

Molecular Structure and Conformational Composition of Methyl Chloroacetate: An Electron-Diffraction and *ab Initio* Molecular Orbital Investigation

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Abstract

The molecular structure and conformational composition of methyl chloroacetate, $\text{H}_2\text{ClC}-\text{C}(=\text{O})-\text{O}-\text{CH}_3$, have been determined by gas-phase electron diffraction (GED), using results from *ab initio* molecular orbital calculations (HF, MP2 and MP3/6-311+G(d,p)) to obtain constraints on some of the structural parameters. The molecules exist in the gas-phase at 25 °C as a mixture of two stable conformers: syn with C–Cl eclipsing C=O and gauche with C–H approximately eclipsing C=O. In both of these conformers O–CH₃ is also eclipsing C=O. The experimentally observed conformational composition at 25 °C was 36(8) % syn and 64(8) % gauche (parenthesised values are 2σ), corresponding to a free energy difference between conformers of $\Delta G^\circ_{\text{exp}} = 1.4(9)$ kJ/mol. The corresponding theoretical values obtained for ΔG° are 1.1 kJ/mol (HF), 2.3 kJ/mol (MP2), and 2.4 kJ/mol (MP3). The results for the principal distances ($r_{\text{h}1}$) and angles ($\angle_{\text{h}1}$) for the major gauche conformer obtained from the combined GED/*ab initio* study (2σ uncertainties) are $r(\text{CO}-\text{CCl}) = 1.502(9)$ Å, $r(\text{C}-\text{H}) = 1.084(6)$ Å (average value), $r(\text{C}-\text{Cl}) = 1.782(4)$ Å, $r(\text{C}=\text{O}) = 1.213(4)$ Å, $r(\text{CO}-\text{O}) = 1.346(4)$ Å, $r(\text{CH}_3-\text{O}) = 1.468(10)$ Å, $\angle\text{C}-\text{C}-\text{Cl} = 110.0(6)^\circ$, $\angle\text{C}-\text{C}=\text{O} = 124.7(6)^\circ$, $\angle\text{C}-\text{C}-\text{O} = 108.3(10)^\circ$, $\angle\text{C}-\text{O}-\text{C} = 115.9(8)^\circ$, $\phi(\text{Cl}-\text{C}-\text{C}=\text{O}) = 111(2)^\circ$, $\phi(\text{C}-\text{O}-\text{C}=\text{O}) = 3(3)^\circ$.

1. Introduction

In the past we have studied molecules containing one or more carbonyl groups and attempted to find factors determining the conformation of such compounds. Among these are molecules with the general formula $\text{ClH}_2\text{C}-\text{C}(=\text{O})\text{R}$, where R = H, CH₃, a phenyl group or a Cl atom [1-4]. In these compounds conformers where C–Cl and C=O have different positions relative to each

other have been observed. In some of these compounds more than one conformer has been observed. In addition to the earlier studied compounds, we have now investigated methyl chloroacetate, $\text{ClH}_2\text{C}-\text{C}(=\text{O})-\text{O}-\text{CH}_3$, where $\text{R} = \text{OCH}_3$, (Figure 1) using GED and *ab initio* molecular orbital calculations. Our results are presented in the following.

Experimental

A commercial sample of methyl chloroacetate (99%) was obtained from Aldrich Chemical Co and used without further purification. The electron diffraction experiments were performed using the Oregon State University apparatus with an r^3 sector and Kodak Electron Image plates. The nominal acceleration voltage was 60 kV and the nozzle-tip temperature was 25 °C. The voltage/distance calibration was done with CO_2 as a reference. Experimental parameters, namely temperatures, nozzle-to-plate distances, weighting functions for creating weight matrices, correlation parameters, final scaling factors and electron wavelengths are listed in Table 1. Data reduction was performed using standard routines [5,6] employing published scattering factors [7]. Data analysis was carried out using the program “ed@ed”[8]. Experimental intensity and radial distribution (RD) curves, together with theoretical and difference curves for the final model of the molecules are presented in Figures 2 and 3, respectively.

