Structural Parameters of Methyl Iodide by Infrared Spectroscopy

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A major use of infrared spectroscopy lies in the determination of structural parameters for small molecules. A number of experiments for undergraduates have been described in which structural parameters of molecules are determined from an analysis of their infrared spectra. However, they deal with either linear or triatomic molecules (e.g., *1–4*). This paper describes an experiment in which a careful study of the rotation-vibration spectrum of methyl iodide permits calculation of the following parameters; (1) band origins of the fundamentals, (2) Coriolis coupling constants of the degenerate modes, (3) rotational constants, (4) carbon-hydrogen and carbon-iodine bond lengths, and (5) carbon-hydrogen and carbon-iodine force constants.

Modern Instrumentation

The explosive growth in microcomputer and laser technology has led to a revolution in high resolution infrared spectroscopy. The most precise infrared measurements now available for methyl iodide (8 significant figures or better) have been achieved with Fourier transform (*5*) or infrared laser-radiofrequency double resonance (*6*). Techniques which have been common in other areas of spectroscopy (e.g., Lamb dip (*7*), Zeeman and Stark effects (*8*)) are also being applied to infrared studies. It is probable that advances in Fourier transform techniques (*9*) and tunable lasers (*10*), as well as a determined effort by several commercial suppliers of infrared spectrometers, will eventually lead to the demise of the ubiquitous grating spectrometer for high resolution infrared studies. Nevertheless, many interesting and useful experiments can be performed with a medium resolution grating instrument. The experiment described in this paper can be performed with either a good grating or Fourier transform spectrometer.

Theory

Methyl iodide is a prolate symmetric top. Two quantum numbers are necessary to define the rotational energy of a symmetric top molecule. J determines the total angular momentum of the molecule while K determines the angular momentum about the symmetry axis. These quantum numbers take the values

$$J = 0, 1, 2, 3 \dots .$$

$$K = 0, \pm 1, \pm 2, \dots , \pm J$$

Under low resolution, or in condensed phases, only the effects of vibrational motion are resolved. However, under medium resolution in the gas phase it is often possible to see the rotational transitions which accompany each vibrational transition. The rotational structure depends on the direction of change to the dipole moment. If the dipole moment changes in the direction of the symmetry axis, then the band is called a parallel band; whereas, if the change is at right angles, it is called a perpendicular band.

If the effects of centrifugal distortion and Coriolis coupling are ignored, then the rotation-vibration energy is given by (*11*).

$$E_{rv} = \sum \left(v_i + \frac{d_i}{2} \right) hc v_i + hc \{ B_v J(J + 1) + (A_v - B_v)K^2 \} \quad (1)$$

the first term representing the vibrational energy and the second term representing the rotational energy.

Parallel Bands

Selection rules: for $K = 0$, $\Delta K = 0$, $\Delta J = \pm 1$

for $K \neq 0$, $\Delta K = 0$, $\Delta J = 0, \pm 1$

where J and K denote the rotational angular momentum quantum numbers in the lower vibrational level. There are, therefore, three sets of bands determined by $\Delta J = -1$ (P), $\Delta J = 0$ (Q), and $\Delta J = +1$ (R). For the Q branch eqn. (1) shows that

$$\nu = \nu_0 + J(J+1)(B_{v'} - B_{v''}) + \{(A_{v'} - B_{v'}) - (A_{v''} - B_{v''})\}K^2 \quad (2)$$

The single primes (v') represent upper state rotational constants while the double primes represent lower state rotational constants, and ν_0 is the band origin.

