# Vibrational Spectra of Seven Halomethanes*

**Valdas Sablinskas, Peter Klaeboe, Claus J. Nielsen and Detlev Sülzle**
*Department of Chemistry, University of Oslo, P.O. Box 1033, 0315 Oslo 3, Norway*

---

Seven halogenated methanes $CX_2YZ$ (with X, Y and Z being H, F, Cl, Br or I), all with a plane of symmetry, were synthesized and studied by infrared (IR) and Raman techniques. They belong to point group $C_s$ and have six fundamentals of species $a'$ and three of species $a''$. Some of these molecules were investigated 30–40 years ago, but very little spectroscopic work has been carried out since. The IR spectra were recorded in the region from 3100 to 100 $cm^{-1}$ in the vapour, liquid and crystalline states. Raman spectra, including semi-quantitative polarization measurements on the liquids, were obtained, additional vapour spectra were recorded, and the liquid spectra were also given in the $R(\omega)$ representation. Accurate Raman spectra were recorded of the crystalline phases at temperatures above 78 K, and the external modes in the range 200–10 $cm^{-1}$ were investigated as probes for the phase transitions. The fundamentals of chloroiodomethane have been listed and two crystalline phases were observed for this compound, while only one crystal phase was observed for the other molecules. No plastic phases were detected in any of the compounds. Preliminary results of these investigations are presented.

**Keywords:** *Infrared; Raman spectroscopy; halomethanes; phase transitions*

---

The substituted methanes are among the simplest organic molecules. Because of their small size and straightforward spectra, some of the halogenated methanes were investigated by vibrational spectroscopy 30–40 years ago. Hence, Plyler and Benedict[1] studied the infrared (IR) spectra of several halomethanes in the early 1950s while Meister and co-workers[2,3] published a series of papers on the spectra of these molecules with particular emphasis on the Raman spectra. Scattered spectroscopic work on these molecules, particularly in the crystalline state, has appeared since then.[4,5]

Some of the halomethanes, which are not commercially available, have to our knowledge never been investigated by vibrational spectroscopy. In other molecules, the IR work was performed with low resolution in a restricted range, and the early photographic Raman recordings were limited to the liquid state and gave very uncertain polarization measurements.[6] For these reasons it was decided to synthesize a series of halomethanes with F, Cl, Br and I as substituents, and to record complete IR and Raman spectra in all the three states of aggregation.

Eight halogenated methanes $CX_2YZ$ (with X, Y and Z being H, F, Cl, Br or I), all having a plane of symmetry, were synthesized and studied by IR and Raman techniques. Seven of these compounds are included in this paper. With $C_s$ symmetry these molecules have six fundamentals of species $a'$ and three of species $a''$. Among these compounds, the IR and Raman spectra of dichloroiodomethane have to our knowledge never been studied and chloroiodomethane has previously been investigated in the crystalline state only. Some of the compounds (bromoiodomethane and particularly dichloroiodomethane) were easily coloured after storage, and they reacted to form molecular iodine ($I_2$) when excited by the 514.5 nm argon ion laser line. They were instead illuminated by the 632.8 nm line from a helium–neon laser, but no complete Raman vapour spectrum was obtained for these molecules, particularly as bromoiodomethane has a vapour pressure of a few Torr only. Some preliminary results for the following seven halomethanes: chloroiodo-, bromoiodo- and bromochloromethane (with two hydrogens outside the symmetry plane) and dibromofluoro-, bromodichloro-, dichloroiodo- and dibromochloromethane (with two halogens outside the symmetry plane) are presented. The colour of dichloroiodomethane prevented registration of the low-temperature crystal spectra of this compound.

## Experimental

### Synthesis

The halomethanes were synthesized according to known methods described in the literature,[7–10] except for bromochloromethane, which was commercially available. The final purification of all the compounds involved a careful fractionation in a 1 m spinning band column under a nitrogen atmosphere. The purity of the compounds was subsequently checked by gas-chromatographic analysis (3 m; 3% of SP-2000 on Chromosorb), and was usually better than 99%. The following boiling-points were observed: chloroiodomethane,[7] 381–382 K; bromoiodomethane,[7] 411–412 K; dibromofluoromethane,[8] 338 K; bromodichloromethane,[9] 363 K; dibromochloromethane,[10] 394–395 K and dichloroiodomethane,[9] 313 K/30 mmHg. The compounds were stored under a nitrogen atmosphere at 248 K. In some of the compounds a slight decomposition occurred with time, and they were purified immediately before the spectral investigation by preparative gas chromatography.

### Instrumentation

The IR spectra were recorded with Fourier transform IR spectrometers [Model 88 (4000–400 $cm^{-1}$) and 114c (600–50 $cm^{-1}$)] from Bruker (Karlsruhe, Germany), using TGS (triglycine sulfate) and MCT (mercury cadmium telluride) detectors. The vapours were studied in a 10 cm cell having CsI windows and in a 20 cm cell having polyethylene windows. A multiple-reflection cell with KBr windows capable of giving a 10 m path is currently used for those compounds with low vapour pressures. Infrared liquid spectra were recorded in sealed cells and as a capillary film between KBr plates, whereas the far-IR spectra were obtained in cyclohexane solution in vacuum-tight cells with polyethylene windows.

The Raman spectra were recorded with a triple monochromator spectrometer, Model RT 30, from Dilor (Lille, France), interfaced with a PC from IBM. An argon ion laser, Model 2000, and a helium–neon laser, Model 125 A, both from Spectra-Physics, were employed for excitation, using the 514.5 and 632.8 nm lines. The vapour spectra were recorded at full vapour pressure in cells with windows having Brewster angles, illuminated in a modified multiple-reflection unit from Spex Industries (Edison, NJ, USA). The liquids and solids were investigated in sealed capillaries with use of the 90 and 180° illumination mode. They were also mounted in a cryostat

---

* Presented at the XXVII Colloquium Spectroscopicum Internationale (CSI), Bergen, Norway, June 9–14, 1991.

from Oxford Instruments (Oxford, UK), Model DN 1704, cooled by liquid nitrogen, giving a temperature accuracy of ±0.5 K.

## Results and Discussion

### Internal Modes

As representative examples, some characteristic IR bands of chloroiodomethane in the vapour phase with well-resolved contours are shown in Fig. 1. No Raman spectra in the vapour phase of any of the present halomethanes have previously been published. The vapour spectra of dibromofluoromethane (Fig. 2) and chloroiodomethane (Fig. 3) are presented here. To our knowledge, no spectra have been recorded of dichloroiodomethane, and a Raman spectrum with two polarization directions is reproduced in Fig. 4. As this molecule is slightly coloured and easily forms molecular iodine on irradiation with the 514.5 nm argon line, the spectra were excited with a helium–neon laser. Finally, a Raman crystal spectrum obtained at 90 K of bromoiodomethane, which to our knowledge has never been investigated, is given in Fig. 5.

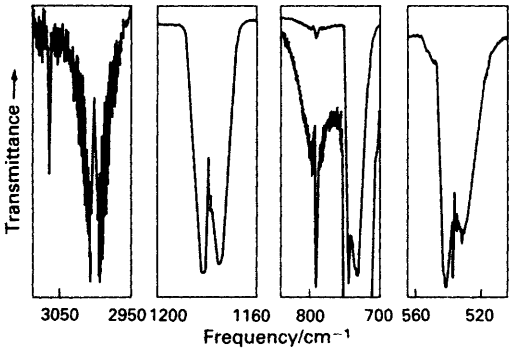

**Fig. 1** IR spectrum of some fundamentals of chloroiodomethane in the vapour phase (resolution 0.4 cm$^{-1}$): path 10 cm and pressure ≈ 2.0 kPa

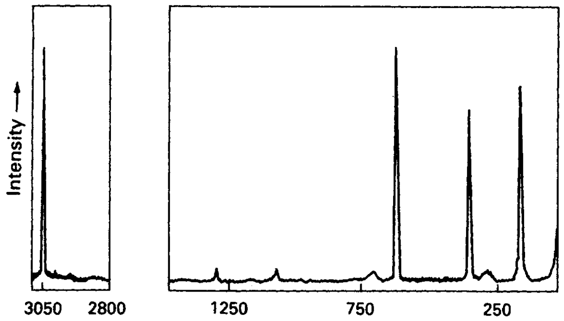

**Fig. 2** Raman spectrum of dibromofluoromethane as a vapour (resolution 2 cm$^{-1}$): pressure 11.0 kPa and excitation line 514.5 nm

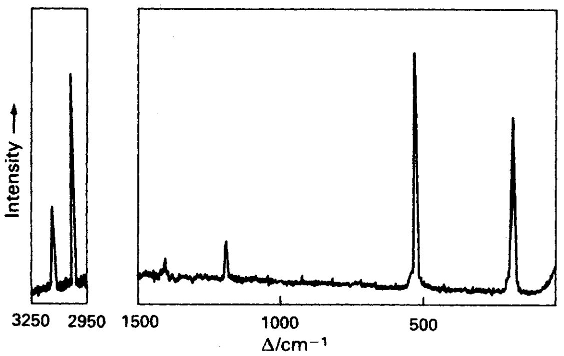

**Fig. 3** Raman spectrum of chloroiodomethane as a vapour (resolution 2 cm$^{-1}$): pressure 4.0 kPa and excitation line 514.5 nm

More detailed spectral results from IR and Raman studies will be published elsewhere.

The fundamental vibrations of chloroiodomethane have previously been observed in Raman spectra for the crystalline phases only[11] and the spectral results for this molecule are listed in Table 1. However, a large number of rotational lines with a spacing of approximately 1.6 cm$^{-1}$ were observed for the IR vapour bands at 3002 cm$^{-1}$ ($\nu_1$) and 790 cm$^{-1}$ ($\nu_9$) and they have not been included in Table 1. In addition, more than one crystal phase was found for this molecule, in agreement with a recent report.[11] The internal modes for these phases are not given here for the sake of brevity, but the external modes are included in Table 2.

In chloroiodomethane, all the three heavy atoms lie in the symmetry plane and the two hydrogens are situated symmetrically outside the plane. The axes of lowest and intermediate moments of inertia will lie in the symmetry plane, and that of the highest moment will be perpendicular to the plane. However, the intermediate axis, situated in the plane, will have a moment of inertia fairly similar to the largest moment, while the smallest moment is approximately 5% of the others. Therefore, this molecule will be nearly an accidental prolate symmetric top, and owing to the low moment of inertia for the $I_A$ axis, it will give well-resolved rotational lines for certain bands.

The fundamentals will divide themselves between six *a*′ and three *a*″ modes, in which the latter modes are depolarized in Raman and give rise to IR vapour bands with *C*-type contours. The in-plane modes of species *a*′ give rise to polarized Raman bands and IR vapour contours that are *A*/*B* hybrids.

There is a marked similarity between the spectra of the three halomethanes investigated, having two hydrogens situated outside the plane: bromochloro-, chloroiodo- and bromoiodomethane. They all have characteristic *C*-type contours for the out-of-plane modes of species *a*″, and *A*/*B* contours for the in-plane modes of species *a*′. Moreover, in each of the compounds, well-resolved rotational fine structures were

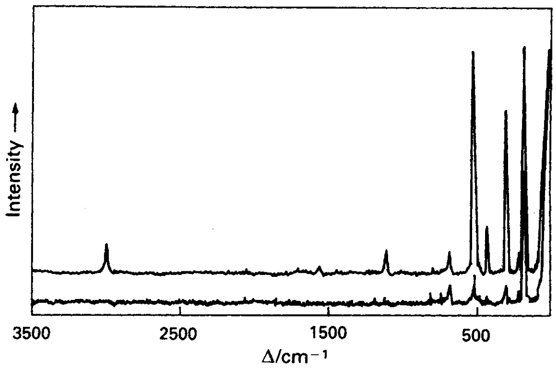

**Fig. 4** Raman spectra of dichloroiodomethane as a liquid in vertical (upper spectrum) and horizontal (lower spectrum) directions of polarization (resolution 4 cm$^{-1}$): excitation line 632.8 nm and 30 mW

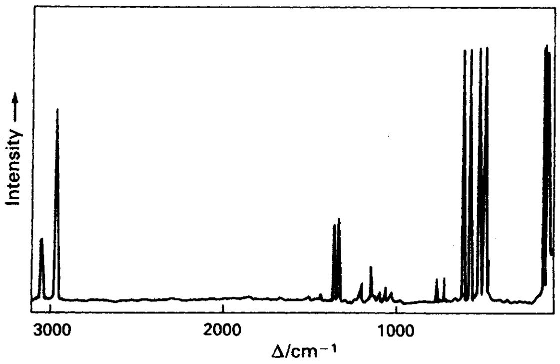

**Fig. 5** Raman spectrum of bromoiodomethane as a crystalline solid at 90 K

**Table 1** Infrared and Raman spectral data for chloroiodomethane

| Infrared |  | Raman |  |  |  |
|---|---|---|---|---|---|
| Vapour | Liquid | Vapour | Liquid | ρ* | Assignment |
|  | 3835 m† |  |  |  | $\nu_7 + \nu_9$ |
|  | 3512 w |  |  |  | $\nu_1 + \nu_5$ |
| 3065 m *C* | 3051 s | 3066 m | 3050 m | 0.2 | $\nu_7$ |
| 3008 m<br>2995 m } *B*‡ | 2980 s | 3001 s | 2978 s | 0.01 | $\nu_1$ |
|  |  |  | 2774 w | P | $2\nu_2$ |
| 2599 w<br>2588 w } *B* | 2574 m |  |  |  | $\nu_2 + \nu_3$ |
|  | 2499 w |  |  |  | $\nu_2 + \nu_8$ |
|  | 2355 m |  |  |  | $2\nu_3$ |
| 2294 w *C* | 2285 m |  |  |  | $\nu_3 + \nu_8$ |
| 2188 w *C*‡ | 2172 s |  |  |  | $\nu_2 + \nu_9$ |
|  | 2109 w |  |  |  | $\nu_2 + \nu_4$ |
| 1981 w | 1977 m |  |  |  | $\nu_3 + \nu_9$ |
|  | 1925 w |  |  |  | $\nu_2 + \nu_5$ |
| 1911 w<br>1900 w } *B* | 1900 w |  |  |  | $\nu_8 + \nu_9$ |
| 1584 vw |  |  | 1578 vw | P | $2\nu_9$ |
| 1474 w<br>1461 w } *B* | 1427 sh |  | 1431 w | P | $2\nu_4$ |
|  | 1395 m | 1412 vw | 1392 m | 0.25 | $\nu_2$ |
| 1384 w<br>1373 w } *B* | 1380 sh |  |  |  | $\nu_3 + \nu_6$ |
| 1223 w<br>1212 w } *B* |  |  | 1252 w | P | $\nu_4 + \nu_5$ |
| 1193 s<br>1183 s } *B* | 1183 † | 1188 m | 1183 m | 0.07 | $\nu_3$ |
| 1074 w *C* | 1111 m |  | 1108 w | 0.6 | $\nu_8$ |
| 1071 w *C* |  |  |  |  |  |
| 1062 w | 1057 w |  | 1056 vw |  | $2\nu_5$ |
|  | 980 w |  |  |  | $\nu_6 + \nu_9$ |
|  | 914 w |  |  |  | $\nu_4 + \nu_6$ |
|  | 848 w |  |  |  |  |
| 790 m, *C*‡ | 789 w |  | 789 w | 0.7 | $\nu_9$ |
| 744 s<br>733 s } *B* | 724 vs§ | 740 vw | 720 m | 0.7 | $\nu_4$ |
| 541 s<br>537 s<br>532 s } *A* | 533 vs§ | 536 s | 531 vs | 0.1 | $\nu_5$ |
|  | 391 w¶ |  | 393 w | P | $2\nu_6$ |
|  | 359 w¶ |  |  |  |  |
|  | 334 m¶ |  | 333 w | P | $\nu_5 - \nu_6$ |
|  | 196 m¶ | 192 s | 196 vs | 0.4 | $\nu_6$ |

* Depolarization ratios in numbers; P, polarized.

† Abbreviations: s, strong; m, medium; w, weak; v, very; and sh, shoulder; *A*, *B* and *C*, vapour phase contours.

‡ Resolved rotational structure for these bands not included.

§ Solution in $CCl_4$.

¶ Solution in cyclohexane.

observed for the symmetric C–H stretches ($\nu_1$) of species *a*′ situated at about 3000 cm$^{-1}$ with a spacing of approximately 1.8 cm$^{-1}$ in bromochloromethane to approximately 1.4 cm$^{-1}$ in bromoiodomethane. Additional resolved rotational bands with irregular spacing were observed in the $CH_2$ rocking modes ($\nu_9$) of species *a*″ situated in the range 860–750 cm$^{-1}$ in the three molecules. The rotational lines making up the *P* and *R* structure of these bands will be discussed elsewhere.

As is apparent from Table 1, the assignments for chloroiodomethane are, in principle, straightforward as is to be expected for a molecule with only five atoms and a symmetry plane. Two of the three *a*″ modes had very characteristic *C*-type contours in the IR vapour spectra with very sharp and intense *Q*-branches, situated at 3065 ($\nu_7$) and at 790 cm$^{-1}$ ($\nu_9$), whereas the third mode ($\nu_8$) gave rise to a weak band at 1074 cm$^{-1}$, apparently with *C*-type contours. They all gave rise to depolarized bands in the Raman spectra of the liquid. No Raman vapour bands were detected for $\nu_8$ and $\nu_9$ as expected for the *a*″ modes, but a distinct band was observed for $\nu_7$ at 3066 cm$^{-1}$.

The in-plane modes of species *a*′ were observed in the IR vapour spectra at 3002 ($\nu_1$), 1189 ($\nu_3$), 740 ($\nu_4$) and 537 cm$^{-1}$ ($\nu_5$), while 1412 ($\nu_2$) and 192 cm$^{-1}$ ($\nu_6$) were observed in the Raman spectrum of the vapour. A number of these bands had typical *B*-type contours in the IR vapour spectra. The Raman counterparts observed in the liquid were all definitely polarized except for the band at 720 cm$^{-1}$ with $\rho = 0.7$. Sharp Raman vapour bands were observed for the *a*′ modes, except for $\nu_4$ attributed to C–Cl stretch, which surprisingly was very weak in Raman.

A marked intensity change between the IR bands $\nu_7$ and $\nu_1$ was observed in the liquid state relative to vapour. Hence, the integrated IR vapour intensity of the 3002 cm$^{-1}$ band with a *B*-type contour relative to that at 3065 cm$^{-1}$ with a *C*-type contour was approximately 50 : 1, whereas in the liquid state the ratio was approximately 1 : 10, giving the asymmetric $CH_2$ stretch ($\nu_7$) an enhancement of 500 from vapour to liquid. Apparently, the dipole–dipole interactions in the liquid, active between the polar molecules of chloroiodomethane, lead to a large increase in the dipole change during the

**Table 2** External modes of halomethanes, recorded as Raman spectra of the crystals and the $R(\omega)$ representation of the liquid

| Halomethane | $p_{vap}$/kPa | $T_{melt}$/K | $\nu_{external}$/ cm$^{-1}$ | $T_{transition}$/ K | $\nu_{external}$/ cm$^{-1}$ | $R(\omega)$*/ cm$^{-1}$ |
|---|---|---|---|---|---|---|
| $CH_2ClI$ | 4.0 | 203 | 39 m† | 155 | 16 w | 49 |
| | | | 46 m | | 25 w | |
| | | | 51 m | | 36 w | |
| | | | 56 s | | 45 w | |
| | | | 77 m, bd | | 60 s | |
| | | | 108 m | | 70 s | |
| | | | 117 m | | 82 vw, bd | |
| | | | 121 m | | 95 vw, bd | |
| $CH_2BrI$ | 0.2 | 257 | 12 s | | | 37 |
| | | | 18 w | | | |
| | | | 23 w | | | |
| | | | 39 m | | | |
| | | | 45 m | | | |
| | | | 55 w | | | |
| | | | 64 s | | | |
| $CH_2ClBr$ | 9.0 | 180 | 15 vs | | | 51 |
| | | | 28 w | | | |
| | | | 32 w | | | |
| | | | 58 s | | | |
| | | | 82 s | | | |
| | | | 111 w, bd | | | |
| $CHBr_2F$ | 11.0 | 192 | 16 w | | | 38 |
| | | | 27 s | | | |
| | | | 33 s | | | |
| | | | 36 w | | | |
| | | | 39 s | | | |
| | | | 52 m, bd | | | |
| | | | 61 w, bd | | | |
| | | | 97 w, bd | | | |
| $CHCl_2Br$ | 5.0 | 220 | 25 sh | | | 53 |
| | | | 36 bd | | | |
| | | | 56 bd | | | |
| | | | 63 sh | | | |
| | | | 85 w | | | |
| $CHBr_2Cl$ | 2.0 | 245 | 33 bd | | | 43 |
| | | | 50 bd | | | |
| | | | 77 w | | | |

* Band position [for meaning of the $R(\omega)$ representation see refs. 9 and 10].

† Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; and bd, broad.

asymmetric $CH_2$ stretch. No comparable enhancement was observed in the Raman spectra.

As is apparent from Table 1, the observed IR bands not assigned as fundamentals can in most instances be explained as binary combination bands or overtones. Only two of these bands (333 and 393 cm$^{-1}$) were observed in Raman. The bands at 334 (IR) and 333 cm$^{-1}$ (Raman) can be explained as the difference $\nu_5 - \nu_6$, for which the corresponding sum was hidden by $\nu_4$. This is supported by the fact that these bands disappear in the low-temperature crystals.

## External Modes

The low-temperature Raman spectra were carefully recorded for all the present halomethanes, except for dichloroiodomethane. Considerable changes in position and intensities of the Raman bands in the whole region 3000–100 cm$^{-1}$ were observed on going from the liquid to the crystalline state, and frequent examples of band splittings were observed. The most significant changes between the liquid and crystalline states occurred invariably in the low-frequency range, caused by the external modes active in the crystal. The external modes observed below 100 cm$^{-1}$ for all the six halomethanes are listed in Table 2.

Different cooling procedures between ambient and 78 K were carried out, ranging from very slow cooling of approximately 1 K min$^{-1}$ to shock-freezing in liquid nitrogen and subsequent slow annealing to higher temperatures. As is apparent from Table 2, only one low-temperature crystal was observed for each of the compounds, except for chloroiodomethane, for which two crystalline phases were observed. A third anisotropic phase (IV) was reported for this molecule in the temperature range above 185 K, but below the assumed plastic phase described by Torrie *et al.*[11] This phase (IV) was obtained by heating phase III to 185 K, and it was apparently metastable. In spite of numerous attempts, this phase was not observed in the present work. The sample obtained by Torrie *et al.*[11] was, in most instances, condensed from a vapour on a cold window whereas our substance was a liquid contained in a capillary that was initially cooled from ambient temperature. Our crystalline phases 1 and 2 for chloroiodomethane were identical with the phases II and III reported.[11] We observed a reversible phase transition between the phases 1 and 2 at 155 K.

In most bands, the internal modes were split in the high-temperature phase 1, but no splitting was detected in the low-temperature phase 2. The phase transitions for chloroiodomethane are currently being studied by differential scanning calorimetry. It was also observed that the Raman intensity of $\nu_9$ (at 789 cm$^{-1}$ attributed to $CH_2$ rock) was reduced by an order of magnitude from phase 2 to 1. This is also apparent from the earlier spectra.[11] Probably, the $CH_2$ rocking motions are hindered in the crystal lattice of phase 1.

The plastic phase reported[11] for chloroiodomethane was not verified in our spectra. On the contrary, at temperatures below 245 K our sample was a liquid (although of fairly high viscosity), as verified by rapidly removing the capillary from the cryostat. Moreover, the Raman spectra in the range

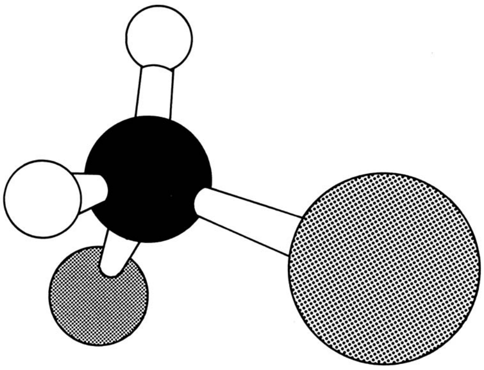

**Fig. 6** Molecular structure of chloroiodomethane

245–203 K were identical with those of the liquid. Each of the six halomethanes were carefully investigated with the purpose of detecting plastic crystalline phases, but to no avail. Apparently, the dihalo- and the trihalomethanes investigated deviate too much from spherical symmetry, because of the bulky halogens, to favour plastic crystalline phases (Fig. 6).

A striking similarity was observed between the low-frequency Raman spectrum of bromoiodomethane and the low-temperature phase (phase 2) of chloroiodomethane, as is apparent from Table 2. It is assumed tentatively that these crystals are isomorphous.

The low-frequency spectra of bromodichloro- and dibromochloromethane were similar, giving only a few broad bands in each instance. In these two trihalomethanes the three halogen atoms are of comparable size, and they can easily form a disordered crystal and therefore give broad, diffuse bands. In the third of the trihalomethanes studied (dibromofluoromethane), however, an ordered crystal is expected because of the large differences in size between fluorine and bromine, in agreement with the sharp external modes observed for this compound. The low-frequency spectrum of dibromofluoromethane was indeed similar to those of the dihalomethanes. The spectra of the liquids were plotted in the $R(\omega)$ formalism developed by Lund *et al.*[12] and used by them and other workers in a large number of systems (for a recent review see ref. 13). This reduction of the Raman spectrum leads to a 'removal' of the Rayleigh intensity (the mathematical treatment is not included here for the sake of brevity) and treats the intensity above 10 cm$^{-1}$ as Raman scattering in a density of state format.

In this representation, a broad, apparently librational, band was observed in the 35–55 cm$^{-1}$ region in all the halomethanes studied, for which the maxima are listed in Table 2. These $R(\omega)$ bands represented an envelope of the librational external bands of each crystal, as is demonstrated in Fig. 7, and is a result of the similar density of states of the liquids and the crystals.

## Conclusion

Three halomethanes that have hydrogens outside the symmetry plane: chloroiodo-, bromoiodo- and bromochloromethane, and four molecules with two halogens outside the symmetry plane: dibromofluoro-, bromodichloro-, dichloroiodo- and dibromochloromethane, were synthesized, and preliminary IR and Raman spectral results are presented. Members of the former group had very low moments of inertia about the *A* axis, and well-resolved rotational fine structures were observed in the IR vapour spectra.

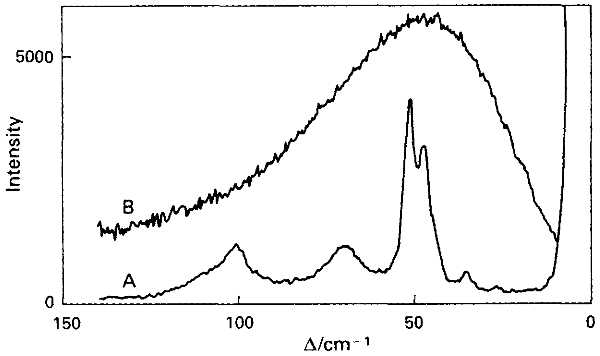

**Fig. 7** Low frequency Raman spectrum of chloroiodomethane, recorded at 195 K, showing A, phase 2 and B, a liquid spectrum at 210 K in the $R(\omega)$ representation (resolution 2 cm$^{-1}$): excitation line, 514.5 nm

The spectral results for chloroiodomethane are presented in detail. For the remaining compounds the crystal spectra in Raman obtained at low temperatures are presented. Except for chloroiodomethane, in which two phases were observed, only one crystal phase was detected for each compound, and no plastic phase was observed for any of the seven halomethanes. The lattice modes in Raman were compared with the liquid state spectra, presented in the $R(\omega)$ representation.

Two of the authors (V. S. and D. S.) have received financial support from the Royal Norwegian Council for Science and Technology (NTNF). A travel grant to V. S. from the Norwegian Academy for the Learned Societies is acknowledged.

## References

1 Plyler, E. K., and Benedict, W. S., *J. Res. Natl. Bur. Stand.*, 1951, **47**, 202.
2 Weber, A., Meister, A. G., and Cleveland, F. F., *J. Chem. Phys.*, 1953, **21**, 930.
3 Murata, H., Palm, A., and Meister, G., *J. Chem. Phys.*, 1955, **23**, 702.
4 LeBlanc, L. M., and Anderson, A., *J. Raman Spectrosc.*, 1990, **21**, 693.
5 LeBlanc, L. M., and Anderson, A., *J. Raman Spectrosc.*, 1991, **22**, 355.
6 Pontarelli, D. A., Meister, A. G., Cleveland, F. F., Voelz, F., Bernstein, R. B., and Sherman, R. H., *J. Chem. Phys.*, 1952, **20**, 1949.
7 Miyano, S., and Hashimoto, H., *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2869.
8 Schlosser, M., and Heinz, G., *Chem. Ber.*, 1971, **104**, 1934.
9 Sülzle, D., *Tetrahedron Lett.*, 1987, **28**, 2769.
10 Fedorynski, M., Poplawska, M., Nitschke, K., Kowalski, W., and Makosza, M., *Synth. Commun.*, 1977, **7**, 287.
11 Torrie, B. H., Prystupa, D. A., Clark, J., Taylor, S., and Wong, Y. V., *J. Raman Spectrosc.*, 1990, **21**, 423.
12 Lund, P.-A., Faurskov Nielsen, O., and Praestgaard, E., *Chem. Phys.*, 1978, **28**, 167.
13 Brooker, M. H., Faurskov Nielsen, O., and Praestgaard, E., *J. Raman Spectrosc.*, 1988, **19**, 71.

*Paper 1/02983E*
*Received June 18, 1991*
*Accepted August 5, 1991*