Structure Analysis

Molecular Orbital Calculations: To determine the number of stable conformers, and also to get starting values for the parameters in the model used in the least-squares electron-diffraction refinements, *ab initio* molecular orbital calculations were performed using the Gaussian98 [9] program with a 6-311+G(d,p) basis set and Hartree-Fock and Møller-Plesser (MP2 and MP3) level of theory. Four stable conformers were observed, but two of these conformers were higher in energy than the other two (approximately 40 kJ/mol higher). The high energy conformers have the $\text{O}-\text{CH}_3$ and the $\text{C}=\text{O}$ bonds anti to each other. MP2 and MP3 calculations were performed only for the two low-energy conformers. These two conformers are depicted in Figure 1. The results for important geometrical parameters from the *ab initio* calculations are given in Table 2.

Normal Coordinate analysis: Vibrational quantities are an important part of the model used to analyse the experimental data. *Ab initio* frequency calculations (HF/6-311+G(d,p)) provided theoretical force fields for the molecular vibrations. To calculate the required vibrational parameters (amplitudes, perpendicular amplitude corrections and centrifugal distortions) from these force fields, the program SHRINK [10,11] was used. The force constants for bonds were scaled by 0.9. The calculated vibrational quantities were used to convert the r_a distances used in the electron diffraction model to the geometrically consistent r_{h1} distances [11].

Analysis of the gas-phase electron diffraction data: Only the two low-energy forms of methyl chloroacetate (Figure 1) observed in the theoretical calculations were included in the model used in the analysis of the experimental electron-diffraction data. These two forms have the O-CH₃ bond eclipsing the carbonyl bond. In one of the low-energy conformers the C-Cl bond is eclipsing the C=O bond (syn conformer), while in the other form the C-H bond is approximately eclipsing the C=O bond, and C-Cl and C=O are therefore gauche to each other (gauche conformer).

The parameters used to define the model for the gauche conformer are given in Table 2. The structure of the syn conformer was defined by applying calculated differences between related parameters for the gauche and the syn conformers obtained in the *ab initio* calculations (MP3/6-311+G(d,p)).

In the model used the C-H_{methyl} bonds were assumed to be equal. The same assumption was also used for the C-C-H_{methyl} angles. The least squares refinements were performed using the program ed@ed [8]. Values for the independent parameters are given in Table 2 and the important interatomic distance values are given in Table 3.

Intensity curves calculated for the final model are shown in Figure 2, together with experimental and difference curves. Figure 3 contain the corresponding RD-curves, and the correlation matrix for the refined parameters is given in Table 4.

Discussion

In Table 2 parameter values obtained for methyl chloroacetate (GED, r_{hl} -values) are shown together with theoretical values from the MP3/6-311+G(d,p) calculations. Most experimental parameter values are as expected. $r(\text{C}=\text{O})$ is calculated shorter than the experimental value, but this has been observed in many of these molecules. The $\text{O}-\text{CH}_3$ bond distance is found to be surprisingly long, both compared with calculated values and with experimental values observed in related molecules [12, 13]. We have no good explanation for this.

A good fit between the experimental and the theoretical intensity and RD-curves was obtained using a model with only the two low-energy conformers found in the *ab initio* calculations. This is not surprising since the other two conformers, where $\text{O}-\text{CH}_3$ is anti to $\text{C}=\text{O}$, were found to be more than 40 kJ/mol higher in energy. The two conformers found experimentally both have the methoxy group syn to the carbonyl group, in one conformer the $\text{C}-\text{Cl}$ bond is syn to $\text{C}=\text{O}$, in the other $\text{C}-\text{Cl}$ is gauche to $\text{C}=\text{O}$ (Figure 1). The conformational composition observed experimentally is 36(8)% syn conformer, 64(8)% gauche conformer, corresponding to a free energy difference of $\Delta G^\circ_{\text{exp}} = 1.4(9)$ kJ/mol. The theoretical values for ΔG° found in our *ab initio* calculations are: 1.1 kJ/mol (HF), 2.3 kJ/mol (MP2), and 2.4 kJ/mol (MP3). All these theoretical values are therefore close to our experimental result for the conformational composition. In Figure 3 the experimental and theoretical RD-curves for methyl chloroacetate are shown.

