

Conformers, Vibrational Spectra and Laser-induced Rotamerization of CH₂ClCOOH

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Ab initio molecular orbital (MO) calculations with a 6-31G* basis set have been carried out for CH₂ClCOOH. Structures and energies of relevant conformations have been determined by gradient geometry refinement and some conformationally dependent geometry trends discussed. The results agree with reported experimental data and provide a good insight for the intramolecular interactions which determine the relative stability of the various conformers. The normal mode analysis based on the 6-31G* harmonic force field is used to review previous assignments of the vibrational spectra of the various conformers and to interpret previous experimental findings (A. Kulbida and A. Nosov, *J. Mol. Struct.*, 1992, **265**, 17) on the laser-induced rotamerization of the chloroacetic acid monomer trapped in an argon matrix.

The rotamerization of chloroacetic acid monomer has been studied experimentally by electron diffraction and microwave spectroscopy in the mid-seventies^{1,2} and quite recently by vibrational spectroscopy (IR; argon matrix).³ An *ab initio* SCF-MO study carried out with the STO-3G minimum basis set⁴ and a molecular mechanics study⁵ have also been undertaken, focusing on the conformational preferences of this molecule. While these studies have understood a number of relevant questions, some important points remain to be understood, in particular:

(i) The precise characterization of the three experimentally observed conformers (Fig. 1).

(ii) The nature of the main intramolecular effects which determine their relative energies.

(iii) The detailed description of the vibrational normal modes and their vibrational coupling.

(iv) The interpretation of the changes observed in the vibrational spectra of CH₂ClCOOH trapped in an argon matrix when the sample is irradiated with a CO laser in the $\nu(\text{C}=\text{O})$ region.³

The *ab initio* results and the normal mode analysis presented here for the CH₂ClCOOH monomer aim at a better understanding of these structural and spectroscopic problems.

Computational Methods

The *ab initio* MO calculations were done in a VAX 8530 computer using the GAUSSIAN 92 program system⁶ and the 3-21G, 3-21G* [$\zeta^d(\text{Cl}) = 0.75$] and 6-31G* basis sets.^{7,8}

The equilibrium molecular geometries were obtained by the gradient relaxation method of Pulay⁹ using Berny's algorithm¹⁰ which evaluates the gradient analytically. The maximum residual internal coordinate forces are always less than $3 \times 10^{-4} E_h a_0$ ($1 E_h = 2625.5001 \text{ kJ mol}^{-1}$; $1 \text{ bohr} \approx 5.29177 \times 10^{-11} \text{ m}$) or $E_h \text{ rad}^{-1}$. Under these conditions, the absolute errors in bond lengths and bond errors with respect to the true equilibrium geometrical parameters are less than 1 pm and 0.1°, respectively. The stopping criterion for the SCF iterative process required a density matrix convergence of less than 10^{-8} .

The 6-31G* cartesian harmonic force constants were calculated for all the studied conformations and converted to internal coordinates using the program TRANSFORMER.¹¹ This program also prepared the input data for the normal coordinate analysis programs used in this study (BUILD-G and VIBRAT¹²). As usual, vibrational frequencies calculated using the 6-31G* basis set were higher than the experimental values. The force-field scaling procedure adopted here to improve the frequency fit was that of ref. 13 and 14: the force constants were grouped according to the type of the associated coordinates (coupling constants, in a single group), a separate scaling factor was ascribed to each group and the complete set of scaling factors was adjusted, by least-squares minimization, to reproduce the experimental frequencies. The FG eigenvalues, $\lambda_i = 4\pi^2\nu_i^2$, were weighted by $1/\lambda_i^2(\text{obs.})$ in all refinements. The scaling factors evaluated using the experimental information obtained for the most stable form of the chloroacetic acid monomer are listed in Table 1. These factors were also used to scale the force constants of the less

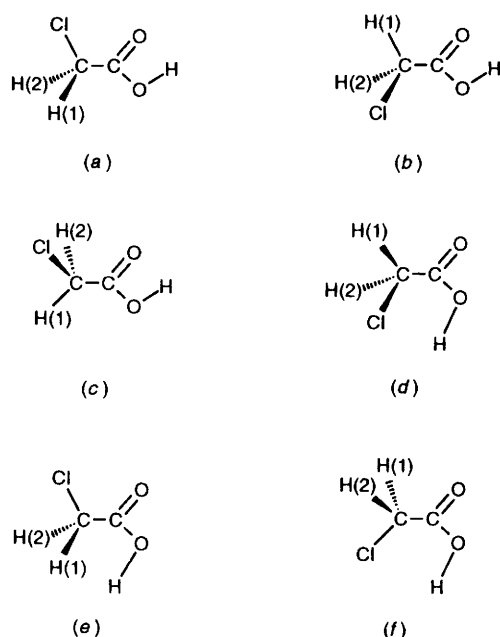


Fig. 1 Relevant conformations of chloroacetic acid. Forms (a) and (b) correspond to the two most stable forms in both gaseous and argon-matrix-isolated phases.^{1–5} A third conformer was found to be present in significant amounts in the conformational equilibrium, though its precise characterization has been a source of controversy: ref. 1 and 2 suggest it corresponds to form (c); ref. 3–5 assume it is either (d) or (f). Form (e) has been suggested as a high-energy conformer, despite the fact that it has never been found experimentally.

Table 1 6-31G* scaling factors^a

parameter	scaling factor
C—C	0.944
C=O	0.745
C—O	0.657
O—H	0.777
C—Cl	0.795
C—H	0.821
C—C=O	0.718
O=C—O	0.804
C—O—H	0.832
Cl—C—C	0.913
H—C—C	0.794
C—C(=O)O	0.860
O=C—O—H	0.687
Cl—C—C=O	0.796

^a For the scaling procedure and assumed transferability of scaling factors between conformers see Computational Methods. The scaling factor for the interaction force constants is 0.742.

stable isomers, thus assuming full transferability of the scaling factors between rotational isomers.

