

Scientific paper

Anharmonic Vibrational Properties of Chlorocarbonyl Ketene Conformers Using Second-order Perturbation Theory

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Abstract

The present paper reports main results of a comprehensive study of the structure and vibrational spectra of the stable conformers of chlorocarbonyl ketene computed using second-order perturbation theory treatment based on quadratic, cubic and semidiagonal quartic force constants. It is found that the *s-trans* conformer is more stable than the *s-cis* conformer by -0.69 kcal/mol. The vibrationally averaged bond lengths and bond angles, both for the *cis* and *trans* conformers, are within 0.005 Å and 0.14° , respectively, of the equilibrium geometry. The *ab initio* and DFT based anharmonic vibrational analysis using second-order perturbation theory provides reliable frequencies (r.m.s. deviation ± 20 cm $^{-1}$) and assignments to the vibrational bands. DFT calculations using the same method and basis function for the harmonic frequencies and anharmonic corrections give frequencies in better agreement with the experimental values than those in which the harmonic frequencies from a high level quantum mechanical method (B97-1/aug-cc-pVTZ) are coupled with anharmonic corrections from a cheap model (B3LYP/6-31+G**); the r.m.s. deviation in the latter case is ± 47 cm $^{-1}$. The errors in the calculation of the fundamental modes are reflected in the overtones and combination bands. Some spectroscopic constants namely, the anharmonic constants, rotational constants and rotation-vibration coupling constants of the two conformers have been calculated by density functional theory and compared with literature, where available.

Keywords: Chlorocarbonyl ketene; Conformers; Anharmonic frequencies; Spectroscopic constants; DFT; Perturbation theory

1. Introduction

Ketenes are fascinating and versatile reactive intermediates in a variety of reactions.^{1–4} Substituted ketenes are highly reactive species with properties often different from those of ketene itself and as such have prompted a number of mechanistic⁵ and theoretical studies.^{6,7} In an earlier communication,⁸ we have reported quantum chemical studies on the effect of substituents on structural, chemical and spectroscopic characteristics of di-substituted ketenes. Pietri et al.⁹ have reported photolysis of chloroformyl ketene resulting in the formation of carbon suboxide and explained the reaction path on the basis of *ab initio* calculations. Brown et al.¹⁰ have suggested the possible existence of high-carbon content compounds like ketenes in the interstellar space. We have earlier reported^{11,12} results of anharmonic vibrational analysis of some cyanides and related molecules of astrophysical significance. Apart from the inherent interest in more thoroughly cha-

racterizing a chemically interesting group of rather unstable molecule, the spectral data are potentially important as a basis for future astrophysical studies of such molecules. Badawi et al.^{13–15} have computed vibrational spectra of some substituted ketenes in the harmonic approximation and have also drawn conclusion about their structural stability. However, significant mismatch between the experimental and their calculated frequencies due to the neglect of anharmonicity raises doubt about their vibrational assignments.

Several effective approaches going beyond the harmonic levels have been adopted during the last years to account for the anharmonicity effects. These include Car-Parrinello molecular dynamics (CPMD) method of Jeziarska et al.,¹⁶ a mixed quantum-classical density matrix evolution (DME) method of Mavri and Grdadolnik¹⁷ limited to quantization of the OH motion in one dimension and variational method of Stare and Mavri¹⁸ for numerical solving of the vibrational time-independent Schrodinger

equation in one and two dimensions. For small molecules converged rovibrational levels have been obtained by fully variational methods of Bowman et al.^{19–22} However, for large molecules the variational vibrational SCF (VSCF)²³ and second-order perturbation^{24,25,30} treatments have been the most successful approaches. The second-order perturbation theory (PT2) provides closed expressions for most of the spectroscopic parameters required for the analysis of the experimental frequencies. However, for correct results, this approach requires complete quartic development which is the most practical representation of the potential for large molecules. As noticed by Handy et al.^{26,27} and Barone,³⁰ the predictions by the second-order perturbation theory after the inclusion of the quartic potential derivable from analytical second derivatives can be closer to experiment than their variational counterparts.

We have earlier reported¹⁶ the vibrationally averaged structure and the results of anharmonic analysis of the vibrational spectrum of ketene by density functional theory using second order perturbation theory. In the present communication, we are reporting the results of anharmonic analysis of the vibrational spectra of the *cis* and *trans* conformers of chlorocarbonyl ketene using *ab initio* and DFT methods.

2. Methodology

The potential energy function for an anharmonic oscillator may be written as

$$V = \frac{1}{2} \sum_{ij} f_{ij} S_i S_j + \frac{1}{6} \sum_{ijk} f_{ijk} S_i S_j S_k + \frac{1}{24} \sum_{ijkl} f_{ijkl} S_i S_j S_k S_l + \quad (1)$$

$\{S_i\}$ represent a displacement internal coordinate and f_{ij} , f_{ijk} and f_{ijkl} etc. are the quadratic, cubic and quartic etc. force constants. Using the Dunham potential functions, the energy of an anharmonic oscillator is given by

$$E_{n_1, n_2, \dots} = \sum_i \nu_{0i} \left(n_i + \frac{1}{2} \right) + \sum_{\substack{i,k \\ k \geq i}} X_{ik} \left(n_i + \frac{1}{2} \right) \left(n_k + \frac{1}{2} \right) + \quad (2)$$

where X_{ii} and X_{ik} are the diagonal and non-diagonal anharmonicity constants. While X_{ii} characterizes anharmonicity of the given vibration, the coefficients X_{ik} characterize coupling between different normal modes resulting from anharmonicity and are determined from cubic and quartic force constants. The fundamental frequencies of the anharmonic oscillator are given by

$$\nu_i' = \nu_{0i} + 2X_{ii} + \frac{1}{2} \sum_{j \neq i} X_{ij} \quad (3)$$

The rotational – vibrational couplings may be determined in terms of the rotational, and rotation-vibration interaction constants.

