JOURNAL OF MOLECULAR SPECTROSCOPY 45, 65–70 (1973)

A Vibrational Analysis of Trichloroiodomethane

RICHARD H. MANN AND PETER M. MANIS[1]

Department of Chemistry, Boston University, Boston, Massachusetts 02215

The infrared and Raman spectra of CCl_3I have been recorded. Band assignments have been made on the basis of the infrared results, and the Raman spectrum has been interpreted in terms of the fundamentals of CCl_3I, with additional bands being assigned to decomposition products of CCl_3I. A Urey–Bradley force constant calculation has been made, transferring results from the earlier work of Ngai and Mann.

INTRODUCTION

A recent study of tetrahalomethanes in this laboratory (*1*) yielded a transferable Urey–Bradley force field (UBFF) for eighteen tetrahalomethanes. It was found that agreement between calculated and observed frequencies was poorest for iodine-containing members of the series, there being three which were included in the calculations: CI_4, CF_3I, and CF_2I_2. It was hoped that vibrational data could be obtained for other iodotetrahalomethanes and then that these molecules be included in the normal coordinate calculations.

As it turns out, most iodotetrahalomethanes are rather unstable molecules, being easily photodecomposed as well as being air and heat sensitive. Herein is reported for the first time the vibrational spectra and band assignments of trichloroiodomethane, perhaps the least unstable of those iodotetrahalomethanes which have not been studied to date.

PREPARATION OF CCl_3I

The synthesis of CCl_3I was performed following Pullman and West (*2*). Identification of the CCl_3I was established by its boiling point of 142°C and by its absorption in the ultraviolet at 324 nm as reported by Hazeldine (*3*). A mass spectrum using a Hitachi RMU-6L spectrometer showed major peaks corresponding to the fragments CCl, CCl_2, CCl_3, I, C_2Cl_4 and C_2Cl_5, the latter two indicating some contamination of C_2Cl_6 in the sample. The gas chromatogram of CCl_3I showed, in addition to the main peak, trace amounts of CS_2, CCl_4, I_2 and C_2Cl_6, the latter two being decomposition products.

---

[1] Participant in the National Science Foundation Undergraduate Research Participation Program, Summer, 1971.

RECORDING OF SPECTRA

The mid-infrared spectrum (2000–350 cm^{-1}) was recorded on a Perkin-Elmer Model 521 grating spectrometer, using a KBr cell with a 0.5 mm spacer. The spectrum was traced several times in succession, and very little evidence was found of decomposition due either to heating in the beam or to contact with air during the recording of the spectra. The far-infrared measurements were made with a Perkin-Elmer Model 301 grating spectrometer in the region 500–120 cm^{-1}, using a globar source and Golay detector. The sample was contained in 0.1 mm polyethylene cells, and some decomposition of the sample was noted over the period of time needed to record the spectrum.

The Raman spectrum was recorded on a Jarrell-Ash Model 25-300 spectrometer, with a Spectra-Physics Model 125 He–Ne laser used for the exciting ratiation. The samples were enclosed in quartz capillaries, and extensive decomposition of the CCl_3I was noted such that a new sample was required after approximately 10 min of irradiation. The spectra obtained were thus rich in bands of the major decomposition products C_2Cl_6 and I_2, as well as CCl_3I.

OBSERVED SPECTRA AND DISCUSSION OF ASSIGNMENTS

Because of the excessive decomposition of the CCl_3I during the Raman measurements, these results are not considered to be useful in assigning the fundamental frequencies. Upon analysis of the infrared spectrum, however, values have been obtained for the CCl_3I fundamentals, and the observed Raman spectrum has been interpreted in terms of the infrared results for CCl_3I and also the reported Raman spectra of the two major decomposition products C_2Cl_6 and I_2, and of a secondary contaminent CCl_4.

In order to aid in the assignment of the infrared frequencies, use was made of the UBFF (*1*) obtained from the tetrahalomethanes. Of the seven UBFF force constants for CCl_3I, four (K_{CI}, K_{CCl}, H_{ClCCl} and F_{ClCl}) were transferred from the other molecules. The remaining three were estimated by taking combinations of related force constants:

$$\begin{aligned} H_{ICCl} &= \tfrac{1}{4}(H_{ICI} + 3H_{ClCCl}), \\ F_{ICl} &= \tfrac{1}{4}(F_{II} + 3F_{ClCl}), \qquad (1) \\ \rho_{CCl_3I} &= \tfrac{1}{4}(\rho_{CI_4} + 3\rho_{CCl_4}), \end{aligned}$$

where the force constants on the r.h.s. are also transferred from the earlier work. The frequencies predicted for this set of force constants are given in Table I. These can be compared with the observed infrared bands displayed in Table II. It is clear that the symmetric and antisymmetric stretches ν_1 and ν_4 are to be found in the strong absorption between 825 and 650 cm^{-1}. From the spectrum of a thin film of the CCl_3I the frequencies of 755 cm^{-1} for ν_4 and 687 cm^{-1} for ν_1 were obtained.

