

Wolfgang Förner · Hassan M. Badawi
Abdulaziz A. Al-Saadi · Sk. Asrof Ali

Vibrational assignments and derived potential energy distributions for tri- and difluoromethyl ketene by density functional calculations

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Abstract The structures of 3,3,3-trifluoromethyl ketene and 3,3-difluoromethyl ketene were studied by utilizing ab initio calculations with the 6-311++G** basis set at the (B3LYP) Density Functional level. Full optimization was performed for both molecules in their ground and transition states. Energy optimization of the systems under investigation shows that trifluoromethyl ketene exists only in the *cis* conformation (fluorine atom eclipses the ketene group). Difluoromethyl ketene was predicted to have two stable conformations: the *cis* (hydrogen atom eclipses the ketene group) and the *gauche* (fluorine atom eclipses the ketene group) form. The conformational stability of the molecules was found to be governed mainly by electrostatic and molecular orbital interactions. The vibrational frequencies were computed and complete assignments were provided on the basis of normal coordinate calculations and comparison with similar molecules. The potential energy distributions (PED) among symmetry coordinates were derived for the stable conformations of the two molecules.

Keywords Vibrational spectra and assignments · Rotational barriers · Trifluoromethyl ketene · Difluoromethyl ketene

Introduction

The interesting electronic structure and chemical reactivity of ketenes have been demonstrated in the literature. [1, 2, 3, 4, 5, 6, 7, 8, 9] Many simple substituted ketenic molecules have been isolated experimentally, characterized, and used to produce other ketenic and organic systems. [10, 11, 12, 13, 14, 15, 16, 17, 18, 19] The importance of ketenes as well as aldehydes [20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34] and isocyanates

[35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51] in synthetic chemistry has attracted attention in order to study their properties and structural stabilities for many years.

When conjugation is the predominant force, as in acrolein, [20, 23] formyl ketene [9] and formyl isocyanate, [51] the molecules are found to exist as a mixture of the planar *cis* and *trans* conformations. In these compounds, it is clear that the π - π interaction between the C=O bond and vinyl -C=C-, the ketene -C=C=O or the isocyanate -N=C=O groups greatly stabilizes the planar forms with a relatively high rotational barrier. In comparison, the C-N barrier in the isocyanates is much lower than the C-C barrier in the vinyl derivatives and ketenes. This significant difference between the two rotational barriers is due to the difference in the strength of the partial π character of the C-N bond as compared to that of the C-C bond. This difference is the result of the electronegativity change on going from the C-C to the C-N bond.

In the case of halomethyl isocyanates, the molecules were found to exist in only one conformation with minimum interaction between the halogen atom and the lone pair. [49, 50] For example, for chloromethyl isocyanate the *trans* conformation (chlorine atom eclipses the nitrogen lone pair) was found to be the stable conformation. [49] Difluoromethyl isocyanate was also predicted to exist in the *trans* conformation in which the hydrogen atom eclipses the lone pair. [50] In haloacetaldehyde systems, [24, 25] it was found that the planar *s-trans* conformation (the halogen atom eclipses the aldehydic hydrogen) is the form with the lowest energy. The steric effect (the repulsive force between the halogen atom and the carbonyl group) would destabilize the *cis* form of the molecule.

3,3,3-Trifluoromethyl ketene has been reported to be an important intermediate. [52, 53] The rate of hydration of the molecule was observed experimentally using UV spectroscopy. [53] Moreover, the reactivity of trifluoromethyl ketene was studied using molecular orbital methods, and the substituent effect of the CF₃ group in the

W. Förner · H.M. Badawi (✉) · A.A. Al-Saadi · Sk.A. Ali
Department of Chemistry,
King Fahd University of Petroleum and Minerals,
Dhahran 31261, Saudi Arabia
e-mail: hbadawi@kfupm.edu.sa

system was compared to a series of other substituents theoretically. [3] As a continuation of these studies, we investigated the structure of 3,3,3-trifluoromethyl ketene and 3,3-difluoromethyl ketene to understand the nature of the forces that control the conformational behavior of such important molecular systems. We carried out normal coordinate calculations by utilizing ab initio density functional calculations and derived the potential energy distributions among symmetry coordinates. The vibrational assignments of the normal modes were made for both molecules. The results of the work are presented herein.

Ab initio calculations

The GAUSSIAN 98 program [54] running on an IBM RS/6000 43P model 260 workstation, was used to carry out the LCAO-MO-SCF DFT-B3LYP calculations. The extended 6-311++G** basis set was employed to optimize the structures and predict the energies and dipole moments of trifluoromethyl ketene and difluoromethyl ketene in their stable conformations. The calculations were extended to the Density Functional B3LYP level. From full energy optimization the *cis* conformation of trifluoromethyl ketene was found to be the energy minimum for the system, whereas both the *cis* and the *gauche* conformations were the stable conformers in difluoromethyl ketene (Fig. 1). The calculated structural parameters in the molecules are shown in Tables 1 and 2. Moreover, the optimized geometrical parameters of trifluoromethyl ketene were compared to the corresponding values obtained from experimental data for trifluoroacetaldehyde [55] as in Table 1. The optimized structural parameters were used to compute vibrational frequencies at the DFT-B3LYP/6-311++G** level. Normal coordinate calculations were then carried out to derive the potential energy distributions for the molecules in their stable conformations.

Asymmetric torsional potential function

The potential scan for the internal rotation about the C–C single bond was obtained by allowing the OCCC dihedral angle (ϕ) to vary from 0° (*cis* position) to 180° (*trans* position). Full geometry optimizations at each of the fixed dihedral angles (ϕ) of 15° , 30° , 45° , 60° , 75° , 90° , 105° , 120° , 135° , 150° , and 165° were carried out at DFT-B3LYP/6-311++G** level in both systems. The barrier to interconversion and the relative energies in difluoromethyl ketene were calculated and are shown in Table 3. The torsional potential was represented as a Fourier cosine series in the dihedral angle (ϕ): $V(\phi) = V_0 + \sum(V_n/2)[1 - \cos(n\phi)]$, where V_0 is the relative energy at the *cis* conformation, and the potential coefficients from V_1 to V_6 are considered adequate to describe the potential function. The results of the energy optimizations were used to calculate the six coefficients by least-squares fitting for the systems (Table 4). The poten-

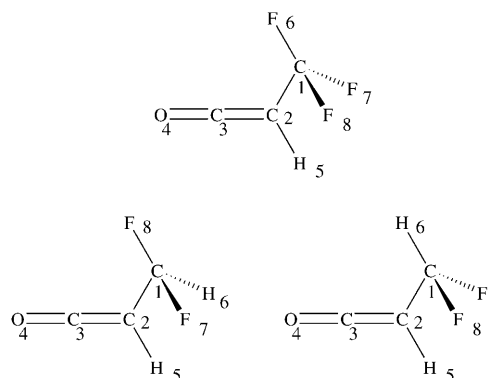


Fig. 1 Atom numbering for trifluoromethyl ketene (*upper*) and difluoromethyl ketene (*lower*) in the *cis* (*right*) and the *gauche* (*left*) conformations

Table 1 Calculated structural parameters, total dipole moment, and rotational constants for the *cis* conformation of trifluoromethyl ketene

Parameter ^a	B3LYP/6-311++G** <i>Cis</i>	Electron diffraction ^b <i>Cis</i>
Bond length (Å)		
$r(C_1-C_2)$	1.484	1.540±0.020
$r(C_2-C_3)$	1.317	
$r(C_3-O_4)$	1.154	
$r(C_2-H_5)$	1.081	1.09 (assumed to be constant)
$r(C_1-F_6)$	1.353	1.332±0.007
$r(C_1-F_7)$	1.354	1.332±0.007
$r(C_1-F_8)$	1.354	1.332±0.007
Bond angle (deg)		
($C_1C_2C_3$)	121.656	
($C_2C_3O_4$)	181.103	
($C_1C_2H_5$)	119.160	
($C_3C_2H_5$)	119.184	120.0 (assumed to be constant)
($C_2C_1F_6$)	111.681	
($C_2C_1F_7$)	112.104	
($C_2C_1F_8$)	112.104	
($F_6C_1F_7$)	107.342	108.7±1
($F_6C_1F_8$)	107.342	108.7±1
($F_7C_1F_8$)	105.922	108.7±1
($C_3C_2C_1F_6$)	0.0	0.0
($C_3C_2C_1F_7$)	120.510	
($C_3C_2C_1F_8$)	-120.510	
Dipole moment (Debye)		
μ_t	2.1	
Rotational constants (MHz)		
<i>A</i>	5428	
<i>B</i>	1681	
<i>C</i>	1657	

^a Calculated total energy, zero-point correction, and the sum of total and zero point energies (in Hartrees) of the *cis* conformer of trifluoromethyl ketene at DFT-B3LYP/6-311++G** level are -489.79721, 0.03794, and -489.75927, respectively

^b Data was obtained for trifluoromethylacetaldehyde (fluoral), see ref [55]

tial functions of trifluoromethyl ketene and difluoromethyl ketene are shown in Fig. 2.

Vibrational frequencies and normal coordinate analyses

Both trifluoromethyl ketene and difluoromethyl ketene in their *cis* conformations have C_s symmetry. The 18 vibrational modes span the irreducible representations: 12 A' and 6 A'' . The A' modes should be polarized while the A'' modes are depolarized in the Raman spectra of the liquid. However, the *gauche* conformation in difluoromethyl ketene has C_1 symmetry. All the eighteen vibrational modes in difluoromethyl ketene belong to the A

Table 2 Calculated structural parameters, total dipole moment, and rotational constants for the *cis* and *trans* conformations of difluoromethyl ketene

Parameter	B3LYP/6-311++G**	
	<i>Cis</i>	<i>Gauche</i>
Bond length (Å)		
$r(C_1-C_2)$	1.484	1.489
$r(C_2-C_3)$	1.314	1.316
$r(C_3-O_4)$	1.157	1.156
$r(C_2-H_5)$	1.083	1.082
$r(C_1-H_6)$	1.091	1.092
$r(C_1-F_7)$	1.377	1.380
$r(C_1-F_8)$	1.377	1.372
Bond angle (deg)		
$(C_1C_2C_3)$	121.859	122.084
$(C_2C_3O_4)$	179.996	180.802
$(C_1C_2H_5)$	119.425	119.629
$(C_2C_1H_6)$	114.020	113.460
$(C_2C_1F_7)$	110.651	111.223
$(C_2C_1F_8)$	110.651	110.579
$(C_3C_2C_1H_6)$	0.0	131.508
$(C_3C_2C_1F_7)$	121.707	119.954
$(C_3C_2C_1F_8)$	-121.717	-121.680
Dipole moment (Debye)		
μ_t	1.4	2.8
Rotational constants (MHz)		
A	8815	7928
B	1906	2259
C	1690	1962

Table 3 Computed total, zero-point corrections (Hartrees), relative energies, and rotational barriers (kcal mol⁻¹) in difluoromethyl ketene

	B3LYP/6-311++G**		
	<i>Cis</i>	<i>Gauche</i> ^a	<i>TS</i> ^b
Total energy	-390.51751	-390.51622	-390.51402
Relative energy	0.80949		
<i>cis-gauche</i> barrier	2.19001		
<i>gauche-cis</i> barrier	1.38052		
Zero-point correction	0.04634	0.04629	0.04599
Sum of total and zero-point energies	-390.47118	-390.46993	-390.46803
Corrected relative energy	0.78439		
Corrected <i>cis-gauche</i> barrier	1.97666		
Corrected <i>gauche-cis</i> barrier	1.19227		

^a The CCCO dihedral angle of the *gauche* conformer was calculated to be 131.51°

^b The CCCO dihedral angle of the transition state was calculated to be 67.57°

representation and are polarized in the Raman spectrum of the liquid.

Normal coordinate analyses were carried out for the stable conformers of the molecules in order to provide a complete assignment of the fundamental vibrational frequencies. A computer program was written for this purpose by following Wilson's method. [56] The cartesian coordinates for the stable conformers together with the normal modes (in cartesian coordinates) and the frequencies from the GAUSSIAN 98 output were used as an input in the program. A complete set of internal coordinates (Tables 5 and 6) was used to form symmetry coordinates (Tables 7 and 8) in our molecular systems.

The normal modes were next transformed to mass-weighted cartesian coordinates, which were then used to calculate the force constant matrix. This was diagonalized and its eigenvectors and eigenvalues were used in the further calculations. Following this step the force constant matrix was transformed to internal coordinates. To ensure correctness, this transformation was checked numerically in both directions. At this point the force constant matrix in internal coordinates could be scaled if desired, back-transformed to mass weighted cartesians and diagonalized again to get scaled frequencies and normal modes. The matrix was finally transformed to symmetry coordinates where again all possible numerical checks were performed.

In the next step the normal modes were also transformed to symmetry coordinates. Finally, the potential energy distribution (PED) for each normal mode among

Table 4 Calculated potential constants (kcal mol⁻¹) for the asymmetric torsion in trifluoromethyl ketene and difluoromethyl ketene

Potential constants	B3LYP/6-311++G**	
	Trifluoromethyl ketene ^a	Difluoromethyl ketene
V_1		0.115
V_2		1.077
V_3	1.315	1.289
V_4		0.012
V_5		-0.021
V_6		-0.022

^a Because all potential constants, except V_3 , related to the trifluoro-derivative are of a very low value, they were omitted

Fig. 2 Potential curve for the internal rotation in trifluoromethyl ketene (solid line; note, that the “gauche” minimum at 120° is identical to the *cis* form) and difluoromethyl ketene (dashed line) as determined by ab initio calculations at B3LYP/6-311++G** level

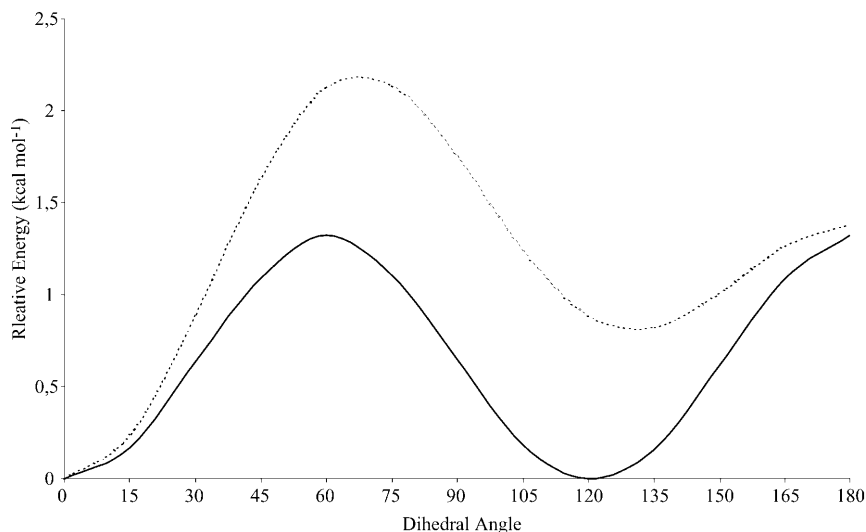


Table 5 Internal coordinate definitions (see Fig. 1 for atom denotation) for trifluoromethyl ketene

No.	Coordinate	Definition
1	C ₁ -C ₂	stretch R
2	C ₂ -C ₃	stretch P
3	C ₃ -O ₄	stretch T
4	C ₂ -H ₅	stretch D
5	C ₁ -F ₆	stretch Q ₁
6	C ₁ -F ₇	stretch Q ₂
7	C ₁ -F ₈	stretch Q ₃
8	C ₁ C ₂ C ₃	bend γ
9	C ₂ C ₃ O ₄	bend σ
10	C ₁ C ₂ H ₅	bend ρ
11	C ₃ C ₂ H ₅	bend δ
12	C ₂ C ₁ F ₆	bend α ₁
13	C ₂ C ₁ F ₇	bend α ₂
14	C ₂ C ₁ F ₈	bend α ₃
15	F ₆ C ₁ F ₇	bend β ₁
16	F ₆ C ₁ F ₈	bend β ₂
17	F ₇ C ₁ F ₈	bend β ₃
18	C ₂ =C ₃ =O ₄	wag χ
19	H ₅ C ₁ C ₂ C ₃	wag π
20	F ₆ C ₁ C ₂ C ₃ F ₇ C ₁ C ₂ C ₃ F ₈ C ₁ C ₂ C ₃	(CF ₃) torsion τ

Table 6 Internal coordinate definitions (see Fig. 1 for atom denotation) for difluoromethyl ketene

No.	Coordinate	Definition
1	C ₁ -C ₂	stretch R
2	C ₂ -C ₃	stretch P
3	C ₃ -O ₄	stretch T
4	C ₂ -H ₅	stretch D
5	C ₁ -H ₆	stretch Q ₁
6	C ₁ -F ₇	stretch Q ₂
7	C ₁ -F ₈	stretch Q ₃
8	C ₁ C ₂ C ₃	bend γ
9	C ₂ C ₃ O ₄	bend σ
10	C ₁ C ₂ H ₅	bend ρ
11	C ₃ C ₂ H ₅	bend δ
12	C ₂ C ₁ H ₆	bend α ₁
13	C ₂ C ₁ F ₇	bend α ₂
14	C ₂ C ₁ F ₈	bend α ₃
15	H ₆ C ₁ F ₇	bend β ₁
16	H ₆ C ₁ F ₈	bend β ₂
17	F ₇ C ₁ F ₈	bend β ₃
18	C ₂ =C ₃ =O ₄	wag χ
19	H ₅ C ₁ C ₂ C ₃	wag π
20	H ₆ C ₁ C ₂ C ₃ F ₇ C ₁ C ₂ C ₃ F ₈ C ₁ C ₂ C ₃	(CHF ₂) torsion τ

the symmetry coordinates was calculated and is given in Tables 9, 10 and 11. A complete vibrational assignment of the fundamentals was proposed. The assignments were made based on calculated PED, infrared band intensities, Raman line activities and depolarization ratios. The data of the vibrational assignments are also given in Tables 9, 10 and 11.

Calculation of vibrational spectra

To calculate the Raman spectra we used the frequencies ν_j , the scattering activities S_j and the depolarization ratios ρ_j as calculated on DFT-B3LYP level (6-311++G** basis set for all). Then, the Raman cross-sections

$(\partial\sigma_j/\partial\Omega)$, which are proportional to the intensities, [57, 58] are given as:

$$\partial\sigma_j/\partial\Omega=(2^4\pi^4/45)(\nu_o-\nu_j)^4(h/8\pi^2c\nu_j)S_j[(1-\rho_j)/(1+\rho_j)]/[1-\exp(-h\nu_j/k_B T)]$$

Since we use only relative intensities, we calculated them as:

$$I_j=(\partial\sigma_j/\partial\Omega)/(\partial\sigma_{jm}/\partial\Omega)$$

where jm denotes the normal mode having the largest Raman cross-section. As laser wavelength we took $\lambda_o=514.5$ nm ($\nu_o=1/\lambda_o$), which corresponds to an argon ion laser. We assumed the temperature to be $T=300$ K in the case of 3,3-difluoromethyl ketene.

The line shapes were then calculated as Lorentzians (L) with a width of $\Delta\nu=12\text{ cm}^{-1}$. Thus, the final spectrum is calculated as:

$$I(\nu) = \sum_j I_j L(\nu - \nu_j)$$

$$L(\nu - \nu_j) = (1/\pi)(\Delta\nu/2) / [(\nu - \nu_j)^2 + (\Delta\nu/2)^2]$$

$$\int_{-\infty}^{+\infty} L(\nu) d\nu = 1$$

where j runs over all normal modes. For the plots we used a grid step size of 10 cm^{-1} , but not when a spectral line appeared between two consecutive grid points. In this case we inserted 12 points with step size 0.5 cm^{-1} into this interval which include the exact location of the center of the line.

Table 7 Symmetry coordinates for trifluoromethyl ketene

Spe- cies	Description	Symmetry coordinate ^a
A'	C-H stretch	$S_1=D$
	C-C stretch	$S_2=R$
	C=C=O symmetric stretch	$S_3=P+T$
	C=C=O antisymmetric stretch	$S_4=P-T$
	CF ₃ symmetric stretch	$S_5=Q_1+Q_2+Q_3$
	CF ₃ antisymmetric stretch	$S_6=2Q_1-Q_2-Q_3$
	C=C-H in-plane bend	$S_7=\rho-\delta$
	C=C-C in-plane bend	$S_8=2\gamma-\rho-\delta$
	C=C=O in-plane bend	$S_9=\sigma$
	CF ₃ symmetric deformation	$S_{10}=\alpha_1+\alpha_2+\alpha_3-\beta_1-\beta_2-\beta_3$
	CF ₃ antisymmetric deformation	$S_{11}=\beta_1+\beta_2-2\beta_3$
	CF ₃ rock	$S_{12}=2\alpha_1-\alpha_2-\alpha_3$
A''	C=C-H out-of-plane bend (wag)	$S_{13}=\pi$
	C=C=O out-of-plane bend (wag)	$S_{14}=\chi$
	CF ₃ antisymmetric stretch	$S_{15}=Q_2-Q_3$
	CF ₃ antisymmetric deformation	$S_{16}=\beta_1-\beta_2$
	CF ₃ rock	$S_{17}=\alpha_2-\alpha_3$
	CF ₃ torsion	$S_{18}=\tau$

^a Not normalized

Table 8 Symmetry coordinates for difluoromethyl ketene

Species	Description	Symmetry coordinate ^a
A'	C-H ₅ stretch	$S_1=D$
	C-C stretch	$S_2=R$
	C=C=O symmetric stretch	$S_3=P+T$
	C=C=O antisymmetric stretch	$S_4=P-T$
	CF ₂ symmetric stretch	$S_5=Q_2+Q_3$
	C-H ₆ stretch	$S_6=Q_1$
	C=C-H in-plane bend	$S_7=\rho-\delta$
	C=C-C in-plane bend	$S_8=2\gamma-\rho-\delta$
	C=C=O in-plane bend	$S_9=\sigma$
	CH ₆ in-plane bend	$S_{10}=[(6)^{1/2}-2]\beta_3-[(6)^{1/2}+2]\alpha_1+\alpha_2+\alpha_3+\beta_1+\beta_2$
	CF ₂ deformation	$S_{11}=[(6)^{1/2}+2]\beta_3-[(6)^{1/2}-2]\alpha_1-\alpha_2-\alpha_3-\beta_1-\beta_2$
	CF ₂ rock	$S_{12}=\alpha_2+\alpha_3-\beta_1-\beta_2$
A''	C=C-H out-of-plane bend (wag)	$S_{13}=\pi$
	C=C=O out-of-plane bend (wag)	$S_{14}=\chi$
	CF ₂ antisymmetric stretch	$S_{15}=Q_2-Q_3$
	C-H ₆ out-of-plane bend	$S_{16}=\alpha_2-\alpha_3+\beta_1-\beta_2$
	CF ₂ twist	$S_{17}=\alpha_2-\alpha_3-\beta_1+\beta_2$
	CHF ₂ torsion	$S_{18}=\tau$

^a Not normalized

For the infrared spectrum we used the intensities as given by the DFT-B3LYP/6-311++G** calculations and converted them to relative transmittance. The Boltzmann distribution was then used to superimpose the spectra of the *cis* and the *gauche* conformers of difluoromethyl ketene. Accordingly, the total line intensity was calculated as a function of frequency. For $N+1$ different energy minima we have:

$$I(\nu) = \sum_{l=0}^N g_l I_l(\nu) e^{-\Delta E_l/k_B T} / \sum_{l=0}^N g_l e^{-\Delta E_l/k_B T}$$

where $I_l(\nu)$ are the line intensities for the respective minima, $\Delta E_l=E_l-E_0$, and g_l is a degeneracy factor. The g_l value for the trifluoro- and difluoromethyl ketene in the *cis* conformation is unity, whereas it is 2 for the nonplanar *gauche* conformer. Additionally, E_l represents the total energy of conformer l corrected with the corresponding zero-point energy. The label $l=0$ is given to the lowest energy conformer. For the temperature, $T=300\text{ K}$ was used. The calculated vibrational Raman and infrared

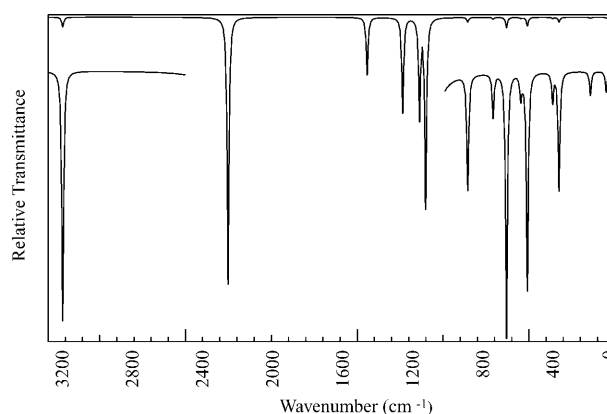


Fig. 3 Calculated vibrational IR spectrum of trifluoromethyl ketene at the DFT-B3LYP/6-311++G** level

Table 9 Calculated vibrational frequencies (cm^{-1}) at B3LYP/6-311++G** level for the *cis* conformer of trifluoromethyl ketene

Symm.	No.	Fre- quency	IR intensity ^a	Raman activity	Depol. ratio	Ob- served ^b	PED ^c
A'	ν_1	3215	26.4	77.6	0.2	3160	100% C–H str. (S_1)
	ν_2	2252	714.5	12.6	0.7		97% C=C=O antisymm. str. (S_4)
	ν_3	1442	154.3	8.4	0.1		43% C=C=O symm. str. (S_3), 25% C=C–H in-plane bend (S_7), 24% C–C str. (S_2)
	ν_4	1235	256.3	0.4	0.7	1298	17% CF_3 symm. str. (S_5), 22% C–C str. (S_2), 17% CF_3 symm. def. (S_{10}), 17% C=C–H in-plane bend (S_7), 14% CF_3 antisymm. str. (S_6)
	ν_5	1136	265.2	6.5	0.3	1197	22% CF_3 antisymm. str. (S_6), 36% C=C=O symm. str. (S_3), 17% C=C–H in-plane bend (S_7), 11% CF_3 symm. str. (S_5)
	ν_6	1100	155.2	11.5	0.3		35% C=C–H in-plane bend (S_7), 34% CF_3 antisymm. str. (S_6)
	ν_7	856	12.1	6.5	0.1	841	45% CF_3 symm. str. (S_5), 21% C–C str. (S_2), 10% CF_3 antisymm. str. (S_6), 10% C=C=O in-plane bend (S_9)
	ν_8	709	4.7	5.3	0.2	707	32% CF_3 symm. def. (S_{10}), 23% CF_3 symm. str. (S_5), 18% C=C=O in-plane bend (S_9), 12% C=C–C in-plane bend (S_8)
	ν_9	535	0.6	0.6	0.7	531	69% CF_3 antisymm. def. (S_{11}), 12% CF_3 antisymm. str. (S_6)
	ν_{10}	509	13.9	2.4	0.1		30% C=C=O in-plane bend (S_9), 33% CF_3 symm. def. (S_{10}), 27% C–C str. (S_2)
	ν_{11}	361	3.1	1.5	0.6	255	62% CF_3 rock (S_{12}), 17% CF_3 antisymm. def. (S_{11}), 11% C=C=O in-plane bend (S_9)
	ν_{12}	142	2.6	1.7	0.7		65% C=C–C in-plane bend (S_8), 19% C=C=O in-plane bend (S_9), 16% CF_3 rock (S_{12})
A''	ν_{13}	1101	355.8	2.8	0.7	1194	77% CF_3 antisymm. str. (S_{15}), 13% CF_3 antisymm. def. (S_{16})
	ν_{14}	630	28.0	0.6	0.7		23% C=C–H wag (S_{13}), 31% CF_3 rock (S_{17}), 15% CF_3 antisymm. str. (S_{15}), 14% CF_3 torsion (S_{18})
	ν_{15}	547	2.5	1.3	0.7		88% C=C=O wag (S_{14})
	ν_{16}	508	9.4	1.3	0.7	529 ^d	56% CF_3 antisymm. def. (S_{16}), 22% C=C–H wag (S_{13}), 14% CF_3 torsion (S_{18})
	ν_{17}	324	12.6	0.7	0.7	320	60% CF_3 rock (S_{17}), 25% C=C–H wag (S_{13}), 15% CF_3 antisymm. def. (S_{16})
	ν_{18}	50	2.2	2.4	0.7	65	74% CF_3 torsion (S_{18}), 26% C=C–H wag (S_{13})

^a Infrared intensities and Raman activities are calculated in Km mol^{-1} and $\text{\AA}^4 \text{amu}^{-1}$, respectively

^b Observed Raman frequencies (cm^{-1}) in the gas phase for trifluoroacetaldehyde (fluoral) are obtained from reference [60]

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

^d IR frequency

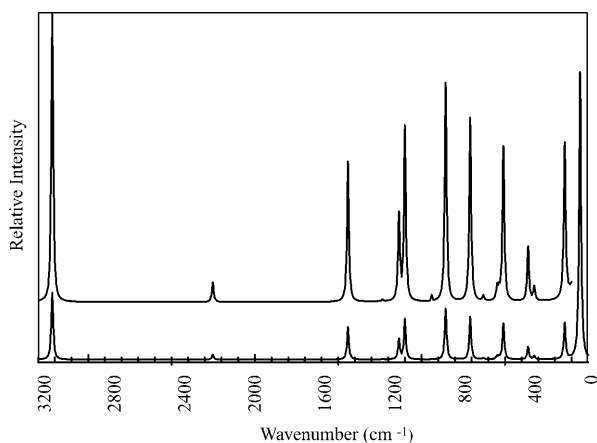


Fig. 4 Calculated vibrational Raman spectrum of trifluoromethyl ketene at the DFT-B3LYP/6-311++G** level

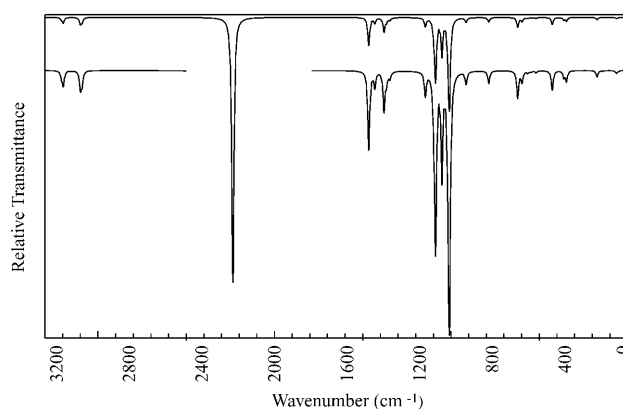


Fig. 5 Calculated vibrational IR spectrum of difluoromethyl ketene at 300 K at the DFT-B3LYP/6-311++G** level

spectra of the *cis*-trifluoromethyl ketene are shown in Figs. 3 and 4, while the spectra of the difluoromethyl ketene mixture (65% *cis* and 35% *gauche*) at 300 K are shown in Figs. 5 and 6.

Discussion

The interesting properties of organoiscyanate molecules [33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51] recently prompted us to investigate the conformational and structural stabilities of

Table 10 Calculated vibrational frequencies (cm⁻¹) at B3LYP/6-311++G** level for the *cis* conformer of difluoromethyl ketene

Symm.	No.	Fre- quency	IR intensity ^a	Raman activity	Depol. ratio	PED ^b
A'	v ₁	3196	19.9	76.5	0.2	100% C–H ₅ str. (S ₁)
	v ₂	3100	24.8	73.5	0.2	100% C–H ₆ str. (S ₆)
	v ₃	2234	752.7	13.1	0.7	97% C=C=O antisymm. str. (S ₄)
	v ₄	1466	108.6	4.2	0.1	24% C=C=O symm. str. (S ₃), 34% C–H ₆ in-plane bend (S ₁₀), 15% C=C–H in-plane bend (S ₇), 14% C–C str. (S ₂), 13% CF ₂ rock (S ₁₂)
	v ₅	1332	1.3	7.6	0.2	23% C–H ₆ in-plane bend (S ₁₀), 31% CF ₂ rock (S ₁₂), 29% C=C=O symm. str. (S ₃), 13% C=C–H in-plane bend (S ₇)
	v ₆	1143	7.8	7.5	0.6	55% C=C–H in-plane bend (S ₇), 17% C–C str. (S ₂), 16% C=C=O symm. str. (S ₃)
	v ₇	1087	229.1	4.0	0.1	40% C–C str. (S ₂), 18% C=C=O symm. str. (S ₃), 15% CF ₂ symm. str. (S ₅)
	v ₈	1052	141.7	14.3	0.2	60% CF ₂ symm. str. (S ₅)
	v ₉	630	3.0	4.9	0.1	41% C=C=O in-plane bend (S ₉), 17% C=C–C in-plane bend (S ₈), 13% C–C str. (S ₂), 12% CF ₂ symm. str. (S ₅), 10% CF ₂ def. (S ₁₁)
	v ₁₀	565	3.4	0.8	0.6	26% CF ₂ rock (S ₁₂), 29% CF ₂ def. (S ₁₁), 18% C=C=O in-plane bend (S ₉), 11% CF ₂ symm. str. (S ₅), 11% C–H ₆ in-plane bend (S ₁₀)
	v ₁₁	426	22.2	2.2	0.3	47% CF ₂ def. (S ₁₁), 17% CF ₂ rock (S ₁₂), 15% C–H ₆ in-plane bend (S ₁₀), 14% C–C str. (S ₂)
	v ₁₂	173	8.7	2.5	0.7	66% C=C–C in-plane bend (S ₈), 28% C=C=O in-plane bend (S ₉)
A''	v ₁₃	1346	9.8	3.8	0.8	67% C–H ₆ wag (S ₁₆), 33% CF ₂ twist (S ₁₇)
	v ₁₄	1008	274.0	4.2	0.8	94% CF ₂ antisymm. str. (S ₁₅)
	v ₁₅	622	37.0	1.7	0.8	15% CF ₂ twist (S ₁₇), 33% C=C–H wag (S ₁₃), 28% CHF ₂ torsion (S ₁₈), 11% C–H ₆ wag (S ₁₆)
	v ₁₆	548	0.1	0.6	0.8	94% C=C=O wag (S ₁₄)
	v ₁₇	346	14.5	1.2	0.8	49% CF ₂ twist (S ₁₇), 28% C=C–H wag (S ₁₃), 21% C–H ₆ wag (S ₁₆)
	v ₁₈	63	4.1	2.3	0.8	65% CHF ₂ torsion (S ₁₈), 35% C=C–H wag (S ₁₃)

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

^b PED values are obtained by using calculated frequencies at B3LYP level

Table 11 Calculated vibrational frequencies (cm⁻¹) at B3LYP/6-311++G** level for the *gauche* conformer of difluoromethyl ketene

Symm.	No.	Fre- quency	IR intensity ^a	Raman activity	Depol. ratio	PED ^b
A	v ₁	3206	16.9	84.9	0.2	100% C–H ₅ str. (S ₁)
	v ₂	3090	34.3	120.7	0.2	67% C–H ₆ str. (S ₆), 33% CF ₂ symm. str. (S ₅)
	v ₃	2239	753.6	12.2	0.7	97% C=C=O antisymm. str. (S ₄)
	v ₄	1432	40.6	8.1	0.1	44% C=C=O symm. str. (S ₃), 29% C=C–H in-plane bend (S ₇), 16% C–C str. (S ₂)
	v ₅	1380	102.1	4.2	0.7	51% C–H ₆ in-plane bend (S ₁₀), 19% C–H ₆ wag (S ₁₆), 14% CF ₂ rock (S ₁₂)
	v ₆	1366	30.9	5.9	0.7	76% C–H ₆ wag (S ₁₆), 14% C–H ₆ in-plane bend (S ₁₀)
	v ₇	1146	48.0	12.5	0.3	49% C=C–H in-plane bend (S ₇), 13% C=C=O symm. str. (S ₃)
	v ₈	1096	105.4	5.1	0.4	22% CF ₂ symm. str. (S ₅), 19% C=C=O symm. str. (S ₃), 14% C=C–H in-plane bend (S ₇), 10% C–H ₆ str. (S ₆)
	v ₉	1014	291.1	7.3	0.4	71% CF ₂ antisymm. str. (S ₁₅), 11% CF ₂ symm. str. (S ₅)
	v ₁₀	915	32.7	8.0	0.04	42% C–C str. (S ₂), 16% CF ₂ rock (S ₁₂), 12% C=C=O symm. str. (S ₃), 10% CF ₂ symm. str. (S ₅)
	v ₁₁	786	33.6	2.8	0.7	23% CF ₂ rock (S ₁₂), 21% C=C=O in-plane bend (S ₉), 20% C=C–C in-plane bend (S ₈)
	v ₁₂	598	29.2	3.2	0.2	11% C=C=O in-plane bend (S ₉), 21% C=C–H wag (S ₁₃), 21% C=C=O wag (S ₁₄)
	v ₁₃	548	3.1	2.8	0.5	59% C=C=O wag (S ₁₄), 24% CF ₂ def. (S ₁₁)
	v ₁₄	519	6.0	0.8	0.7	23% C=C–H wag (S ₁₃), 29% CF ₂ def. (S ₁₁), 20% C=C=O wag (S ₁₄), 10% CHF ₂ torsion (S ₁₈)
	v ₁₅	429	10.2	0.7	0.6	30% C=C=O in-plane bend (S ₉), 20% CF ₂ twist (S ₁₇), 18% CF ₂ rock (S ₁₂), 10% C–H ₆ in-plane bend (S ₁₀)
	v ₁₆	361	17.8	1.3	0.6	49% CF ₂ twist (S ₁₇), 28% C=C–H wag (S ₁₃), 10% CF ₂ rock (S ₁₂)
	v ₁₇	143	1.1	1.6	0.7	65% C=C–C in-plane bend (S ₈), 20% C=C=O in-plane bend (S ₉)
	v ₁₈	51	1.0	2.0	0.7	81% CHF ₂ torsion (S ₁₈), 18% C=C–H wag (S ₁₃)

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

^b PED values are obtained by using calculated frequencies at B3LYP level

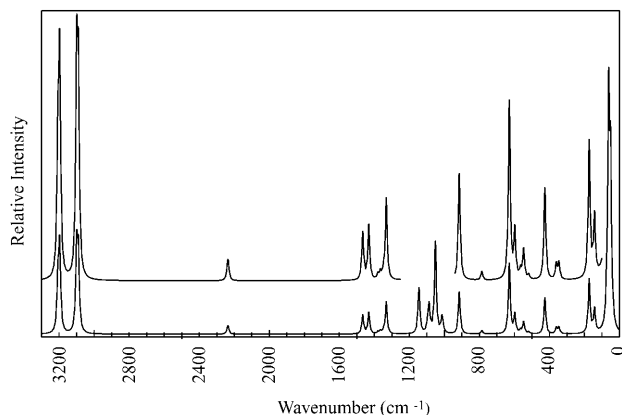


Fig. 6 Calculated vibrational Raman spectrum of difluoromethyl ketene at 300 K at the DFT-B3LYP/6-311++G** level

isocyanatoacetaldehyde, chloromethyl isocyanate, difluoromethyl isocyanate and formyl isocyanate. [48, 49, 50, 51] The conformational behavior of these compounds depends greatly on the extent of interactions between the substituent and both the π -system of the isocyanate group and the lone pair on the nitrogen. In isocyanatoacetaldehyde the *cis-cis* conformation (isocyanate group eclipses the carbonyl group) was found to be the lowest energy form with the carbonyl oxygen being oriented away from the lone pair. [48] The potential surface governing internal rotation about the C–N bond in chloromethyl isocyanate was calculated to be consistent with a single minimum corresponding to a structure having the chlorine atom *gauche* or near-*cis* to the –NCO moiety [49]. From a more recent study, difluoromethyl isocyanate was predicted to exist only in the *trans* conformation, again with minimum repulsive interaction between the fluorine atoms and the electron lone pair on the nitrogen. [50]

In the case of formyl isocyanate, the molecule was predicted to have a *cis* \leftrightarrow *trans* conformational equilibrium. [51] The molecule was found to have the *cis* (carbonyl oxygen eclipses the isocyanato group) conformer as the lower energy form, with the carbonyl oxygen being away from the electron lone pair. A similar conformational equilibrium was predicted for formyl ketene with a relatively higher rotational barrier. [9] The conjugation stabilization force in such systems stabilizes the planar forms and considerably restricts the internal rotation of the –CHO group.

The electronic structure of trifluoromethyl ketene fascinated us. On first sight, we expected that the *trans* conformer (a fluorine atom eclipses the ketenic hydrogen) should be more stable than the *cis* form (a fluorine atom eclipses the C=C=O moiety). However, closer inspection shows that actually the reverse was true. As shown in Table 12, the negatively charged F_6 atom in the *cis* conformer is calculated to be quite close to the positive C_3 atom. Moreover, in both conformers the repulsion between the negative F_6 and O_4 atoms is rather small due to the large distances between them. Thus, the C_3 – F_6 and

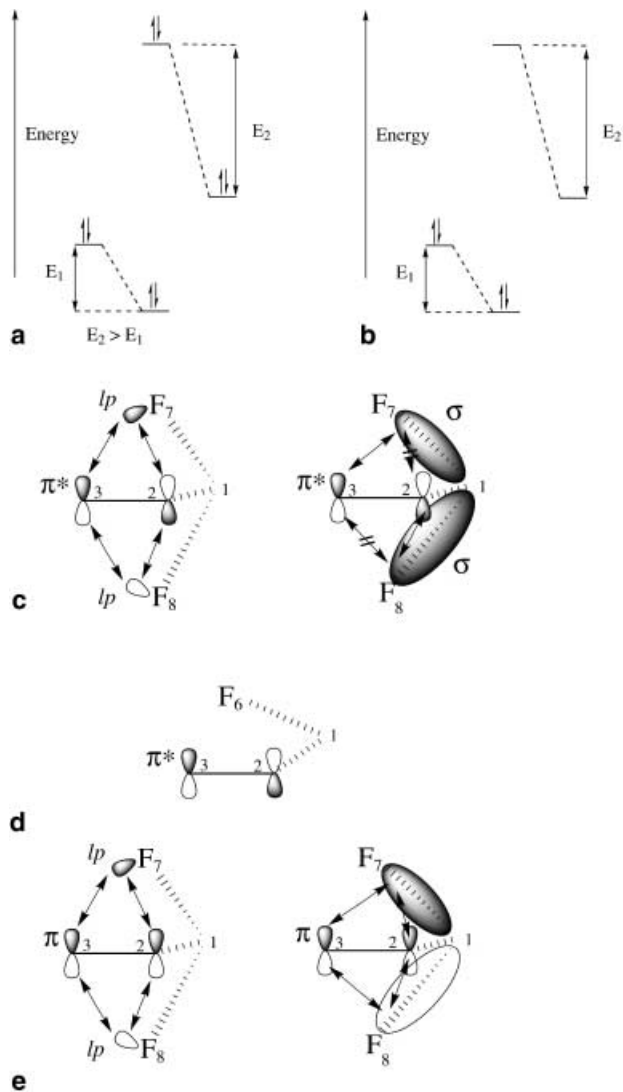


Fig. 7a–e Orbital interactions in trifluoromethyl ketene. **a** Destabilizing interaction between two filled orbitals. **b** Stabilizing interaction between a filled and an unfilled orbital. **c** MO interaction of fluorine lone pairs (and C–F σ orbitals) with the π^* orbital of the C–C π -bond in the *trans* conformation of trifluoromethyl ketene. **d** MO interaction of fluorine lone pairs (and C–F σ orbitals) with the π^* orbital of the C–C π -bond in the *cis* conformation of trifluoromethyl ketene. **e** MO interaction of fluorine lone pairs (and C–F σ orbitals) with the π orbital of the C–C π -bond in the *trans* conformation of trifluoromethyl ketene

C_3 – F_7 (F_8) electrostatic attractions dominate the F_6 – O_4 repulsion in both cases. The corresponding stabilization is larger in the *cis* conformer than in the *trans* one, because the absolute values of the charges are larger and the C–F distance is smaller in the *cis* form. However, this simple electrostatic argument explains only why the *cis* is more stable than the *trans* form, not why *cis* is a minimum but *trans* a maximum in the potential curve (Fig. 2). A closer look at the MO interactions in the system provides an explanation for this result.

As is well known, the interactions between two filled orbitals destabilize (Fig. 7a), while those between a

Table 12 Total atomic charges and selected non-bonded distances calculated at B3LYP/6-311++G** level for *cis* and *trans* conformations of trifluoromethyl ketene and difluoromethyl ketene

Atom	<i>cis</i>	<i>trans</i> ^a	Atom	<i>cis</i>	<i>trans</i>
Trifluoromethyl ketene			Difluoromethyl ketene		
C ₁	0.098	0.125	C ₁	-0.261	-0.210
C ₂	0.029	0.048	C ₂	0.141	0.065
C ₃	0.189	0.135	C ₃	0.102	0.193
O ₄	-0.179	-0.166	O ₄	-0.181	-0.175
H ₅	0.220	0.218	H ₅	0.225	0.173
F ₆	-0.164	-0.137	H ₆	0.224	0.220
F ₇	-0.099	-0.112	F ₇	-0.125	-0.133
F ₈	-0.099	-0.112	F ₈	-0.125	-0.133
Non-bonded distance (Å)			Non-bonded distance (Å)		
F ₆ -C ₃	2.678		H ₆ -C ₃	2.624	
F ₆ -O ₄	3.403		H ₆ -O ₄	3.416	
F ₈ -C ₃		2.976	F ₈ -C ₃		2.963
F ₈ -O ₄		3.818	F ₈ -O ₄		3.793

^a Transition state

filled and an unfilled orbital stabilize (Fig. 7b) a system. Candidates for such interactions in our system are the lone pairs at fluorine, the σ, σ^* orbitals of the C-F bond and the π, π^* orbitals of the C=C π bond. Being flanked by a CF₃ group at one end and a C=O bond at the other, the C=C bond can be considered as quite electron deficient, making it an ideal system to interact with F lone pairs or the σ orbitals of the C-F bond. However, as Fig. 7c shows, in the *trans* conformer neither of them can efficiently overlap with the π^* orbital due to geometry, while in the *cis* form F₆ lies in the nodal plane of the π^* orbital (Fig. 7d). Thus, there are no efficient stabilizing orbital interactions and we have to concentrate on the destabilizing ones. In the case of the destabilizing interactions there is a significant difference between the *cis* and the *trans* form. Again in the *cis* conformer the lone pair at F₆ and the C-F₆ σ orbital are exactly in the nodal plane of the π orbital and are symmetric with respect to this plane, while π is antisymmetric. Therefore, in the *cis* form there are no efficient destabilizing orbital interactions present as compared to that in the *trans* conformer. Furthermore, any arbitrary rotation away from the fully symmetric *cis* form destroys the symmetry of the C-F σ orbital or the F₆ lone pair, increasing destabilizing interactions. Hence, *cis* must be a true energy minimum.

On the contrary, in the *trans* form, as shown in Fig. 7e, there are destabilizing interactions present, and thus the *trans* conformer has to be thermodynamically less preferable than the *cis* form. Additionally, Fig. 7e indicates that any rotation out of the fully symmetric *trans* form would reduce these destabilizing effects, and thus the *trans* form is a maximum in the potential curve. Given the fact that the distances between the atoms indicate comparatively small effects due to the discussed orbital interactions, one would expect to find small barriers as predicted in our calculations. The difference in MO interactions between the two forms we have just viewed above surely dominates any electrostatic attractive inter-

actions between the fluorine and the ketenic hydrogen atom because the latter are of roughly the same strength in both conformers.

An electron diffraction study for trifluoroacetaldehyde concluded that the *cis* conformation (fluorine eclipses the aldehyde group) was the preferred conformation for the system. [55] The results obtained from the electron diffraction experiment were reasonably consistent with the microwave study. [59] As a result this experimental conclusion supports our prediction for the stability of trifluoromethyl ketene.

In the case of the difluoro derivative, the steric effects play a competitive role with the MO orbital interactions in determining the conformational stability in difluoromethyl ketene. The question of which bond, C-H₆ or C-F, eclipses the ketenic hydrogen (C-H₅) or the CCO group is also important, because the different effects of steric hindrance might outweigh those due to MO interactions. In difluoromethyl ketene the low minima are expected at such angles, for which either CH₆ or CF eclipses the ketenic CCO group and the C-H₆ bond is staggered relative to the other two bonds of the difluoromethyl (CHF₂) rotor.

In the lowest energy *cis* conformation of difluoromethyl ketene, the small H₆ atom opposes the CCO group while the more bulky C-F bonds eclipse the C-H₅ bond. The second, lower energy *gauche* conformer with an HCCC dihedral angle of 131° has the C-F₈ eclipsing the CCO moiety. It is higher in energy than the *cis* conformer, because here the bulky F₈ opposes the CCO group. However, although in both forms the ketenic CCO group is in an eclipsed position, the two are the lower energy forms, because they are the only forms where no destabilizing interactions between the fluorine lone pairs and the π orbitals of the C=C double bond occur. In the *cis* case no lone pair points to the C=C double bond, while in the higher *gauche* (HCCC is 120°) case the F₈ lone pair lies in the nodal plane of the C=C bond (see Fig. 7d).

The other *gauche* conformer (HCCC is 60°) and the *trans* structure both suffer from the aforementioned destabilizing interactions. The *trans* form has two such interactions, while the high energy *gauche* structure has only one. Since these interactions are rather small in difluoromethyl ketene, not the *trans* form is higher in energy, but the *gauche* structure (HCCC of 60°). The reason for this is simply that the bulky C-F₇ bond eclipses C-H₅ in the case of the high energy *gauche* form, while in the *trans* case only C-H₆ is eclipsing C-H₅. While MO interactions would give the *gauche*-60 structure the lower energy, their effects are outweighed by the larger steric hindrance in the *gauche* form, making it higher in energy than the *trans* structure. Since in both *gauche*-60 and *trans*, any rotation out of their respective positions would lower the destabilizing effects and finally drive them into one of the minima, the two structures are maxima, with *gauche*-60 being higher in energy than *trans*.

We calculated the vibrational frequencies and derived the PED values among symmetry coordinates in the low

energy conformers of the two molecules. Some of the vibrations were clearly pure, and their assignments were easily made possible only based on the PED values as shown in Tables 9, 10 and 11, and others were predicted to be mixed with neighboring modes.

The C–H stretching modes of the two molecules were calculated to have the highest Raman activities. Only one C–H stretching mode is in the Raman spectrum of trifluoromethyl ketene and was calculated to be at $3,215\text{ cm}^{-1}$. While in difluoromethyl ketene Raman spectrum there are two C–H stretches that were calculated at $3,196\text{ cm}^{-1}$ for the ketenic C–H stretch and at $3,100\text{ cm}^{-1}$ for the other C–H stretch for the *cis* conformer.

The highest calculated IR intensities in the tri- and difluoromethyl ketene IR spectra were assigned to the --C=C=O antisymmetric stretching vibrations with PED values of 97%. Furthermore, the C=C–C in-plane bending modes of the *cis* conformers of both molecules were calculated at 142 cm^{-1} for the trifluoro derivative and 173 cm^{-1} for the difluoro one. The --C=C=O symmetric stretching mode in the trifluoro system was of a clear assignment and was calculated at $1,442\text{ cm}^{-1}$ with 43% PED. In the case of the difluoro-derivative, the assignment of this --C=C=O mode was not straightforward based on the calculated PED and could be assigned to either ν_4 or ν_5 . However, the --C=C=O symmetric stretching mode could be assigned to the ν_4 with the higher IR intensity as one might expect for such a vibration. Then, the assignment of ν_5 could be predicted from the PED values in Table 9 to the C–H₆ in-plane bending.

Several vibrational modes in trifluoromethyl ketene were calculated to be mixed with other modes. The assignments of such modes could be clarified with the help of the observed frequencies obtained from the gas phase Raman spectrum of trifluoroacetaldehyde (fluoral). [60] For example, ν_4 in our trifluoro system could be referred to either the C–C stretching or the CF₃ symmetric stretching. In fluoral, the experimental frequency assigned to the CF₃ symmetric stretching mode was $1,298\text{ cm}^{-1}$. Therefore, ν_4 in trifluoromethyl ketene could be assigned to CF₃ symmetric stretching. However, the C–C stretching vibration can be assigned with confidence to the 856 cm^{-1} frequency since the corresponding vibration in fluoral was observed at 841 cm^{-1} . [60] Similarly, the CF₃ antisymmetric stretching mode and the C=C–H in-plane bending mode were calculated to couple with each other in ν_5 and ν_6 . Experimentally, the CF₃ antisymmetric stretching mode was found at $1,197\text{ cm}^{-1}$, which is closer to the frequency of ν_5 in trifluoromethyl ketene (Table 9). Thus, ν_5 and ν_6 can be assigned to the antisymmetric CF₃ stretching and the in-plane C=C–H bending modes, respectively.

The assignment of some of the CF₃ vibrational modes below $1,000\text{ cm}^{-1}$ was obvious from derived PED values. The calculated wavenumbers at 535 and 361 cm^{-1} were referred to the CF₃ antisymmetric deformation and the CF₃ rock, respectively. The CF₃ symmetric deformation in fluoral was observed at 707 cm^{-1} ; hence the CF₃ symmetric deformation in trifluoromethyl ketene could

be assigned to ν_8 . This leaves us with the assignment of ν_{10} to the --C=C=O in-plane bending vibration.

The calculated PEDs for difluoromethyl ketene in the *cis* conformation provided excellent help for the assignments of most of the skeletal vibrations (see Table 10). The frequencies ν_6 , ν_7 , ν_8 , ν_9 and ν_{11} can with little doubt be assigned to the C=C–H in-plane bending (55% PED), the C–C stretching (40% PED), the CF₂ symmetric stretching (60% PED), the C=C=O in-plane bending (41% PED) and the CF₂ deformation (47% PED), respectively. This should then assign ν_{10} at 565 cm^{-1} to the CF₂ rocking mode. The remaining frequency at $1,332\text{ cm}^{-1}$ in the *cis* conformer of the difluoro system (ν_5) can be referred with confidence to the C–H₆ in-plane bending.

Many vibrational modes in the *gauche* form of the difluoro derivative, however, were difficult to assign based only on the calculated PEDs, especially for the region below $1,000\text{ cm}^{-1}$, at which a large degree of coupling of many bending modes was found (Table 11). From the experimental IR frequencies of chlorocarbonyl ketene obtained in the xenon matrix, [19] the C=C–H wag was observed at 531 cm^{-1} for the *cis* and 556 cm^{-1} for the *trans* conformers. The observed modes were weak in the IR spectrum. This information leads to the assignment of the C=C–H wag of the *gauche* difluoromethyl ketene to the depolarized wavenumber at 519 cm^{-1} . Therefore, from the calculated PEDs, the C=C=O in-plane bending was assigned to ν_{12} . Then, the CF₂ rock and the CF₂ twist could be assigned to ν_{11} and ν_{15} , respectively. This approximate assignment leads one to assign ν_8 at $1,096\text{ cm}^{-1}$ to the symmetric CF₂ stretching.

Many of the bending modes of A'' symmetry in the tri- and the difluoromethyl ketene spectra were calculated to have a very low degree of mixing and their assignments are shown in Tables 9 and 10. Among these modes only the C=C–H wag was of a low PED value in trifluoromethyl ketene. The C=C–H wagging mode was predicted to be at 630 and 622 cm^{-1} in the trifluoro and difluoro systems, respectively. The lowest vibrational mode in the spectra of the two molecules was the asymmetric torsion. The CF₃ asymmetric torsion in the spectrum of trifluoromethyl ketene was calculated to be at 50 cm^{-1} , and the CHF₂ asymmetric torsion in the difluoro spectrum was predicted to be at 63 cm^{-1} in the *cis* form and 51 cm^{-1} in the *gauche* form. The asymmetric torsion modes were predicted to have a relatively small degree of contribution from the C=C–H wagging mode as shown in Tables 9, 10 and 11.

Finally, we were able to provide reasonable vibrational assignments for the normal modes of the stable conformers of tri- and difluoromethyl ketene based on normal coordinate analysis. Good agreements were noticed when the calculated frequencies of trifluoromethyl ketene were compared to the experimental ones of fluoral, especially for the vibrational modes associated to the CF₃ moiety.

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