

COMPUTATIONAL STUDY OF SUBSTITUENT EFFECTS AND VIBRATIONAL ANALYSIS OF FORMYL HALOKETENES AND FORMYL METHYLKETENE

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الخلاصة:

تعتبر الكيتينات وسطا مستقرا في عدد كبير من التفاعلات العضوية الهامة حيث أن السلوك البنائي الفريد لهذه المركبات جعل منها حقلا رحبا للعديد من الأبحاث المعملية والنظرية في العقدين الأخيرين. لقد وُظفت حسابات *ab initio* النظرية في البحث الحالي لدراسة السلوك البنائي لمركبات الفورميل كلورو، الفورميل فلورو والفورميل ميثيل كيتين باستخدام مستوى الحسابات DFT-B3LYP/6-311++G**. لقد وُجد في المركبات الثلاثة أنفة الذكر أن الشكل البنائي المستوي هو الأفضل حراريا مع حاجز عالٍ للطاقة اللازمة للانتقال من أحد الشكلين البنائين المستويين إلى الآخر. بالإضافة إلى ما سبق فقد تم حساب الأطياف الاهتزازية لخليط الـ *cis* و الـ *trans* للمركبات التي تحت الدراسة، وتم تحديد جميع صيغها الاهتزازية بناءً على القيم المحسوبة لتوزيع الطاقة الكامنة عبر إحداثيات التناظر في هذه المركبات، والمقارنة مع مركبات شبيهة.

ABSTRACT

The structural stability and conformational behavior of formyl fluoro-, formyl chloro- and formyl methylketene were investigated by utilizing *ab initio* calculations with the 6-311++G** basis set at the Density Functional (B3LYP) level. From our calculations, the three molecular systems were predicted to exist in the planar conformations with a relatively high energy barrier. The vibrational frequencies were computed at the DFT-B3LYP/6-311++G** level, and the calculated vibrational infrared and Raman spectra of the *cis-trans* mixtures of the three molecular systems were plotted. Complete vibrational assignments were made for the stable conformers of the molecules on the basis of normal coordinate calculations and derived potential energy distributions.

INTRODUCTION

The interesting structure and the reactivity behavior of several substituted ketenes have been the subject of many investigations in the past years [1-15]. The great attention paid to these molecular systems is a result of the important role they play in synthetic chemistry [1-10]. Mainly, ketenes are capable to undergo the (2+2) cycloaddition reactions with different unsaturated compounds to produce various types of four-membered ring compounds. Ketenes can also undergo nucleophilic addition reactions with different nucleophiles [1].

We recently investigated the structural stability and computed the vibrational spectra of two series of ketenes [11-15]. The stability of conjugated ketenes, such as formyl ketene [12], vinyl ketene [13] and halocarbonyl ketenes [14], were found to be largely governed by the conjugation effect that maintains the planar conformation and restricts the rotation around the C-C single bond. The energetic barrier in these molecules was predicted to be of the order of 10 kcal/mol. The two planar conformations in formyl ketene and halocarbonyl ketenes were predicted to be approximately of the same stability [12-14], while the relative energy in vinyl ketene was calculated to be much higher as compared to formyl derivatives. This difference in the magnitude of the relative energies is attributed to the repulsive hydrogen-hydrogen interaction in the *cis* conformation of vinyl ketene [13]. However, when conjugation is absent, mono-, di- and trifluoromethyl ketenes as well as chloromethyl ketene were found to have a considerably lower rotational barrier (about 3 kcal/mol) [11,15]. In such non-conjugated systems the *gauche* conformation is expected to be a stable form. Steric effect, the intramolecular electrostatic attraction and the molecular orbital destabilization were thought to play competitive roles in controlling the stability of this series of ketenes [11,15].

As a continuation of our interest in ketenes, we investigated in the present work the conformational behavior and structure of formyl fluoroketene, formyl chloroketene and formyl methylketene for the purpose of comparison. In this work, we carried out *ab initio* optimizations of the energies for all the stable conformers as well as the transition states of the molecules. From the data the relative conformational stabilities and the barriers to internal rotations were determined at the DFT-B3LYP level. Additionally, vibrational frequencies were calculated, and complete assignments were made for all the normal modes by using normal coordinate calculations. We also calculated the vibrational infrared and Raman spectra of the mixtures of the stable conformers of each molecule. The results of the work are presented herein.

AB INITIO CALCULATIONS

Ab initio density functional calculations were carried out using the GAUSSIAN 98 program, running on an IBM RS/6000 43P model 260 workstation and the B3LYP/6-311++G** basis set. From full energy optimizations and calculations of energy barriers, the *cis* conformation (the carbonyl oxygen eclipses the ketenic group) and the *trans* conformation of formyl fluoro-, formyl chloro- and formyl methylketene were found to be the energy minima (Figures 1 and 2). The optimized structural parameters were used to compute the vibrational frequencies of the three molecules at the DFT-B3LYP level of calculations. Normal coordinate analyses were then carried out for the stable conformers of the molecules to derive the potential energy distributions (PEDs). Complete sets of internal coordinates (Figure 1) were used to form symmetry coordinates (Tables 1 and 2).