Results and Discussion

Geometries and Energies

The *ab initio* calculations account for four different stable conformations of the chloroacetic acid monomer molecule

(Fig. 1) and indicate that the first and the second more stable forms correspond to an *s-cis* O=C—O—H axis. These are the *syn/s-cis* (SC) and *skew/s-cis* (SKC) conformers, respectively (Table 2), in consonance with previous studies.^{1–5}

While the agreement between experimental² and calculated geometries is generally good (Table 3), the following specific comments should now be made:

(i) The inclusion of d orbitals on the chlorine atom improves considerably on the C—Cl bond length and Cl—C—C angle, thus stressing the relevance of polarization orbitals in MO calculations of geometries of α -chlorosubstituted carbonyl compounds.

(ii) As usual,^{1,5} at the 6-31G* level of calculation, the C—O and C—Cl bond lengths are too short, but the C—C=O, C—C—O and C—O—H angles show a much better agreement with experiment.

(iii) The calculated value of the Cl—C—C=O dihedral angle for the SC conformer (0°) deviates appreciably from the experimental refined value (10°, ref. 2). This deviation may be due to a large amplitude torsional motion about the C_α—C bond, as the empirical value results from statistically averaged displacements from the energy minimum (see also footnote of Table 3). In consonance with this large amplitude motion, the diagonal force constant for the Cl—C—C=O dihedral angle has a comparatively low value (0.201, scaled value).

(iv) A similar reasoning applies to the deviations found for the SKC form between the calculated values of the Cl—C—C=O dihedral angle and its measured value.²

Table 2 Calculated and experimental conformational energy differences (kJ mol⁻¹)^a

	3-21G	MP2/3-21G	3-21G*	MP2/3-21G*	6-31G*	MP2/6-31G*	exp. ^b
$\Delta E_{\text{SKC-SC}}$	1.69	3.61	4.92	6.10	1.49	2.52	4.85
$\Delta E_{\text{AT/SKT-SC}}^c$	25.48	24.68	28.37	25.75	18.17	16.09	7.66
$\Delta E_{\text{ST-SC}}^c$	41.22	37.55	40.77	37.57	35.20	32.70	24.84 ^d
$\Delta E_{\text{SKC-SKC}}$	9.20	7.38	5.90	4.93	2.43	2.20	—
$\Delta E_{\text{SKT-SKT}}$	0.88	0.13	0.44	0.06	—	—	—

^a Second-order Møller–Plesset energies (MP2) were obtained using the corresponding SCF optimized geometries. ^b Ref. 2. ^c $\Delta E_{\text{AT-SC}}$ for 6-31G* calculations; $\Delta E_{\text{SKT-SC}}$ for 3-21G and 3-21G* calculations (see text). ^d Calculated value (molecular mechanics; PF1 force field³).

Table 3 Calculated (6-31G*) and experimental geometries^a

parameter ^b	SC		SKC calc.	ST calc.	AT calc.
	calc.	exp. ^c			
C—C	151.3	150.8	151.2	152.2	152.6
C=O	118.0	122.3	118.5	117.4	118.1
C—O	133.0	135.2	132.2	133.6	131.7
O—H	95.0	97.0	95.2	94.8	95.0
C—Cl	176.6	177.8	178.2	176.3	178.7
C—H(1)	108.0	109.0	107.6	108.2	107.8
C—H(2)	108.0	109.0	107.9	108.2	107.8
C—C=O	127.4	126.1	123.5	125.7	118.1
O=C—O	123.7	123.3	123.8	121.4	122.4
C—C—O	108.9	110.6	112.6	112.9	119.5
C—O—H	108.5	105.8	108.6	113.3	112.9
Cl—C—C	113.3	112.5	111.9	113.5	115.9
H(1)—C—C	108.8	109.5	108.7	109.2	108.1
H(2)—C—C	108.8	109.5	109.8	109.2	108.1
C—C(=O)O	180.0	180.0	182.2	180.0	180.0
O=C—O—H	0.0	0.0	-2.2	180.0	180.0
Cl—C—C—O	0.0	10.0 ^d	120.0 ^e	0.0	180.0
H(1)—C—C=O	121.2	120.0	0.5	120.8	58.9
H(2)—C—C=O	-121.2	-120.0	-120.6	-120.8	-58.9

^a Bond lengths in pm; angles in degrees. ^b See Fig. 1 for atom numbering. ^c Ref. 2. In this experimental study, all geometric parameters except the Cl—C—C—O dihedral angle were assumed to be equal in the various conformers. ^d This value corresponds to a statistical average of the dihedral angle varying during the large amplitude torsional motion about the C_α—C bond. ^e The experimentally determined value is 131, ref. 2.

However, in this case, the torsional motion about the $C_\alpha-C$ bond is not symmetrical with respect to the equilibrium $Cl-C-C=O$ dihedral angle. The MO results point to a larger increase in energy when the chlorine atom moves towards the hydroxy-group oxygen.

At the 3-21G level, the third and fourth conformers correspond to the *skew/s-trans* (SKT) and *syn/s-trans* (ST) forms [Fig. 1(d) and (e)], and the *gauche/s-cis* (GC) and *anti-trans* (AT) forms [Fig. 1(c) and (f)], previously proposed as possible conformers,²⁻⁴ correspond to first-order saddle points in the potential-energy surface, *i.e.* to conformational transition states. The larger 6-31G* basis set yields minima at the ST and AT geometries (Table 2).

The ST form does not deserve much attention here, as it corresponds to a high-energy form not yet observed experimentally and has never been studied theoretically in detail, its existence as a high-energy form being never questioned. In contrast, the AT form has been the subject of considerable controversy and is spectroscopically detectable,^{2,3} thus justifying particular attention.

In consonance with present calculations, previous theoretical and molecular mechanics studies^{4,5} strongly suggest that the third more stable form should not be the GC form (see Fig. 1) proposed in the electron diffraction study.² The question is whether the third more stable form corresponds to the symmetric AT form or to the SKT form. On one hand, AT represents a better candidate, considering similar α -fluorosubstituted carbonyl compounds whose structures are well characterized and usually have a fluorine atom in the *anti* position.^{16,17} On the other hand, for an $R_1R_2R_3C_\alpha(=O)X$ fragment, carbonyl eclipsed structures are generally favoured relatively to carbonyl staggered structures, due to group orbital interactions.¹⁸ On the whole, the SKT form appears to be the best candidate. However, the 6-31G* potential energy profile for the internal rotation about the $C_\alpha-C$ bond for a fixed *s-trans* $O=C-O-H$ axis has minima for two planar structures (ST and AT). While the 3-21G and 3-21G* calculations yield minima at the two equivalent-by-symmetry SKT forms ($Cl-C-C=O$ dihedral angle is *ca.* 150°), the calculated energy barrier separating these forms (<1 kJ mol⁻¹; see Table 2) is below the zeroth vibrational level for the $C_\alpha-C$ torsion, making the distinction irrelevant in practical terms.

Comparison of the calculated geometries of the various conformers leads to the following conclusions:

(i) The much higher energies of the *s-trans* conformers suggest that the most unfavourable intramolecular interactions should be the $H\dots H(O)$ non-bonding interactions. They should also be mainly responsible for the increase of energy in going from the AT (or SKT) to the ST form (see Fig. 1 and Table 1). In fact, in the latter two short distances $H\dots H(O)$ occur, while in the SKT form only one is present and in the AT conformer none. Moreover, the single short $H\dots H(O)$ distance present in the SKT form is longer than the $H\dots H(O)$ distances in the ST form [note that longer $H\dots H(O)$ distances correlate with smaller $H-C-C=O$ dihedral angles]. The relative importance of the $H\dots H(O)$ repulsive interactions in the various conformers correlate with their $C-C$ bond lengths and $H-C-C$, $C-C-O$ and $C-O-H$ angles. In fact, the calculated values for these structural parameters in all but the AT (SKT) form follow the order: $SC < SKC < ST$.

In the AT form, the larger chlorine atom leads to the highest values calculated for the above-mentioned geometrical parameters, as the $Cl-C-C-O-H$ fragment lies in the same plane. However, the $Cl\dots H(O)$ interactions do not seem to be so important in energy terms as they are in geometric terms. This is easily understood considering that this inter-

action has two main contributions with opposite signs: an attractive and essentially dipolar interaction, and a repulsive and steric one.

(ii) Other unfavourable intramolecular interactions with important geometric implications are the $Cl\dots O=$ and $Cl\dots O-$ repulsive interactions. Both of these are also dipolar and steric in nature. However, the quantification of their relative importance is neither simple nor relevant.

The $Cl\dots O$ interactions reflect mainly in the relative values of the $Cl-C-C$, $C-C=O$ and $C-C-O$ angles in the two *s-cis* forms, when both the $H\dots H(O)$ and $Cl\dots H(O)$ interactions are not present. Considering the internal rotation about the $C_\alpha-C$ bond for a fixed *s-cis* $O=C-O-H$ axis, the calculations show that the $C-C=O$ and $C-C-O$ angles attain their maximum values for the SC and *anti/s-cis* (AC) conformations, respectively. As is easily anticipated, the calculated values for the SKC conformer are in between those of the SC and AC forms. These results indicate a relatively more important $Cl\dots O=$ interaction in the SC form and a comparatively more important $Cl\dots O-$ interaction in the AC form. Considering that an ester oxygen is usually more negative and sterically more important than a carbonyl oxygen,^{19,20} the presence of a stronger $Cl\dots O-$ repulsive interaction in the SKC conformer can justify its higher energy when compared with the SC form, in spite of an extra stabilizing interaction which will be referred to in (iii).

(iii) It is well known that the mesomerism within the $C(=O)O$ fragment in carboxylic acids and esters (Fig. 2) is very sensitive to the substituent and to its relative position with respect to the carbonyl group, usually contributing in a significant way to the stabilization of the molecule. Considering the relative values of the $C=O$ and $C-O$ bond lengths in the various conformers of chloroacetic acid (Table 3), it can be concluded that the contribution of the canonical form II (Fig. 2) is less important when the chlorine atom is *syn* with respect to the carbonyl oxygen atom, *i.e.* when the $Cl-C$ and $C=O$ bond dipole moments are parallel. This dipolar repulsion causes relevant changes in the vibrational properties, as will be pointed out later.

In summary, the main intramolecular interactions which determine the relative stability of the different conformers of chloroacetic acid are $H\dots H(O)$ and $Cl\dots O$ (both $O=$ and $-O-$) repulsive (steric and dipolar) interactions, and the mesomerism within the carboxylic group. The high energy of the *s-trans* forms is mainly determined by the $H\dots H(O)$ interactions, while the balance between the $Cl\dots O$ repulsions and the mesomerism within the $C(=O)O$ group determines the relative stability of the two *s-cis* forms, leading to a more stable SC form.

Vibrational Frequencies

Vibrational spectra of chloroacetic acid in the liquid and solid phases, where dimeric structures dominate, were studied previously in great detail.^{5,21-23} In contrast, the vibrational spectrum of the monomer has not received much attention. Though previous infrared (IR) spectroscopic³ and molecular

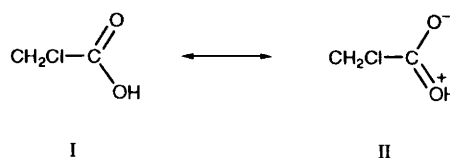


Fig. 2 Canonical forms of chloroacetic acid showing the mesomerism within the carboxylic group

mechanics⁴ studies clarified important points, a detailed vibrational analysis of this molecule has not yet been carried out, hence the relevance of the present study.

In consonance with earlier electron diffraction results² three conformers were found to contribute to the IR spectrum of monomeric chloroacetic acid.³ Considering the results now obtained, these forms should be the *s-cis* conformers (SC and SKC) plus the AT form, the latter being present in a very small amount at low temperatures.

As the SC, AT and ST configurations belong to the C_s point group, their 18 normal modes span the irreducible representations, $12A' + 6A''$. The remaining forms are non-symmetric (C_1 point group). Table 4 shows the local C_s symmetry coordinates used for all conformers.

The calculated *ab initio* frequencies and potential-energy distribution (PED) for the various studied conformers are shown in Table 5. This table includes the IR³ or molecular mechanics⁴ frequencies and those now obtained with the scaled force fields. The latter show a general agreement with the experimental values to within 2–3% for all conformers.

Region below 1000 cm^{-1}

The lowest normal mode corresponds to the $\tau(\text{C}-\text{C})$ torsion, its calculated frequency in the SC form fitting perfectly the experimental value of ref. 1 (62 cm^{-1}). In this conformer, there is a significant contribution from the $\gamma(\text{C}=\text{O})$ out-of-plane coordinate. In the SKC form, the $\tau(\text{C}-\text{C})$ torsion mixes with the $\delta(\text{C}-\text{C}-\text{Cl})$ coordinate. The AT form is essentially pure (Table 5).

As the $\delta(\text{C}-\text{C}-\text{Cl})$ and $\delta(\text{C}-\text{C}=\text{O})$ modes have not been observed experimentally, the molecular mechanics frequencies⁵ were used in the scaling of the *ab initio* force field. These vibrations are less delocalized in the SKC form than in the symmetric conformers, SC and AT (Table 5). In these forms, the PED contributions from the $\nu(\text{C}-\text{Cl})$ stretching in the $\delta(\text{C}-\text{C}=\text{O})$ mode are 24 and 31%, respectively.

The mixture of $\tau(\text{C}-\text{O})$ with $\gamma(\text{C}=\text{O})$ and $\gamma(\text{CH}_2)$ (these coordinates are A'' in the C_s forms) is appreciably dependent on the conformation. In particular, the $\gamma(\text{CH}_2)$ mode has similar PED values (62 and 64% of this coordinate) in the SC and AT forms, with additional important terms from $\gamma(\text{C}=\text{O})$ (29 and 19%, respectively). In the SKC form, a dominant contribution of $\gamma(\text{CH}_2)$ (72%) mixes with $\delta(\text{O}-\text{C}=\text{O})$ (the

scaled *ab initio* frequency of this mode, which is not observed experimentally,³ is 927 cm^{-1}).

In the SC form, the $\gamma(\text{C}=\text{O})$ coordinate mixes with $\gamma(\text{CH}_2)$ (26%) and $\tau(\text{C}-\text{O})$ (16%). In the AT form, a single additional term from $\gamma(\text{CH}_2)$ (34%) adds in, and in the SKC form, a contribution from $\nu(\text{C}-\text{Cl})$, equally important as $\gamma(\text{C}=\text{O})$, occurs.

The $\tau(\text{C}-\text{O})$ vibration is essentially pure in the AT form, and well localized in the SC conformer, with additional contributions from $\gamma(\text{C}=\text{O})$ (35%) and $\gamma(\text{CH}_2)$ (15%). On the other hand, in the SKC form, a completely delocalized vibration assigned to this mode occurs at 511 cm^{-1} , mixing with almost similar amounts from $\gamma(\text{C}=\text{O})$, $\delta(\text{O}-\text{C}=\text{O})$, $\nu(\text{C}-\text{Cl})$, and $\nu(\text{C}-\text{C})$.

In conclusion, in the SC and AT forms, $\gamma(\text{CH}_2)$ and $\gamma(\text{C}=\text{O})$ mix appreciably, but, in the AT form, none of these coordinates mix with either $\tau(\text{C}-\text{C})$ or $\tau(\text{C}-\text{O})$. In contrast, in the SC form, $\tau(\text{C}-\text{O})$ and $\tau(\text{C}-\text{C})$ mix appreciably with $\gamma(\text{C}=\text{O})$, and $\tau(\text{C}-\text{O})$ has an additional important contribution from $\gamma(\text{CH}_2)$. In the SKC form, the $\gamma(\text{CH}_2)$ does not mix with $\gamma(\text{C}=\text{O})$ or with any of the torsions. However, as the chlorine atom no longer lies in the $\text{O}=\text{C}-\text{O}$ plane, a contribution from $\nu(\text{C}-\text{Cl})$ arises in the $\gamma(\text{C}=\text{O})$ mode. As will be pointed out later, these findings are relevant to the understanding of the rotamerization of the chloroacetic acid monomer trapped in an argon matrix.³

The *ab initio* results also suggest that the frequencies previously assigned to the $\tau(\text{C}-\text{O})$ and $\delta(\text{O}=\text{C}-\text{O})$ vibrations in the SC form (at 605 and 611 cm^{-1} , respectively³) should now be interchanged. Also, the IR bands of the SKC form at 509 and 585 cm^{-1} , previously ascribed to the $\gamma(\text{C}=\text{O})$ and $\tau(\text{C}-\text{O})$ modes,³ are now assigned to $\tau(\text{C}-\text{O})$ and $\delta(\text{O}=\text{C}-\text{O})$. In addition, the band of the AT form observed at 526 cm^{-1} is now associated with the $\gamma(\text{C}=\text{O})$ mode instead of $\delta(\text{O}=\text{C}-\text{O})$.³ In turn, the latter vibration is calculated at 610 cm^{-1} and ascribed to the 596 cm^{-1} IR band³ which was previously assigned to the $\tau(\text{C}-\text{O})$ torsion whose calculated value, 452 cm^{-1} , indicates a much lower frequency.

For the SC and AT conformers, the present calculations confirm previous assignments of the $\nu(\text{C}-\text{C})$ stretching mode to the IR bands appearing at 892 and 852 cm^{-1} , respectively³ (calculated values: 894 and 862 cm^{-1}), as well as of the $\nu(\text{C}-\text{Cl})$ stretching mode to the IR bands at 793 and 771

Table 4 Local C_s symmetry coordinates^a

coordinate		symmetry	composition ^b
S_1	$\nu(\text{O}-\text{H})$	A'	$\Delta(\text{O}-\text{H})$
S_2	$\nu(\text{CH}_2)$, as	A''	$\Delta[\text{C}-\text{H}(1)] - \Delta[\text{C}-\text{H}(2)]$
S_3	$\nu(\text{CH}_2)$, s	A'	$\Delta[\text{C}-\text{H}(1)] + \Delta[\text{C}-\text{H}(2)]$
S_4	$\nu(\text{C}=\text{O})$	A'	$\Delta(\text{C}=\text{O})$
S_5	$\nu(\text{C}-\text{O})$	A'	$\Delta(\text{C}-\text{O})$
S_6	$\nu(\text{C}-\text{C})$	A'	$\Delta(\text{C}-\text{C})$
S_7	$\nu(\text{C}-\text{Cl})$	A'	$\Delta(\text{C}-\text{Cl})$
S_8	$\delta(\text{CH}_2)$	A'	$5\Delta(\text{HCH}) - \Delta[\text{H}(1)\text{CCl}] - \Delta[\text{H}(2)\text{CCl}] - \Delta[\text{H}(1)\text{CC}] - \Delta[\text{H}(2)\text{CC}] - \Delta(\text{CCl})$
S_9	$\omega(\text{CH}_2)$	A'	$\Delta[\text{H}(1)\text{CCl}] + \Delta[\text{H}(2)\text{CCl}] - \Delta[\text{H}(1)\text{CC}] - \Delta[\text{H}(2)\text{CC}]$
S_{10}	$t(\text{CH}_2)$	A''	$\Delta[\text{H}(1)\text{CCl}] - \Delta[\text{H}(2)\text{CCl}] - \Delta[\text{H}(1)\text{CC}] + \Delta[\text{H}(2)\text{CC}]$
S_{11}	$\gamma(\text{CH}_2)$	A''	$\Delta[\text{H}(1)\text{CCl}] - \Delta[\text{H}(2)\text{CCl}] + \Delta[\text{H}(1)\text{CC}] - \Delta[\text{H}(2)\text{CC}]$
S_{12}	$\delta(\text{C}-\text{C}-\text{Cl})$	A'	$4\Delta(\text{CCCl}) - \Delta[\text{H}(1)\text{CCl}] - \Delta[\text{H}(2)\text{CCl}] - \Delta[\text{H}(1)\text{CC}] - \Delta[\text{H}(2)\text{CC}]$
S_{13}	$\delta(\text{C}-\text{O}-\text{H})$	A'	$\Delta(\text{COH})$
S_{14}	$\delta(\text{O}=\text{C}-\text{O})$	A'	$2\Delta(\text{OCO}) - \Delta(\text{CC}=\text{O}) - \Delta(\text{CCO})$
S_{15}	$\delta(\text{C}-\text{C}=\text{O})$	A'	$\Delta(\text{CC}=\text{O}) - \Delta(\text{CCO})$
S_{16}	$\gamma(\text{C}=\text{O})$	A''	$\Delta(\text{C}=\text{O})$ out of the $\text{C}-\text{C}-\text{O}$ plane
S_{17}	$\tau(\text{C}-\text{O})$	A''	$\Delta(\text{O}=\text{C}-\text{O}-\text{H})$
S_{18}	$\tau(\text{C}-\text{C})$	A''	$\Delta(\text{Cl}-\text{C}-\text{C}=\text{O})$

^a See Fig. 1 for atom numbering; ν , stretching; δ , bending; ω , wagging; t , twisting; γ , rocking; τ , torsion. ^b Normalizing factors are not presented in the table.

Table 5 Calculated (6-31G*) vibrational frequencies (ν/cm^{-1}) and PED (%)^a

	SC			SKC			ST			AT		
	ν	PED	ν	ν	PED	ν	ν	PED	ν	ν	PED	
$\nu(\text{O}-\text{H})$ (a')	3570	1 [100]	3574 (17)	1 [100]	3612	1 [100]	3596 (90)	1 [100]	3596 (90)	1 [100]		
$\nu(\text{CH}_2)$ as (a'')	3034 (-9) ^b	2 [100]	3070 (26) ^b	2 [92]	3006	2 [100]	3061 ^c	2 [100]	3061 ^c	2 [100]		
$\nu(\text{CH}_2)$ s (a')	2980 (9) ^b	3 [100]	2993 (23) ^b	3 [93]	2954	3 [100]	3000 ^d	3 [100]	3000 ^d	3 [100]		
$\nu(\text{C}=\text{O})$ (a')	1806	4 [94]	1788 (13)	4 [93]	1830	4 [95]	1798 (8)	4 [94]	1798 (8)	4 [94]		
$\delta(\text{CH}_2)$ (a')	1429 (1)	8 [103]	1425 ^b	8 [100]	1419	8 [113]	1400 ^e	8 [121]	1400 ^e	8 [121]		
$\delta(\text{C}-\text{O}-\text{H})$ (a')	1352 (-2)	13 [10] + 9 [38] + 5 [20]	1220 (27) ^d	13 [51] + 10 [25] + 5 [15]	1269	13 [56] + 9 [28] + 5 [16]	1192 ^f	13 [52] + 5 [25] + 6 [12]	1192 ^f	13 [52] + 5 [25] + 6 [12]		
$\omega(\text{CH}_2)$ (a')	1278 ^b	9 [46] + 13 [41]	1278 (9)	9 [96]	1344	9 [63] + 5 [20] + 6 [17]	1278 (-10) ^g	9 [102]	1278 (-10) ^g	9 [102]		
$\nu(\text{C}-\text{O})$ (a')	1196 (1)	10 [93]	1130 (-7) ^e	10 [66] + 5 [20] + 13 [14]	1200	10 [95]	1191 ^h	10 [94]	1191 ^h	10 [94]		
$\nu(\text{CH}_2)$ (a')	929	11 [62] + 16 [29]	1360 (-6)	5 [34] + 6 [20] + 13 [17] + 14 [16]	1092	5 [46] + 13 [28] + 9 [12]	1348 (14)	5 [47] + 13 [40] + 6 [19] + 14 [13]	1348 (14)	5 [47] + 13 [40] + 6 [19] + 14 [13]		
$\nu(\text{C}-\text{C})$ (a')	894 (2)	6 [49] + 7 [24] + 5 [12]	927 (106) ^f	11 [72] + 15 [12]	933	11 [63] + 16 [25]	920 ^g	11 [64] + 16 [19]	920 ^g	11 [64] + 16 [19]		
$\nu(\text{C}-\text{Cl})$ (a')	794 (1)	7 [55] + 12 [20] + 15 [18] + 6 [12]	860 (50) ^f	6 [48] + 5 [26]	889	6 [49] + 7 [23] + 5 [14]	862 (10)	6 [50] + 5 [24] + 7 [14]	862 (10)	6 [50] + 5 [24] + 7 [14]		
$\tau(\text{C}-\text{O})$ (a')	613 (2)	17 [89] + 16 [35] + 11 [15]	668 (17)	7 [38] + 17 [35] + 14 [17] + 16 [20]	810	7 [54] + 15 [17] + 12 [17] + 6 [13]	758 (-13)	7 [64] + 12 [19] + 15 [23]	758 (-13)	7 [64] + 12 [19] + 15 [23]		
$\delta(\text{O}-\text{C}-\text{O})$ (a')	606 (1)	14 [65]	570 (-15)	17 [16] + 16 [22] + 14 [21] + 7 [17] + 6 [10]	366	17 [85] + 16 [23]	452 ^h	17 [98]	452 ^h	17 [98]		
$\nu(\text{C}-\text{O})$ (a')	489 (-3)	16 [68] + 11 [26] + 17 [16]	820 (407) ^f	16 [44] + 7 [43] + 12 [15]	625	14 [62]	610 (14)	14 [73] + 12 [14]	610 (14)	14 [73] + 12 [14]		
$\delta(\text{C}-\text{C}=\text{O})$ (a)	384 (5) ^g	15 [37] + 7 [24] + 14 [13]	379 (-24) ^g	15 [84] + 11 [15]	384	15 [36] + 7 [25] + 14 [12]	400 ^g	15 [58] + 11 [34]	400 ^g	15 [58] + 11 [34]		
$\delta(\text{C}-\text{C}-\text{Cl})$ (a)	220 (-4) ^h	12 [66] + 15 [34]	217 (-6) ^h	12 [71] + 16 [16] + 15 [10]	223	12 [68] + 15 [32]	249 ^h	12 [64] + 15 [20]	249 ^h	12 [64] + 15 [20]		
$\tau(\text{C}-\text{C})$ (a')	62 ⁱ	18 [88] + 16 [12]	48 (20) ^j	18 [66] + 12 [19]	72	18 [88] + 16 [12]	33 ^g	18 [97]	33 ^g	18 [97]		

^a ν , stretching; δ , bending; ω , wagging; τ , twisting; ρ , rocking; τ , torsion. Symmetry of each normal mode applies only to C_s conformers (SC, ST, AT). The calculated frequencies presented in the table were obtained with scaled force constants, see Table 1 for scaling factors; note that the scaling procedure does not alter the relative order of non-scaled *ab initio* frequencies. Values in brackets after the calculated frequency correspond to calc. - exp. frequency differences. Except for the ST form that corresponds to a high-energy form not yet experimentally observed, omitted differences correspond to zero values, i.e. to exact agreement between calculated and experimental frequencies. Unless otherwise indicated, experimental frequencies were taken from ref. 1, 3 and 5. PED values are indicated in brackets after the number of the corresponding coordinates (see Table 4 for numbering and definition of these). PED values smaller than 10% are not presented. ^b For the evaluation of the calc. - exp. frequency difference, the value obtained with the PFI molecular mechanics force field³ was used. ^c In the evaluation of the calc. - exp. frequency difference, the experimental value was obtained by microwave spectroscopy.^{1,4} In the IR spectrum of this conformer, there is a band at ca. 1230 cm^{-1} that was not previously assigned³ and may also correspond to this calculated frequency. ^d Other IR bands were assigned to this mode in ref. 3, namely at 1158 and 1113 cm^{-1} . ^e The molecular mechanics result³ presented in the table is probably wrong. ^f Not observed. ^g Other possible assignment is the IR band observed at 1260 cm^{-1} , as proposed in ref. 3.

cm^{-1} ³ (calculated values: 794 and 758 cm^{-1}). In contrast, the $\nu(\text{C}-\text{Cl})$ vibration of the SKC form, previously associated with the 585 cm^{-1} IR band,³ is now ascribed to the IR band at 651 cm^{-1} .³ In turn, the $\delta(\text{O}=\text{C}-\text{O})$ mode corresponds to the 585 cm^{-1} IR band [the calculated frequencies of $\nu(\text{C}-\text{Cl})$ and $\delta(\text{O}=\text{C}-\text{O})$ are 668 and 570 cm^{-1} , respectively; Table 5].

One important consequence of the assignments now made is that the frequencies of the $\nu(\text{C}-\text{Cl})$ vibrations correlate well with the inverse of the corresponding C-Cl bond lengths (Fig. 3). In particular, the two *syn* forms (SC and ST) which possess the shortest C-Cl bond lengths originate the highest $\nu(\text{C}-\text{Cl})$ frequencies. These are a direct result of stronger C-Cl bonds which, in turn, are due to reduced polarizations of these bonds caused by parallel alignment of the C-Cl and C=O bond dipole moments in these forms. As we shall see, a similar correlation holds also for $\nu(\text{C}=\text{O})$.

1000–1800 cm^{-1} Region

This spectral region includes the CO stretching modes [$\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$], the CH_2 bending vibrations [scissoring, $\delta(\text{CH}_2)$; wagging, $\omega(\text{CH}_2)$; twisting $t(\text{CH}_2)$] and the $\delta(\text{C}-\text{O}-\text{H})$ in-plane bending mode.

The calculations showed that $\nu(\text{C}=\text{O})$ and $\delta(\text{CH}_2)$ are pure modes in all conformers (Table 5). As for $\nu(\text{C}-\text{Cl})$, the calculated relative $\nu(\text{C}=\text{O})$ frequencies correlate well with the inverse of the corresponding C=O bond lengths (Fig. 3), a result which can be explained in a similar way. In addition, $t(\text{CH}_2)$ in the C_s conformers (SC, AT and ST), and $\omega(\text{CH}_2)$ in the SKC and AT forms correspond also to pure modes. The $t(\text{CH}_2)$ mode in the SKC form and the $\omega(\text{CH}_2)$ vibration in the two *syn* forms (SC and ST) mix mainly with $\nu(\text{C}-\text{O})$,

$\delta(\text{C}-\text{O}-\text{H})$, and $\nu(\text{C}-\text{C})$. In turn, $\delta(\text{C}-\text{O}-\text{H})$ and $\nu(\text{C}-\text{O})$ mix appreciably in all forms. In the *syn* forms, the lower frequency mode is ascribed to $\nu(\text{C}-\text{O})$, and in the SKC and AT forms, the $\nu(\text{C}-\text{O})$ coordinate contributes mainly to the higher frequency mode.

In consonance with the present results, a revision of previous assignments³ is now proposed (Table 5). The main changes are:

(i) In the SC form, the IR band at 1111 cm^{-1} , previously assigned to the $\delta(\text{C}-\text{O}-\text{H})$ mode,³ is now ascribed to $\nu(\text{C}-\text{O})$, this assignment being consistent with the high intensity of the IR band.³ The $\delta(\text{C}-\text{O}-\text{H})$ vibration (calculated value: 1352 cm^{-1}) is now ascribed to the 1354 cm^{-1} IR band that was previously assigned to $\omega(\text{CH}_2)$ (the calculated frequency for the latter mode, probably not observed, is 1278 cm^{-1}). These two coordinates, $\delta(\text{C}-\text{O}-\text{H})$ and $\omega(\text{CH}_2)$, mix appreciably in the SC form. In addition, the $\delta(\text{CH}_2)$ mode (calculated value: 1429 cm^{-1}) is now ascribed to the 1428 cm^{-1} band, earlier assumed to be due to $\nu(\text{C}-\text{O})$.³

(ii) The assignments previously made for the SKC form are essentially confirmed by the calculations, the exception being $\delta(\text{CH}_2)$ which should not correspond to the 1366 cm^{-1} IR band, but to a higher frequency (the calculated value 1425 cm^{-1} agrees quite well with the molecular mechanics result⁵). The 1366 cm^{-1} band is now reassigned to the $\nu(\text{C}-\text{O})$ vibration (calculated value 1360 cm^{-1}).

(iii) For the AT form, the calculations confirm the assignments of the 1790 cm^{-1} IR band to $\nu(\text{C}=\text{O})$ ³ (calculated value: 1798 cm^{-1}), and of the intense IR band at 1334 cm^{-1} to $\nu(\text{C}-\text{O})$. In addition, the calculations show that the $\delta(\text{CH}_2)$ vibration should correspond to a band near 1400 cm^{-1} (not observed). Thus, the IR band at 1288 cm^{-1} , previously assigned to that mode, is now ascribed to $\omega(\text{CH}_2)$ (calculated value 1278 cm^{-1}).

2800–3600 cm^{-1} Region

This spectral region includes the $\nu(\text{O}-\text{H})$ and $\nu(\text{CH}_2)$ vibrations. The $\nu(\text{CH}_2)$ modes (symmetric and antisymmetric) have not been assigned in the previous IR study.³ The present calculations predict that the frequencies of these modes are larger for the SKC form and have their lowest values for the ST conformer. In addition, the order of the calculated $\nu(\text{O}-\text{H})$ frequencies in the various experimentally observed conformers is $\text{AT} \gg \text{SKC} > \text{SC}$.

In the AT and SKT forms, the proximity of the chlorine and of the hydroxy-group hydrogen atoms closing the five-membered ring $\text{Cl}-\text{C}-\text{C}-\text{O}-\text{H}$ leads to weak intramolecular hydrogen bonding interactions, thus contributing to lower the $\nu(\text{O}-\text{H})$ frequencies in these forms. On the contrary, the anti-parallel alignment of the C=O and OH bond dipole moments in the *s-cis* forms polarizes the O-H bonds, thus reducing their force constants and lowering their frequencies. In order to predict the relative order of the $\nu(\text{O}-\text{H})$ frequencies in the various conformers, the basis set should correctly reproduce the balance between these subtle interactions. While the 6-31G* calculations improve significantly over the smaller basis sets by doubling the 3-21G and 3-21G* overlap populations, they still yield a small Cl...H(O) overlap population for the AT form (0.0148 *e*). Larger basis sets with diffuse orbitals should be considered before an assessment of the basis set effect on these interactions, hydrogen bonding and bond dipole interactions, is definitely made.

Rotamerization of Chloroacetic Acid trapped in an Argon Matrix upon Irradiation in the $\nu(\text{C}=\text{O})$ Region

The results of a recent study on the rotamerization of chloroacetic acid trapped in an argon matrix, upon irradiation in

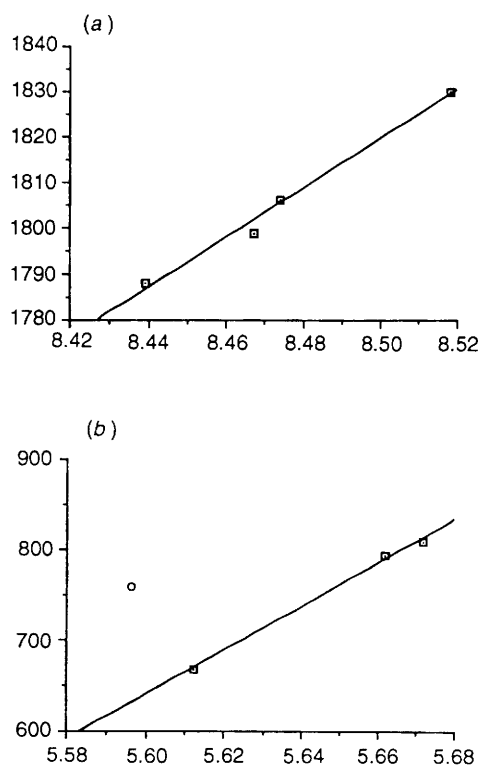


Fig. 3 Correlation of (a) $\nu(\text{C}=\text{O})$ with $1/R(\text{C}=\text{O})$, and (b) $\nu(\text{C}-\text{Cl})$ with $1/R(\text{C}-\text{Cl})$. The point that does not fit in the straight line in (b) corresponds to the AT form. This apparent anomaly is in consonance with the occurrence of a hydrogen bond involving the chlorine atom, as suggested in the text.

the $\nu(\text{C}=\text{O})$ region with the 1805 cm^{-1} CO laser line,³ can be summarized as follows:

(i) Irradiation of the sample deposited in an argon matrix at 13 K leads to both $\text{SC} \Rightarrow \text{SKC}$ and $\text{SC} \Rightarrow \text{AT}$ rotamerizations.

