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Conformational stability from variable temperature infrared spectra of krypton solutions of 1,3-dichloropropane

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Abstract

The infrared spectra ($3500\text{--}400\text{ cm}^{-1}$) of krypton solutions of 1,3-dichloropropane, $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$, at variable temperatures (-105 to $-150\text{ }^\circ\text{C}$) have been recorded. Additionally, the far infrared spectra ($500\text{--}70\text{ cm}^{-1}$) of the gas and solid have been recorded. All of the fundamental vibrations of the C_2 conformer (*gauche*–*gauche*) and many of those for the C_1 form (*gauche*–*trans*) have been assigned. By utilizing seven pairs of fundamentals for these two conformers in the krypton solutions, an enthalpy difference of $272 \pm 27\text{ cm}^{-1}$ ($3.25 \pm 0.32\text{ kJ/mol}$) has been obtained for the C_2 versus C_1 conformer with the C_2 conformer the more stable form. For the C_{2v} conformer (*trans*–*trans*), the enthalpy difference has been determined to be $383 \pm 38\text{ cm}^{-1}$ ($4.58 \pm 0.46\text{ kJ/mol}$). It is estimated that there is $62 \pm 2\%$ of the C_2 form, $33 \pm 2\%$ of the C_1 form and $5 \pm 1\%$ of the C_{2v} conformer present at ambient temperature. Equilibrium geometries and total energies of the three stable conformers have been determined from ab initio calculations with full electron correlation by the perturbation method to second order as well as by hybrid density functional theory calculations with the B3LYP method using a number of basis sets. The MP2 calculations predict the C_1 conformer stability to be slightly higher than the experimentally determined value whereas for the C_{2v} conformer the energy difference is much larger than the experimental value. The B3LYP calculations predict a better energy difference for both the C_1 and C_{2v} conformers than the MP2 values. A complete vibrational assignment is proposed for the C_{2v} conformer and many of the fundamentals have been identified for the C_1 and C_2 forms based on the force constants, relative intensities and rotational-vibrational band contours obtained from the predicted equilibrium geometry parameters. The r_0 structural parameters are estimated from ab initio MP2/6-311 + G(d,p) calculations and comparisons are made with the parameters obtained by electron diffraction technique. The spectroscopic and theoretical results are compared to the corresponding properties for some similar molecules.

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Keywords: 1,3-Dichloropropane; Conformational stability; Ab initio calculations; Structural parameters

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¹ Taken in part from the thesis of C. Zheng which will be submitted to the Department of Chemistry in partial fulfillment of PhD degree.

1. Introduction

Recently we [1] participated in a vibrational study of 1,3-dichloropropane, $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$,

utilizing infrared and Raman spectroscopy. Earlier Thorbjørnsrud et al. [2] reported a very extensive vibrational study of several 1,3-dihalopropanes which included 1,3-dichloropropane, followed by a detailed vibrational study [3] of the far infrared spectrum of 1,3-dichloropropane by some of these same authors. In these earlier studies [2–5] predictions from ab initio calculations were not utilized to support the vibrational assignment, so we [1] used ab initio MP2(frozen core)/6-31 + G(d) calculations to predict the normal modes for three of the four possible conformers of 1,3-dichloropropane (Fig. 1). These calculations predicted the approximate relative stabilities of GG (75%), TG (18%), TT (6%) and nearly zero percent for the GG' form (both chlorine atoms on the same side of the CCC skeleton) of C_s symmetry since the predicted energy difference is so large [1]. Here G (*gauche*) and T (*trans*) refer to the orientation of the two chloromethyl groups relative to the plane of the three carbon atoms. Although the result seemed somewhat unusual they were consistent with the previously reported [6] conformer stabilities of GG (73%), TG (24%), and less than 10% of the TT form and zero percent of the GG' rotamer which were obtained from electron diffraction studies of the gas at 38 °C. There can be little doubt that the GG (C_2 symmetry) form is the most

stable conformer, but the percent populations of the various conformers is probably $\pm 10\%$ ($\pm 4\%$ by E.D. investigators [6]) which indicates large experimental uncertainties in the amount of the TG (C_1) and TT(AA) (C_{2v}) conformers present in the gas phase at ambient temperature. There has been a conformational study of liquid 1,3-dichloropropane using wide-angle X-ray scattering [7] and the GG conformer predominates ($82 \pm 2\%$) with a significant amount of the GT form ($18 \pm 2\%$) present at -20 °C, but there was no experimental evidence to support the existence of the TT staggered conformer. Thus, the conformer concentrations in the liquid appear to be significantly different from those in the gas.

Since we have shown that variable temperature infrared studies of rare gas solutions give excellently determined enthalpy differences for conformational changes which are usually very similar to values obtained in the gas phase [8–12], we initiated such a study of 1,3-dichloropropane. We were interested in comparing these values with those previously reported experimentally as well as with those obtained from various ab initio calculations. These calculations have been carried out with a variety of basis sets at the level of the restricted Hartree–Fock (RHF) and with electron correlation by the perturbation method [13] to the second order (MP2) to obtain the geometric parameters, harmonic force constants, infrared intensities, Raman activities, depolarization ratios and vibrational frequencies. Hybrid density functional theory (DFT) calculations have also been carried out by the B3LYP method to obtain conformational energy differences and vibrational frequencies. The results of these spectroscopic and theoretical studies are reported herein.

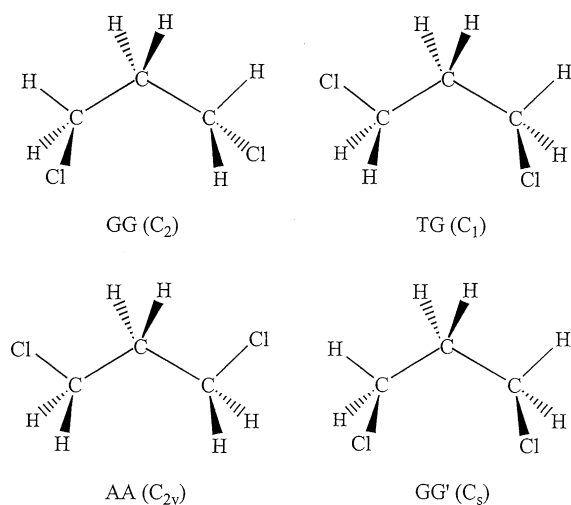


Fig. 1. The four conformers of 1,3-dichloropropane.

2. Experimental

The sample of 1,3-dichloropropane was purchased from Aldrich Chemical Co., Milwaukee, WI, with a stated purity of 99%. The sample was further purified by means of a low-pressure low-temperature fractionation column and the purity of the sample was checked by mass and NMR spectra. The sample was kept in the dark at low temperature until it was used.

The mid-infrared spectrum of the gas was obtained from 3500 to 400 cm^{-1} on a Perkin–Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beamsplitter and a DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen gas. The spectrum of the gas was obtained with the sample contained in a 10 cm cell fitted with CsI windows. The theoretical resolution used to obtain the spectrum of the gas was 1.0 cm^{-1} , usually 100 interferograms were collected and averaged and the data were transformed with a boxcar truncation function. The observed fundamental frequencies are listed in Tables 1–3.

The temperature studies of the sample dissolved in krypton solutions from -105 to -150 $^{\circ}\text{C}$ were conducted on a Bruker model IFS 66 Fourier transform spectrometer equipped with a Globar source, a Ge/KBr beamsplitter and a TGS detector. The temperature studies were performed in a specially designed cryostat cell which consisted of a copper cell with a 4 cm path length and wedged silicon windows sealed to the cell with indium gaskets. The temperature was monitored with two Pt thermoresistors. The complete cell is connected to a pressure manifold to allow for the filling and evacuation of the cell. After the cell is cooled to the designated temperature, a small amount of sample is condensed into the cell. Next, the manifold and the cell are pressurized with krypton, which immediately starts condensing in the cell, allowing the compound to dissolve in krypton.

The far infrared spectra of the gas and solid (Fig. 2) were recorded on the previously described Perkin–Elmer model 2000 spectrometer. A grid beamsplitter and a cryostat cell with polyethylene windows was used to record the spectrum of the solid with the sample being deposited on a silicon substrate at 77 K and multiple annealings were performed in order to obtain a good polycrystalline solid. For the spectrum of the gas, the sample was contained in a 10 cm cell equipped with polyethylene windows. The spectra were recorded at a spectral resolution of 1.0 cm^{-1} . Typically, 256 scans were used for both the sample and reference data to give a satisfactory signal-to-noise ratio. The interferograms were averaged and then transformed with a boxcar truncation function.

3. Ab initio calculations

The LCAO-MO-SCF restricted Hartree–Fock calculations were performed with the GAUSSIAN 98 program [14] using Gaussian-type basis functions. The energy minima with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all the geometric parameters using the gradient method of Pulay [15]. Calculations were also carried out with full electron correlation by the perturbation method [13] to second order up to the 6-311 + G(2df,2pd) basis set. DFT calculations made with the GAUSSIAN 98 program [14] were restricted to the hybrid B3LYP method. The determined energy differences that resulted from these various calculations are listed in Table 4.

In order to obtain a complete description of the molecular motions involved in the fundamental modes of 1,3-dichloropropane, a normal coordinate analysis has been carried out. The force field in Cartesian coordinates was obtained with the GAUSSIAN 98 program [14] from the MP2/6-31G(d) calculation. The internal coordinates shown in Fig. 3 were used to form the symmetry coordinates listed in Table 5. The B-matrix elements [16] were used to convert the ab initio force field from Cartesian coordinates into the force field in designated internal coordinates. These force constants were used to reproduce the ab initio vibrational frequencies for the three conformers which are given in Tables 1–3. The diagonal elements of the force field in internal coordinates were then multiplied by scaling factors of 0.88 for the CH stretches, 1.0 for heavy atom bends and 0.90 for all other modes. The geometrical average of the scaling factors was applied to the off-diagonal force constants. The calculation was repeated to obtain the fixed scaled force field, scaled vibrational frequencies and potential energy distributions (PEDs) given in Tables 1–3.

The infrared spectra were predicted from the MP2(full)/6-31G(d) calculations. Infrared intensities were calculated based on the dipole moment derivatives with respect to the Cartesian coordinates. The derivatives were taken from the ab initio calculations transformed to normal coordinates by:

$$\left(\frac{\partial \mu_u}{\partial Q_i}\right) = \sum_j \left(\frac{\partial \mu_u}{\partial X_j}\right) L_{ij}$$

Table 1

Observed and calculated frequencies (cm^{-1}) and potential energy distributions (PEDs) for the GG (C_2) conformer of 1,3-dichloropropane

| | Description | Ab initio ^a | Fixed scaled ^b | IR int. ^c | Raman act. ^d | Obs. gas | Obs. Kr | Contour | | | PED ^e |
|---|---|------------------------|---------------------------|----------------------|-------------------------|----------|---------|---------|-----|----|--|
| | | | | | | | | A | B | C | |
| A | ν_1 *CH ₂ antisymmetric stretch | 3234 | 3034 | 3.5 | 37.3 | 3014 | 3009 | – | 100 | – | 99S ₁ |
| | ν_2 *CH ₂ symmetric stretch | 3166 | 2970 | 4.4 | 139.7 | 2973 | 2966 | – | 100 | – | 99S ₂ |
| | ν_3 CH ₂ symmetric stretch | 3110 | 2917 | 8.6 | 92.3 | 2925 | 2919 | – | 100 | – | 100S ₃ |
| | ν_4 *CH ₂ deformation | 1547 | 1468 | 2.2 | 19.9 | 1449 | 1449 | – | 100 | – | 97S ₄ |
| | ν_5 CH ₂ deformation | 1529 | 1451 | 8.5 | 13.0 | 1427 | 1423 | – | 100 | – | 97S ₅ |
| | ν_6 *CH ₂ wag | 1415 | 1343 | 15.2 | 1.5 | 1322 | 1319 | – | 100 | – | 77S ₆ , 22S ₈ |
| | ν_7 *CH ₂ twist | 1340 | 1273 | 0.04 | 24.9 | – | – | – | 100 | – | 47S ₇ , 30S ₈ |
| | ν_8 CH ₂ twist | 1219 | 1157 | 0.6 | 10.9 | 1135 | 1135 | – | 100 | – | 40S ₈ , 47S ₇ |
| | ν_9 *CH ₂ rock | 1065 | 1017 | 0.1 | 1.4 | 1014 | 1011 | – | 100 | – | 55S ₉ , 17S ₁₀ , 12S ₁₂ |
| | ν_{10} CCC symmetric stretch | 917 | 870 | 11.0 | 7.0 | 871 | 869 | – | 100 | – | 64S ₁₀ , 24S ₉ |
| | ν_{11} CCl stretch | 741 | 706 | 13.0 | 16.2 | 692 | 689 | – | 100 | – | 77S ₁₁ , 10S ₁₃ |
| | ν_{12} CCC bend | 476 | 466 | 0.4 | 2.5 | 467 | 467 | – | 100 | – | 49S ₁₂ , 26S ₁₃ , 11S ₁₁ , 11S ₉ |
| | ν_{13} CCCI bend | 227 | 225 | 3.1 | 1.1 | 217 | – | – | 100 | – | 61S ₁₃ , 34S ₁₂ |
| | ν_{14} CH ₂ Cl torsion | 63 | 60 | 2.1 | 1.6 | 63 | – | – | 100 | – | 95S ₁₄ |
| B | ν_{15} *CH ₂ antisymmetric stretch | 3234 | 3034 | 3.4 | 49.3 | 3015 | 3009 | 97 | – | 3 | 99S ₁₅ |
| | ν_{16} CH ₂ antisymmetric stretch | 3172 | 2975 | 21.7 | 35.5 | 2979 | 2971 | 6 | – | 94 | 52S ₁₆ , 47S ₁₇ |
| | ν_{17} *CH ₂ symmetric stretch | 3160 | 2964 | 3.7 | 72.9 | 2972 | 2966 | 14 | – | 86 | 52S ₁₇ , 48S ₁₆ |
| | ν_{18} *CH ₂ deformation | 1548 | 1469 | 15.5 | 0.0003 | 1451 | 1445 | 65 | – | 35 | 100S ₁₈ |
| | ν_{19} CH ₂ wag | 1443 | 1370 | 0.4 | 2.2 | 1362 | 1360 | 67 | – | 33 | 69S ₁₉ , 14S ₂₂ , 14S ₂₁ |
| | ν_{20} *CH ₂ wag | 1379 | 1308 | 48.1 | 2.4 | 1285 | 1282 | 54 | – | 46 | 94S ₂₀ |
| | ν_{21} *CH ₂ twist | 1229 | 1167 | 0.5 | 1.2 | 1155 | 1152 | 7 | – | 93 | 79S ₂₁ |
| | ν_{22} CCC antisymmetric stretch | 1146 | 1090 | 2.9 | 2.8 | 1081 | 1080 | 100 | – | 0 | 63S ₂₂ , 14S ₁₉ , 11S ₂₃ |
| | ν_{23} CH ₂ rock | 1033 | 983 | 10.6 | 0.7 | 974 | 970 | 64 | – | 36 | 37S ₂₃ , 28S ₂₄ , 11S ₂₂ |
| | ν_{24} *CH ₂ rock | 845 | 803 | 32.1 | 4.4 | 801 | 799 | 93 | – | 7 | 55S ₂₄ , 19S ₂₅ , 15S ₂₃ |
| | ν_{25} CCl stretch | 700 | 664 | 14.3 | 6.1 | 657 | 653 | 59 | – | 41 | 72S ₂₅ , 17S ₂₃ |
| | ν_{26} CCCI bend | 373 | 364 | 1.9 | 0.9 | 357 | – | 100 | – | 0 | 66S ₂₆ , 21S ₂₇ |
| | ν_{27} CH ₂ Cl torsion | 196 | 188 | 6.4 | 0.6 | 175 | – | 87 | – | 13 | 74S ₂₇ , 17S ₂₆ |

Asterisk indicates CH₂ motions from CH₂Cl groups.^a Frequencies from MP2(full)/6-31G(d) calculation.^b Scaling factors of 0.88 for CH stretches, 1.0 for heavy atom bends and 0.90 for all other modes.^c Calculated infrared intensities in km/mol.^d Calculated Raman activities in Å⁴/amu.^e Values less than 10% are omitted.

Table 2

Observed and calculated frequencies (cm^{-1}) and potential energy distributions (PEDs) for the TG (C_1) conformer of 1,3-dichloropropane

| | Description | Ab initio ^a | Fixed scaled ^b | IR int. ^c | Raman act. ^d | Obs. gas | Obs. Kr | Contour | | | PED ^e |
|------------|--|------------------------|---------------------------|----------------------|-------------------------|----------|---------|---------|----|----|---|
| | | | | | | | | A | B | C | |
| ν_1 | *CH ₂ antisymmetric stretch | 3234 | 3034 | 4.8 | 27.9 | 3015 | 3009 | 11 | 31 | 58 | 54S ₁ , 39S ₁₅ |
| ν_2 | *CH ₂ symmetric stretch | 3151 | 2956 | 13.8 | 104.1 | 2951 | 2951 | 1 | 78 | 21 | 51S ₂ , 45S ₁₇ |
| ν_3 | CH ₂ symmetric stretch | 3119 | 2926 | 5.0 | 87.9 | 2929 | 2929 | 4 | 73 | 23 | 95S ₃ |
| ν_4 | *CH ₂ deformation | 1555 | 1476 | 4.6 | 3.5 | 1444 | 1444 | 6 | 43 | 51 | 54S ₄ , 36S ₁₈ |
| ν_5 | CH ₂ deformation | 1543 | 1464 | 8.6 | 21.1 | 1431 | 1427 | 59 | 4 | 37 | 66S ₅ , 31S ₁₈ |
| ν_6 | *CH ₂ wag | 1399 | 1328 | 27.3 | 3.5 | 1313 | 1312 | 33 | 61 | 6 | 48S ₆ , 25S ₂₀ , 23S ₈ |
| ν_7 | *CH ₂ twist | 1269 | 1206 | 1.1 | 6.3 | 1198 | 1195 | 0 | 92 | 8 | 46S ₇ , 14S ₁₉ , 10S ₆ |
| ν_8 | CH ₂ twist | 1350 | 1281 | 8.1 | 5.5 | 1269 | 1266 | 58 | 1 | 41 | 13S ₈ , 31S ₇ , 23S ₆ , 10S ₂₀ |
| ν_9 | *CH ₂ rock | 1105 | 1052 | 0.3 | 3.1 | 1042 | 1040 | 2 | 1 | 97 | 41S ₉ , 18S ₁₀ , 16S ₂₃ , 14S ₇ |
| ν_{10} | CCC symmetric stretch | 1032 | 983 | 10.5 | 3.0 | 976 | 976 | 70 | 30 | 0 | 28S ₁₀ , 17S ₂₄ , 15S ₂₃ |
| ν_{11} | CCl stretch | 784 | 747 | 11.4 | 13.2 | 737 | 736 | 42 | 23 | 35 | 42S ₁₁ , 21S ₉ , 10S ₂₃ |
| ν_{12} | CCC bend | 243 | 240 | 0.9 | 0.7 | 238 | – | 45 | 53 | 2 | 38S ₁₂ , 30S ₂₆ , 14S ₁₃ , 13S ₂₇ |
| ν_{13} | CCCl bend | 279 | 272 | 1.6 | 1.7 | 273 | – | 14 | 75 | 11 | 63S ₁₃ , 14S ₂₇ , 10S ₁₁ |
| ν_{14} | CH ₂ Cl torsion | 86 | 82 | 3.8 | 1.2 | 81 | – | 1 | 47 | 52 | 61S ₁₄ , 25S ₂₇ |
| ν_{15} | *CH ₂ antisymmetric stretch | 3220 | 3020 | 6.2 | 55.5 | 3001 | 2995 | 8 | 17 | 75 | 57S ₁₅ , 40S ₁ |
| ν_{16} | CH ₂ antisymmetric stretch | 3183 | 2986 | 6.8 | 62.8 | 2982 | 2988 | 0 | 39 | 61 | 88S ₁₆ |
| ν_{17} | *CH ₂ symmetric stretch | 3157 | 2962 | 13.1 | 54.5 | 2972 | 2966 | 34 | 8 | 58 | 51S ₁₇ , 42S ₂ |
| ν_{18} | *CH ₂ deformation | 1548 | 1469 | 2.3 | 6.8 | – | – | 78 | 20 | 2 | 33S ₁₈ , 44S ₄ , 23S ₅ |
| ν_{19} | CH ₂ wag | 1445 | 1371 | 10.2 | 3.4 | 1357 | 1354 | 82 | 3 | 15 | 55S ₁₉ , 15S ₆ , 12S ₂₀ , 10S ₂₂ |
| ν_{20} | *CH ₂ wag | 1358 | 1290 | 15.9 | 11.2 | 1274 | 1272 | 74 | 25 | 1 | 47S ₂₀ , 20S ₂₁ , 19S ₈ |
| ν_{21} | *CH ₂ twist | 1205 | 1144 | 0.8 | 7.2 | 1134 | 1129 | 48 | 41 | 11 | 59S ₂₁ , 23S ₈ |
| ν_{22} | CCC antisymmetric stretch | 1131 | 1074 | 2.4 | 5.6 | 1064 | 1065 | 90 | 10 | 0 | 71S ₂₂ |
| ν_{23} | CH ₂ rock | 828 | 790 | 23.6 | 5.1 | 786 | 786 | 85 | 14 | 1 | 16S ₂₃ , 26S ₂₅ , 23S ₂₄ , 12S ₉ |
| ν_{24} | *CH ₂ rock | 910 | 864 | 12.5 | 3.6 | 863 | 861 | 76 | 22 | 4 | 38S ₂₄ , 28S ₁₀ |
| ν_{25} | CCl stretch | 718 | 682 | 15.7 | 9.3 | 676 | 668 | 49 | 51 | 0 | 42S ₂₅ , 21S ₉ , 10S ₂₃ |
| ν_{26} | CCCl bend | 454 | 443 | 7.3 | 2.3 | 435 | 434 | 99 | 0 | 1 | 41S ₂₆ , 33S ₁₁ , 14S ₂₃ |
| ν_{27} | CH ₂ Cl torsion | 129 | 124 | 2.5 | 0.5 | 119 | – | 49 | 9 | 42 | 38S ₂₇ , 33S ₁₄ , 11S ₁₂ |