It seems likely that either the 390- or the 358-cm^{-1} band corresponds to ν_2, if one is to accept the calculated predictions. Further, it would appear that the band at 284 cm^{-1} corresponds to ν_5, with either 224 or 205 cm^{-1} being ν_3, and one of the pair of bands at 188 and 171 cm^{-1} corresponding to ν_6.

An analysis of the spectra of the two major decomposition products is useful in selection of fundamentals from these pairs of bands. It is seen that ν_{12} of C_2Cl_6 occurs

TABLE I

FUNDAMENTAL FREQUENCIES AND FORCE CONSTANTS FOR CCl_3I

Frequency and symmetry	Predicted from[a] (Ngai–Mann)	Assignment with[b] 390 and 224(I)	Assignment with[b] 358 and 205(II)	Calculated frequencies[c] using assignment I
$\nu_1(a_1)$	679	684	684	678
$\nu_2(a_1)$	392	390	358	406
$\nu_3(a_1)$	223	224	205	225
$\nu_4(e)$	770	755	755	768
$\nu_5(e)$	261	284	284	267
$\nu_6(e)$	186	188	188	191
Average error		10.0	14.7	9.9

	K_{CI}	K_{CCl}	H_{ClCCl}	H_{ICCl}	F_{ClCl}	F_{ICl}	ρ
Starting force constants	1.309	2.017	0.089	0.082	0.652	0.569	−0.273
Final force constants[d]	(1.309)	(2.017)	(0.089)	0.064	(0.651)	0.552	−0.215
Errors in calculated force constants[e]				0.059		0.086	−0.169

[a] Force constants used were either transferred from Ref. (*1*) or estimated by means of Eq. (1).

[b] The average error is the average difference between the assigned and the predicted values using the starting force constants.

[c] The average error is the average difference between the assigned and the calculated values after refinement of the three unique force constants H_{ICCl}, F_{ICl} and ρ.

[d] The values in parenthesis were not allowed in the force constant refinement.

[e] Errors estimated as in Ref. (*1*).

at 169 cm^{-1} (*4*), and this would suggest that the 171 cm^{-1} band be assigned to C_2Cl_6, leaving the band at 188 cm^{-1} to be assigned to ν_6 of CCl_3I.

The strong band at 205 cm^{-1} is proposed to be due to the I_2 formed by decomposition, with the stretching vibration becoming active due to formation of a donor–acceptor complex with the undecomposed CCl_3I. The appearance of an infrared vibrational band at ~200 cm^{-1} is a common phenomena for I_2 dissolved in polar or highly polarizable organic solvents (5). This assignment would then leave the band at 224 cm^{-1} to be ν_3, this band being supperimposed on the decomposition band due to ν_9 of C_2Cl_6, reported at 223 cm^{-1}. An alternative assignment would be to have the band at 205 cm^{-1} to be ν_3 plus the I_2 band, with the 224 cm^{-1} vibration being due entirely to C_2Cl_6. The decision on the assignment in favor of ν_3 being found at 224 cm^{-1} is made on the basis that it yields better agreement in the assignment of the overtones and combinations. For example, no assignment with ν_3 at 205 cm^{-1} could explain the band at 513 cm^{-1}, whereas with ν_3 equal to 224 cm^{-1} this band is readily assigned to $\nu_3 + \nu_5$. In addition, the absorption at 1597 cm^{-1} can only be explained by $2\nu_1 + \nu_3$ when ν_3 is equal to 224 cm^{-1}.

In the case of the bands at 390 cm^{-1} and 358 cm^{-1} the choice of 390 cm^{-1} as ν_2 is made because it lies closer to the value predicted from the transferred UBFF. As can be seen from Table II, either band can yield satisfactory assignments of the overtones and combinations.