(ii) Irradiation of the annealed sample, *i.e.* after the $\text{SC} \Rightarrow \text{SKC}$ rotamerization, does not produce any change.

(iii) Irradiation during sample deposition leads mainly to $\text{SC} \Rightarrow \text{SKC}$ conversion.

(iv) No evidence was found for the $\text{SC} \Rightarrow \text{ST}$ rotamerization.

From these results, the following main conclusions were drawn:³

(i) Only the SC form converts to other forms by irradiation in the $\nu(\text{C}=\text{O})$ region.

(ii) Restricted-free-volume conditions make the $\text{SC} \Rightarrow \text{AT}$ rotamerization more important. Unlike the non-symmetric SKC conformer, the AT form can be embedded in the primarily occupied volume. In less restricted-free-volume situations, *e.g.* during sample deposition, the $\text{SC} \Rightarrow \text{SKC}$ rotamerization dominates.

As suggested previously,³ the $\nu(\text{C}=\text{O})$ mode of the SC conformer of chloroacetic acid interacts with the first overtone of $\gamma(\text{CH}_2)$ (a'), through a Fermi resonance mechanism. The calculations presented herein confirm that the best candidate for this interaction with the $\nu(\text{C}=\text{O})$ mode is, in fact, the first overtone of $\gamma(\text{CH}_2)$ [compare the frequencies of $2\gamma(\text{CH}_2)$ and $\nu(\text{C}=\text{O})$, Table 5]. Thus, by irradiating the sample at 1805 cm^{-1} , energy is transferred not only to the C=O stretching, but also to the $\gamma(\text{CH}_2)$ mode through its first overtone. Then, as the $\gamma(\text{CH}_2)$ fundamental belongs to the same symmetry species (a') as the $\tau(\text{C}-\text{C})$ and $\tau(\text{C}-\text{O})$ torsions, irradiation in the $\nu(\text{C}=\text{O})$ region is effective in promoting rotamerization. A different mechanism of direct energy transfer from $\nu(\text{C}=\text{O})$ to the torsions, involving high-order overtones of these vibrations should not be definitively excluded, as the interactions with the matrix cage may reduce the symmetry of the molecule, thus destroying the symmetry constraint for intermolecular vibrational energy transfer. However, the proposed mechanism appears more attractive as it does not require an additional hypothesis (interaction with matrix cage) and is suggested strongly by the calculations. Moreover, this mechanism also explains why only the SC conformer rotamerizes. In fact, in this form, $\gamma(\text{CH}_2)$ is considerably mixed with $\nu(\text{C}=\text{O})$, and this mode with $\tau(\text{C}-\text{O})$. In turn, $\tau(\text{C}-\text{C})$ has a significant contribution from $\nu(\text{C}=\text{O})$ (see Table 5). Hence, the overall result of this sequence of processes is the transfer of energy from the first overtone of the $\gamma(\text{CH}_2)$ mode [in Fermi resonance with $\nu(\text{C}=\text{O})$] to the torsions which promote the rotamerizations [$\tau(\text{C}-\text{C})$ and $\tau(\text{C}-\text{O})$]. In contrast, in the SKC form, $\gamma(\text{CH}_2)$ does not mix appreciably with any relevant coordinate (see Table 5), thus the rotamerization cannot occur. As symmetry restrictions do not apply to this form (note that all modes are totally symmetric), potential-energy distribution between internal coordinates is not constrained by symmetry to the relevant modes of rotamerization, thus enabling us to understand the different PED behaviour of the SC and SKC forms. Finally, in the AT form, while $\gamma(\text{CH}_2)$ and $\nu(\text{C}=\text{O})$ mix with each other, these two coordinates do not mix with torsions, which, interestingly enough, are pure vibrations in this conformation. Hence, also for this form, rotamerization should not be induced by laser irradiation in the $\nu(\text{C}=\text{O})$ region.

The results now presented seem to confirm a previous hypothesis which states that a concerted rotation about the $\text{C}_\alpha-\text{C}$ and $\text{C}-\text{O}$ bonds should be involved in the $\text{SC} \Rightarrow \text{AT}$ rotamerization,³ in opposition to a multi-step process involving separate $\text{C}_\alpha-\text{C}$ and $\text{C}-\text{O}$ rotamerizations corresponding

to $\text{S} \rightarrow (\text{SK}) \rightarrow \text{A}$ and $\text{C} \rightarrow \text{T}$ individual processes, one at a time. In fact, as was shown above, the AT form cannot be obtained from the SKC form upon laser irradiation in the $\nu(\text{C}=\text{O})$ region, following the $\text{SC} \rightarrow \text{SKC} \rightarrow \text{AT}$ mechanism. In turn, the alternative way of obtaining the SKT form from the SC conformer is *via* the ST form ($\text{SC} \rightarrow \text{ST} \rightarrow \text{SKT} \rightarrow \text{AT}$), but the first step of this reaction does not occur as the CO laser photon energy (*ca.* 22 kJ mol^{-1}) is not high enough to promote the $\text{SC} \Rightarrow \text{ST}$ transformation.

The authors thank Prof. A. Kulbida, Institute of Physics, University of St. Petersburg, for his comments and useful suggestions on a draft version of this paper. They are grateful for computer assistance provided by the Centro de Informática da Universidade de Coimbra (CIUC), and to Junta Nacional de Investigação Científica e Tecnológica (JNICT), Lisboa, for financial support.

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