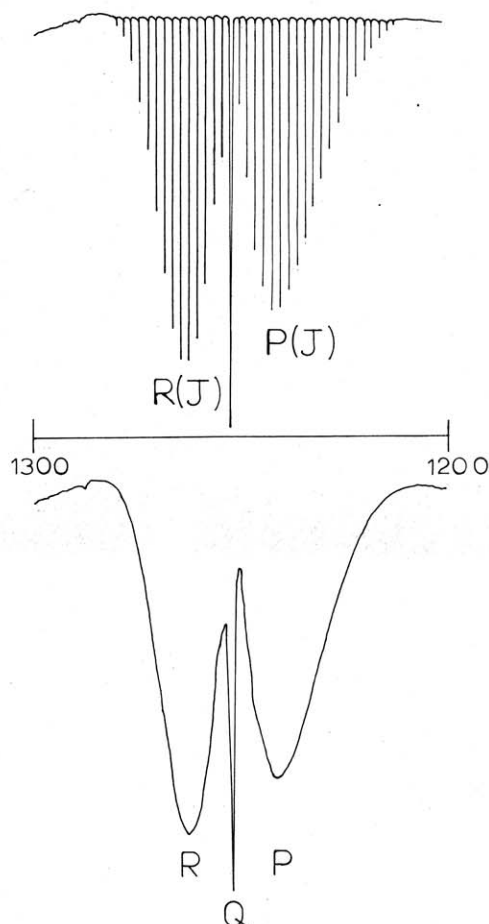The rotational constants in the lower and upper states are very similar; therefore, eqn. (2) predicts a narrow Q band

Figure 1. ν_2 of methyl iodide under high (top) and medium (bottom) resolution.
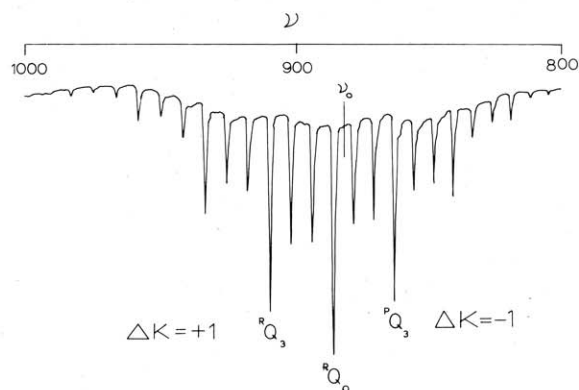
Figure 2. ν_6 of methyl iodide showing the effect of nuclear spin.

formed from the superposition of many coincident sub-bands. The formulae for the P and R bands predict groups of lines of a given J but various K appearing at approximately the same position. Overall a parallel band is expected to appear as in Figure 1a. Because most spectrometers are unable to resolve the P and R sub-bands a parallel band actually looks like Figure 1b, i.e., only the band envelope is observed.

Perpendicular Bands

Selection rules: $\Delta K = \pm 1, \quad \Delta J = 0, \pm 1$

For each value of K there are two sets of P, Q, R branches corresponding to $\Delta K = \pm 1$.

Under medium resolution, the transitions corresponding to $\Delta J = \pm 1$ give an unresolved background and only the $\Delta J = 0$ transitions need to be considered. These give a series of sharp sub-bands whose measured zero positions (i.e., $J = 0$) are given by

$$\nu_0{}^{sub} = \nu_0 + (A_{v'} - B_{v'}) \pm 2 (A_{v'} - B_{v'})K$$
$$+ \{(A_{v'} - B_{v'}) - (A_{v''} - B_{v''})\}K^2 \quad (3)$$

where the + refers to $\Delta K = +1$ (R sub-branch) and the − refers to $\Delta K = -1$ (P sub-branch). If $A_{v'} = A_{v''}$ and $B_{v'} = B_{v''}$, then the perpendicular band gives rise to a series of Q branches separated by $2(A - B)$ superimposed on an unresolved background of P and R branches as in Figure 2. The symbolism $^PQ_3$ means that $\Delta K = -1$, $\Delta J = 0$, $K'' = 3$.

Coriolis Coupling[1]

Equation (3) predicts that all of the perpendicular bands will have the same spacing, $2(A - B)$; however, in a perpendicular band the effect of Coriolis coupling is not negligible. It introduces an additional *vibrational* angular momentum $\zeta_i \hbar$ $(-1 \leq \zeta_i \leq 1)$ about the symmetry axis. ζ_i is called the Coriolis coupling constant for vibration ν_i. This results in the frequencies of the Q branches being given by

$$\nu_0{}^{sub} = \nu_0 + A_{v'} (1 - 2\zeta_i) - B_{v'} \pm 2\{A_{v'}(1 - \zeta_i) - B_{v'}\}K$$
$$+ \{(A_{v'} - B_{v'}) - (A_{v''} - B_{v''})\}K^2 \quad (4)$$

Effect of Nuclear Spin

As can be seen in Figure 2 the perpendicular bands show an intensity alternation strong, weak, weak, strong. ... The threefold symmetry axis gives rise to the periodicity of the alternation (12). Because the nuclear spin of the proton is $\frac{1}{2}$, the rotational levels with $K = 0, 3, 6, \ldots$ have twice the sta-

[1] Coriolis coupling arises from the Coriolis force, that force which must be introduced when describing the motion of a body which moves (vibrates in this case) relative to a rotating reference frame. Vibrational angular momentum of degenerate vibrations can interact with rotational angular momentum about the symmetry axis in first order. If ζ is negative, there is a speeding up of the rotation of the vibrating moment about the symmetry axis leading to an increase in the rotational spacing. A positive value corresponds to a slowing down of the rotation and a decrease in the rotational spacing.

tistical weight of those with $K = 1, 2, 4, 5, \ldots$. They are, therefore, twice as intense.

Structure Determination

This experiment determines the molecular structure of methyl iodide by infrared spectroscopy. There are a number of other methods for determining molecular structure of which microwave spectroscopy is the most important.

For the last thirty years, microwave spectroscopy has played a preeminent role in the accurate determination of structural parameters for small molecules in the gas phase. Several reasons for this situation include the extreme accuracy with which transition frequencies, and hence rotational constants, can be measured, the very narrow line widths at low gas pressures, the high sensitivity of detectors, and the ability to resolve easily transitions due to isotopically substituted molecules. If ground state rotational constants are available for several isotopic species and if it is assumed that there is negligible change in bond lengths and angles upon isotopic substitution, then the ground state r_0 structure can be obtained directly by simultaneous solution of the moment equations. Choosing different sets of isotopically substituted species gives different sets of r_0 values, mainly due to zero-point vibrational effects (13). When each of the atoms can be substituted, the changes in the rotational constants can be used to determine the substitution structure r_s (14, 15). Only when all the rotation-vibration interaction constants are available can the isotopically invariant equilibrium structure r_e be determined. The relationship between these different structures is rather complicated (16).

Experimental

Spectra should be run at two pressures, a high pressure to observe the combinations and overtones, a low pressure to determine accurately the strong fundamentals. It is essential that the temperature in the beam be measured, because it may differ significantly from ambient temperature. The results below were obtained using a Perkin-Elmer 457 operating in the narrow slit mode with ten times abscissa expansion. The cell was a 10-cm gas cell with KBr windows containing 15 torr pressure of methyl iodide.

The closest spacing of any of the rotational fine structure is about 7 cm^{-1} so that any spectrometer with a resolution better than 5 cm^{-1} which can scan to 500 cm^{-1} and has the option of either expanding the abscissa scale or driving an auxiliary chart recorder should be adequate for this experiment.

Analysis

(1) Assignment

Three parallel and three perpendicular fundamentals are expected. All of the observed bands should first be divided into parallel or perpendicular types and then assigned as fundamentals, combinations, or overtones.

(2) Parallel Bands

For each of the parallel bands the frequency of the Q branch should be measured as well as the spacing between the maxima in the P and R branches. It can be shown (17) that

$$\Delta \nu_{PR} = 2.470\sqrt{BT} \quad (5)$$

where B is in cm^{-1} and T in K. The rotational constant B can, therefore, be determined from the measured spacings.

(3) Perpendicular Bands

It is necessary to assign values of K to the sub-bands. This is facilitated by the fact that $^RQ_0$ forms a strong line near ν_0 (Fig. 2). On the low frequency side of ν_5, there is a clear change in spacing. This is due to overlapping with $\nu_3 + \nu_6$ (18). Care must be taken in numbering these sub-bands so as not to include any due to $\nu_3 + \nu_6$ in the analysis of ν_5.

When analyzing perpendicular bands it is common to use the relationships

$$^RQ_K - {}^PQ_K = 4\{A_{v'}(1 - \zeta_i) - B_{v'}\}K \quad (6)$$

$$^RQ_K + {}^PQ_K = 2\nu_0 + 2\{A_{v'}(1 - 2\zeta_i) - B_{v'}\}$$
$$+ 2\{A_{v'} - B_{v'}) - (A_{v''} - B_{v''})\}K^2 \quad (7)$$

However, these can be very wasteful of observed data. (They do not use $^RQ_0$, and they require the same value of K to be available in both the R and P sub-branches). With presently available calculators and computers it is a simple job to fit the frequencies of the sub-bands directly to eqn. (4) to determine the coefficients. The coefficient of K^2 in eqn. (4) or (7) shows how good an assumption it is to ignore changes in rotational constants between the ground and excited states.

For the methyl halides the Coriolis coupling constants obey the relationship (19).

$$\zeta_4 + \zeta_5 + \zeta_6 = \frac{B}{2A} \quad (8)$$

If it is assumed that the rotational constants are the same in the upper and lower states, then eqn. (8) can be used to show that

$$2\sum_{i=1}^{3} \{A(1 - \zeta_i) - B\} = 6A - 7B \quad (9)$$

The value of the left-hand side of this equation is known from fitting either eqn. (4) or eqn. (6) to the sub-bands in the perpendicular bands, and the value of B is known from the spacing in the parallel bands; therefore, the value of A can be determined.

Once A and B are known, then the linear term in eqn. (4) gives ζ_i, and the constant term gives ν_0.

(4) Bond Lengths

The rotational constants are related to the moments of inertia which, in turn, are related to the structural parameters. Assuming that the angles around carbon are tetrahedral, then the two moments of inertia are given by

$$I_A = \frac{16.858}{A} = 8m_H r^2_{CH}/3 \quad (10)$$

$$I_B = \frac{16.858}{B} = 5m_H r^2_{CH}/3 + m_I r^2_{CI} - \frac{(m_I r_{CI} - m_H r_{CH})^2}{M} \quad (11)$$

where I_i is in μ Å^2, A and B in cm^{-1}, m_i and M represent the mass of atom i and the molecule in μ while r_i is the bond length in Å. Equation (10) is solved for r_{CH}, and then this value is substituted into eqn. (11) to give r_{CI}.

(5) Force Constants

The carbon-hydrogen and carbon-iodine force constants can be estimated by treating the molecule as a diatomic in two different ways. If the "diatomic" is considered to be H(CH$_2$I), then

$$k_{CH} = 4\pi^2 c^2 \nu_1^2 \, \mu_1/N$$

where c is the velocity of light in cm s^{-1}, μ_1 the reduced mass in amu, ν_1 the frequency in cm^{-1}, N is Avogadro's number and

$$\frac{1}{\mu_1} = \frac{1}{m_H} + \frac{1}{m_{CH_2 I}}$$

Similarly, if the "diatomic" is (CH$_3$)I then

$$k_{CI} = 4\pi^2 c^2 \nu_3^2 \mu_3/N$$

where

$$\frac{1}{\mu_3} = \frac{1}{m_{CH_3}} + \frac{1}{m_I}$$

The frequencies ν_1 and ν_3 are chosen because they correspond to the totally symmetric carbon-hydrogen and carbon-iodine stretching modes. The values derived by this simple approach are surprisingly close to those derived from the full harmonic force field (20).

The values obtained for all the parameters in a careful run are given in Table 1 and compared with several high resolution determinations.

Two Variants

(1) *Easier Variant:* If the influence of Coriolis coupling is ignored as well as the dependence of the rotational constants on vibrational state, then the spacing in each of the perpendicular bands is simply 2(A-B). Taking the average for the

Table 1. Derived Parameters for Methyl Iodide [a]

	This work				Literature	
ν_1	2971.3		$\Delta\nu_1$ 21.2	$\pm$ 0.2	2971.29	(25)
ν_2	1252.2		$\Delta\nu_2$ 21.7	$\pm$ 0.2	1250.75	(26)
ν_3	532.7		$\Delta\nu_3$ 21.7	$\pm$ 0.2	533.21	(26)
$2\nu_2$	2487.2		$\Delta(2\nu_2)$ 21.8	$\pm$ 0.2	2486.50	(26)
$2\nu_5$	2841.6		$\Delta(2\nu_5)$ 21	$\pm$ 1	2843.25	(26)
B	0.255 ± 00.005				0.25021559	(27)
A	5.001 ± 0.014				5.1734	(21)
ζ_4	0.043 ± 0.009				0.059	(26)
ζ_5	-0.198 ± 0.013				-0.2444	(28)
ζ_6	0.180 ± 0.006				0.2103	(6)
	0.167 ± 0.008 (from $\nu_2 + \nu_6$)				0.200	(29)
	0.16 ± 0.01 (from $\nu_3 + \nu_6$)				0.2019	(28)
$\zeta_{5,6}$	-0.10 ± 0.08 (from $\nu_5 + \nu_6$)				-0.044	(26)
ν_4	3060.3				3060.0924	(5)
ν_5	1439.5				1438.1	(26)
ν_6	882.1				882.917	(6)
$\nu_2 + \nu_6$	2132.1				2132.176	(29)
$\nu_3 + \nu_6$	1409.1				1409.7	(30)
$\nu_5 + \nu_6$	2319.9				2319.5	(26)
$(A_4 - B_4) - (A_0 - B_0)$			-0.0334 ± 0.003		-0.0347	(18)
$(A_5 - B_5) - (A_0 - B_0)$			-0.0140 ± 0.01		-0.04590	(28)
$(A_6 - B_6) - (A_0 - B_0)$			0.0358 ± 0.001		0.03559	(6)
r_{CH}	1.120 ± 0.003				1.088	(21)
r_{CI}	2.11 ± 0.03				2.1423	(21)
k_{CH}	5.21				5.44	(20)
k_{CI}	2.24				2.39	(20)

[a] All values in cm^{-1} except ζ_i (unitless), r_i (Å) and k_i (millidyne/Å).

Table 2. Structural Parameters Obtained Using Easier Variant

$B = 0.255$ cm^{-1},	$A = 4.96$ cm^{-1}
$r_{CH} = 1.12$ Å,	$r_{CI} = 2.11$ Å

Table 3. Structural Parameters Obtained Using Harder Variant

$r_{CH} = 1.086$ Å
$r_{CI} = 2.144$ Å
HCH $= 111°$ 50'

three fundamental perpendicular bands and using the value of B from eqn. (5) gives the value of A. It is easy to show that despite the large variations in the spacings of the three perpendicular bands this simple procedure gives a surprisingly good value for A. Table 2 shows the structural parameters using this simple approach.

(2) *Harder Variant:* Combining the A and B obtained here with B tabulated for an isotopic species (21) removes the need to constrain the angles around the carbon atom. The equations for the moments of inertia are now somewhat more complicated (22) than eqns. (10) and (11). The resulting set of three simultaneous nonlinear equations can be solved in a relatively straightforward manner (23). Structural parameters obtained using A and B from CH_3I and B from CD_3I (24) are given in Table 3.

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