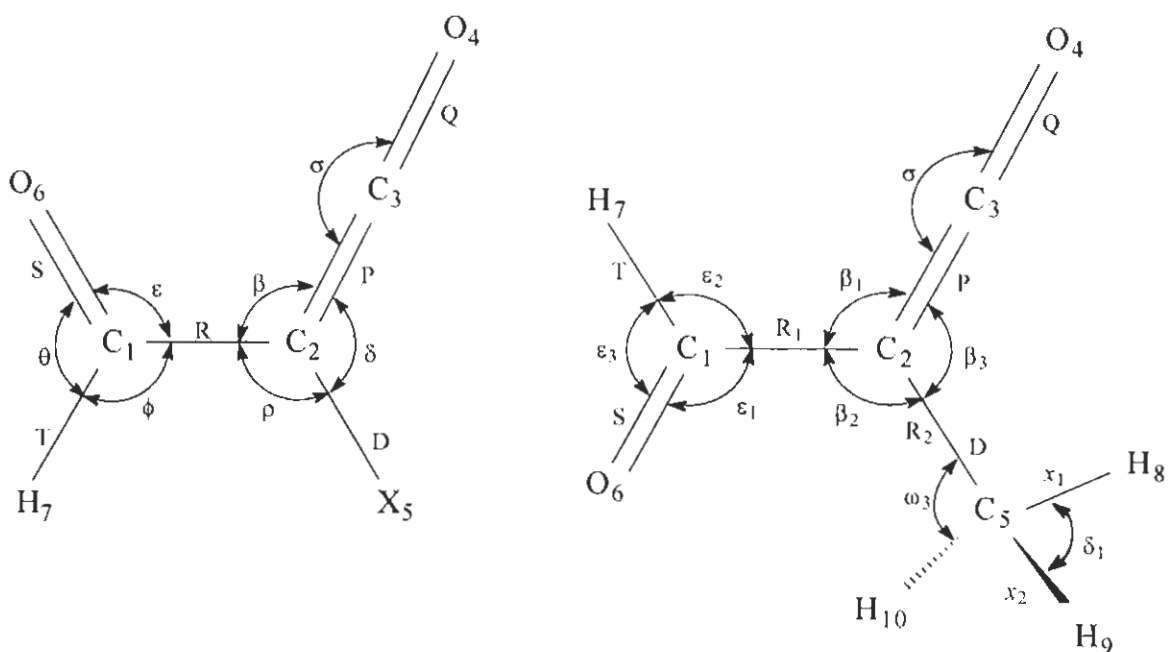


Figure 1. Atom numbering and internal coordinate definitions for formyl fluoroketene ($X=F$) and formyl chloroketene ($X=Cl$) in the cis form (left), and formyl methylketene in the trans form (right).