In Table 5 the experimental conformation for $\text{ClH}_2\text{C}-\text{C}(=\text{O})\text{R}$, $\text{R} = \text{H}, \text{CH}_3, \text{Ph}, \text{Cl}$ and OCH_3 are shown. In the first three of these molecules the predominant conformer is the one where the $\text{C}-\text{Cl}$ and the $\text{C}=\text{O}$ bonds are pointing away from each other in an anti or gauche position. In these three molecules there is only one large bond dipole originating on each of the two central carbon atoms, and these bond dipoles are expected to point away from each other. The angle between the two dipoles will probably depend on the size of R , that is on the steric repulsion between R and Cl . Since $\text{Ph} > \text{CH}_3 > \text{H}$, we may expect the $\text{Cl}-\text{C}-\text{C}-\text{R}$ torsion angle to decrease from $\text{R} = \text{H}$ to $\text{R} = \text{Ph}$. This is indeed what is observed, the $\text{Cl}-\text{C}-\text{C}-\text{R}$ torsion angle is 180° in chloroacetaldehyde [1], $139(7)^\circ$ in chloroacetone [2] and $112(7)^\circ$ in 2-chloro-1-phenylethanone [3]. When $\text{R} = \text{Cl}$ or $\text{R} = \text{OCH}_3$ we have two bond dipoles on the terminal carbon atom.

Therefore, some of the conformer where the C-Cl and C-R bonds are pointing away from each other is also expected. Since C-Cl is a stronger dipole than C-OCH₃ we expect to have a larger amount of this second conformer for R = Cl. This is what is observed. In chloroacetyl chloride [4] (R = Cl) 77(7)% of the conformer where C=O and C-Cl is coplanar is present in the gas phase, while in methyl chloroacetate (R = OCH₃) only 36(8)% of this conformer is observed. For the two molecules with R = Cl or R = OCH₃ the gauche torsion angle has almost the same value (116(8)^o and 111(3)^o, respectively). For methyl chloroacetate this is in good agreement with the *ab initio* results. It is close to the value observed for R = Ph [3]. Since Ph is larger than OCH₃ this indicates that steric repulsion is not the only factor determining the value of this torsion angle.

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Table 1 Experimental parameters for methyl chloroacetate

nozzle to plate distance/mm	300.01	747.35
nozzle temperature/°C	25	25
nominal electron wavelength/Å	0.0498	0.0498
data interval/Å ⁻¹	0.25	0.25
no. of plates	4	3
$s_{\min}/\text{Å}^{-1}$	2.0	9.0
$s_{\max}/\text{Å}^{-1}$	15.0	27.0
$s_{w1}/\text{Å}^{-1}$	4.0	11.0
$s_{w2}/\text{Å}^{-1}$	13.0	23.2
Correlation parameter	-0.0454	0.4749
Scale factor ^a	1.290(15)	0.808(30)

a) Values in parentheses are the estimated standard derivations

Table 2. Structural parameters obtained from electron diffraction (GED) refinements (gauche conformer) and theoretical calculations (6-311+G(d,p)) for the gauche and syn conformer of methyl chloroacetate.

Parameter ^a	GED (r_{hi}/\angle_{hi})		Ab initio(r_e/\angle_e)					
	Gauche conformer		Gauche conformer			Syn conformer		
			HF	MP2	MP3	HF	MP2	MP3
$r(C_1-C_2)$	1.502	(9)	1.513	1.513	1.516	1.519	1.521	1.514
$r(C-H)$	1.084	(6)	1.080	1.090	1.091	1.090	1.091	1.081
$r(C-Cl)$	1.782	(4)	1.787	1.782	1.785	1.763	1.767	1.771
$r(C=O)$	1.213	(4)	1.182	1.211	1.198	1.206	1.193	1.177
$r(C_2-O_3)$	1.346	(4)	1.313	1.344	1.334	1.350	1.341	1.321
$r(C_4-O_3)^b$	1.468	(10)	1.420	1.438	1.430	1.439	1.430	1.420
$\Delta(C-H)$	0.002		0.002	0.001	0.002	-0.001	0.001	0.001
$\angle HC_1H$	111.5		111.3	111.5	111.5	108.6	108.6	108.6
$\angle C_2C_1H_{projec}$	120.0		119.0	120.0	122.0	120.0	121.0	118.0
$\angle C_2C_1Cl$	110.0	(6)	110.8	109.4	109.7	112.5	112.7	113.3
$\angle C_1C_2O_8$	124.7	(6)	123.3	124.8	124.3	127.4	127.1	126.8
$\angle C_1C_2O_3$	108.3	(10)	112.0	110.4	111.0	107.9	108.4	108.5
$\angle O_3C_4H$	105.6		105.7	105.3	105.6	105.3	105.6	105.7
$\angle C_2O_3C_4$	115.9	(8)	117.6	114.3	115.0	114.2	114.8	117.5
$\phi(O_8C_2C_1Cl)$	111	(2)	111	102	106	0	0	0
$\phi(O_8C_2O_3C_4)$	3	(3)	-3	-3	-3	0	0	0
$\phi(C_2O_3C_4H_{10})$	180		-179	-179	-179	180	180	180
α (G)	64	(8)						

a) Distances are in Ångström (Å) and angles are in degree (°). Uncertainties are given as 2σ .