TABLE II

OBSERVED INFRARED FREQUENCIES AND ASSIGNMENTS FOR CCl_3I

C_2Cl_6(obsd)[a]	CCl_3I assignments with 390 and 223	CCl_3I(obsd)[b,c]	CCl_3I assignments with 358 and 205	
1752	[C_2Cl_6]	1752 vw,sh	same[d]	
	1698 $2\nu_4 + \nu_6$	1697 s	same	
	1592 $2\nu_1 + \nu_3$	1597 w	$2\nu_1 + \nu_3$	1573
	1510 $2\nu_4$	1510 s	same	
	1439 $\nu_1 + \nu_4$	1441 s	same	
	?	1379 vvw	same	
	1368 $2\nu_1$	1358 w	same	
	1252 $\nu_1 + 2\nu_5$	1261 s	same	
	1227 $\nu_4 + \nu_5 + \nu_6$	1223 m	same	
1209	[C_2Cl_6]	1207 vw	same	
	1156 $\nu_1 + \nu_5 + \nu_6$	1156 m,sh	same	
1128	[C_2Cl_6]	1129 m	same	
1017, 1117	1060 $\nu_1 + 2\nu_6$	~1073 vs,br	same	
1000	[C_2Cl_6]	992 w	same	
	968 $\nu_1 + \nu_5$	965 m	same	
	921 $\nu_2 + \nu_4 - \nu_3$	926 m	$2\nu_5 + \nu_2$	926
	908 $\nu_1 + \nu_3$	909 w	$2\nu_2 + \nu_6$	904
	872 $\nu_1 + \nu_6$	884 w,sh	$\nu_1 + \nu_3$	889
	854 $3\nu_5$ 862 $\nu_2 + \nu_5 + \nu_6$	854 s	$3\nu_5$	854
678–804	ν_1, ν_4	825– 650 vvs	same	
	600 $2\nu_6 + \nu_3$	609 s	$2\nu_3 + \nu_6$	598
	531 $\nu_4 - \nu_3$	535 m	$\nu_2 + \nu_6$	546
	508 $\nu_3 + \nu_5$	513 vw	?	
	472 $\nu_5 + \nu_6$	480 m	same	
373	390 ν_2	390 m	$\nu_3 + \nu_6$	393
	365 $\nu_4 - \nu_2$	358 w	ν_2	
278	284 ν_5	284 w	same	
223	224 ν_3	224 w	[C_2Cl_6]	
	205 [I_2]	205 s	ν_3	205
	188 ν_6	188 m	same	
169	169 [Cl_2Cl_6]	171 m	same	

[a] Reference (*4*).

[b] The upper bands were observed on the PE 521, the lower bands on the PE 301.

[c] The notation is as follows: v, very; s, strong; m, medium; w, weak, br, broad; sh, shoulder.

[d] "Same" indicates that the assignments are identical for both sets of fundamentals.

It can be seen from Table II that all of the major infrared bands with the exception of a very weak feature at 1379 cm^{-1} have been assigned to the CCl_3I molecule or to C_2Cl_6 and I_2. All of the major ir bands of C_2Cl_6 are in fact observed at least weakly (with the possible exception of the 373 cm^{-1} band, which may be lost in the envelope of the 390 cm^{-1} CCl_3I band) indicating that some decomposition was present.

TABLE III

FUNDAMENTAL FREQUENCIES OF CCl_3I AND POTENTIAL ENERGY DISTRIBUTION

Band	Frequency (cm^{-1})	Symmetry (C_{3v})	Urey–Bradley potential energy distribution (%)[a]
ν_1	684	a_1	CI(38), CCl(32)
ν_2	390	a_1	ICl(40), CCl(26), ClCl(16), CI(12)
ν_3	224	a_1	ClCl(56), ICl(16), CI(13)
ν_4	755	e	CCl(80)
ν_5	284	e	ICl(43), ClCl(27), ICCl(10)
ν_6	188	e	ClCl(46), ICl(32), ClCCl(15), ICCl(10)

[a] Notation is the same as in Ref. *(1)*.

One may use the fundamentals of CCl_3I (Table III) obtained from the infrared to help explain the observed Raman spectrum. It can be seen in Table IV that the observed bands apparently are due to CCl_3I, and its decomposition products C_2Cl_6, I_2 and CCl_4. It can be seen that most of the major Raman bands of C_2Cl_6 are observed with the polarized band at 434 cm^{-1} most assuredly being ν_2 (a_{1g}), the strongest Raman band in C_2Cl_6. The polarized band observed at 405 cm^{-1} apparently is the first overtone of the I_2 vibration appearing via the Resonance Raman effect (7), although it may be that ν_2 of CCl_3I (which should be polarized) is contributing to this band. The depolarized

