].

### COSX group motions

These are the most important group vibrations to be discussed as most of the bands of this group are red shifted on deuteration. As far as we know, no data are available in the literature for the bands of the COSD group.

The SH stretching vibrational mode is seen as a weak band in the vapor and is medium in the liquid phase (Table 1). The frequency in the liquid phase is lower than the frequency in the vapor phase. The SD stretching vibration must have the characteristics of the SH stretching mode. Therefore the band centred at 1865 cm$^{-1}$ (in liquid) and at 1890 cm$^{-1}$ (in vapor) is assigned to the SD stretching motion. The increase in frequency in going from liquid to vapor phase is the normal behaviour of SH groups observed in other systems [6, 8] containing this group. The frequency ratio i.e. $\nu_{SH}/\nu_{SD}$ is 1.37 and 1.36 for the liquid and vapor phase respectively.

The carbonyl stretching vibration is about 35 cm$^{-1}$ higher in the vapor phase than in the liquid phase (Table 1). Similar behaviour of this band has been observed in other thiolacids [6, 8]. The other important mode of

the COSX group to be discussed is the C—S stretching vibration. It should be strong in Raman spectra. The only band in the appropriate region is centred at 575 cm$^{-1}$ in the $d_3$- and $d_4$-species but at 626 cm$^{-1}$ in the $d_0$- and $d_1$-species (Table 1).

The CSH in-plane bending motion merits little discussion while its corresponding out-of-plane analogue is the most controversial motion to be discussed. The band positioned at 830 cm$^{-1}$ in $d_0$- and $d_3$- species (Table 1) is red shifted on deuteration and appears at 658 cm$^{-1}$ in the corresponding $d_1$ and $d_4$ species respectively. The frequency ratio of these bending motions is 1.26.

Crowder et al. [9] on the basis of their normal coordinate analysis assigned a band at 288 cm$^{-1}$ (calc.) to the CSH out of plane deformation, while the assignment made by Mecke and Spiesecke [2] to this mode is at 525 cm$^{-1}$. The possibility of assigning the 525 cm$^{-1}$ band to this mode is ruled out as this band has been observed in our Raman spectra of both the $d_0$- and $d_1$-species (Table 2). The only band in the appropriate region which is red shifted on deuteration is at 451 cm$^{-1}$ and hence could safely be assigned to the CSH out of plane bending motion and the corresponding CSD band appears at 299 cm$^{-1}$ in the $d_1$-species. Hence the Crowder et al. [9] assignment of 445 cm$^{-1}$ and 430 cm$^{-1}$ to CSH and OCS bending motions respectively needs to be changed. The band at 430 cm$^{-1}$ which is not influenced by deuteration may be assigned to the OCS bending vibration. The frequency ratio of the $\delta_{CSH}$ and $\delta_{CSD}$ vibrations is 1.50 and the comparison of frequency ratios shows that the deuteration effect follows the order: $\delta_{CSH(O/P)} > \nu_{SH} > \delta_{CSH(I/P)}$ The results of the deuteration effect on the COSX group vibrations are summarized in Table 2.

## NMR STUDIES

The NMR spectra of $CH_3COSH$ were investigated in $CS_2$ solution using TMS as a reference in the temperature range $+22°C$ to $-93°C$. The signals corresponding to SH and $CH_3$ protons were observed at the $\delta$ value of 4.90

**TABLE 2**

Deuteration effects on the COSH group vibrations

| Mode[a] | Species | | | | Frequency ratio $(d_0/d_1)$ |
| --- | --- | --- | --- | --- | --- |
| | $d_0$ | $d_1$ | $d_3$ | $d_4$ | |
| SH str | 2565 | 1865 | 2565 | 1865 | 1.37 |
| CSH(I/P)def | 830 | 658 | 845 | 645 | 1.26 |
| CSH(O/P)def | 451 | 299 | 442 | — | 1.50 |
| C—S str | 628 | 628 | 575 | 575 | 1.0 |

[a]Abbreviations: I/P, in-plane; O/P, out of plane; str, stretch; def, deformation.

ppm and 2.30 ppm respectively. The half bandwidth of the SH proton increased on lowering the temperature. It was of the order of 0.5 Hz at $+22°C$ and 3 Hz at $-93°C$. The increase may be due to the molecular association through S—H $\cdots$ O type hydrogen bonding as has been observed by infrared spectral studies [10]. The NMR spectra of neat $CH_3COSH$ (TMS as reference) in the temperature range $+38°C$ to $+83°C$ showed signals for the SH and $CH_3$ protons at $\delta$ values of 5.25 ppm and 2.35 ppm respectively. We failed to observe the signal for the OH proton. A comparison of $\delta$ values of SH and $CH_3$ protons in different media is given in Table 3.

TABLE 3

$\delta$ Values (in ppm) of SH and $CH_3$ protons of $CH_3COSH$ in different media[a]

| Medium | Temperature | SH proton | CH, proton |
|---|---|---|---|
| Carbondisulphide[b] | $+22°C$ | 4.90 | 2.30 |
| pure liquid | $+38°C$ | 5.25 | 2.38 |
| Chloroform[c] | $+37°C$ | 4.70 | 2.33 |

[a]TMS as reference.
[b]30% *w/v*.
[c]19% *w/v*.

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