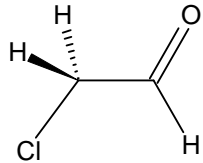
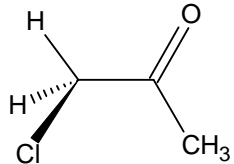
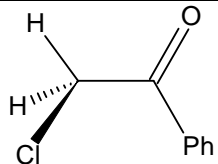
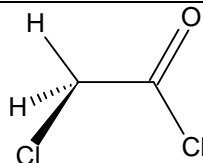
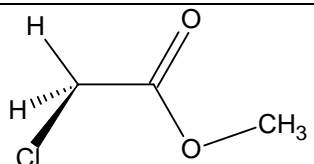
b) $\Delta(C-H) = r(C-H_{9,10,11}) - r(C-H_{6,7})$

Table 3. Important distances obtained from electron diffraction (GED) refinements for the gauche and syn conformer

	Gauche conformer				Syn conformer			
	r_a		l	$l_{theoretical}$	r_a		l	$l_{theoretical}$
r(C–H)	1.081	(6)	0.074	0.074	1.079	(6)	0.074	0.074
r(C=O)	1.212	(4)	0.036	0.036	1.208	(4)	0.035	0.035
r(C ₂ –O ₃)	1.345	(4)	0.043	0.043	1.352	(4)	0.043	0.043
r(C ₄ –O ₃)	1.467	(10)	0.047	0.047	1.468	(10)	0.047	0.047
r(C ₁ –C ₂)	1.501	(9)	0.048	0.048	1.505	(9)	0.048	0.048
r(C–Cl)	1.782	(4)	0.049	(6) 0.049	1.763	(4)	0.047	(6) 0.048
r(O ₈ ···O ₃)	2.291	(8)	0.048	0.048	2.292	(8)	0.048	0.048
r(C ₁ ···O ₃)	2.308	(11)	0.061	0.061	2.277	(12)	0.061	0.061
r(C ₂ ···C ₄)	2.387	(12)	0.061	0.061	2.391	(12)	0.061	0.061
r(C ₁ ···O ₈)	2.405	(11)	0.057	0.057	2.435	(11)	0.056	0.056
r(C ₂ ···Cl)	2.694	(12)	0.081	0.081	2.729	(12)	0.063	(14) 0.066
r(O ₈ ···C ₄)	2.747	(13)	0.087	(14) 0.090	2.745	(13)	0.087	(14) 0.090
r(Cl···O ₃)	3.056	(19)	0.192	(19) 0.203	3.886	(9)	0.040	0.066
r(Cl···O ₈)	3.580	(31)	0.229	0.229	3.001	(25)	0.101	(19) 0.108
r(C ₁ ···C ₄)	3.684	(11)	0.066	0.066	3.664	(11)	0.066	0.066
r(Cl···C ₄)	4.399	(19)	0.174	0.174	5.116	(10)	0.081	0.081

a) Distances are in Ångström (Å) and uncertainties are given as 2σ .

Table 5 Conformational composition for molecules with the general formula $\text{ClH}_2\text{C}-\text{C}(=\text{O})\text{R}$

	Position of Cl relative to C=O		Reference
R = H	94(7)% anti, $\phi = 180^\circ$		1
R = CH ₃	95(8)% gauche, $\phi = 139(7)^\circ$		2
R = Ph	90(11)% gauche, $\phi = 112(7)^\circ$		3
R = Cl	23(7)% gauche, $\phi = 116(8)^\circ$ 77(7)% syn, $\phi = 0$		4
R = O-CH ₃	64(8)% gauche, $\phi = 111(3)^\circ$ 36(8)% syn, $\phi = 0$		This work