TABLE IV

OBSERVED RAMAN FREQUENCIES AND ASSIGNMENTS VOR CCl_3I, C_2Cl_6, CCl_4 AND I_2

CCl_3I (obsd)	Assignment for CCl_3I[a]	C_2Cl_6[b]	CCl_4[c]	I_2[d]
		976(3)p $\nu_1(a_{1g})$		
~825(vvw)[e]	$[\nu_7\ C_2Cl_6]$?	858(16)dp $\nu_7(e_g)$		
687(w,br)p	$\nu_1(a_1)$			
458(w)	$[\nu_1\ CCl_4]$		458(vs)p $\nu_1(a_1)$	
434(w)p	$[\nu_2\ C_2Cl_6]$	431(100)p $\nu_2(a_{1g})$		
405(w)p	$\nu_2(a_1)$, $[2\nu\ I_2]$			420(s)p 2ν
		340(56)dp $\nu_8(e_g)$		
314(vw)	$[\nu_4\ CCl_4]$		314(s)dp $\nu_4(d_2)$	
288(w)dp	$\nu_5(e)$			
224(w)	$\nu_3(a_1)$, $[\nu_9\ C_2Cl_6]$, $[\nu_2\ CCl_4]$	223(42)dp $\nu_9(e_g)$	218(s)dp $\nu_2(e)$	
202(m)p	$[\nu\ I_2]$			211(s)p ν
~170(m,br)	$\nu_6(e)$?			
137(m)	$[\nu_1 - \nu_4\ CCl_4]$?			
113(w)	$2\nu_3 - \nu_5$?			
83(s)	$[\nu_2 - \nu_8\ C_2Cl_6]$	90(m)dp $\nu_2 - \nu_8(e_g)$		

[a] Decomposition bands are designated by brackets.

[b] Reference *(4)*; the figures in parentheses give relative intensities.

[c] Reference *(6)*.

[d] Reference *(7)*.

[e] The notation is as follows: v, very; s, strong; m, medium; w, weak; br, broad; p, polarized; and dp, depolarized.

band observed at 288 cm^{-1} is unequivocally ν_5 of CCl_3I, since no decomposition product has a band close to this frequency.

FORCE CONSTANT CALCULATIONS

Upon determination of the correct assignment for the fundamentals, a force constant calculation was made for CCl_3I to determine the values of the three unique force constants for CCl_3I: H_{ICCl}, F_{ICl} and ρ_{CCl_3I}. As can be seen in Table I, the final values obtained for F_{ICl} and ρ are quite close to those predicted by Eq. (1). The value for H_{ICCl} is much lower than predicted, but the calculated error is very large. This large uncertainty is due in part to the fact that the Jacobian matrix element for all six frequencies is very large for this term. The obtained potential energy distribution (Table III) is similar to that found for the other tetrahalomethanes, with nonbonding (F) contributions generally being predominant with respect to bending (H) and intramolecular tension (ρ) contributions.

One other calculation was made in which the iodine related force constants (K_{CI}, H_{ICI}, H_{ICF}, F_{II}, F_{IF}, $\rho_{CF_2I_2}$, ρ_{CF_3I} and ρ_{CI_4}) from the three molecules (CF_2I_2, CF_3I, and CI_4) in the previous study and the three unique force constants of CCl_3I were adjusted. In this calculation, the remaining force constants (K_{CF}, K_{CCl}, H_{FCF}, H_{ClCCl}, F_{FF}, and F_{ClCl}) were transferred from Ngai and Mann. As it turned out, there was almost no change in the calculated frequencies and force constants from those obtained in the earlier study.

CONCLUSIONS

Acknowledging the problems encountered with decomposition of the compound, it nevertheless appears that a reasonable assignment of the fundamental vibrations of CCl_3I has been obtained. As with the other iodotetrahalomethanes, the transferability of Urey–Bradley force constants is less successful than with the tetrahalomethane compounds containing only F, Cl, and Br. While it may be possible to obtain the vibrational spectra for other iodine containing tetrahalomethanes, similar problems of instability are sure to be encountered.

ACKNOWLEDGMENTS

Appreciation is expressed to Professor R. C. Lord of Massachusetts Institute of Technology for use of his infrared equipment. Thanks are also extended to Professor William Risen of Brown University for making available his Raman instrumentation.

RECEIVED: June 20, 1972

REFERENCES

1. L. H. NGAI AND R. H. MANN, *J. Mol. Spectrosc.* **38**, 322 (1971).
2. B. J. PULLMAN AND B. O. WEST, *J. Inorg. Nucl. Chem.* **19**, 262 (1961).
3. R. N. HASZELDINE, *J. Chem. Soc.* 1764 (1953).
4. (a) R. A. CARNEY, E. A. PIOTROWSKI, A. G. MEISTER, J. H. BRAUN AND F. F. CLEVELAND, *J. Mol. Spectrosc.* **7**, 209 (1961). (b) F. WATARI AND K. AIDA, *J. Mol. Spectrosc.* **24**, 503 (1967).
5. V. LORENZELLI, *Compt. Rend.* **258**, 5386 (1964).
6. G. HERZBERG, "Infrared and Raman Spectra," Van Nostrand, Princeton, N. J., p. 311, 1945.
7. O. S. MORTENSEN, *J. Mol. Spectrosc.* **39**, 48 (1971).