The anharmonic force fields and spectroscopic constants have been calculated by using the second order Perturbation theory (PT2) implemented in Gaussian03W²⁹ software. The implementation of a fully automated code for the building of anharmonic force constants and their use in a second-order perturbative evaluation of vibrational parameters has been described in details by Barone.³⁰ Anharmonic force fields are computed by exploiting the linear relationship between normal and cartesian displacement coordinates. The second-derivative matrix over normal modes is given as

$$\Phi = \mathbf{L}^+ \mathbf{M}^{-1/2} \mathbf{F} \mathbf{M}^{-1/2} \mathbf{L}$$

where \mathbf{M} is the diagonal matrix of atomic masses, and \mathbf{L} is the matrix of (columnwise) eigenvectors of the mass weighted cartesian force constant matrix $\mathbf{M}^{-1/2} \mathbf{F} \mathbf{M}^{-1/2}$. Starting from analytical second derivatives, the third and semidiagonal fourth derivatives needed for second-order perturbation have been computed by a finite difference approach which scales linearly with the number of modes. A tight geometry optimization with residual gradients less than 10^{-7} hartree/bohrs (or radian) is a mandatory prerequisite for reliable anharmonic analysis irrespective of the specific quantum mechanical method (RHF or DFT). The vibrational Hamiltonian \mathbf{H}_{vib} is taken as a sum of zeroth order harmonic term ($\mathbf{H}_{\text{vib}}^0$) and successive terms containing the contributions of cubic, quartic etc., components of the potential ($\mathbf{H}_{\text{vib}} = \mathbf{H}_{\text{vib}}^0 + \mathbf{H}_{\text{vib}}^1 + \mathbf{H}_{\text{vib}}^2$). The second order term includes a kinetic contribution arising from the vibrational angular momentum. Starting from the solutions $|v_i^0\rangle$ of the harmonic problem the vibrational wave functions $|v_i\rangle = |v_i^0\rangle + |v_i^1\rangle + |v_i^2\rangle$ are obtained by the second-order perturbation theory. The vibrotational Hamiltonian $\mathbf{H}_{\text{vibrot}}$ obtained by adding the rotational energy term is used to get the vibrotational eigen functions and energies. The calculations were conducted using B3LYP and B97-1 procedures with 6-31+G**, 6-311++G** and aug-cc-pVTZ basis sets involving diffuse functions and polarization functions and by *ab initio* method RHF/6-311++G**. The suggestion of Barone¹⁸ that best results can be obtained by using hybrid functionals (B3LYP, B97-1 etc) and large basis sets combined with anharmonic corrections using less expensive method B3LYP/6-31+G* was also tested. The forms of vibrations were analyzed using the software GaussView version 2.0.³¹

3. Results and Discussion

The experimental infrared spectrum of chlorocarbonyl ketene at 10 K in argon and xenon matrices has been reported by Pietri et al.⁹ during a photo-isomerization study. They assigned the two sets of absorption bands showing opposite behavior during the photo-isomerization experiment to the *s-cis* and *s-trans* conformers.

mers. Quantum chemical calculations using MP2/D95* were also conducted by these authors to obtain molecular geometries of the *s-cis* and *s-trans* conformers in the electronic ground and first excited states. Spectral assignments to some prominent absorption peaks of the two conformers were also given. No experimental data seems to be available for the molecular geometry of the stable conformers of chlorocarbonyl ketene. Al-Saadi and Badawi^{13,32} predicted molecular geometries of the two rotational isomers of chlorocarbonyl ketene using B3LYP/6-311++G** and MP2/6-311++G** calculations and compared them with the experimental geometries of an analogous molecule propenoyl chloride from electron diffraction³³ and microwave³⁴ measurements. Discrepancies are observed in the values of the geometrical parameters reported by these authors in the two publications.^{13, 32} No anharmonic analysis has so far been reported in the literature for the vibrational spectra of chlorocarbonyl ketene. The results of our anharmonic calculations on the *s-cis* and *s-trans* conformers of chlorocarbonyl ketene using HF and density functional methods are given in Tables 1–6. The numbering on atoms in these tables are in accordance with Figures 1a and 1b for the *s-trans* and *s-cis* conformers, respectively. The optimized and vibrationally averaged geometrical parameters, harmonic and anharmonic vibrational frequencies and spectroscopic constants of the *s-cis* and *s-trans* conformers of chlorocarbonyl ketene are being discussed separately. A reasonab-

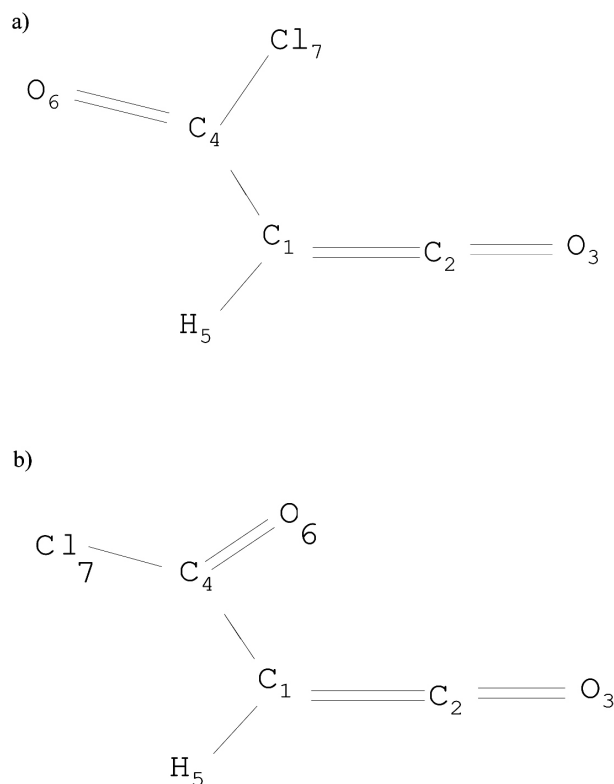


Fig. 1 *s-trans* (a) and *s-cis* (b) conformers of chlorocarbonyl ketene

le agreement with the experimental frequencies has, in general, been obtained.