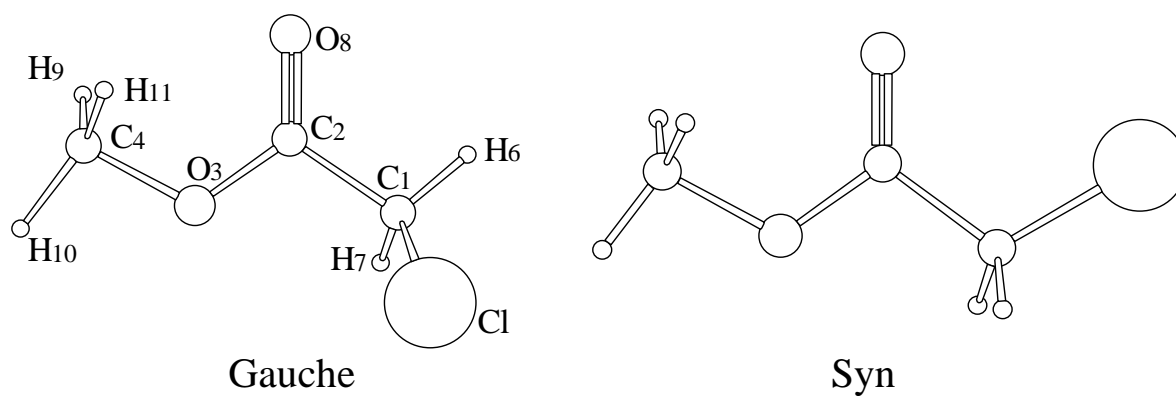


Figure 1:

Diagram showing the numbering scheme and the two conformers of methyl chloroacetate

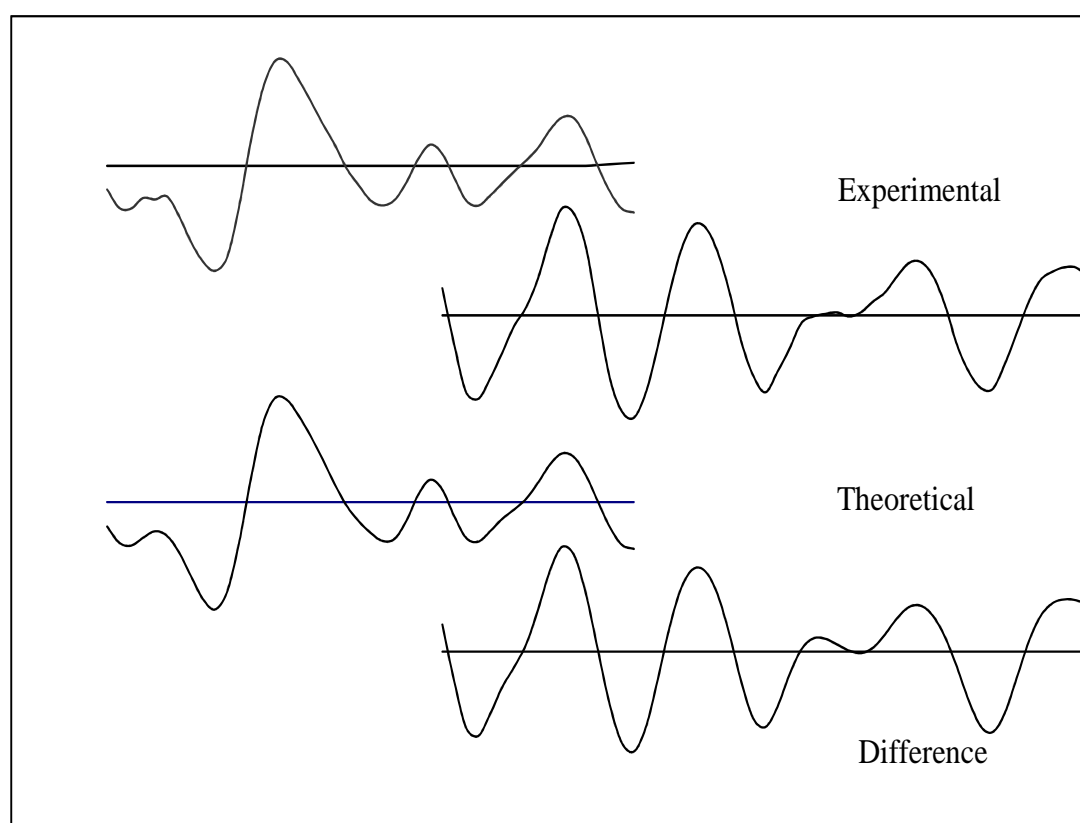


Figure 2:

Experimental intensity curves, $s^4 I_t(s)$, for methyl chloroacetate, together with theoretical curve calculated from the final model and difference curves. Difference curves are experimental minus theoretical

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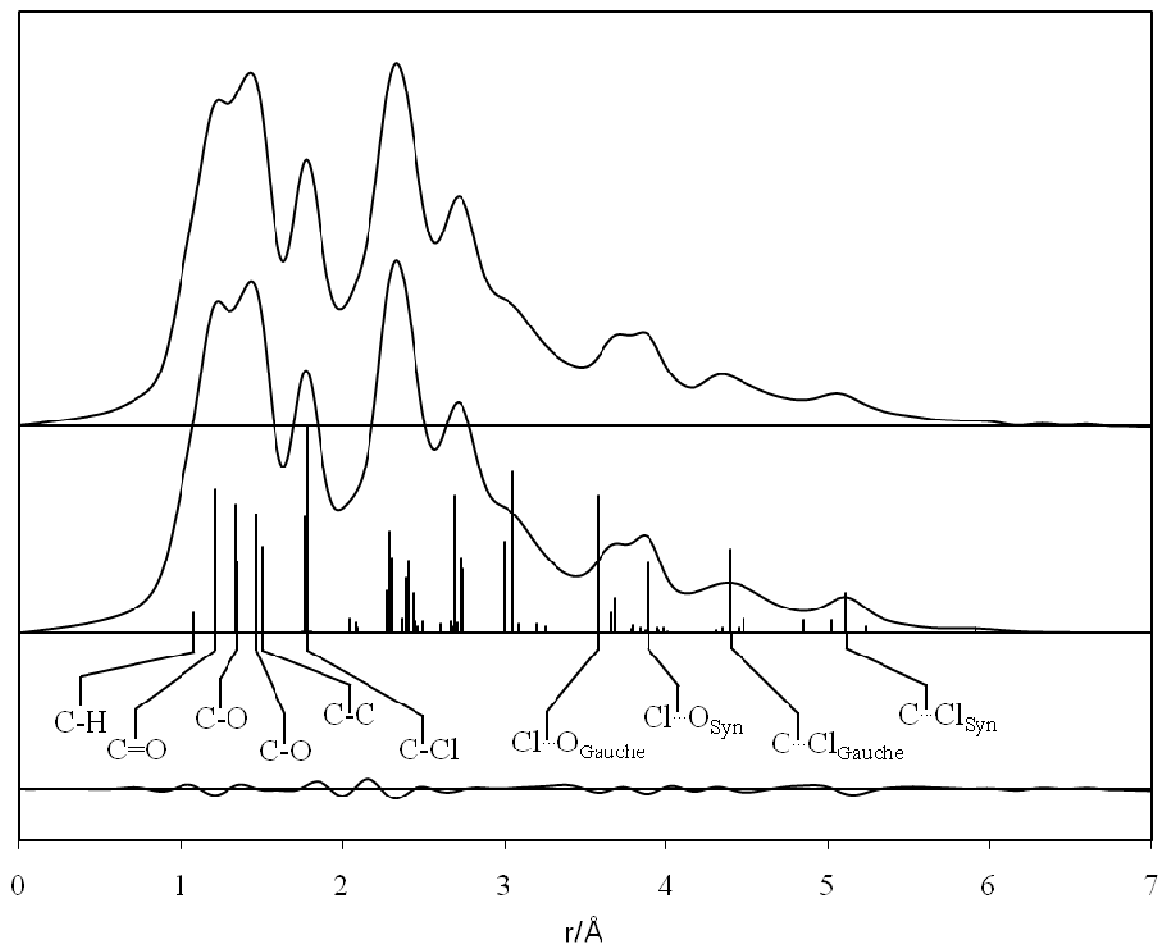


Figure 3:

Radial distribution curves for methyl chloroacetate. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region $0 \leq s/\text{\AA}^{-1} \leq 2.00$ and $B/\text{\AA}^2 = 0.002$. Difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights.