

## 1.03 HEAT CAPACITY OF CHLOROMETHANE BY IR AND ACOUSTIC INTERFEROMETRY

(5 points)

### Relevant lecture courses and topics in physical chemistry

When carrying out this experiment, you will find it helpful to have some understanding of selection rules in IR spectroscopy and an elementary knowledge of Statistical Mechanics; it also draws upon simple ideas from symmetry. Relevant lecture courses: Symmetry I (2nd year, Michaelmas term), Symmetry II (2nd year, Hilary term), Statistical Thermodynamics (2nd year, Hilary term), Atomic and Molecular Spectroscopy (2nd year, Hilary term),

<http://ptcl.chem.ox.ac.uk/~hmc/tlab/experiments/103.html>

### Outline

The heat capacity of a gas can be measured in several different ways. In this experiment you will use two quite different methods and compare the results. Infrared spectra of most gases are simple to obtain, and if the molecule is not too large, can be analyzed to yield information on the vibrational energy levels in the gas; the heat capacity can then be calculated using statistical mechanics. In the second approach to be used, the heat capacity is found by measuring the speed of sound in the gas using an acoustic interferometer.

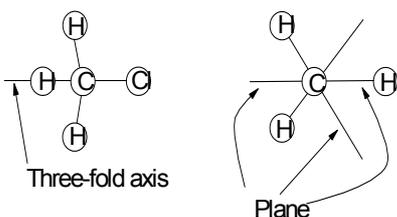


Fig. 1. Symmetry elements in chloromethane.

## Safety/COSHH

Chloromethane (methyl chloride) is a narcotic. In the event of a serious leak, tell a demonstrator or technician immediately and evacuate the area.

There is more detailed information on chloromethane at <http://ptcl.chem.ox.ac.uk/MSDS/CH/chloromethane.html>.

## Preparation

Start by reading through these instructions carefully. You may find it helpful to review the relevant sections of lecture courses on Statistical Mechanics and Molecular Spectroscopy. Remind yourself what is meant by P, Q and R branches, parallel and perpendicular bands, heat capacities and equipartition.

## General References

1. *Symmetry and Spectroscopy*, D. Harris and M.D.Bertolucci, Dover, New York (1989). [Copies in the libraries at Corpus, New, Queen's and the RSL].
2. *Infrared and Raman Spectra of Polyatomic Molecules*, G.Herzberg, Van Nostrand, New York (1945) p.312. [Copies in BNC, Corpus, Hertford, LMH, Lincoln, Magdalen, Merton, Queen's, Somerville, St Anne's, St Catherine's, St Peter's, Trinity, RSL, Hooke Mf 5]
3. *Chemical Applications of Group Theory*, F.A.Cotton, Interscience, New York (1990), 71. [Copies in Balliol, Corpus, LMH, Lincoln, Magdalen, Merton, Somerville, St Anne's, SEH, St Hugh's, St Peter's, Trinity, RSL, Hooke Ce 4]
4. Ref 2. p314.
5. *Fundamentals of Molecular Spectroscopy*, C.N.Banwell, McGraw Hill, London, 4th Edn. (1994) [Copies in LMH, Magdalen, St Anne's, St Catherine's, St Hugh's, St Peter's, RSL, Hooke Cd 6]
6. *Physical Chemistry*, R.S.Berry, S.A.Rice and J.Ross, John Wiley, New York (2000). [Copies in Balliol, BNC, Corpus, LMH, RSL, Hooke Ca 101]
7. Ref 5, p.763.
8. *Fundamentals of Ultrasonics*, J.Blitz, Butterworths, London 2nd edn. (1967), p.90. [Copies in Merton, RSL]
9. Ref. 6, p.1080.
10. *Absorption and Dispersion of Ultrasonic Waves*, K.F.Herzfeld and T.A.Litovitz, Academic Press, New York (1959), p.109. [Copies in Corpus, RSL]

## Theory

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### Vibrations of chloromethane [1,2]

Chloromethane has the symmetric top structure shown in Fig. 1. The molecule has a three-fold axis of symmetry and two equal moments of inertia. In group theory nomenclature [3] it belongs to  $C_{3v}$ .