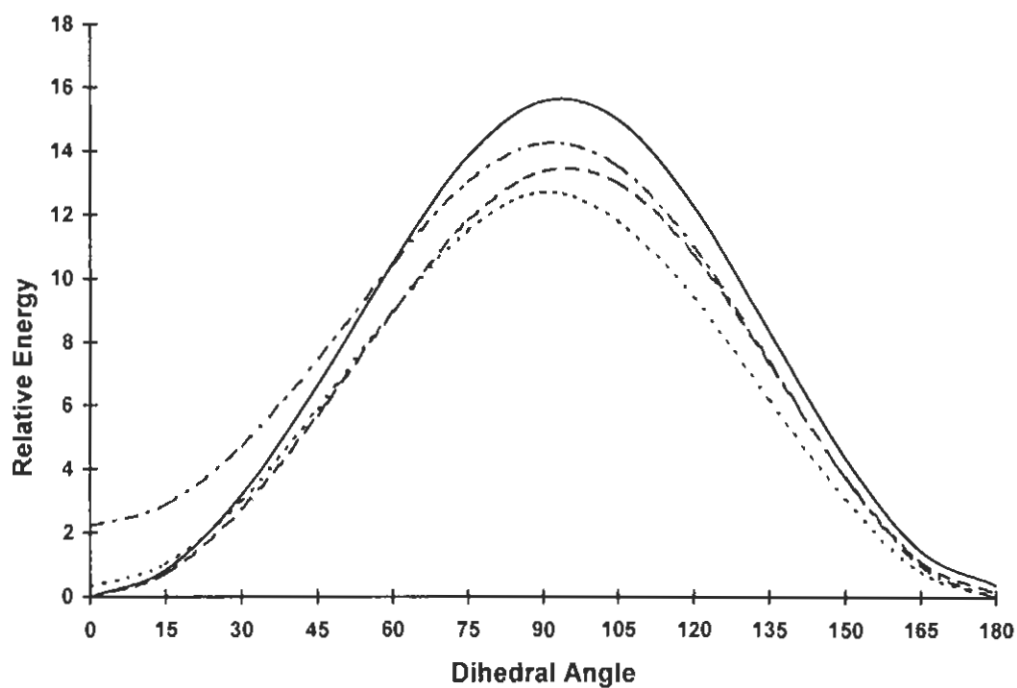


Figure 2. Potential functions for the asymmetric torsions in formyl fluoroketene (solid), formyl chloroketene (dashed), formyl methylketene (dashed-dotted) and formyl ketene (dotted) as determined by *ab initio* calculations with the B3LYP/6-311++G** level, the potential function of formyl ketene was obtained from Ref. [12].

Table 1. Symmetry coordinates for formyl fluoroketene (X=F) and formyl chloroketene (X=Cl).

Description			Symmetry Coordinate ^{a,b}
A'	C-X	stretch	$S_1 = D$
	C-H	stretch	$S_2 = T$
	C=O	stretch	$S_3 = S$
	C-C	stretch	$S_4 = R$
	C=C=O	antisymmetric stretch	$S_5 = P - Q$
	C=C=O	symmetric stretch	$S_6 = P + Q$
	C=C-X	deformation (scissor)	$S_7 = \beta + \rho - 2\delta$
	C-H	in-plane bend	$S_8 = \varphi - \theta$
	C-C=O	in-plane bend	$S_9 = \varphi + \theta - 2\varepsilon$
	C=C-X	in-plane bend (rock)	$S_{10} = \beta - \rho$
	C=C=O	in-plane bend	$S_{11} = \sigma$
A''	C=C-X	out-of-plane bend (wag)	$S_{12} = \pi$
	C-H	out-of-plane bend (wag)	$S_{13} = \omega$
	C=C=O	out-of-plane bend (wag)	$S_{14} = \chi$
		asymmetric torsion	$S_{15} = \tau$

^a Not normalized.

^b See ref. [12,14] for the definitions of wag and torsion internal coordinates.

Table 2. Symmetry coordinates for formyl methylketene.

Description			Symmetry Coordinate ^a
A'	CCC	symmetric stretch	$S_1 = R_1 + R_2$
	CCC	antisymmetric stretch	$S_2 = R_1 - R_2$
	C=O	stretch	$S_3 = S$
	C-H _{ald}	stretch	$S_4 = T$
	C=C=O	antisymmetric stretch	$S_5 = P - Q$
	C=C=O	symmetric stretch	$S_6 = P + Q$
	CH ₃	antisymmetric stretch	$S_7 = 2x_1 - x_2 - x_3$
	CH ₃	symmetric stretch	$S_8 = x_1 + x_2 + x_3$
	C-H _{ald}	in-plane bend	$S_9 = \varepsilon_2 - \varepsilon_3$
	C-C=O	in-plane bend	$S_{10} = \varepsilon_2 + \varepsilon_3 - 2\varepsilon_1$
	C ₁ -C ₂ =C ₃	in-plane bend	$S_{11} = 2\beta_1 - \beta_2 - \beta_3$
	C ₅ -C ₂ =C ₃	in-plane bend	$S_{12} = \beta_2 - \beta_3$
	CH ₃	antisymmetric deformation	$S_{13} = 2\delta_3 - \delta_1 - \delta_2$
	CH ₃	symmetric deformation	$S_{14} = \delta_1 + \delta_2 + \delta_3 - \omega_1 - \omega_2 - \omega_3$
	CH ₃	in-plane bend (rock)	$S_{15} = 2\omega_1 - \omega_2 - \omega_3$
	C=C=O	in-plane bend	$S_{16} = \sigma$
A''	C=C=O	out-of-plane bend (wag)	$S_{17} = \pi_1$
	C ₅ -C ₂ =C ₃	out-of-plane bend (wag)	$S_{18} = \pi_2$
	C-H _{ald}	out-of-plane bend (wag)	$S_{19} = \pi_3$
	CH ₃	antisymmetric stretch	$S_{20} = x_2 - x_3$
	CH ₃	antisymmetric deformation	$S_{21} = \delta_1 - \delta_2$
	CH ₃	rock	$S_{22} = \omega_2 - \omega_3$
	CH ₃	torsion	$S_{23} = \tau_1$
		asymmetric torsion	$S_{24} = \tau_2$

^a Not normalized.

The normal coordinate analyses were previously described in details [11-15]. The computation of the potential energy distributions (PEDs) has been also described in our previous work [11-15].

At 300 K, The mixture of formyl fluoroketene contains 72% *cis* and 28% *trans*, and that of the chloride derivative contains 60% of the *cis* and 40% of the *trans* conformer. However, at 300 K, the percentage of the *trans* conformer of formyl methylketene was calculated to be of 97%, with only 3% of the less preferably *cis* conformer.