Asterisk Indicates CH₂ motions from CH₂Cl groups.^a Frequencies from MP2(full)/6-31G(d) calculation.^b Scaling factors of 0.88 for CH stretches, 1.0 for heavy atom bends and 0.90 for all other modes.^c Calculated infrared intensities in km/mol.^d Calculated Raman activities in Å⁴/amu.^e Values less than 10% are omitted.

Table 3

Observed and calculated frequencies (cm^{-1}) and potential energy distributions (PEDs) for the TT (C_{2v}) conformer of 1,3-dichloropropane

| Description | | | Ab initio ^a | Fixed scaled ^b | IR int. ^c | Raman act. ^d | Obs. gas | obs.Kr | Contour | | | PED ^e |
|----------------|------------|--|------------------------|---------------------------|----------------------|-------------------------|----------|--------|---------|-----|-----|---|
| | | | | | | | | | A | B | C | |
| A ₂ | ν_1 | *CH ₂ antisymmetric stretch | 3212 | 3013 | — | 0.5 | — | — | — | — | — | 100S ₁ |
| A ₁ | ν_2 | *CH ₂ symmetric stretch | 3152 | 2957 | 33.3 | 75.6 | 2955 | 2951 | — | 100 | — | 89S ₂ , 11S ₃ |
| A ₁ | ν_3 | CH ₂ symmetric stretch | 3135 | 2941 | 0.003 | 129.6 | — | — | — | 100 | — | 89S ₃ , 11S ₂ |
| A ₁ | ν_4 | *CH ₂ deformation | 1554 | 1475 | 0.06 | 33.1 | — | — | — | 100 | — | 70S ₄ , 29S ₅ |
| A ₁ | ν_5 | CH ₂ deformation | 1566 | 1485 | 5.7 | 0.1 | — | — | — | 100 | — | 70S ₅ , 30S ₄ |
| A ₁ | ν_6 | *CH ₂ wag | 1389 | 1319 | 25.1 | 2.8 | 1308 | 1305 | — | 100 | — | 100S ₆ |
| A ₂ | ν_7 | *CH ₂ twist | 1196 | 1135 | — | 10.3 | — | — | — | — | — | 69S ₇ , 18S ₈ , 11S ₉ |
| A ₂ | ν_8 | CH ₂ twist | 1364 | 1294 | — | 18.6 | — | — | — | — | — | 67S ₈ , 27S ₇ |
| A ₂ | ν_9 | *CH ₂ rock | 870 | 825 | — | 1.0 | — | — | — | — | — | 83S ₉ , 14S ₈ |
| A ₁ | ν_{10} | CCC symmetric stretch | 1099 | 1054 | 0.6 | 4.8 | 1046 | 1043 | — | 100 | — | 74S ₁₀ , 14S ₁₃ , 10S ₁₂ |
| A ₁ | ν_{11} | CCl stretch | 856 | 820 | 8.3 | 22.2 | 815 | 815 | — | 100 | — | 73S ₁₁ , 15S ₁₂ |
| A ₁ | ν_{12} | CCC bend | 310 | 301 | 1.4 | 4.3 | 302 | — | — | 100 | — | 38S ₁₂ , 29S ₁₁ , 19S ₁₀ , 13S ₁₃ |
| A ₁ | ν_{13} | CCCl bend | 139 | 138 | 3.3 | 2.1 | 139 | — | — | 100 | — | 63S ₁₃ , 35S ₁₂ |
| A ₂ | ν_{14} | CH ₂ Cl torsion | 125 | 119 | — | 0.9 | — | — | — | — | — | 98S ₁₄ |
| B ₁ | ν_{15} | *CH ₂ antisymmetric stretch | 3222 | 3023 | 18.4 | 34.2 | 3004 | 2997 | — | — | 100 | 78S ₁₅ , 22S ₁₆ |
| B ₁ | ν_{16} | CH ₂ antisymmetric stretch | 3190 | 2993 | 0.1 | 109.0 | — | 2991 | — | — | 100 | 78S ₁₆ , 22S ₁₅ |
| B ₂ | ν_{17} | *CH ₂ symmetric stretch | 3146 | 2952 | 33.3 | 75.6 | 2951 | 2951 | 100 | — | — | 100S ₁₇ |
| B ₂ | ν_{18} | *CH ₂ deformation | 1549 | 1469 | 2.8 | 0.3 | — | — | 100 | — | — | 99S ₁₈ |
| B ₂ | ν_{19} | CH ₂ wag | 1442 | 1369 | 32.2 | 1.3 | 1354 | 1354 | 100 | — | — | 48S ₁₉ , 44S ₂₀ |
| B ₂ | ν_{20} | *CH ₂ wag | 1298 | 1232 | 4.2 | 1.8 | 1226 | 1222 | 100 | — | — | 55S ₂₀ , 45S ₁₉ |
| B ₁ | ν_{21} | *CH ₂ twist | 1339 | 1270 | 2.9 | 0.03 | — | — | — | — | 100 | 74S ₂₁ , 20S ₂₃ |
| B ₂ | ν_{22} | CCC antisymmetric stretch | 1100 | 1043 | 6.2 | 6.6 | 1036 | 1030 | 100 | — | — | 90S ₂₂ |
| B ₁ | ν_{23} | CH ₂ rock | 780 | 740 | 3.8 | 0.3 | 742 | 742 | — | — | 100 | 46S ₂₃ , 35S ₂₄ , 14S ₂₇ |
| B ₁ | ν_{24} | *CH ₂ rock | 1114 | 1057 | 1.8 | 2.6 | 1048 | 1046 | — | — | 100 | 53S ₂₄ , 26S ₂₃ , 21S ₂₁ |
| B ₂ | ν_{25} | CCl stretch | 766 | 728 | 47.2 | 8.0 | 716 | 711 | 100 | — | — | 95S ₂₅ |
| B ₂ | ν_{26} | CCCl bend | 385 | 380 | 8.7 | 0.007 | 375 | — | 100 | — | — | 92S ₂₆ |
| B ₁ | ν_{27} | CH ₂ Cl torsion | 109 | 103 | 1.5 | 0.09 | 104 | — | — | — | 100 | 85S ₂₇ |

Asterisk indicates CH₂ motions from CH₂Cl groups.^a Frequencies from MP2(full)/6-31G(d) calculation.^b Scaling factors of 0.88 for CH stretches, 1.0 for heavy atom bends and 0.90 for all other modes.^c Calculated infrared intensities in km/mol.^d Calculated Raman activities in Å⁴/amu.^e Values less than 10% are omitted.

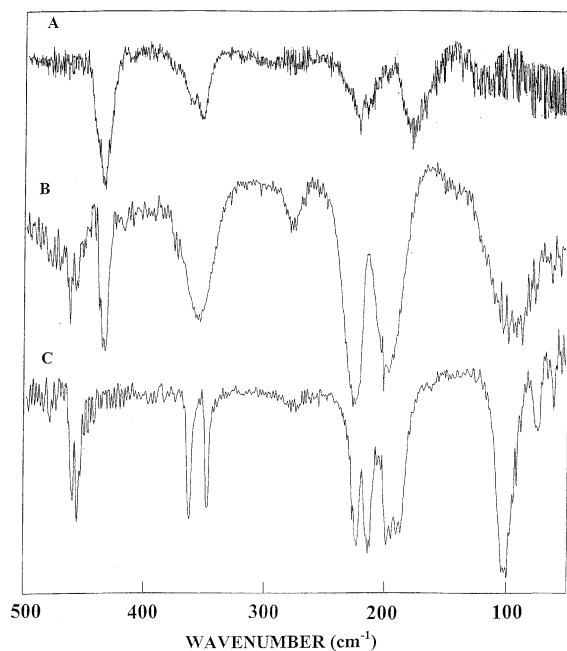


Fig. 2. Far infrared spectra of 1,3-dichloropropane from 50 to 500 cm^{-1} : (A) gas; (B) amorphous solid; (C) annealed solid.

where Q_i is the i th normal coordinate, X_j is the j th Cartesian displacement coordinate, and L_{ij} are elements of transformation matrix between the Cartesian displacement coordinates and normal coordinates. The infrared intensities were then calculated by:

$$I_i = \frac{N\pi}{3c^2} \left[\left(\frac{\partial \mu_x}{\partial Q_i} \right)^2 + \left(\frac{\partial \mu_y}{\partial Q_i} \right)^2 + \left(\frac{\partial \mu_z}{\partial Q_i} \right)^2 \right]$$

The predicted infrared spectra of the pure GG, GT and TT conformers are shown in Fig. 4E, D and C, respectively. The predicted spectrum of the mixture of the three conformers is shown in Fig. 4B. These spectra can be compared to the experimental spectra of the sample dissolved in liquefied krypton at -110°C shown in Fig. 4A. As a whole, the simulated infrared spectrum closely resembles the observed spectrum, which provides excellent evidence for the quality of the ab initio calculations.

4. Vibrational assignment

To determine the conformations stabilities of the different forms of 1,3-dichloropropane it is necessary

to assign bands to each one of the rotamers. However, since the GG conformer is in such a large abundance [6,7] and the TT form in very low abundance, it is not easy to confidently assign bands to the TG and TT rotamers. Also, because the two ClCH_2 groups are separated by the CH_2 group, many of the fundamentals for the three conformers have very similar frequencies. Nevertheless, by using the ab initio predicted frequencies, the observed and predicted infrared gas phase band contours (Fig. 5) and the band intensities from the infrared spectrum, it has been possible to provide a reasonably complete vibrational assignment for the two major conformers, i.e. GG and TG forms. Additionally, some of the fundamentals have been identified for the other conformer.

For the major conformer GG (C_2) there is little question of the assignments of the fundamentals except where they are nearly degenerate such as the two CH_2 deformations (ν_4 , A and ν_{18} , B) of the CH_2Cl groups which are predicted to be only one wavenumber apart. The ν_{18} fundamental at 1451 cm^{-1} with an excellent A/C contour (Fig. 6) and the ν_5 fundamental at 1427 cm^{-1} with the B-type band contour are readily discernable but ν_4 which also must have a B contour is not apparent. The Q-branch at 1444 cm^{-1} is probably ν_5 of the TG conformer. However in the infrared spectrum of the krypton solution there is a well-defined shoulder at 1448 cm^{-1} which is probably due to ν_4 of the GG form. By using the infrared band contours and the data from the krypton solution where the band centers can be clearly identified (Figs. 6 and 7) and closely spaced bands are resolved, it was possible to give confident assignments for all of the fundamentals of the GG conformer (Table 1) as well as most of those for the TG form (Table 2). The spectral comparisons was particularly important in the region from 800 to 625 cm^{-1} (Fig. 7) where it is not possible to determine the number of bands which are present in the gas. Thus the challenge was to identify bands which could be assigned to the TT (C_{2v}) conformer which is in very low abundance.

There are several bands observed in the infrared spectrum of the krypton solution which have not been assigned to either the GG (C_2) or TG (C_1) conformers with the most pronounced one at 815 cm^{-1} . There is

Table 4

Calculated energies and energy difference for the five conformers of 1,3-dichloropropane

| Method/basis set | <i>gauche</i> – <i>gauche</i> (C_2) | <i>trans</i> – <i>gauche</i> (C_1) | <i>trans</i> – <i>trans</i> (C_{2v}) | <i>gauche</i> – <i>gauche'</i> (C_s) |
|--------------------------|---|--|--|--|
| MP2/6-31G(d) | –1036.753658 0 | –1036.752435 268 | –1036.751463 482 | –1036.746250 1626 |
| MP2/6-31 + G(d) | –1036.764049 0 | –1036.762704 295 | –1036.761572 544 | –1036.756535 1649 |
| MP2/6-311G(d,p) | –1037.031862 0 | –1037.030495 300 | –1037.029510 516 | –1037.024697 1573 |
| MP2/6-311 + G(d,p) | –1037.039283 0 | –1037.037768 333 | –1037.036731 560 | –1037.032019 1594 |
| MP2/6-311G(2d,2p) | –1037.133114 0 | –1037.131532 347 | –1037.130256 627 | –1037.125771 1612 |
| MP2/6-311 + G(2d,2p) | –1037.137890 0 | –1037.136239 362 | –1037.134954 644 | –1037.130525 1616 |
| MP2/6-311G(2df,2pd) | –1037.245533 0 | –1037.243827 374 | –1037.242522 661 | –1037.238135 1624 |
| MP2/6-311 + G(2df,2pd) | –1037.250145 0 | –1037.248376 388 | –1037.247067 676 | –1037.242757 1621 |
| B3LYP/6-31G(d) | –1038.334771 0 | –1038.333709 233 | –1038.332744 445 | –1038.327868 1515 |
| B3LYP/6-31 + G(d) | –1038.340653 0 | –1038.339714 206 | –1038.338848 396 | –1038.333850 1493 |
| B3LYP/6-311G(d,p) | –1038.425477 0 | –1038.424312 256 | –1038.423273 484 | –1038.419012 1419 |
| B3LYP/6-311 + G(d,p) | –1038.427735 0 | –1038.426644 239 | –1038.425659 456 | –1038.421229 1428 |
| B3LYP/6-311G(2d,2p) | –1038.434930 0 | –1038.433860 235 | –1038.432867 453 | –1038.428448 1423 |
| B3LYP/6-311 + G(2d,2p) | –1038.436467 0 | –1038.435432 227 | –1038.434472 438 | –1038.429951 1430 |
| B3LYP/6-311G(2df,2pd) | –1038.441126 0 | –1038.440104 224 | –1038.439195 424 | –1038.434744 1401 |
| B3LYP/6-311 + G(2df,2pd) | –1038.442687 0 | –1038.441693 218 | –1038.440825 409 | –1038.436286 1405 |

also another one at 1222 cm^{-1} as well as weak ones at 711 and 1305 cm^{-1} . These four bands were assigned as ν_{11} (CCl stretch), ν_{20} ($^*\text{CH}_2$ wag), ν_{25} (CCl stretch), and ν_6 ($^*\text{CH}_2$ wag), respectively. A few other bands were assigned for the TT form but these four initial ones were the ones whose relative intensities were measured for the enthalpy determination.

5. Conformational stabilities

The 736 cm^{-1} band can be confidently assigned to the C_1 (TG) conformer which was then combined with the 653 , 689 and 799 cm^{-1} bands which are confidently assigned to C_2 (GG) conformer were

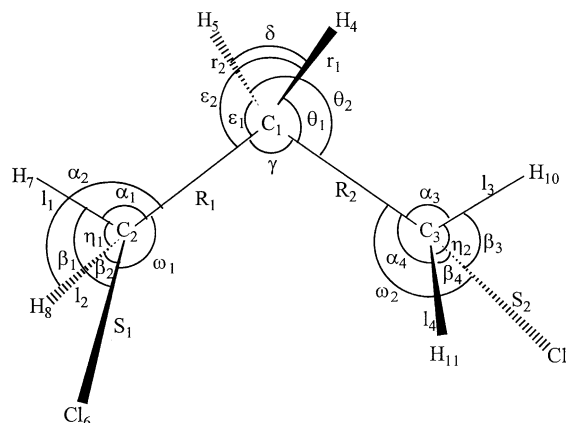


Fig. 3. Internal coordinates used for normal coordinate analysis for 1,3-dichloropropane.

Table 5
Symmetry coordinates for 1,3-dichloropropane

| | Description | Symmetry coordinate ^a |
|----------------|--|--|
| A ₂ | *CH ₂ antisymmetric stretch | $S_1 = l_1 - l_2 + l_3 - l_4$ |
| A ₁ | *CH ₂ symmetric stretch | $S_2 = l_1 + l_2 + l_3 + l_4$ |
| A ₁ | CH ₂ symmetric stretch | $S_3 = r_1 + r_2$ |
| A ₁ | *CH ₂ deformation | $S_4 = 4\eta_1 - \alpha_1 - \alpha_2 - \beta_1 - \beta_2 + 4\eta_2 - \alpha_3 - \alpha_4 - \beta_3 - \beta_4$ |
| A ₁ | CH ₂ deformation | $S_5 = 4\delta - \theta_1 - \theta_2 - \varepsilon_1 - \varepsilon_2$ |
| A ₁ | *CH ₂ wag | $S_6 = \alpha_1 + \alpha_2 - \beta_1 - \beta_2 + \alpha_3 + \alpha_4 - \beta_3 - \beta_4$ |
| A ₂ | *CH ₂ twist | $S_7 = \alpha_1 - \alpha_2 - \beta_1 + \beta_2 + \alpha_3 - \alpha_4 - \beta_3 + \beta_4$ |
| A ₂ | CH ₂ twist | $S_8 = \theta_1 - \theta_2 - \varepsilon_1 + \varepsilon_2$ |
| A ₂ | *CH ₂ rock | $S_9 = \alpha_1 - \alpha_2 + \beta_1 - \beta_2 + \alpha_3 - \alpha_4 + \beta_3 - \beta_4$ |
| A ₁ | CCC symmetric stretch | $S_{10} = R_1 + R_2$ |
| A ₁ | CCl stretch | $S_{11} = S_1 + S_2$ |
| A ₁ | CCC bend | $S_{12} = \gamma$ |
| A ₁ | CCCl bend | $S_{13} = \omega_1 + \omega_2$ |
| A ₂ | CH ₂ Cl torsion | $S_{14} = \tau_1 + \tau_2$ |
| B ₁ | *CH ₂ antisymmetric stretch | $S_{15} = l_1 - l_2 - l_3 + l_4$ |
| B ₁ | CH ₂ antisymmetric stretch | $S_{16} = l_1 + l_2 - l_3 - l_4$ |
| B ₂ | *CH ₂ symmetric stretch | $S_{17} = r_1 - r_2$ |
| B ₂ | *CH ₂ deformation | $S_{18} = 4\eta_1 - \alpha_1 - \alpha_2 - \beta_1 - \beta_2 - 4\eta_2 + \alpha_3 + \alpha_4 + \beta_3 + \beta_4$ |
| B ₂ | CH ₂ wag | $S_{19} = \theta_1 + \theta_2 - \varepsilon_1 - \varepsilon_2$ |
| B ₂ | *CH ₂ wag | $S_{20} = \alpha_1 + \alpha_2 - \beta_1 - \beta_2 - \alpha_3 - \alpha_4 + \beta_3 + \beta_4$ |
| B ₁ | *CH ₂ twist | $S_{21} = \alpha_1 - \alpha_2 - \beta_1 + \beta_2 - \alpha_3 + \alpha_4 + \beta_3 - \beta_4$ |
| B ₂ | CCC antisymmetric stretch | $S_{22} = R_1 - R_2$ |
| B ₁ | CH ₂ rock | $S_{23} = \theta_1 - \theta_2 + \varepsilon_1 - \varepsilon_2$ |
| B ₁ | *CH ₂ rock | $S_{24} = \alpha_1 - \alpha_2 + \beta_1 - \beta_2 - \alpha_3 + \alpha_4 - \beta_3 + \beta_4$ |
| B ₂ | CCl stretch | $S_{25} = S_1 - S_2$ |
| B ₂ | CCCl bend | $S_{26} = \omega_1 - \omega_2$ |
| B ₁ | CH ₂ Cl torsion | $S_{27} = \tau_1 - \tau_2$ |

Shown for the highest symmetry TT (C_{2v}) conformer, reduced to A and B symmetry blocks for GG (C₂) conformer and no separation of symmetry blocks for the TG (C₁) conformer. Asterisk indicates CH₂ moieties from CH₂Cl groups.

^a Not normalized.

used for the enthalpy determination. Also, the bands at 711, 816, 1222 and 1305 cm⁻¹ with low intensities which are rather isolated were initially used for the enthalpy determination of the C_{2v} (TT) conformer. These bands were utilized to obtain the enthalpy differences between the conformers on the basis of decreasing intensity with lowering the temperature. In order to obtain the enthalpy difference, spectral data were measured at every five degree interval beginning at -105 to -150 °C. When data were collected below -130 °C it was evident that the sample was freezing on the windows so the intensity data used for the enthalpy determinations were limited to temperatures above -130 °C. These sets of intensity data were fit to the van't Hoff equations, $-\ln K = \Delta H/RT - \Delta S/R$, where K is the intensity ratio of C₂/C₁ or C₂/C_{2v}, assuming that ΔH is not

a function of temperature. The value obtained from the 1222 cm⁻¹ band was variable and those for both the 816 and 1305 cm⁻¹ were relatively small which indicates interference from underlying combination and/or overtone bands. Therefore only the 711 cm⁻¹ band gave reasonable results for the C_{2v} conformer. By using a least squares fit and the slopes of the van't Hoff plot, ΔH value of 272 ± 11 cm⁻¹ (3.25 ± 0.14 kJ/mol) and 383 ± 19 cm⁻¹ (4.58 ± 0.23 kJ/mol) were obtained for the C₂/C₁ and C₂/C_{2v} pairs with the C₂ conformer the most stable form followed by the C₁ and C_{2v} conformers. The uncertainty reported in Table 6 is the statistical uncertainty. There is a low chance of interference of the measured bands from combination and overtone bands since relatively low frequency bands were used. Thus, it is expected that the ΔH values are reasonably

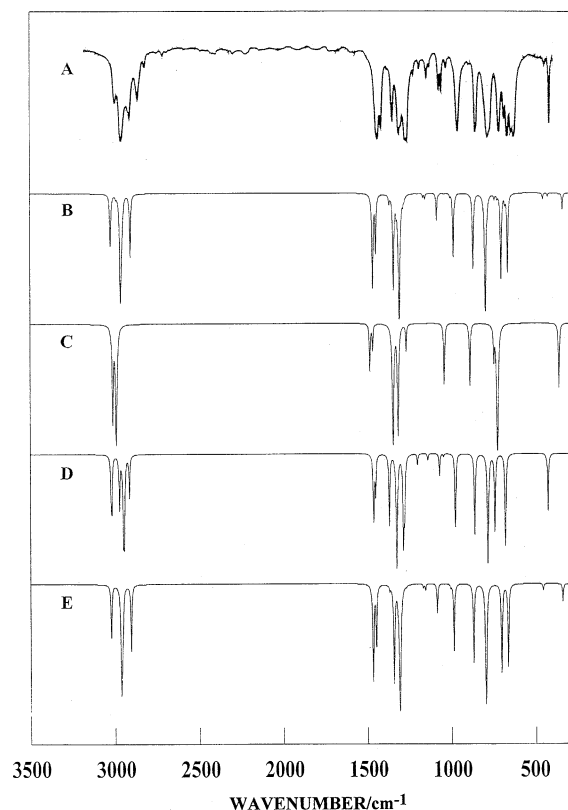


Fig. 4. Mid-infrared spectra of 1,3-dichloropropane: (A) observed infrared spectrum of the krypton solution; (B) simulated spectrum of a mixture of three conformers with ΔH of 272 cm^{-1} for TG and ΔH of 383 cm^{-1} for TT relative to the most stable GG form; (C) calculated spectrum for pure TT form (C_{2v}); (D) calculated spectrum for pure TG form (C_1); (E) calculated spectrum for pure GG form (C_2).

accurate but at least a ten percent uncertainty is a more realistic error value. Thus the final values of $272 \pm 27\text{ cm}^{-1}$ ($3.25 \pm 0.32\text{ kJ/mol}$) and $383 \pm 38\text{ cm}^{-1}$ ($4.58 \pm 0.46\text{ kJ/mol}$) are obtained for the enthalpy differences for the C_1 and C_{2v} rotamers, respectively, to the most stable C_2 conformer. These values are comparable to those obtained from the theoretical ab initio values reported in Table 4. From these enthalpy differences and the classical multiplicities of C_2 (2), C_1 (4) and C_{2v} (1) for 1,3-dichloropropane it is estimated that there is $62 \pm 2\%$ of the C_2 form, $33 \pm 2\%$ of the C_1 rotamer, and $5 \pm 1\%$ of the C_{2v} conformer present at ambient temperature. These values are significantly different from the values previously reported [6,7].

6. Discussion

The previously reported energy differences between the C_2 (GG) and C_1 (GT) forms of 1,3-dichloropropane obtained from the electron diffraction study [6] of $1.1 \pm 0.2\text{ kcal/mol}$ ($385 \pm 70\text{ cm}^{-1}$) and $4.7 \pm 0.2\text{ kJ/mol}$ ($393 \pm 17\text{ cm}^{-1}$) from wide-angle X-ray scattering [7] agree reasonable well with the determined enthalpy difference of $272 \pm 27\text{ cm}^{-1}$ ($3.25 \pm 0.32\text{ kJ/mol}$). The listed uncertainty of 17 cm^{-1} from the X-ray scattering study [7] is undoubtedly too small. For agreement with the value reported herein would require an uncertainty about six times the value given which seems to be a more realistic error particularly since it is clear that there is a significant amount of a third conformer present which was not considered in the X-ray studies. The ab initio predicted energy difference between these two most abundant conformers ranges from a low value of 268 cm^{-1} (MP2/6-31G(d)) to a high value of 388 cm^{-1} (MP2/6-311 + G(2df,2pd)) whereas the predictions from the hybrid DFT calculations have a smaller range of 206 cm^{-1} (B3LYP/6-31 + G(d)) to 256 cm^{-1} (B3LYP/6-311G(d,p)). Considering the expected error from the theoretical predicted energy difference the experimentally determined value agrees with the theoretical value.

The energy difference between the C_2 (GG) and C_{2v} (TT) conformers has been obtained experimentally and predicted from molecular mechanics calculations [6,17] with values of $1.5 \pm 0.5\text{ kcal/mol}$ ($525 \pm 175\text{ cm}^{-1}$) and 2.21 kcal/mol (773 cm^{-1}), respectively. Therefore the experimentally determined value has a very large range from 350 to 800 cm^{-1} . The experimental value obtained in this study is $383 \pm 38\text{ cm}^{-1}$ ($4.58 \pm 0.46\text{ kJ/mol}$) which is on the low side of the previously reported value. It should be noted that this value is significantly lower than the ab initio predicted energy differences which ranged from a low value of 482 cm^{-1} (MP2/6-31G(d)) to a high value of 676 cm^{-1} (MP2/6-311 + G(2df,2pd)). However the hybrid DFT calculations predicted energy differences which ranged from a low value of 396 cm^{-1} (B3LYP/6-31 + G(d)) to a high value of 484 cm^{-1} (B3LYP/6-311G(d,p)) with most of the values in the lower range. Therefore the B3LYP predictions of

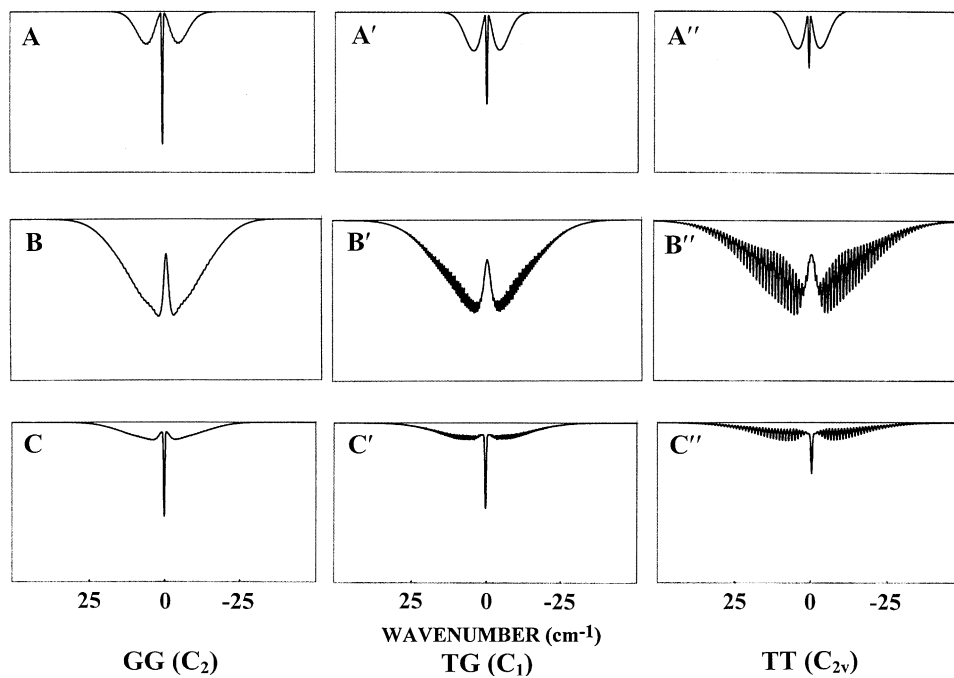


Fig. 5. Predicted pure A-, B- and C-type infrared contours for the GG, TG and TT conformers for 1,3-dichloropropane.

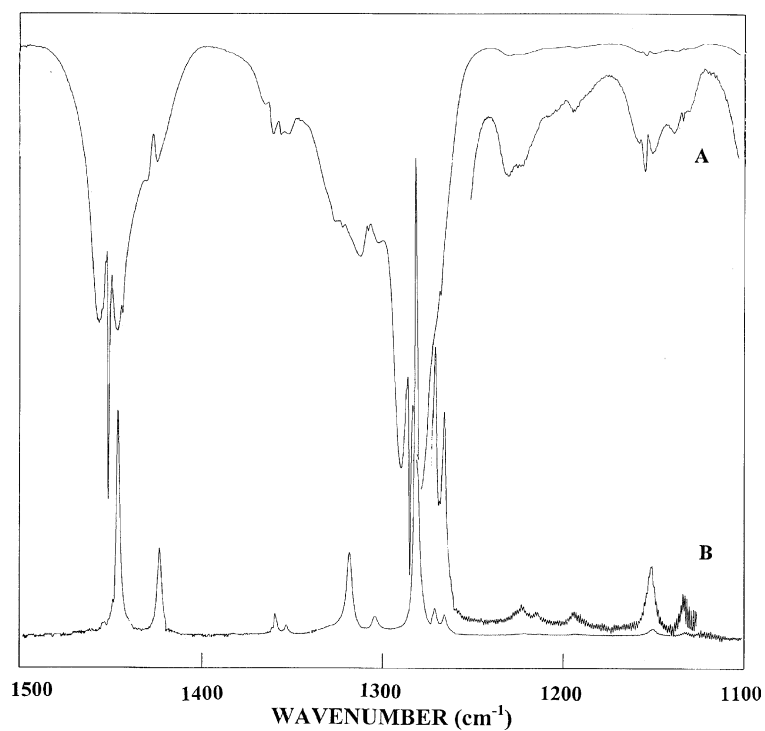


Fig. 6. Mid-infrared spectra of 1,3-dichloropropane in 1100–625 cm^{-1} region: (A) gas in transmittance; (B) Kr solution in absorbance.

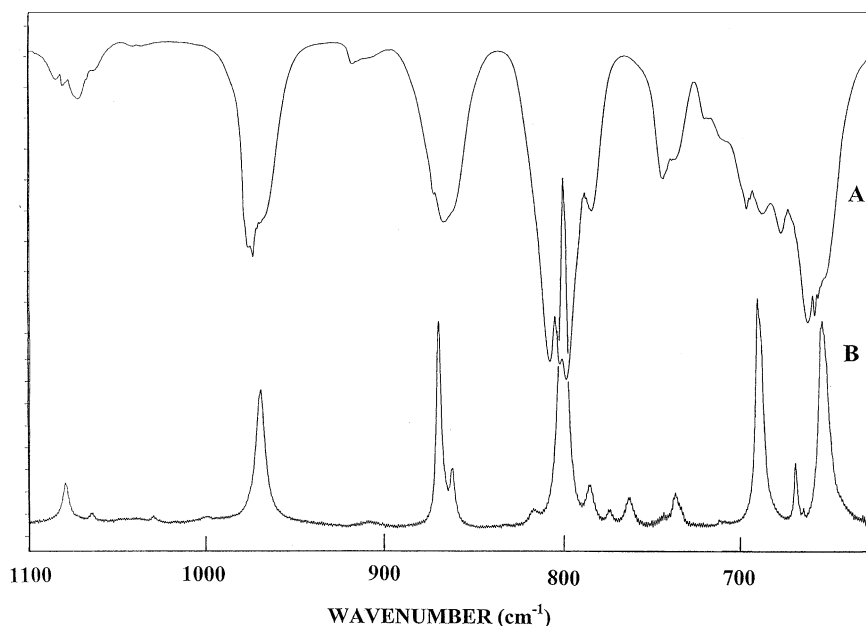


Fig. 7. Mid-infrared spectra of 1,3-dichloropropane in 1500–1100 cm^{-1} region: (A) gas in transmittance; (B) Kr solution in absorbance.

the energy differences seem to be in better agreement with the experimentally determined values.

By utilizing only two scaling factors of 0.88 for the CH stretches, 0.90 for the CH bends and heavy atom stretches, with 1.0 for the remaining modes. The frequencies of the vibrations of A symmetry of the C_2 form are predicted with an average difference of 9.7 cm^{-1} from the observed values which represents an average error of only 0.7%. For the vibrations of B symmetry for the C_2 conformer

the average difference in the predicted and observed frequencies is slightly higher with a value of 11.9 cm^{-1} which is an error of 0.8%. A significant amount of this error arises from the predicted frequencies for the carbon–hydrogen stretches. Nevertheless there are some vibrations which are poorly predicted such as the CH_2 wag (ν_{20}) at 1308 cm^{-1} but clearly observed at 1285 cm^{-1} . A similar poor prediction for the corresponding vibration ($^*\text{CH}_2$ wag, ν_6) of A symmetry which is

Table 6

Temperature and intensity ratios for the conformational study of C_2/C_1 and C_2/C_{2v} conformers of 1,3-dichloropropane dissolved in liquid krypton

| Conformer pair | | GG (C_2)/TG (C_1) | | | GG (C_2)/TT (C_{2v}) | | |
|---------------------------------|------------------------------|---------------------------|---------------|---------------|------------------------------|---------------|---------------|
| T ($^{\circ}\text{C}$) | $1000/T$ (K^{-1}) | $I_{653/736}$ | $I_{799/736}$ | $I_{689/736}$ | $I_{970/711}$ | $I_{799/711}$ | $I_{689/711}$ |
| –105.0 | 5.9471 | 10.512 | 12.942 | 8.608 | 97.98 | 362.25 | 122.68 |
| –110.0 | 6.1293 | 11.476 | 14.552 | 9.376 | 102.46 | 385.64 | 126.78 |
| –115.0 | 6.3231 | 11.969 | 14.811 | 9.748 | 119.40 | 459.96 | 145.80 |
| –120.0 | 6.5295 | 13.282 | 16.537 | 10.723 | 128.76 | 502.24 | 156.61 |
| –125.0 | 6.7499 | 14.439 | 18.291 | 11.700 | 149.20 | 591.91 | 180.98 |
| ΔH (cm^{-1}) | | 271 ± 16 | 284 ± 29 | 259 ± 15 | 371 ± 30 | 432 ± 30 | 344 ± 31 |

Average enthalpy differences $272 \pm 11 \text{ cm}^{-1}$ ($3.25 \pm 0.14 \text{ kJ/mol}$) for TG (C_1) and $383 \pm 19 \text{ cm}^{-1}$ ($4.58 \pm 0.23 \text{ kJ/mol}$) for TT (C_{2v}) conformers with respect to the most stable GG (C_2) form.

predicted at 1343 cm^{-1} but observed at 1322 cm^{-1} . There is also a significant error of 14 cm^{-1} for the predicted frequency of the CCl stretch, ν_{11} . Finally it should be noted that these predicted frequencies agree better with the observed values than those which were obtained earlier from the electron diffraction study [6] from transferred force constants.

Since the structural parameters are nearly the same for all three conformers, one expects the force constants to have similar values with exception for a few of the angles. This is exactly what is found for the predicted values where the differences among the stretching force constants for the three conformers averages less than one percent, the same is true for the bending constants with the exception of γ (CCC), ε_1 ($\text{C}_2\text{C}_1\text{H}_5$), θ_2 ($\text{C}_3\text{C}_1\text{H}_5$) and ω_1 ($\text{Cl}_6\text{C}_2\text{C}_1$) as well as ω_2 ($\text{C}_1\text{C}_3\text{Cl}_9$) for the C_{2v} conformer. For γ the values are 10.6 and 19.9% smaller for the C_1 and C_{2v} forms, respectively, compared to the value (0.923 mdyn/\AA) of this force constant for the C_2 conformer. For ε_1 the values are 5.5% smaller for the C_1 and C_{2v} forms, for θ_2 the C_{2v} form has a smaller value of 5.5% and the C_1 form a smaller value of 4.8%. For ω_1 the values are 9.8 and 11.6% smaller for the C_1 and C_{2v} forms, respectively, whereas for ω_2 the value is 11.6% smaller than the value for this force constant for the C_2 conformer. Thus, these significantly different force constants for the CCC and CCl bends results in quite different values for the fundamentals associate with the bending motions of these atoms. For this reason the low frequency spectra for most haloalkanes provide the most definitive information on the presence of conformers in the fluid states.

For the C_2 conformer the mixing of the symmetry coordinates with only five vibrations having significant contributions from three symmetry coordinates and only one mode (ν_{12} , CCC bend) with contributions from four symmetry coordinates. The only vibration which has less than 40% from the major contributor is ν_{23} (CH_2 rock) with 37% from S_{23} and 28% from S_{24} the other rock ($^*\text{CH}_2$ rock, ν_{24}). Even less mixing is predicted for the C_{2v} conformer with four modes having significant contributions from three symmetry coordinates and again the CCC bend, ν_{12} , with major contributions from four symmetry coordinates. However, the TG conformer (C_1) without any symmetry element except for identity

has extensive mixing with 10 modes with contributions from three symmetry coordinates and five with contributions from four. This makes the descriptions for ν_8 and ν_{23} somewhat arbitrary. Nevertheless most of the other modes have the major contributions of 40% or more.

In the earlier electron diffraction study [6] the authors provided the force constants for calculating the fundamental frequencies for the three conformers of 1,3-dichloropropane which were transferred from other molecules [18,19]. The values for these force constants are listed in Table 7 along with those predicted from the MP2/6-31G(d) ab initio calculations for the C_2 conformer. The transferred force constants gave reasonable predictions for the fundamental frequencies for the C_2 form except for the symmetrical torsion which is predicted at 145 cm^{-1} but observed at 175 cm^{-1} . The experimental value agrees well with the ab initio predicted frequency of 188 cm^{-1} for this mode. The transferred force constants are in reasonable agreement with ab initio predicted values except for the two stretch/stretch constants, the $^*\text{C}-\text{C}/\text{C}^*\text{CH}$ stretch/bend, and all three of the bend/bend constants. The transferred $^*\text{C}-\text{C}/\text{C}^*\text{C}-\text{Cl}$ stretch/stretch constant is a factor of three times larger than the predicted value whereas the transferred $\text{C}-\text{C}/\text{C}-^*\text{C}$ constant is three times smaller than the predicted value. There is also a major difference for the transferred $\text{H}^*\text{CCl}/\text{H}^*\text{CCl}$ bend/bend where the value is $0.097\text{ mdyn \AA rad}^{-2}$ compared to the predicted value of $0.653\text{ mdyn \AA rad}^{-2}$. Similarly for the $\text{C}^*\text{CH}/\text{H}^*\text{CCl}$ bend/bend constant the transferred value is positive and twice the predicted value whereas the predicted value is negative. These differences clearly indicate the importance of obtaining the interaction force constants from ab initio calculations.

In the earlier far infrared study [3] of 1,3-dichloropropane where the infrared spectra were recorded from a benzene solution, bands were reported at 65, 79, 138, 180, 188, 220, 271 and 300 cm^{-1} . The 65 and 79 cm^{-1} bands are undoubtedly the CH_2Cl symmetric torsional modes of the C_2 and C_1 conformers, respectively, whereas the CH_2Cl antisymmetric torsions are observed at 119 and 175 cm^{-1} , respectively, in the far infrared spectrum of the gas. The latter band probably corresponds to the 180 cm^{-1} previously reported

Table 7
Valence force constants for 1,3-dichloropropane

| Constant | Transferred values ^a | Ab initio values ^b |
|---|---------------------------------|-------------------------------|
| <i>Stretch (mdyn Å⁻¹)</i> | | |
| *C–C ^c | 4.57 | 4.411 |
| *C–Cl | 3.18 | 3.276 |
| *C–H | 4.85 | 4.972/4.934 |
| C–H | 4.55 | 4.780 |
| <i>Bend (mdyn Å rad⁻²)</i> | | |
| *CC*C | 0.90 | 0.923 |
| *CCH | 0.68 | 0.555/0.547 |
| C*CH | 0.67 | 0.602/0.575 |
| C*CCl | 1.17 | 0.926 |
| H*CH | 0.45 | 0.508 |
| HCH | 0.55 | 0.513 |
| H*CCl | 0.79 | 0.653/0.627 |
| <i>Stretch/stretch (mdyn Å⁻¹)</i> | | |
| *C–C/*C–Cl (common *C) | 0.730 | 0.230 |
| *C–C/C–*C (different *C) | 0.064 | 0.196 |
| <i>Stretch/bend (mdyn Å rad⁻¹)</i> | | |
| *C–Cl/C*CCl (common *C) | 0.73 | 0.233 |
| *C–Cl/H*CCl (common *C) | 0.33 | 0.211/0.205 |
| *C–C/*CC*C | 0.35 | 0.269 |
| *C–C/C*CCl (common *C) | 0.29 | 0.191 |
| *C–C/C*CH (common *C) | 0.26 | 0.094/0.114 |
| <i>Bend/bend (mdyn Å rad⁻²)</i> | | |
| *CC*C/C*CH (common *C) | –0.124 | 0.060/–0.024 |
| C*CH/H*CCl (common *CH) | 0.105 | –0.052/–0.067 |
| H*CCl/H*CCl (common *C, different H) | 0.097 | 0.653 |

^a Ref. [6].

^b This study.

^c Asterisk indicates carbon atom with chlorine atom attached.

[3]. However, the spectrum of the gas does not have any absorption corresponding to the 188 cm⁻¹ band reported [3] earlier. It should be noted that the 273 and 139 cm⁻¹ bands are not apparent in the spectrum of the gas but are relatively

pronounced in the spectrum of the amorphous solid (Fig. 2). Also the ν_{12} fundamental of the most stable C_2 conformer is not apparent in the spectrum of the gas with the pressure/pathlength used to measure the far infrared spectrum, but it is a pronounced band in the spectrum of the amorphous solid (Fig. 2). It remains in the spectrum of the polycrystalline solid whereas the ν_{26} mode at 435 cm⁻¹ of the C_1 conformer clearly disappears with annealing of the amorphous sample. Finally it should be noted that the splittings of ν_{13} , ν_{26} and ν_{12} of the C_2 conformer of the polycrystalline should indicate that there are at least two molecules in the primitive cell.

We have found that the ab initio MP2/6-31G(d) calculations provide predicted barriers to internal rotation around carbon–carbon bonds to usually better than 200 cm⁻¹ and for many cases better than 100 cm⁻¹ with the experimentally determined barriers. Therefore we obtained the predicted barriers to rotation of one of the CH₂Cl moieties which generates the most stable C_2 conformer (GG) at about –120°, the C_1 conformer (TG) at approximately 0° and the GG' form (C_s) at about 120° (Fig. 8) from both the MP2/6-31G(d) and MP2/6-31 + G(d) calculations. The barriers from the MP2/6-31G(d) calculations are somewhat higher than those from the similar calculation with diffuse functions but the most noticeable difference is the MP2/6-31 + G(d) calculations does not predict any well in the potential function for the C_s form. A rather similar result was obtained from the molecular mechanics calculations [17]. It is expected that the potential function obtained from the MP2/6-31G(d) calculation is similar to the one that would be obtained experimentally from torsional transition and dihedral angles.

For a large number of substituted hydrocarbons, we [20] have recently showed that ab initio MP2/6-311 + G(d,p) calculations predicts the C–H bond distances for more than 50 different C–H bonds to within about 0.002 Å to the experimental determined values, r_0 , obtained from ‘isolated’ carbon–hydrogen stretching frequencies [21]. By using these predicted parameters along with the microwave determined rotational constants it is possible to obtain r_0 structural parameters for many compounds with a limited number of rotational constants. In order to

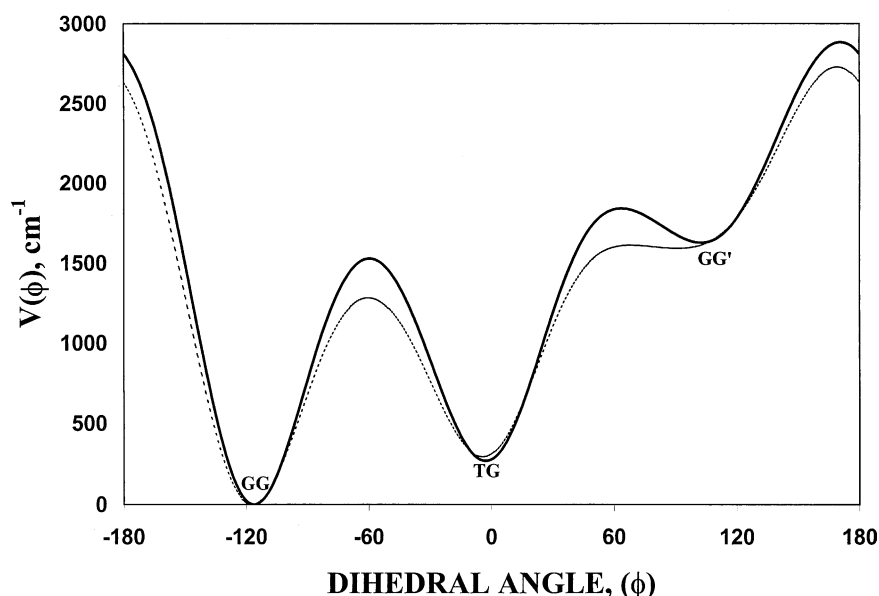


Fig. 8. Calculated potential functions (solid curve, from MP2(full)/6-31G(d) and dotted curve, from MP2(full)/6-31 + G(d)) governing internal rotation of one CH₂Cl rotor in 1,3-dichloropropane with the other CH₂Cl rotor in *gauche* orientation. Dihedral angle $\sim 0^\circ$ defined for the TG conformer.

reduce the number of independent variables, the structural parameters are separated into sets according to their types. Bond lengths in the same set keep their relative ratio, and bond angles and torsional angles in the same set keep their differences in degrees [22]. This assumption is based on the fact that the errors from ab initio calculations are systematic. By utilizing this procedure from chloropropane, the r_0 structural parameters were obtained for both the *trans* and *gauche* conformers [24] with the fit of 25 rotational constants from five isotopomers, i.e. ³⁷Cl, ³⁵Cl, and ¹³C for each of the three different carbon atoms. The difference in the predicted carbon–carbon and carbon–chlorine distances and those obtained from the fit of the microwave data was an elongation of both of these bonds of 0.007 Å. Similarly the predicted parameters were obtained for chloroethane where the structural parameters have been well determined from microwave data [23–25] and the differences were slightly smaller with values of 0.004 Å, again with the predicted parameters too short. Therefore we have estimated the r_0 parameters from the ab initio MP2/6-311 + G(d,p) predicted parameters by keeping the C–H values at the predicted distances and angles and have added

0.007 Å to the carbon–carbon and carbon–chlorine distances which should be the higher limit. These estimated parameters are listed in Table 7 and it is expected that the heavy atom distances should be accurate to 0.003 Å, the carbon–hydrogen distances to 0.002 Å and the angles to 0.5°.

From an earlier electron diffraction study [6], average structural parameters (r_g , $\angle\alpha$) for the three conformers were obtained. Since there is very little of the C_{2v} conformer (TT) present at ambient temperature, these parameters are essentially for the C_2 (GG) and C_1 (TG) conformers and they are also listed in Table 8 for comparison to the estimated r_0 parameters. There is very little predicted difference in the heavy atom parameters for the C_2 and C_1 forms so these average values should be good for comparison to either the C_2 or C_1 forms. The average C–C distance of 1.532 ± 0.008 Å from the electron diffraction study is within the estimated value of 1.524 ± 0.003 Å but it is believed that the shorter value is the better value based on the determined distances for this parameter for other molecules. Similarly the average C–Cl distance of 1.798 ± 0.006 Å is well within the estimated

Table 8

Structural parameters (Å and degree), rotational constants (MHz) and dipole moments (Debye) for GG, TG and TT rotamers of 1,3-dichloropropane

| | MP2(full)/6-311 + G(d,p) | | | Estimated ^a r_0 | | | Average ^b r_g and $\angle\alpha$ |
|--|--------------------------|--------|----------|------------------------------|-----------|-----------|---|
| | GG | TG | TT | GG | TG | TT | |
| $r(\text{C}_1\text{C}_2)$ | 1.517 | 1.517 | 1.519 | 1.524(3) | 1.524(3) | 1.526(3) | 1.532(8) |
| $r(\text{C}_1\text{C}_3)$ | 1.517 | 1.518 | 1.519 | 1.524(3) | 1.525(3) | 1.526(3) | 1.532(8) |
| $r(\text{C}_2\text{Cl}_6)$ | 1.786 | 1.782 | 1.782 | 1.793(3) | 1.789(3) | 1.789(3) | 1.798(6) |
| $r(\text{C}_3\text{Cl}_9)$ | 1.786 | 1.786 | 1.782 | 1.793(3) | 1.793(3) | 1.789(3) | 1.798(6) |
| $r(\text{C}_1\text{H}_4)$ | 1.095 | 1.093 | 1.093 | 1.095(2) | 1.093(2) | 1.093(2) | 1.124(12) |
| $r(\text{C}_1\text{H}_5)$ | 1.095 | 1.096 | 1.093 | 1.095(2) | 1.096(2) | 1.093(2) | 1.124(12) |
| $r(\text{C}_2\text{H}_7)$ | 1.090 | 1.092 | 1.091 | 1.090(2) | 1.092(2) | 1.091(2) | 1.124(12) |
| $r(\text{C}_2\text{H}_8)$ | 1.089 | 1.089 | 1.091 | 1.089(2) | 1.089(2) | 1.091(2) | 1.124(12) |
| $r(\text{C}_3\text{H}_{10})$ | 1.090 | 1.092 | 1.091 | 1.090(2) | 1.092(2) | 1.091(2) | 1.124(12) |
| $r(\text{C}_3\text{H}_{11})$ | 1.089 | 1.090 | 1.091 | 1.089(2) | 1.090(2) | 1.091(2) | 1.124(12) |
| $\angle\text{C}_2\text{C}_1\text{C}_3$ | 114.2 | 112.5 | 110.7 | 114.2(5) | 112.5(5) | 110.7(5) | 112.9(10) |
| $\angle\text{C}_1\text{C}_2\text{Cl}_6$ | 111.2 | 110.6 | 110.8 | 111.2(5) | 110.6(5) | 110.8(5) | 111.6(2) |
| $\angle\text{C}_1\text{C}_3\text{Cl}_9$ | 111.2 | 111.7 | 110.8 | 111.2(5) | 111.7(5) | 110.8(5) | 111.6(2) |
| $\angle\text{C}_2\text{C}_1\text{H}_4$ | 109.2 | 109.8 | 109.7 | 109.2(5) | 109.8(5) | 109.7(5) | 108.8 |
| $\angle\text{C}_2\text{C}_1\text{H}_5$ | 108.1 | 109.1 | 109.7 | 108.1(5) | 109.1(5) | 109.7(5) | 108.8 |
| $\angle\text{C}_3\text{C}_1\text{H}_4$ | 108.1 | 109.9 | 109.7 | 108.1(5) | 109.9(5) | 109.7(5) | 108.8 |
| $\angle\text{C}_3\text{C}_1\text{H}_5$ | 109.2 | 107.8 | 109.7 | 109.2(5) | 107.8(5) | 109.7(5) | 108.8 |
| $\angle\text{C}_1\text{C}_2\text{H}_7$ | 110.6 | 110.8 | 111.2 | 110.6(5) | 110.8(5) | 111.2(5) | 109.9 |
| $\angle\text{C}_1\text{C}_2\text{H}_8$ | 111.1 | 111.3 | 111.2 | 111.1(5) | 111.3(5) | 111.2(5) | 109.9 |
| $\angle\text{C}_1\text{C}_3\text{H}_{10}$ | 110.6 | 111.1 | 111.2 | 110.6(5) | 111.1(5) | 111.2(5) | 109.9 |
| $\angle\text{C}_1\text{C}_3\text{H}_{11}$ | 111.1 | 110.5 | 111.2 | 111.1(5) | 110.5(5) | 111.2(5) | 109.9 |
| $\angle\text{H}_4\text{C}_1\text{H}_5$ | 107.9 | 107.6 | 107.5 | 107.9(5) | 107.6(5) | 107.5(5) | 108.8(7) |
| $\angle\text{H}_7\text{C}_2\text{H}_8$ | 109.4 | 109.2 | 109.1 | 109.4(5) | 109.2(5) | 109.1(5) | 108.3(1) |
| $\angle\text{H}_{10}\text{C}_3\text{H}_{11}$ | 109.4 | 109.1 | 109.1 | 109.4(5) | 109.1(5) | 109.1(5) | 108.3(1) |
| $\angle\text{H}_7\text{C}_2\text{Cl}_6$ | 107.0 | 107.4 | 107.2 | 107.0(5) | 107.4(5) | 107.2(5) | 107.8(1) |
| $\angle\text{H}_8\text{C}_2\text{Cl}_6$ | 107.3 | 107.5 | 107.2 | 107.3(3) | 107.5(5) | 107.2(5) | 107.8(1) |
| $\angle\text{H}_{10}\text{C}_3\text{Cl}_9$ | 107.0 | 107.3 | 107.2 | 107.0(5) | 107.3(5) | 107.2(5) | 107.8(1) |
| $\angle\text{H}_{11}\text{C}_3\text{Cl}_9$ | 107.3 | 107.0 | 107.2 | 107.3(5) | 107.0(5) | 107.2(5) | 107.8(1) |
| $\tau\text{Cl}_6\text{C}_2\text{C}_1\text{C}_3$ | 63.6 | −177.2 | 180.0 | 63.6(5) | −177.2(5) | 180.0(5) | |
| $\tau\text{Cl}_9\text{C}_3\text{C}_1\text{C}_2$ | 63.6 | −65.5 | 180.0 | 63.6(5) | −65.5(5) | 180.0(5) | |
| $\tau\text{H}_7\text{C}_2\text{C}_1\text{Cl}_6$ | 118.8 | 118.9 | 119.1 | 118.8(5) | 118.9(5) | 119.1(5) | |
| $\tau\text{H}_8\text{C}_2\text{C}_1\text{Cl}_6$ | −119.5 | −119.4 | −119.1 | −119.5(5) | −119.4(5) | −119.1(5) | |
| $\tau\text{H}_{10}\text{C}_3\text{C}_1\text{Cl}_9$ | 118.8 | 119.8 | 119.1 | 118.8(5) | 119.8(5) | 119.1(5) | |
| $\tau\text{H}_{11}\text{C}_3\text{C}_1\text{Cl}_9$ | −119.5 | −119.0 | −119.1 | −119.5(5) | −119.0(5) | −119.1(5) | |
| <i>A</i> | 6151.2 | 9629.4 | 15,809.1 | | | | |
| <i>B</i> | 1443.3 | 1096.6 | 894.7 | | | | |
| <i>C</i> | 1350.2 | 1028.6 | 860.5 | | | | |
| $ \mu_a $ | 0.000 | 0.892 | 0.000 | | | | |
| $ \mu_b $ | 2.533 | 1.964 | 2.170 | | | | |
| $ \mu_c $ | 0.000 | 0.857 | 0.000 | | | | |
| $ \mu_t $ | 2.533 | 2.321 | 2.170 | | | | |

^a See text for adjustment values.

^b Ref. [6].

value of 1.793 ± 0.003 Å for this distance. However the C–H distance of 1.124 ± 0.012 Å is entirely too long and the predicted values from the MP2/6-311 + G(d,p) ab initio calculations are

expected to be within 0.002 Å of the accurate values. Both the $\angle\text{CCC}$ and $\angle\text{CCCl}$ values of 112.9 ± 1.0 and $111.6 \pm 0.2^\circ$, respectively, are within the average estimated values of

113.7 ± 0.5 and $111.0 \pm 0.5^\circ$. Therefore we believe the estimated r_0 parameters with the smaller uncertainty are better values than those obtained from the electron diffraction study. Since the two chloride atoms have quadruple moments and two of the three conformers present would have B-type microwave spectra it would be incredibly difficult to assign the microwave spectra to obtain the rotational constants for better refining the estimated r_0 values. Thus, these estimated parameters are probably as good a value that can be obtained for 1,3-dichloropropane.

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