A non-linear N-atom molecule has  $(3N - 6)$  normal modes of vibration. The 9 normal modes in chloromethane are three parallel vibrations, (of symmetry  $A_1$ ), in which the direction of the dipole moment change is parallel to the symmetry axis of the top, and three degenerate pairs of perpendicular vibrations (of symmetry E), in which there is a change in dipole moment at right angles to the symmetry axis. Both classes of vibration are infrared active (recall that a change in dipole moment is necessary), so there should be six strong bands in the spectrum.

### Rotational fine structure [5]

The two types of vibration in chloromethane give rise to different rotational fine structure of their bands. For a diatomic molecule, we can characterize molecular rotations in terms of a single quantum number  $J$  (the total angular momentum of the molecule), but for non-linear molecules a second quantum number  $K$  (the angular momentum about the axis of the top) is required.  $K$  is a component of  $J$ , and can therefore never be greater than  $J$ .

The selection rules for parallel vibrations are:

$$\Delta v = \pm 1; \quad \Delta J = 0, \pm 1; \quad \Delta K = 0$$

where  $v$  is the vibrational quantum number. (The specific selection rule  $\Delta v = \pm 1$  arises from the assumption of pure harmonic motion. This is not of course strictly valid, and low intensity overtones corresponding to  $\Delta v = \pm 2, \pm 3$ , etc will in practice occur).

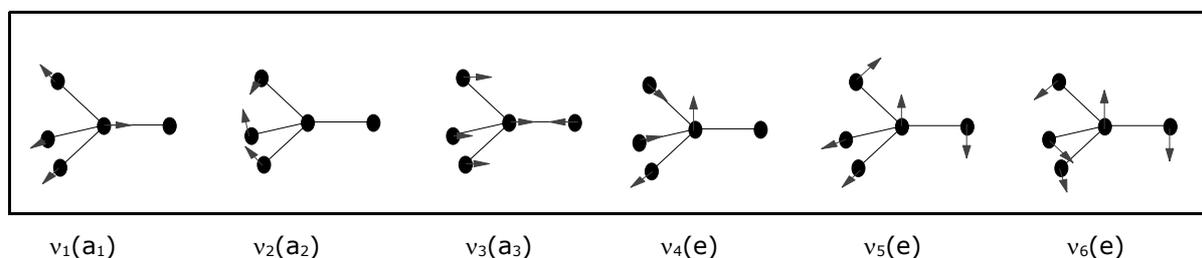


Fig. 2. Normal modes of vibration in chloromethane.

These selection rules define which parallel vibrations are active in the infrared;  $\Delta K = 0$  because rotations about the symmetry axis do not rotate the electric dipole of the

molecule. The selection rules are the same as those for the perpendicular vibrations of linear polyatomics, and the bands exhibit the same P, Q and R branching. The sub-bands corresponding to different values of K are almost exactly superposable. (You could show this using the formula for energy levels in such a molecule,  $E = BJ(J+1) + (A-B)K^2$ ).

In perpendicular vibrations, changes to the dipole at right angles to the symmetry axis occur, and changes in K become possible. The selection rules are:

$$\Delta v = \pm 1; \quad \Delta J = 0, \pm 1; \quad \Delta K = \pm 1$$

In this case the sub-bands are no longer superimposed, but are spread out in two series, the P type and the R type according to the sign of the change in K. When instruments of modest resolving power are used, only the Q branches of these sub-bands are observed, above an envelope of overlapping and unresolved P+R branches. The Q branches form a continuous series through the band origin. They are normally denoted by the letter Q with P or R as superscript, and the lower state K as subscript. Thus  ${}^R Q_0$  is the Q branch in which K changes from 0 to 1, and  ${}^P Q_2$  that in which K changes from 3 to 2. Assignment may generally be made by taking  ${}^R Q_0$  to be the strongest Q branch in the band.