3. 1. Conformational Analysis

The optimized and vibrationally averaged molecular geometries, dipole moments and total energies of the *s-trans* and *s-cis* conformers of chlorocarbonyl ketene using B97-1/6-311++ G**, B97-1/aug-cc-pVTZ, B3LYP/6-31+G**, MP2/6-311++G** and RHF/6-311++G** methods are given in Tables 1(a) and 1(b), respectively. The tables also contain theoretical values of bond lengths and bond angles given in the literature^{9,15} and the experimental values for an analogous molecule propenoyl chloride.^{33,34} It is found that all the theoretical methods presently used give almost identical geometries which are within 0.03 Å in bond length and 3° in bond angle of the experimental geometry of propenoyl chloride. The vibrationally averaged bond lengths for the two conformers are within 0.001–0.005 Å of the optimized parameters, as in the case of ketene.²⁸ Our DFT and MP2 calculations confirm the experimental findings of Pietri et al.⁹ that the *s-trans* conformer is more stable than the *s-cis* conformer. This is in contrast to the findings of Badawi et al.¹⁵ that the *s-cis* conformer is the more stable of the two conformers by about 0.23 kcal/mol. The calculated enthalpy difference 0.69 kcal/mol. (B97-1/6-311++G**) between the *s-cis* and *s-trans* conformers, after incorporating zero-point energy correction, is in better agreement with the experimental estimate of 0.9–1.3 kcal/mol.⁹ in comparison to the theoretical predictions of 0.55 and 0.24 kcal/mol. by Pietri et al.⁹ and Badawi et al.,¹⁵ respectively.

The geometries of the *s-cis* and *s-trans* conformers do not differ significantly except in the angles C₂C₁C₄ and C₄C₁H₅. While the angle C₂C₁C₄ of the *s-cis* conformer is about 4° shorter, the angle C₄C₁H₅ is larger by about 3° than the corresponding angles in the *s-trans* conformer.

3. 2. Harmonic and Anharmonic Fundamental Modes

Two types of calculations were performed to obtain the frequencies and intensities of the fundamental modes, overtones and combination bands for the *s-cis* and *s-trans* conformers of chlorocarbonyl ketene. In the first case, the usual homogeneous model was adopted and both the harmonic frequencies and anharmonic corrections were calculated by using the same method and basis set viz. B97-1/6-311++G**, B3LYP/6-31+G** and RHF/6-311++ G**. In the second case, following Barone,³⁰ the harmonic frequencies computed at a high level of quantum mechanical method and basis set (B97-1/aug-cc-pVTZ) were coupled with anharmonic corrections computed by a cheap model (B3LYP/6-31+G**). The results of calculations together with the experimental frequencies for the *s-trans* and *s-cis* conformers are given in Tables 2 and 3, respectively.

Table 1(a): Molecular geometry, dipole moment and total energy of s-trans conformer of chlorocarbonyl ketene

Bond length/ Bond angle	B97-1/6-311++G** Opt.	B97-1/6-311++G** Aver.	B97-1/aug-cc-pvtz Opt.	B97-1/aug-cc-pvtz Aver.	B3LYP/6-31+G** Opt.	B3LYP/6-31+G** Aver.	MP2/6-311++G** Opt.	MP2/6-311++G** Aver.	RHF/6-311++G** Opt.	RHF/6-311++G** Aver.	Exptl. Values ^a	Literature [9]	Literature [15]
C ₁ -C ₄	1.4486	1.4531	1.4445	1.4476	1.4477	1.4522	1.4475	1.4520	1.4498	1.4538	1.476	1.454	1.466
C ₁ =C ₂	1.3333	1.3357	1.3321	1.3331	1.3354	1.3376	1.3394	1.3404	1.3239	1.3265	1.345	1.346	1.330
C ₂ =O ₃	1.1492	1.1483	1.1481	1.1441	1.1582	1.1572	1.1575	1.1563	1.1215	1.1204	–	1.172	1.153
C ₁ -H ₅	1.0848	1.0822	1.0828	1.0790	1.0852	1.0829	1.0834	1.0786	1.0723	1.0697	1.084	1.078	1.107
C ₁ =O ₆	1.1872	1.1875	1.1867	1.1852	1.1954	1.1958	1.1969	1.1958	1.1650	1.1650	1.192	1.209	1.207
C ₄ -Cl ₇	1.836	1.8418	1.8326	1.8389	1.8319	1.8383	1.8069	1.8120	1.7873	1.7936	1.816	1.811	1.746
C ₄ -C ₁	122.91	122.87	122.37	122.48	123.16	123.13	121.85	121.81	123.30	123.26	122.6	126.6	121.1
C ₁ -C ₂	180.0	176.98	180.0	176.71	180.0	176.95	180.00	176.92	180.0	177.29	–	180.0	178.7
H ₅ -C ₁ -C ₄	119.10	119.13	119.55	119.52	118.87	118.90	119.74	119.71	119.04	119.01	–	120.1	121.4
O ₆ -C ₁ -C ₄	127.25	127.30	127.50	127.50	126.66	126.73	126.50	126.64	125.96	126.02	127.2	126.6	124.0
Cl ₇ -C ₄ -C ₁	112.62	112.56	112.08	112.03	113.14	113.07	112.94	112.93	114.20	114.17	116.3	112.5	113.9
O ₆ -C ₁ -C ₂	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
Cl ₇ -C ₄ -H ₅	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	–	180.0	180.0
μ (Debye)	3.0489	3.0460	3.0460	3.0460	3.0460	3.0460	2.9888	2.9888	2.9849	2.9849	–	–	2.7
E (a.u.)	-725.51647	-725.55205	-725.55205	-725.55248	-725.55248	-725.55248	-724.39376	-724.39376	-723.46747	-723.46747	-724.2621	-724.2621	-725.61893

^avalues obtained from a microwave experiment for a similar molecule, propenyl chloride Ref. [33].

Table 1(b): Molecular geometry, dipole moment and total energy of s-cis conformer of chlorocarbonyl ketene

Bond length/ Bond angle	B97-1/6-311++G** Opt.	B97-1/6-311++G** Aver.	B97-1/aug-cc-pvtz Opt.	B97-1/aug-cc-pvtz Aver.	B3LYP/6-31+G** Opt.	B3LYP/6-31+G** Aver.	MP2/6-311++G** Opt.	MP2/6-311++G** Aver.	RHF/6-311++G** Opt.	RHF/6-311++G** Aver.	Exptl. Values ^a	Literature [9]	Literature [15]
C ₁ -C ₄	1.4553	1.4608	1.4516	1.4528	1.4528	1.4590	1.4528	1.4544	1.4514	1.456	1.484	1.459	1.466
C ₁ =C ₂	1.3339	1.3359	1.3322	1.3402	1.3402	1.3381	1.3402	1.3440	1.3273	1.3298	1.339	1.347	1.322
C ₂ =O ₃	1.1486	1.1467	1.1479	1.1572	1.1572	1.1558	1.1572	1.1559	1.1202	1.1184	–	1.172	1.150
C ₁ -H ₅	1.0817	1.0783	1.0795	1.0804	1.0804	1.0794	1.0804	1.0802	1.0690	1.0659	–	1.085	1.108
C ₁ =O ₆	1.1909	1.1926	1.1901	1.2016	1.2016	1.2010	1.2016	1.2021	1.1699	1.1711	1.192	1.214	1.211
C ₄ -Cl ₇	1.8176	1.8209	1.8160	1.7850	1.7850	1.8186	1.7850	1.7881	1.7720	1.7766	1.772	1.788	1.755
C ₄ -C ₁	118.69	118.55	118.60	117.10	117.10	118.69	117.10	117.11	117.47	117.37	123.4	127.1	121.0
C ₁ -C ₂	180.0	179.32	180.0	179.74	179.74	179.16	179.74	179.72	180.0	178.81	–	180.0	179.6
H ₅ -C ₁ -C ₄	122.79	122.93	122.82	121.20	121.20	122.83	121.20	121.35	123.86	124.0	–	124.0	121.2
O ₆ -C ₁ -C ₄	128.49	128.47	128.50	127.59	127.59	127.97	127.59	127.63	127.17	127.24	125.2	127.1	124.3
Cl ₇ -C ₄ -C ₁	110.86	110.86	110.66	111.20	111.20	111.34	111.20	111.16	112.40	112.34	111.8	115.5	113.0
O ₆ -C ₁ -C ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cl ₇ -C ₄ -H ₅	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	–	0.0	0.0
μ (Debye)	3.2485	3.1118	3.1118	3.1118	3.1118	3.2628	3.4809	3.4809	3.3399	3.3399	–724.26123	–724.26123	–725.61870
E (a.u.)	-725.51540	-725.54899	-725.54899	-725.55166	-725.55166	-725.55166	-724.39319	-724.39319	-723.46814	-723.46814	–724.26123	–724.26123	–725.61870

^avalues obtained from an electron diffraction experiment for a similar molecule, propenyl chloride Ref. [32].

Table 2: Vibrational frequencies, intensities and assignments of s-trans conformer of chlorocarbonyl ketene

Freq- uencies	B97-1/6-311++G**		B3LYP/6-3+G**		RHF/6-311++G**		B971/aug-cc-pvtz ^b		Assignments			
	Argon	Harmonic	Anhar- monic	Harmonic	Anhar- monic	Harmonic	Anhar- monic	Harmonic		Anhar- monic		
	V _{obs}	Int.	V _{calc}	Int.	V _{calc}	Int.	V _{calc}	V _{scal} *	V _{calc}	Int.	V _{calc}	
A'												
V ₁	–	–	3196.8	22.9	3066.5	22.0	3370.3	3250.7	2990.6	3237.8	20.9	3088.8
V ₂	2160	100	2249.6	768.4	2206.6	756.9	2401.5	2368.8	2175.6	2302.1	754.5	2255.2
V ₃	1785	53	1862.6	665.1	1834.9	639.7	2009.1	1987.1	1828.1	1907.5	654.3	1878.6
V ₄	1376	5	1389.9	53.8	1365.6	51.8	1507.8	1480.6	1362.1	1413.0	54.8	1379.7
V ₅	1125	10	1138.0	98.3	1118.2	1149.8	108.7	1129.8	1194.5	1144.2	97.5	1119.5
V ₆	1051	10	1078.6	179.8	1041.3	167.8	1087.3	1175.1	1056.6	1095.2	171.7	1094.3
V ₇	–	–	628.8	5.7	611.6	5.7	717.6	713.6	656.5	613.5	0.1	599.0
V ₈	587	10	585.7	106.6	582.2	107.5	642.6	633.9	583.2	579.3	118.2	571.3
V ₉	–	–	413.9	8.1	411.7	9.1	478.7	474.3	436.4	405.2	9.1	400.0
V ₁₀	–	–	351.1	5.8	347.1	6.3	398.7	396.6	364.9	328.3	4.3	325.8
V ₁₁	–	–	131.1	1.5	126.8	1.7	144.1	143.0	131.6	113.9	2.3	112.2
A''												
V ₁₂	684	9	697.0	44.1	673.0	50.2	779.4	769.4	707.8	687.7	51.03	672.4
V ₁₃	558	6	572.1	12.4	562.2	17.9	556.6	647.0	595.2	534.9	19.59	528.5
V ₁₄	–	–	526.8	11.8	493.6	4.4	515.2	558.8	514.1	507.8	3.13	498.1
V ₁₅	–	–	115.1	5.0	111.2	5.4	121.6	119.9	110.3	51.5	5.63	49.5

* Scaling factor =0.92

^a Ref. [9]^b anharmonic corrections in B3LYP/6-31+G**

Table 3: Vibrational frequencies, intensities and assignments for s-cis chlorocarbonyl ketene

Frequencies	B97-1/6-311+G**			B3LYP/6-3+G**			RHF/6-311++G**			B971/aug-cc-pvtz ^b			Assignments		
	Argon	Harmonic	Anharmonic	Harmonic	Anharmonic	Harmonic	Anharmonic	Harmonic	Anharmonic	Harmonic	Anharmonic				
ν_{obs}	Int.	ν_{calc}	Int.	ν_{calc}	Int.	ν_{calc}	Int.	ν_{calc}	ν_{scal}^*	ν_{calc}	Int.	ν_{calc}			
A'															
ν_1	–	3227.6	28.7	3062.4	3245.6	26.7	3099.9	3407.7	27.8	3286.0	3023.1	3226.7	26.4	3080.9	C–H str.
ν_2	2158	100	2249.8	933.1	2205.9	2231.9	907.3	2188.8	2403.8	1381.2	2369.0	2234.6	37.3	2190.8	C=C=O asym. Str.
ν_3	1748	80	1833.5	377.5	1784.5	1819.7	357.9	1777.9	1973.8	480.4	1940.9	1823.0	333.8	1781.4	C=O str.
ν_4	1361	65	1383.8	261.2	1359.6	1399.4	256.0	1373.5	1503.5	377.9	1464.8	1380.3	252.8	1354.4	C=C=O sym. str.
ν_5	1113	6	1120.3	4.3	1100.4	1128.5	5.9	1160.2	1206.8	35.6	1171.1	1100.8	3.5	1139.7	C–H i.p. bend
ν_6	1004	23	1016.4	184.6	992.5	1026.0	184.4	1007.5	110.4	229.4	1091.2	1003.9	172.9	996.2	C–C str.
ν_7	827	–	839.6	230.7	825.9	834.1	229.0	819.6	938.7	233.1	925.1	851.1	835.5	821.0	C–C–C def., C–C=O def.
ν_8	–	–	515.4	29.5	508.5	506.4	30.2	500.9	578.7	36.1	573.1	527.1	513.6	508.2	C=C=O i.p. bend
ν_9	–	–	438.7	12.1	434.4	432.9	13.5	428.9	499.3	6.7	495.3	455.7	433.9	430.0	Cl C O def., C–Cl str.
ν_{10}	–	–	311.2	4.2	309.3	312.8	4.5	311.5	342.2	3.7	340.8	313.5	309.5	308.3	CCl def.
ν_{11}	–	–	132.3	3.1	130.1	133.0	3.2	131.7	151.3	3.7	150.1	131.1	131.1	130.1	C=C=O i.p. bend
A''															
ν_{12}	660	–	669.3	34.8	657.5	672.2	43.3	664.1	761.9	70.2	754.6	694.3	671.7	663.7	C–C–H o.p. bend, C–Cl wag
ν_{13}	–	–	571.6	3.2	559.9	559.2	25.6	549.9	654.5	8.8	645.9	594.2	570.6	561.4	C=C=O o.p. bend
ν_{14}	531	vw	550.6	28.1	517.7	556.1	2.0	547.0	589.1	30.5	579.1	532.8	554.5	545.5	C–H o.p. bend
ν_{15}	–	–	92.0	2.6	87.8	92.9	2.8	92.8	100.4	2.4	99.2	91.2	90.9	91.1	Asymm. Torsion

* Scaling factor =0.92

^a Ref. [9]^b anharmonic corrections in B3LYP/6-31+G**

It follows from these tables that, both in the case of the *s-cis* as well as *s-trans* conformers, the calculated harmonic frequencies from density functional theory need significant scaling for agreement with the experimental values. The corresponding anharmonic frequencies on the other hand are quite close to the experimental values within $\pm 20 \text{ cm}^{-1}$ and do not need further scaling. The *ab initio* frequencies using Hartree-Fock formalism with 6-311++G** basis set show large deviations from the experimental values, both in the harmonic as well as anharmonic approximations. The anharmonic frequencies in this case need scaling by a factor of 0.92 to match with the experimental frequencies within $\pm 20 \text{ cm}^{-1}$. It also follows from Tables 2 and 3 that coupling of anharmonic correction from a cheap model B3LYP/6-31+G** with harmonic frequencies from B97-1/aug-cc-pVTZ, as in ref. 30, does not give satisfactory agreement with the experimental values; the r.m.s deviation in this case is $\pm 47 \text{ cm}^{-1}$. It

may thus be concluded that calculations using the same method and basis set for harmonic frequencies and anharmonic corrections is superior to the one using different methods and basis sets for the two parts.

Both the *s-cis* and *s-trans* conformations of chlorocarbonyl ketene belong to C_s symmetry groups and have $11A' + 4A''$ normal modes. The assignment of these normal vibrational modes for the *s-trans* and *s-cis* conformers are given Tables 2 and 3, respectively. Our assignment of vibrational bands, both of the *s-cis* and *s-trans* conformers, are in closer agreement with those of Pietri et al.⁹ rather than of Badawi et al.¹⁵ Calculated frequencies of Badawi et al.,¹⁵ in most part, do not agree with the experimental values of chlorocarbonyl ketene.⁹ Pietri et al.⁹ assign a calculated band at 3214 cm^{-1} to C–H stretching mode. However, no such band appears in the experimental infrared spectra.⁹ Present anharmonic calculations for the *s-cis* and *s-trans* conformers predict this band at 3062.4

Table 5: Anharmonicity constants (cm^{-1}) of *s-trans* and *s-cis* conformers of chlorocarbonyl ketene using DFT methods

Anhar. constts	Trans CCK		Cis CCK	
	B97-1/6-311++G**	B3LYP/6-31+G**	B97-1/6-311++G**	B3LYP/6-31+G**
X _{1 1}	-69.88	-63.64	-68.89	-63.33
X _{2 2}	-11.46	-11.23	-11.85	-10.92
X _{3 3}	-12.32	-12.94	-12.60	-12.94
X _{4 4}	-7.37	-7.39	-8.35	-8.48
X _{5 5}	-2.28	-2.99	-1.94	-1.23
X _{6 6}	-2.27	-2.45	-2.47	-2.68
X _{7 7}	-1.17	-0.88	-1.35	-1.33
X _{8 8}	0.36	0.29	0.31	-2.42
X _{9 9}	-0.73	-1.26	-0.32	-0.003
X _{10 10}	0.04	0.21	-0.06	-0.05
X _{11 11}	-0.57	0.29	0.05	0.16
X _{12 12}	-1.64	-0.04	-0.49	-0.04
X _{13 13}	-0.54	0.06	5.90	-5.57
X _{14 14}	-7.23	-3.18	-8.44	-14.58
X _{15 15}	-0.20	-0.26	-0.59	-0.35
X _{1 4}	4.17	3.04	5.29	5.88
X _{1 5}	-19.10	-17.36	-19.29	-17.52
X _{1 12}	-12.27	-8.28	-6.08	-5.24
X _{1 14}	-19.57	-7.32	-24.82	-1.55
X _{3 7}	2.96	3.44	-15.51	-7.65
X _{3 8}	1.12	1.11	-0.40	-0.26
X _{5 9}	1.11	0.88	0.05	0.06
X _{5 13}	4.92	3.07	-29.39	33.94
X _{5 14}	4.11	1.25	2.82	70.40
X _{6 9}	1.55	1.01	0.74	0.81
X _{6 13}	-22.86	-4.64	-2.07	-3.60
X _{6 14}	-19.06	5.91	-3.81	-3.67
X _{7 14}	-8.29	-6.88	-1.21	-0.72
X _{7 15}	-6.54	-5.06	-0.11	0.09
X _{10 14}	-1.17	1.49	0.27	-0.13
X _{11 12}	0.08	0.10	-0.72	-0.56
X _{12 13}	-1.04	1.38	-2.23	3.46
X _{13 14}	12.44	-1.70	-1.40	-15.16
X _{10 15}	0.64	0.51	1.11	1.06
X ₁₄ X ₁₅	5.05	5.10	-2.40	-1.15

Table 6: Rotational constants (MHz) including terms due to quartic centrifugal distortion constants and rotation-vibration coupling constants (MHz) of *s-trans* and *s-cis* conformers of chlorocarbonyl ketene

Rotational constants (MHz)

	<i>s-trans</i>		Ref. [15]	Ref. [24]	<i>s-cis</i>		Ref. [15]	Ref. [24]
	B97-1/ 6-311++G**	B3LYP/ 6-31+G**	B3LYP/6- 311++G**	B3LYP/6- 31++G**	B97-1/6-311 ++G**	B3LYP/6- 31+G**	B3LYP/6- 311++G**	B3LYP/6- 311++G**
A ₀	4847.7	4838.7	3840	4845	9370.4	9380.7	3524	9405
B ₀	2208.3	2185.7	2400	2203	1463.2	1456.6	2490	1464
C ₀	1517.2	1505.6	1476	1514	1265.6	1260.8	1459	1267

Rotation-vibration coupling constants (MHz)

	<i>s-trans</i>						<i>s-cis</i>					
	B97-1/6-311++G**			B3LYP/6-31+G**			B97-1/6-311++G**			B3LYP/6-31+G**		
	a	b	c	a	b	c	a	b	c	a	b	c
α ₁	22.69	2.80	3.52	23.24	2.80	3.55	10.17	3.03	2.43	9.06	2.99	2.38
α ₂	2.57	6.43	3.28	2.90	6.44	3.32	72.13	2.44	3.14	71.80	2.55	3.02
α ₃	19.84	3.37	3.47	19.48	3.44	3.45	18.42	-1.35	-0.73	18.15	-1.39	-0.77
α ₄	-17.90	1.94	-0.67	-16.89	2.06	-0.48	47.03	-0.79	0.49	47.05	-0.55	0.66
α ₅	-30.44	-0.52	-3.16	-27.10	-0.22	-2.63	17.41	-1.58	-0.77	18.13	-1.51	-0.73
α ₆	17.56	3.09	4.53	18.35	3.01	4.47	10.29	4.16	3.95	12.56	4.38	4.15
α ₇	-42.94	0.22	-1.16	-33.64	0.17	-0.86	20.34	0.90	2.11	26.16	0.97	2.26
α ₈	5.46	-0.33	2.35	10.07	-0.23	2.55	59.73	2.21	0.63	65.79	2.30	0.68
α ₉	-13.29	0.71	-1.65	-11.42	0.70	-1.57	-0.04	0.57	0.76	9.11	0.71	1.00
α ₁₀	-14.61	-3.50	-0.89	-12.34	-3.39	-0.55	-1.19	-2.24	0.91	0.95	-2.13	1.00
α ₁₁	-55.75	-3.42	2.64	-63.09	-3.37	2.74	-98.14	-4.75	-0.77	-100.05	-4.66	-0.76
α ₁₂	-4.31	-0.25	-0.72	-4.77	-0.21	-0.80	20.63	0.25	-0.32	20.42	0.11	-0.42
α ₁₃	39.38	-0.93	-1.21	29.23	-1.24	-1.45	-41.52	-1.54	-0.55	-15.51	0.66	-0.06
α ₁₄	21.93	0.55	1.18	21.82	0.77	1.37	-13.16	0.54	0.11	-44.69	-1.65	-0.36
α ₁₅	78.86	-2.77	-1.85	86.92	-2.65	-1.82	14.52	1.87	-3.68	23.03	1.78	-3.55

and 3066.5 cm⁻¹ (Tables 2 and 3), respectively, in close vicinity to the 3070 cm⁻¹ band in ketene which was assigned by us²⁸ to C–H stretch mode.

3. 3. Overtones and Combination Bands

Anharmonic analyses are performed using the second-order perturbation theory for asymmetric tops.³⁵ Fermi resonances have been handled in the usual fashion. That is, near singular terms are eliminated from the expressions for the anharmonic constants X_{ij} and final band origins are obtained by diagonalising the Fermi energy matrix. Some of the overtones and combination bands of the *s-cis* and *s-trans* conformers of chlorocarbonyl ketene are given in Table 4. No experimental values are available for these bands for comparison. The errors in the calculation of the fundamental modes are reflected in the overtones and combination bands. Thus, the results of B97-1/6-311++G** and B3LYP/6-311++G** in the anharmonic approximation are quite close to each other. RHF/ 6-311++G** calculations give very high values for these bands which compare with the DFT values only after sca-

ling with a factor of 0.92. DFT calculations predict Fermi resonance between ν₅ and 2ν₁₃ and ν₄ and 2ν₁₂ frequencies of the *s-trans* conformer. The deperturbed values of these frequencies are 1119.7 and 1123.3 cm⁻¹ and 1362.6 and 1344.3 cm⁻¹, respectively. Similarly, in the case of the *s-cis* conformer, the Fermi resonance is expected between ν₂ and 2ν₅ and ν₅ and ν₁₃ + ν₁₄. The deperturbed values of these frequencies in B97-1/6-311++G** are 2205.0 and 2166.5 cm⁻¹ and 1085.2 and 1076.2 cm⁻¹, respectively.

3. 4. Spectroscopic Constants

Spectroscopic constants namely, the anharmonic constants and rotational and rotation-vibrational coupling constants given in Tables 5 and 6, respectively, may be helpful in future experimentation as no such experimental data is currently available for the *s-trans* and *s-cis* conformers of chlorocarbonyl ketene which, as mentioned earlier, has astrophysical importance.¹⁰

It follows from Table 5 that B97-1/6-311++G** and B3LYP/6-31+G** calculations give a negative value for the diagonal anharmonic constants for the stretching mo-

des of both the *s-trans* and *s-cis* conformers of chlorocarbonyl ketene. However, in the case of frequencies ν_8 and ν_{10} , which have substantial contribution from C=C=O deformation modes, they have small positive values. Lower anharmonic frequencies in both the cases suggest that the cumulative effect of the anharmonic contributions from the non-diagonal terms exceed the contribution of the diagonal terms. A similar observation was made in the case of ketene²⁸.

The rotational constants of the *s-trans* and *s-cis* conformers of chlorocarbonyl ketene, including terms due to quartic centrifugal distortion constants are given in Table 6 and compared with the values reported by Badawi et al.¹⁵ and Al-Saadi et al.³² The table also contains rotation-vibration coupling constants based on second order perturbative vibrational treatment. Rotational constants obtained from different methods and basis sets agree with each other. Present values of rotational constants A_0 , B_0 , C_0 , which contain effects due to zero point vibrations and centrifugal distortions, are quite close to those reported by Al-Saadi et al.³² Badawi et al.,¹⁵ however, report very different values for the rotational constants and seem to be in error.

4. Conclusions

Conformational and vibrational spectral studies have been conducted on the *s-trans* and *s-cis* conformers of chlorocarbonyl ketene by different *ab initio* and density functional theory methods. It is found that the *s-trans* conformer is more stable than the *s-cis* conformer by ~ 0.69 kcal/mol.; this value is in closer agreement with the experimental estimate 0.9–1.3 kcal/mol. than the other previously reported values^{9,15}. The vibrationally averaged bond lengths and bond angles, both for the cis and trans conformers, are within 0.005 Å and 0.14°, respectively, of the equilibrium geometry. The *ab initio* and DFT based anharmonic vibrational analysis using second-order perturbation theory involving quartic, cubic and semidiagonal quartic force constants provides reliable frequencies (r.m.s. deviation ± 20 cm⁻¹) and assignments to the vibrational bands. DFT calculations using the same method and basis function for the harmonic frequencies and anharmonic corrections give frequencies in better agreement with the experimental values than those in which the harmonic frequencies from a high level quantum mechanical method (B97-1/aug-cc-pVTZ) are coupled with anharmonic corrections from a cheap model (B3LYP/6-31+G**); the r.m.s. deviation in the latter case is ± 47 cm⁻¹. The errors in the calculation of the fundamental modes are reflected in the overtones and combination bands. Thus, the *ab initio* anharmonic frequencies from RHF/6-311++G** calculations needed scaling by a factor of 0.92 to match the DFT values. Some spectroscopic constants namely, the anharmonic constants, rotational constants and rota-

tion-vibration coupling constants of the two conformers have been calculated by density functional theory and compared with literature, where available.

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Povzetek

V prispevku obravnavamo kvantno kemijsko študijo struktur in vibracijskih spektrov za stabilne konformacije klorokarbonil ketena. *Ab initio* izračuni so bili izvedeni v okviru DFT približka upoštevajoč popravke drugega reda teorije motenj. Izkazalo se je, da je s-trans konformacija stabilnejša kot s-cis konformacija za 0.69 kcal/mol. Povprečna vibracijska dolžina in kot, ki merita odmik od ravnovesja, sta okoli 0,005 Å in 0.14°. Nekatere spektroskopske konstante, kot so anharmonska konstanta, rotacijska konstanta in rotacijsko-vibracijska sklopitvena konstanta so bile izračunane za obe konformaciji v okviru DFT približka in primerjane s podatki iz literature.

Coriolis coupling constants $Z(I,J)$ (cm^{-1}) for trans-chlorocarbonyl ketene using B97-1/6-311++G**

I	J	Z(I,J)	I	J	Z(I,J)	I	J	Z(I,J)
X-Component			Y-Component			Z-Component		
12	1	0.27851	12	1	0.52459	4	1	0.61378
12	2	-0.01762	12	2	-0.01618	4	2	-0.12471
12	3	-0.75576	12	3	0.15305	4	3	-0.07789
12	4	0.45949	12	4	-0.32105	5	1	-0.70704
12	5	-0.29309	12	5	-0.22957	5	2	0.04843
12	6	-0.06110	12	6	-0.60637	5	3	-0.39567
12	7	0.15758	12	7	-0.22307	5	4	0.08412
12	8	0.11834	12	8	0.33309	6	1	0.22958
12	9	0.05607	12	9	-0.04872	6	2	-0.33829
12	10	-0.08961	12	10	-0.11961	6	3	-0.55650
12	11	-0.01294	12	11	-0.01650	6	4	0.38226
13	1	0.08283	13	1	0.13384	6	5	0.32143
13	2	-0.95479	13	2	0.03892	7	1	0.15185
13	3	0.13960	13	3	-0.01522	7	2	0.71060
13	4	0.20772	13	4	-0.17091	7	3	-0.23437
13	5	0.04260	13	5	0.15043	7	4	-0.19740
13	6	-0.05304	13	6	-0.32991	7	5	-0.24506
13	7	-0.01336	13	7	0.77006	8	1	-0.13326
13	8	-0.09449	13	8	-0.21401	8	2	-0.08079
13	9	-0.01840	13	9	-0.08941	8	3	0.56671
13	10	0.06886	13	10	0.41415	8	4	0.27130
13	11	0.00817	13	11	-0.03688	8	6	-0.27821
14	1	0.36782	14	1	0.68296	8	7	-0.10273
14	2	0.19559	14	2	0.03536	9	2	-0.12690
14	3	0.49028	14	3	-0.07393	9	3	-0.31633
14	4	0.40267	14	4	-0.11754	9	4	-0.20772
14	5	-0.50199	14	5	0.53175	9	5	-0.11554
14	6	0.23588	14	6	0.35381	9	6	-0.08037
14	7	0.04292	14	7	-0.04699	9	7	-0.37831
14	8	-0.23474	14	8	-0.23603	9	8	-0.10846
14	9	-0.10957	14	9	0.06390	10	1	0.13962
14	10	0.20005	14	10	-0.20389	10	2	0.54996
14	11	0.08567	14	11	0.03890	10	4	0.39176
15	1	0.04478	15	1	0.09332	10	5	0.32518
15	2	-0.17880	15	2	0.01734	10	9	-0.55389
15	3	-0.30862	15	3	-0.00768	11	2	-0.16696
15	4	-0.62817	15	4	0.11840	11	3	-0.15392
15	5	-0.44628	15	5	0.20096	11	4	-0.36505
15	6	0.37470	15	6	0.20908	11	5	-0.22677
15	7	-0.09489	15	7	-0.09389	11	6	0.26687
15	8	-0.16685	15	8	0.46016	11	7	0.16669
15	9	-0.18548	15	9	-0.49812	11	8	-0.11859
15	10	0.24804	15	10	0.36728	11	9	-0.57267
15	11	0.06202	15	11	-0.53780	11	10	-0.32703

Coriolis coupling constants $Z(I,J)$ (cm^{-1}) for cis- chlorocarbonyl ketene using B97-1/6-311++G**

I	J	Z(I,J)	I	J	Z(I,J)	I	J	Z(I,J)
X-Component			Y-Component			Z-Component		
12	1	0.18315	12	1	0.34544	4	1	0.65381
12	2	-0.06893	12	2	0.21898	4	2	0.15854
12	3	0.52097	12	3	0.59934	4	3	0.29114
12	4	0.61464	12	4	-0.38719	5	1	-0.67227
12	5	-0.13136	12	5	-0.10169	5	2	-0.19541
12	6	-0.45197	12	6	0.00791	5	3	0.08994
12	7	-0.24864	12	7	0.52240	5	4	0.13316
12	8	-0.08354	12	8	0.16800	6	1	0.25928
12	9	-0.12818	12	9	-0.03567	6	2	-0.24993
12	10	0.07501	12	10	0.09946	6	3	-0.39453
12	11	-0.01089	12	11	0.03001	6	4	0.40812
13	1	-0.06299	13	1	-0.10303	6	5	0.34663
13	2	-0.53075	13	2	0.77514	7	2	0.41755
13	3	-0.05194	13	3	-0.21138	7	3	-0.72753
13	4	0.05249	13	4	0.08523	7	4	-0.27211
13	5	-0.02769	13	5	-0.26706	7	5	-0.28310
13	6	-0.13499	13	6	-0.22560	8	1	0.19897
13	7	0.56438	13	7	0.15073	8	2	-0.73613
13	8	-0.56755	13	8	-0.40990	8	3	-0.20424
13	9	-0.09707	13	9	-0.05325	8	4	-0.17435
13	10	-0.17968	13	10	-0.13333	8	6	0.09186
13	11	0.08691	13	11	0.05506	8	7	0.10719
14	1	0.41135	14	1	0.79542	9	2	-0.21730
14	2	-0.05982	14	2	-0.01203	9	3	-0.34096
14	3	-0.30098	14	3	-0.32135	9	4	-0.04405
14	4	0.44243	14	4	-0.20640	9	5	-0.06506
14	5	-0.51969	14	5	0.27030	9	6	-0.40016
14	6	0.36717	14	6	-0.26904	9	8	0.10430
14	7	0.24863	14	7	-0.17812	10	1	0.08949
14	8	0.23128	14	8	-0.18310	10	2	-0.18471
14	9	0.14039	14	9	-0.03860	10	4	-0.11154
14	10	0.03052	14	10	-0.04987	10	6	0.33956
15	1	0.05636	14	11	-0.08132	10	7	0.03160
15	2	-0.12572	15	1	0.09699	10	9	-0.63194
15	3	0.02357	15	2	0.18698	11	2	0.26274
15	4	-0.28538	15	3	0.02903	11	3	-0.21489
15	5	-0.39962	15	4	0.32965	11	4	0.38972
15	6	0.07748	15	5	0.52614	11	5	0.50018
15	7	-0.33403	15	6	0.39344	11	6	0.07803
15	8	-0.20968	15	7	0.11725	11	7	0.35704
15	9	-0.10334	15	9	-0.47519	11	8	0.23250
15	10	0.27316	15	10	-0.04138	11	9	-0.42559
15	11	0.70178	15	11	0.41620	11	10	0.18526

Nielsen's centrifugal distortion constants (MHz) for s-cis and s-trans conformers of chlorocarbonyl ketene using B97-1/6-311++G**

Trans	Cis	
$D_J \times 10^{-3}$	0.157053	0.103174
$D_{JK} \times 10^{-2}$	0.648810	0.413465
$D_K \times 10^{-3}$	0.011333	0.037930
$R_5 \times 10^{-3}$	-0.772086	-0.555614
$R_6 \times 10^{-4}$	0.114969	0.011338