RESULTS AND DISCUSSION

The stability of some haloketenes, especially, chlorine substituted vinylketenes [16], methylchloroketene [17], dichloroketene [18,19] and fluoroketene [20], has motivated us to investigate the effect of halogen and methyl group substitution on the structural stability of formyl ketene. We have recently investigated the conformational stability of formyl ketene [12]. The molecule was predicted to exist only in the planar forms as a result of the pronounced conjugation effect between the carbonyl and the ketene moieties [12]. From the energy optimization at RHF and MP2 levels, the *cis* conformer was calculated to be slightly higher in energy than the *trans* conformer. However, at the DFT-B3LYP level the *trans* form was predicted to be the more thermodynamically preferred conformation for formyl ketene. It was concluded that the predicted conformational behavior by DFT calculations is more consistent with the idea that eclipsing the two hydrogen atoms in the *cis* form should destabilize the molecule in this conformation. Also, the carbonyl oxygen, not the aldehydic hydrogen, should eclipse the ketenic hydrogen in the *trans* conformation of the molecule [12].

In the present work we studied the effect of some bulky substituents on the direction of the conformational equilibrium and on the height of the rotational barrier in formyl ketene. From the calculated potential functions, the stability of the *cis* conformer relative to the *trans* was predicted to be in the order: fluoride > chloride > formyl > methyl, as shown in Figure 2. Furthermore, the *cis* \leftrightarrow *trans* conformational equilibrium was predicted to reverse as going from the halogen (OHC-CX=C=O) to the formyl (OHC-CH=C=O) to the methyl (OHC-CCH₃=C=O) derivatives. This means that the conformational stability of these molecules is more controlled by dipole-dipole interactions than by steric hinderance. Therefore, the stability of the *cis* conformation in formyl haloketenes is attributed to the repulsive interaction between the carbonyl oxygen C=O and the fluorine or the chlorine atoms. Similarly, the interaction between the C=O and the methyl CH₃ groups in formyl methylketene stabilizes the *trans* conformer, but not the *cis* form of this molecule. In formyl methylketene, the *cis* conformation was predicted to be of about 2 kcal/mol more stable than the *trans* form. Additionally, the conformation in which the carbonyl oxygen is staggered to the methyl moiety in the *trans*-formyl methylketene was found from the calculations of the methyl torsion to be only of about 0.12 kcal/mol lower in energy than the configuration when the C=O is eclipsing one of the methyl hydrogen atoms.

It is interesting to notice that the calculated *cis-trans* barrier is to decrease as going from formyl fluoroketene (15.3 kcal/mol), to formyl chloroketene (13.1 kcal/mol), and finally to formyl methylketene (11.7 kcal/mol). This decrease in the rotational barriers can be explained by the fact that electron-withdrawing substituents strengthen the partial π character along the C-C bond as compared to that in formyl ketene [12]. This certainly leads to a noticeable restriction in the internal rotation in formyl fluoroketene and formyl chloroketene, and hence to

an increase in the barrier. In the case of formyl methylketene, the electron-repelling methyl group seems to slightly influence the π character of the bond as compared to that in formyl ketene, in which the *cis-trans* barrier in both molecules was very comparable and of about 12 kcal/mol. However, the size of the *trans-cis* barrier was of about 14 kcal/mol. Only, the methyl substitution in formyl methylketene was shown to significantly influence the relative stability of the *cis* and the *trans* conformers of the molecule but not, in the same extent, the size of the rotational barrier.

The vibrational wavenumbers of the stable forms of formyl haloketenes and formyl methylketene were calculated at the B3LYP/6-311++G** level, and the vibrational infrared and Raman spectra of the mixtures of the stable conformations in the three molecular systems were plotted as shown in Figures 3 and 4. The vibrational assignments of most of the fundamental vibrations of the investigated systems in their conformations of the lowest energy were straightforward performed based on the calculated PED as shown in Tables 3-5. Some of the calculated modes especially the bending ones were predicted to mix with other vibrations.

In formyl haloketenes, there is only one C-H stretching mode (S_1) that is associated with the aldehydic CHO group. This stretch was calculated to be of the highest Raman activity in the Raman spectra of formyl fluoro- and formyl chloroketenes (Tables 3 and 4). For formyl methylketene, the antisymmetric CH_3 stretching mode (S_7) was calculated to have the highest frequency at 3115 cm^{-1} and 3125 cm^{-1} for *cis* and *trans* formyl methylketenes, respectively. The CH_3 symmetric stretch (S_8) in the methyl derivative was assigned to the band (ν_2) with the highest Raman activity based on the calculated PED values as shown in Table 5. The second highest Raman activity in the formyl methylketene spectrum was assigned to the C-H_{ald} stretching mode (S_4) with a PED value of 100% in the *trans* conformer (Table 5).

The vibrational mode with the highest calculated infrared intensity in the halo molecules in the low energy conformer was calculated to have a PED of 94% antisymmetric $\text{C}=\text{C}=\text{O}$ stretch that agrees very well with the observed very intense band at 2158 cm^{-1} in the infrared spectrum of chlorine substituted vinylketene [16]. The symmetric $\text{C}=\text{C}=\text{O}$ stretch (S_6) was assigned to the calculated lines at 1359 cm^{-1} (PED value of 49% S_6) and at 1334 cm^{-1} (PED value of 56% S_6) in the spectra of the *cis* fluoro- and chloroketenes, respectively. Similarly, in the infrared spectrum of formyl methylketene, the most intense band at 2203 cm^{-1} was assigned with confidence to the antisymmetric $\text{C}=\text{C}=\text{O}$ stretching mode with a 95% PED value for the *trans* form (Figure 3). The experimental result for the same vibration in *trans*-chlorocarbonyl ketene was observed at 2160 cm^{-1} [5]; which supports our prediction.

The situation was more complex for the bending modes, since some of them were calculated to have a high degree of mixing with other vibrations, such as ν_8 and ν_{10} in formyl fluoroketene. Therefore, we made only tentative assignments for the clear spectral features of the bendings in the vibrational spectra of the molecules.

The in-plane C-H_{ald} bending was assigned based on the derived PED values to the wavenumbers ν_4 in formyl halo- and ν_7 in formyl methylketene, respectively (Tables 3-5). The calculated CH_3 in-plane bending modes in formyl methylketene were found to follow the order: antisymmetric deformation (S_{13}) > scissor (S_{14}) > rocking (S_{15}) and were assigned based on the calculated PEDs to the wavenumbers ν_6 , ν_8 and ν_{11} , respectively. The predicted order at the DFT-B3LYP level is noticed to be in fair agreement with the experimental values observed of methacryloyl chloride [21].

The lowest vibrational frequency in the spectra of formyl haloketenes is the asymmetric torsion. This mode (ν_{15}) is predicted at 175 cm^{-1} (for the *cis*) and 157 cm^{-1} (for the *trans*) in the spectra of formyl fluoroketene, while is calculated at 206 cm^{-1} and 260 cm^{-1} for *cis* and *trans*-formyl chloroketene respectively. In the case of the methyl derivative, the asymmetric torsion (S_{24}) was calculated at 57 cm^{-1} for the *cis* and 82 cm^{-1} for the *trans* form.

Table 3. Calculated vibrational frequencies (cm^{-1}) at the B3LYP/6-311++G level for the low energy conformer (the *cis* form) of formyl fluoroketene.**

Symm.	Num.	Freq.	IR Intensity ^a	Raman Activity	Depol. Ratio	Obs ^b	PED ^c
A'	ν_1	2927	63.9	199.6	0.3	2800	100% S ₂
	ν_2	2229	688.2	9.9	0.7		94% S ₅
	ν_3	1737	295.8	36.3	0.4	1724	89% S ₃
	ν_4	1407	55.2	14.1	0.1	1360	73% S ₈
	ν_5	1359	137.5	22.0	0.2		49% S ₆ , 25% S ₄
	ν_6	1229	112.2	4.7	0.7	1158	27% S ₄ , 55% S ₁ , 12% S ₈
	ν_7	790	58.0	9.9	0.2		28% S ₉ , 25% S ₆ , 21% S ₄
	ν_8	710	13.1	2.5	0.2		27% S ₁ , 25% S ₁₁ , 19% S ₇ , 10% S ₆
	ν_9	500	0.6	6.0	0.4	564	30% S ₉ , 19% S ₄ , 19% S ₇ , 17% S ₁₁ , 10% S ₁₀
	ν_{10}	270	8.5	1.1	0.4		32% S ₇ , 26% S ₁₀ , 23% S ₁₁ , 17% S ₉
	ν_{11}	136	3.0	3.6	0.6		44% S ₁₀ , 23% S ₁₁ , 22% S ₇ , 12% S ₉
A''	ν_{12}	995	0.2	4.1	0.8	927	96% S ₁₃
	ν_{13}	526	15.7	1.7	0.8		88% S ₁₄
	ν_{14}	278	0.1	0.4	0.8		96% S ₁₂ , 10% S ₁₄
	ν_{15}	206	16.1	4.0	0.8	158	97% S ₁₅

^a Infrared intensities and Raman activities are calculated in Km mol^{-1} and $\text{A}^1\text{ amu}^{-1}$, respectively.

^b Observed IR frequencies for *trans*-acrolein [22].

^c PED values are obtained by using calculated frequencies at the B3LYP level.

From the calculated torsional frequencies of the investigated ketenes, it is noticed that they are influenced by the nature of the substituents. For example, the torsional frequency of the *cis* conformation was predicted to decrease in the order: fluoride (206 cm⁻¹) > chloride (175 cm⁻¹) > methyl (82 cm⁻¹). It is interesting to notice that this trend is similar to that of the calculated rotational barriers in the three molecular systems.

Table 4. Calculated vibrational frequencies (cm⁻¹) at the B3LYP/6-311++G level for the low energy conformer (the *cis* form) of formyl chloroketene.**

Symm.	Num.	Freq.	IR Intensity ^a	Raman Activity	Depol. Ratio	Obs ^b	PED ^c
A'	ν_1	2940	51.8	144.0	0.3	2800	100% S ₂
	ν_2	2230	783.9	12.6	0.6	(2158)	94% S ₅
	ν_3	1736	297.0	44.7	0.4	1724	92% S ₃
	ν_4	1403	10.1	5.9	0.1	1360	89% S ₈
	ν_5	1334	166.1	16.2	0.2		56% S ₆ , 26% S ₄
	ν_6	1065	45.5	4.6	0.7	1158	43% S ₄ , 31% S ₁ , 10% S ₆
	ν_7	788	65.2	10.9	0.2	564	39% S ₉ , 15% S ₁₁ , 15% S ₆ , 10% S ₁₀ , 10% S ₄
	ν_8	570	9.8	5.5	0.2		36% S ₁₁ , 39% S ₁ , 14% S ₇
	ν_9	446	1.1	7.6	0.2		28% S ₁ , 32% S ₉ , 21% S ₄ , 10% S ₁₁
	ν_{10}	216	4.3	3.1	0.7		46% S ₁₀ , 35% S ₇ , 11% S ₉
	ν_{11}	134	1.3	3.5	0.7		36% S ₇ , 33% S ₁₀ , 25% S ₁₁
A''	ν_{12}	999	0.0	3.2	0.8	927	98% S ₁₃
	ν_{13}	568	20.0	0.7	0.8		85% S ₁₄
	ν_{14}	250	2.0	0.5	0.8		62% S ₁₂ , 22% S ₁₅ , 16% S ₁₄
	ν_{15}	175	11.7	2.7	0.8	158	68% S ₁₅ , 30% S ₁₂

^a Infrared intensities and Raman activities are calculated in Km mol⁻¹ and Å⁴ amu⁻¹, respectively.

^b Observed IR frequencies for *trans*-acrolein [22].

^c PED values are obtained by using calculated frequencies at the B3LYP level.

Table 5. Calculated vibrational frequencies (cm⁻¹) at the B3LYP/6-311++G level for the low energy conformer (the *trans* form) of formyl methylketene.**

Symm.	Num.	Freq.	IR Intensity ^a	Raman Activity	Depol. Ratio	Obs ^b	PED ^e
A'	ν_1	3125	8.4	55.4	0.8	(3016)	99% S ₇
	ν_2	3043	16.2	166.6	0.0	2943	99% S ₈
	ν_3	2921	89.1	132.6	0.4	2831 ^c	100% S ₄
	ν_4	2203	911.1	16.6	0.7	2160 ^d	95% S ₅
	ν_5	1731	521.2	49.6	0.3	1752 ^c	90% S ₃
	ν_6	1503	8.9	3.7	0.7	1459	76% S ₁₃ , 11% S ₁₅
	ν_7	1443	1.4	0.9	0.4	1413 ^c	64% S ₉ , 13% S ₁₃ , 11% S ₆
	ν_8	1415	0.7	2.7	0.7	1365	100% S ₁₄
	ν_9	1340	1.3	19.7	0.2	1361 ^d	44% S ₆ , 21% S ₉
	ν_{10}	1244	134.3	2.4	0.5	1278	72% S ₂
	ν_{11}	1017	39.8	4.6	0.7	1023	69% S ₁₅ , 11% S ₆
	ν_{12}	795	31.5	9.1	0.1	883	58% S ₁ , 21% S ₁₀
	ν_{13}	665	6.6	3.4	0.4	827 ^d	56% S ₁₆ , 20% S ₁₁ , 12% S ₂
	ν_{14}	556	3.3	10.6	0.2	460	43% S ₁₀ , 18% S ₁ , 17% S ₆
	ν_{15}	238	8.6	1.4	0.7		76% S ₁₂ , 20% S ₁₀
	ν_{16}	161	8.5	1.9	0.7		62% S ₁₁ , 34% S ₁₆
A''	ν_{17}	3105	8.2	68.0	0.8	2976	100% S ₂₀
	ν_{18}	1476	9.6	7.5	0.8	1440	91% S ₂₁
	ν_{19}	1058	0.2	0.7	0.8	1055	80% S ₂₂ , 10% S ₁₉
	ν_{20}	983	0.0	1.1	0.8	1020 ^c	88% S ₁₉
	ν_{21}	563	9.9	1.9	0.8		91% S ₁₇
	ν_{22}	335	10.8	2.7	0.8		80% S ₁₈ , 15% S ₂₃
	ν_{23}	160	7.0	0.3	0.8	165	81% S ₂₃ , 11% S ₁₈
	ν_{24}	82	0.1	0.3	0.8	55	98% S ₂₄

^a Infrared intensities and Raman activities are calculated in Km mol⁻¹ and Å⁴ amu⁻¹, respectively.

^b Observed IR frequencies in the gas phase for methacryloyl chloride [21]; the value in brackets is an observed Raman frequency in the gas phase for the same molecule.

^c Observed IR frequencies for chloroacetaldehyde [23].

^d Observed IR frequencies for *trans*-chlorocarbonyl ketene in argon matrix [5].

^e PED values are obtained by using calculated frequencies at the B3LYP level.

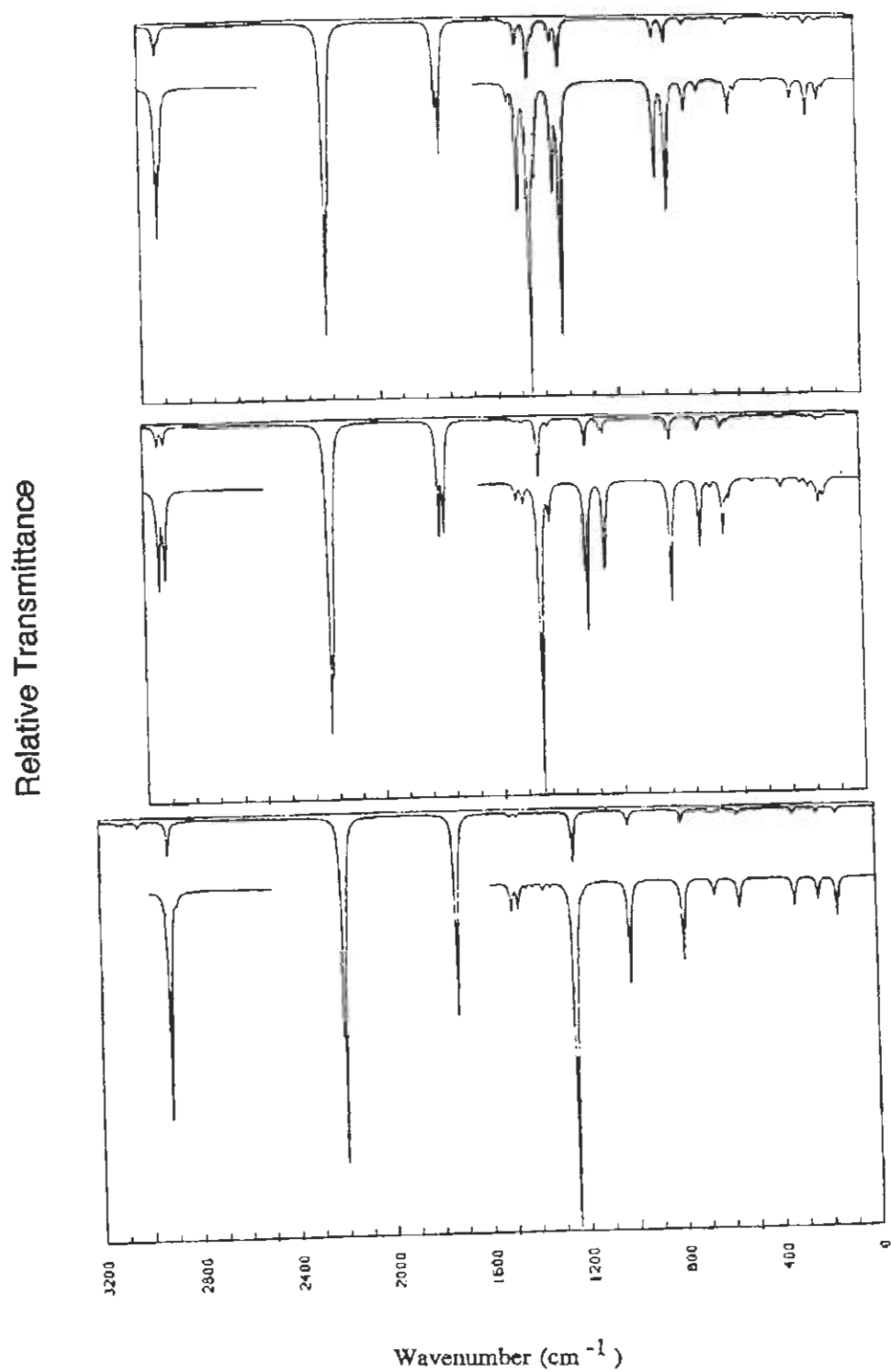
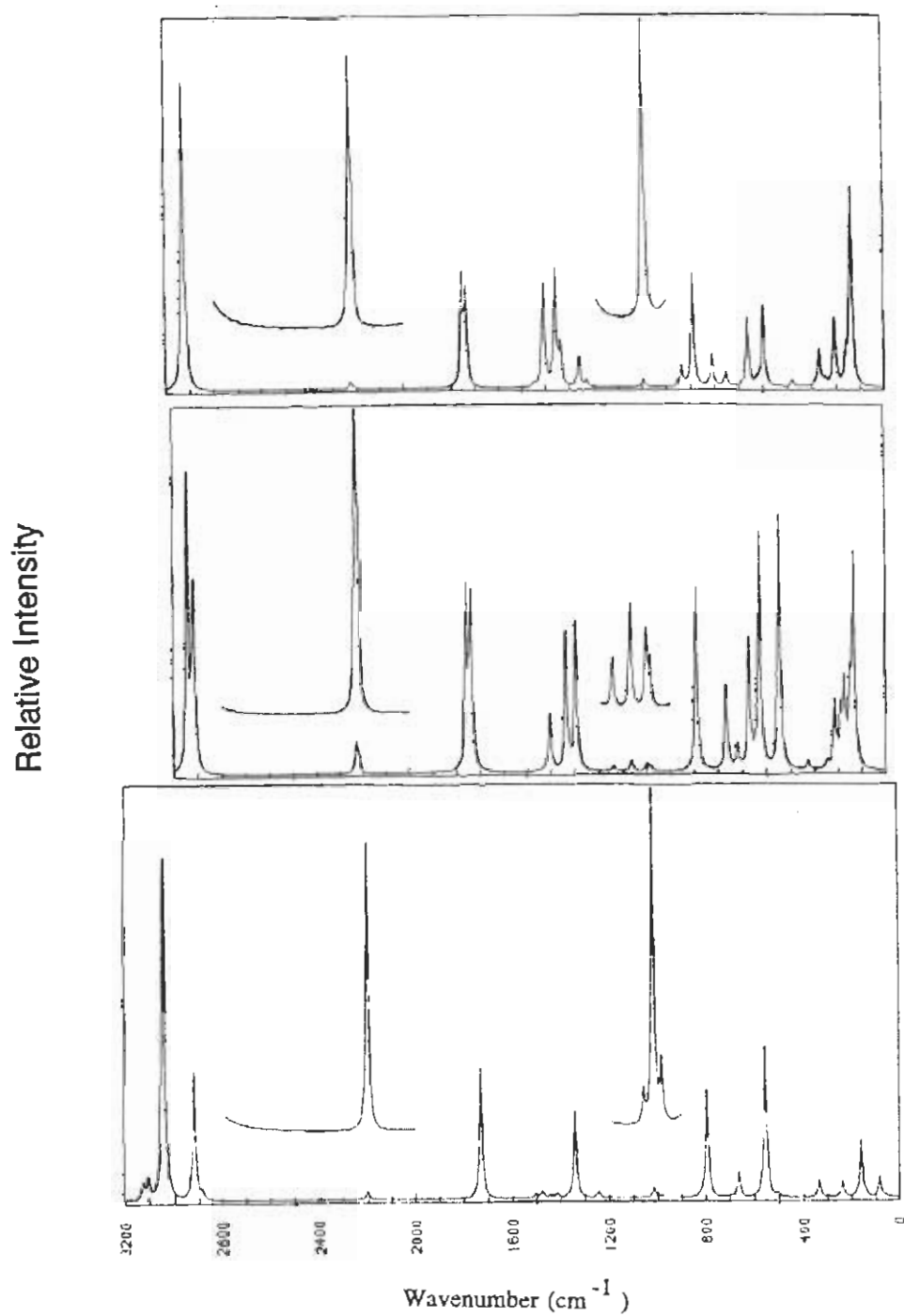


Figure 3: Calculated vibrational infrared spectra of the mixtures of the *cis* and the *trans* conformers of formyl fluoroketene (upper), formyl chloroketene (middle) and formyl methylketene (lower) at 300 K by the DFT-B3LYP/6-311++G** level.



*Figure 4: Calculated vibrational Raman spectra of the mixtures of the cis and the trans conformers of formyl fluoroketene (upper), formyl chloroketene (middle) and formyl methylketene (lower) at 300 K by the DFT-B3LYP/6-311++G** level.*

In conclusion, the *cis* and the *trans* conformations of formyl haloketenes were found to have very comparable energy difference with the conformational equilibrium being directed more to the side of the *cis* form. On the other hand, the *trans* conformer of formyl methylketene was predicted to have more thermodynamic stability than the *cis* form. We provided reliable vibrational assignment for the normal modes of the stable conformers of formyl fluoroketene, formyl chloroketene and formyl methylketene. The derived PED values helped us in making reasonable assignment for many of the vibrational modes, especially in the case of formyl methylketene.

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