A difference of statistical weights of the K levels, analogous to that for linear molecules, can occur in symmetric top molecules. In chloromethane the three-fold axis of symmetry and the spins of the hydrogen nuclei lead to an alternation in peak height in the ratio 2:1:1:2:1:1:2... This can be seen in the perpendicular bands in which the intensities of successive Q branches reflect the population of the K levels from which they originate. Thus the strong lines in a perpendicular band are those with K = 0, 3, 6, etc. This is a further aid in the assignment of the band origin.

Two principal types of interaction disturb the "ideal" pattern described above. Fermi resonance is a resonance interaction between two vibrational levels of similar energy and the same symmetry. This interaction mixes the wavefunctions and "pushes apart" the levels. This can result in a greatly enhanced intensity of an overtone vibration in Fermi resonance with a fundamental. For example, in chloromethane we would expect three parallel and three perpendicular bands. In fact seven strong bands appear, one of which is due to Fermi resonance increasing the intensity of the parallel component of the overtone  $2\nu_5$ . The irregular appearance of the perpendicular fundamental  $\nu_4$  has also been ascribed to Fermi resonance interaction, in this case with the level  $3\nu_6$ .

The second type of interaction is the Coriolis effect, which couples vibrational and rotational motions. This arises when a body moves in a rotating framework and produces a force at right angles to both the direction of motion and to the axis of rotation. In a rotating molecule the motion of an atom in one vibrational mode may give rise to a force in a direction close to that of another mode, and an interaction between the modes may be set up. This occurs between the members of a degenerate pair of perpendicular vibrations in a symmetric top molecule and is an important factor in determining the spacing of the Q branches in perpendicular bands. It may also occur between a parallel

and a perpendicular vibration, if the frequencies of these are close, and an interaction of this type is responsible for irregularities in the  $\nu_5$  band of chloromethane.

### Heat capacity from spectra [6]

It is possible to derive the heat capacity of a molecule from its infrared spectrum in a fairly simple fashion. The heat capacity is related to the degree to which vibrational (and translational and rotational) motion can be excited at a given temperature. You will recall from your first year quantum course that this depends upon the size of the gaps between the relevant energy levels. It follows that, if we can measure these gaps, we can in principle calculate the heat capacity of the molecule.

Finding the gaps is easy - we just record the infrared spectrum of the molecule, and an approximate value for  $\omega_e$  can be read directly off the spectrum. These values of  $\omega_e$  (there are several of them of course, because the molecule has several vibrations, each of which will have its own characteristic vibrational energy) are then fed into a statistical mechanical calculation, as we now show.

The total molecular partition function  $q$  for a set of independent (non-interacting) polyatomic molecules is:

$$q = q^T q^R q^V q^E \quad (1)$$

in which the individual partition functions are the translational, rotational, vibrational and electronic terms. The expression assumes that the energies for the separate motions are independent of one another (thus we are ignoring the minor influence of the Coriolis effect).

It can be shown that  $C_v$  (per mole) is related to the partition function by:

$$C_v = 2RT[\partial \ln q / \partial T]_v + RT^2[\partial^2 \ln q / \partial T^2]_v \quad (2)$$

The translational, rotational, vibrational and electronic contributions to the heat capacity may therefore be calculated and the total heat capacity found from the sum of these terms, since:

$$C_v = C_v^T + C_v^R + C_v^V + C_v^E \quad (3)$$

We now calculate these various heat capacities in turn; this turns out to be fairly trivial except in the case of the vibrations. From a knowledge of the energy levels of a particle in a 3-dimensional box it can be shown that

$$q^T = \frac{V}{h^3} (2\pi mkT)^{\frac{3}{2}} \quad (4)$$

Therefore  $\ln q^T = \frac{3}{2} \ln T + \text{constant} \quad (5)$

(where the constant is independent of T), and hence

$$C_v^T = \frac{3}{2} R \quad (6)$$

This is also the classical (equipartition) value, comprising  $\frac{1}{2}R$  for translation in each Cartesian direction. Such agreement is to be expected since translational levels are extremely closely spaced, so quantisation can be ignored and we can assume classical behaviour.

The rotational levels are also closely spaced, and allowing  $\frac{1}{2}R$  for rotation about each of the three axes, by the equipartition principle:

$$C_v^R = \frac{3}{2} R \quad (7)$$

To calculate the vibrational partition function, we assume chloromethane undergoes independent harmonic oscillation at each fundamental vibration frequency. (We need to consider each vibration separately.) Then the total vibrational partition function is the product of the partition functions for each fundamental vibration  $\nu_i$  and is given by (excluding zero point motion)

$$q_{vib} = \prod_{i=1,9} [1 - \exp^{-h\nu_i/kT}]^{-1} \quad (8)$$

From equation 2, the heat capacity contribution from a single fundamental vibration is therefore given by:

$$C_{v,i} = R \left(\frac{\theta_i}{T}\right)^2 \frac{\exp^{-\theta_i/T}}{[1 - \exp^{-\theta_i/T}]^2} \quad (9a)$$

where  $\theta_i = h\nu_i/k$  is the characteristic vibrational temperature for the particular mode with vibrational frequency  $\nu_i$ . Note that Equation (9a) is a "universal function" of the dimensionless ratio  $T/\theta_i$ : different modes of a molecule have different vibrational frequencies and hence different vibrational temperatures, but  $C_{v,i}$  depends in the same way for all modes upon the "scaled" temperature,  $T/\theta_i$ . The total vibrational heat capacity is simply a sum of the individual contributions:

$$C_v = \sum_{i=1}^9 C_{v,i} \quad (9b)$$

Finally, chloromethane is not appreciably electronically excited at room temperature, so  $q^E = 1$  and hence the electronic contribution to the heat capacity is in practice zero.

### Heat capacity from the speed of sound [8,9]

When sound travels through a gas, molecules move back and forth in the direction of propagation and form what is known as a longitudinal pressure (or compression) wave. To minimize wall and edge effects, the frequencies used in this experiment are around 100 kHz. At these frequencies the time interval between passage of a compression

maximum and minimum is brief. The pressure variation occurs rapidly enough for heat conduction to be negligible, so compression and expansion in the wave are nearly adiabatic processes.

Reversible adiabatic processes in perfect gases obey the expression

$$pV^\gamma = \text{const.} \quad (10)$$

where  $\gamma = C_p/C_v = 1 + R/C_v$  (see Atkins' Physical Chemistry). In terms of mass density  $\rho$  ( $= nM/V$  with  $M$  the molar mass), this is just

$$p/\rho^\gamma = \text{const} \quad (11)$$

Differentiating this expression with respect to  $\rho$ , we find that

$$[\partial p/\partial \rho]_s = \gamma p/\rho \quad (12)$$

(where constant  $S$  follows since adiabatic processes are isentropic). It can be shown that the speed,  $c$ , of a plane longitudinal wave in a homogeneous medium of uniform density  $\rho$  is given by:

$$c^2 = [\partial p/\partial \rho]_s \quad (13)$$

hence, combining equations 12 and 13 with the ideal gas law (in the form  $P = \rho RT/M$ )

$$c^2 = \gamma RT/M \quad (14)$$

A better approximation to the behaviour of real gases is the virial expansion:

$$pV/nRT = 1 + B'p \quad (15)$$

where the second virial coefficient  $B'$  is a measure of the gas imperfection. It can be shown that, in general, equation 13 may be expressed in the form

$$c^2 = [\partial p/\partial \rho]_s = \gamma [\partial p/\partial \rho]_T = -\gamma V^2/nM [\partial p/\partial V]_T \quad (16)$$

With  $(\partial p/\partial V)_T$  from equation (15), equation (16) yields:

$$c^2 = \frac{\gamma}{M} RT [1/(1 - \frac{B'nRT}{V})^2] = \frac{\gamma RT}{M} [1 + 2pB' + \dots] \quad (17)$$

The terms in  $B'$  (and higher) may be eliminated by measuring  $c^2$  at a series of pressures and extrapolating to  $p = 0$ , whereupon the value of  $\gamma$  is that appropriate to a perfect gas, i.e.

$$\gamma_o = 1 + \frac{R}{C_v} \quad (18)$$

thus allowing  $C_v$  to be determined.

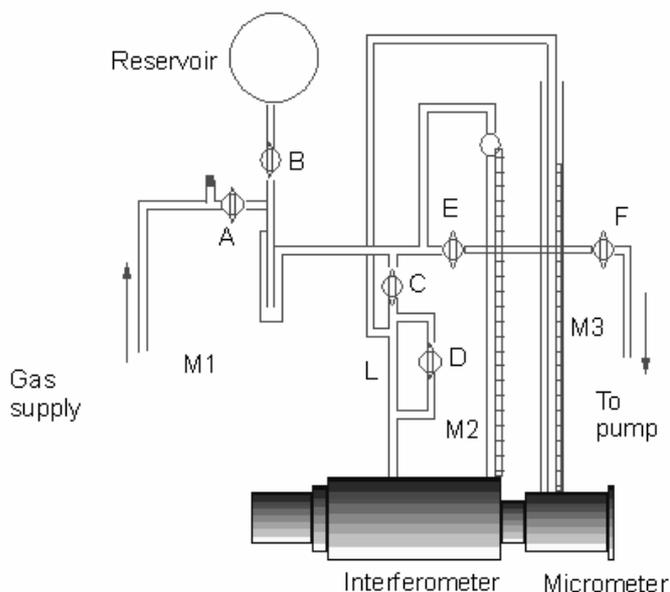
## Procedure

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### Spectroscopic measurements

An absorption cell is provided filled with chloromethane at a suitable pressure. Touch neither the taps on the cell, nor the NaCl cell windows, which are easily marked by fingerprints. Record the ir spectrum of chloromethane at moderate resolution. Also record the principal bands under high resolution on an expanded scale. Use these spectra to measure the frequencies of the bands. (The ideal procedure would be to use a calibrant gas with lines of known frequency as a secondary standard. However, for this experiment it will be sufficient to use the wavenumber scale on the spectrometer.)

Fig. 3 The Interferometer.



### Speed of sound measurements [10]

The acoustic interferometer contains disks of Melinex film to act as sound transmitter and receiver. The receiver is mounted on a rod which can be moved by turning a micrometer, thus changing the distance between transmitter and receiver. As this distance changes, the signal detected by the receiver rises and falls due to interference between transmitted and reflected sound waves. Maxima, which are separated by half a wavelength, are readily recognized, since at a maximum the oscilloscope trace collapses to a straight line.

The apparatus must be pumped out before filling with gas. It is essential this be done SLOWLY to protect the Melinex films. Close the direct connection, D, between the interferometer and the vacuum line leaving the leak, L, open; carefully evacuate the line. When the manometer, M3, is steady, record its height. Close the connection, C, to

the interferometer and the tap, E, connecting the line to the vacuum pump, then carefully fill the line and gas bulb with chloromethane to atmospheric pressure. The technician will supply you with a balloon filled with the gas. Do not bubble gas through the mercury reservoir - chloromethane is a narcotic.

Close tap A and place a Dewar of liquid nitrogen around the trap. Wait five minutes for the chloromethane to collect there (it will appear as a white crystalline powder), then pass any remaining gas slowly through the trap by opening tap E a small amount. Pump for a further minute to remove any traces of air. Close the connection to the pump, open the leak to the interferometer, remove the Dewar and allow the chloromethane to fill the line, gas bulb and interferometer.

Switch on the oscilloscope, amplifier (the small box in the line between detector and oscilloscope) and oscillator; adjust the oscilloscope so that, when transmitted and reflected waves are in phase, the trace is a straight line about 5-10 cm long. If you have difficulty getting a suitable trace, check the settings on, and connections to, the oscilloscope, which are given in Appendix A.

Turn the micrometer to about 6 cm. Slowly move it inwards, recording the positions at which the trace collapses to a straight line. Try to approach the maxima smoothly and from the same direction each time to minimize backlash errors. The change in micrometer reading for successive samples will be very small, so you should do this step with care. Record a series of measurements at pressures from close to atmospheric to the lowest pressure at which satisfactory measurements can be made, pumping out THROUGH THE LEAK each time.

At the end of the experiment close all taps; leave the interferometer evacuated. Isolate the vacuum line from the pump by closing tap F, open the air leak to the pump, then turn it off. Ensure that you have turned off the amplifier, oscillator and oscilloscope.

## **7 Calculations**

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Assign the bands to the normal modes of chloromethane and indicate your assignment on the spectrum. First identify the parallel bands, using the hints given in the theory section: these will have 'smooth' P and R branches, and the Q branch should be visible on at least two of the bands. The perpendicular bands are easily identified by their clearly alternating intensities, and the band origin is identified with the most intense Q-branch line. You will also need to identify, and eliminate from further consideration, the reasonably intense Fermi resonance overtone occurring at around  $2\nu_5$ . If you are unsure about the assignments, and in any case before leaving the laboratory, consult a demonstrator .

Determine and tabulate the positions of the six bands, and hence calculate the characteristic vibrational temperature for each mode. Calculate the vibrational

contributions to the heat capacity for the six fundamental vibrations using equation 9, do not forget to count degenerate vibrations twice. Add together translational, rotational and vibrational contributions to obtain the total heat capacity.

Find the mean of each set of interferometer readings using the following procedure: divide your readings into two groups; if you had twenty readings, divide them into two groups of ten. Now subtract the first from the eleventh, second from the twelfth and so on. Note how many half-wavelengths the result of your subtraction corresponds to. Thus calculate the mean wavelength. Plot  $c^2$  against  $p$  to obtain  $C_v$  (equations 17 and 18), treating units with care. Compare the values of heat capacity obtained by the two methods; comment on the agreement - or lack of it - between the two results. Discuss the magnitude and source of errors in the experiment.

### Appendix A - Oscilloscope Settings

The oscilloscope normally supplied for this experiment is a Gould OS300. If the oscilloscope is different and you cannot get it to function correctly, ask for help from a demonstrator.

Controls on the oscilloscope are left untouched during an experiment, so you should find that it is set up correctly. You may wish to check that the oscilloscope is set up as below. The precise setting is not crucial. If the oval on the screen is well-defined you need not change the settings.

MODE X-Y	All push buttons out
CH1 (X) 1 V cm <sup>-1</sup>	CH2 (Y) 10 V cm <sup>-1</sup>

Triggering (the small sliders to the bottom of the CH1 and CH2 units) either AC or DC

The CH1 input on the oscilloscope should be connected to the right-hand terminal on the frequency source.

The CH2 input on the oscilloscope should be connected to the Output terminal of the amplifier

The LH socket on the frequency source should be connected to the BNC (round) terminal at the rear of the interferometer.

The BNC (round) terminal at the left hand side of the interferometer should be connected to the input terminal on the amplifier.

## **Chemical Properties, Hazards and Emergency Treatment**

Gloves are not necessary for this experiment, but may be worn if you wish. Neoprene or nitrile are both suitable materials.

### **Chloromethane**

Colourless gas. May act as a narcotic if breathed in. Brief exposure to this minor amounts of material is unlikely to have any lasting harmful effect, but you should evacuate the area if the apparatus is broken, or if gas is released into the laboratory in some other way.