

An ab initio vibrational study of rotational isomerism in oxalyl fluoride, $O=CF-CF=O$, and acryloyl fluoride, $O=CF-CH=CH_2$

Charles W. Bock

Chemistry Department, Philadelphia College of Textiles and Science, Philadelphia, PA 19144, USA
and American Research Institute, Marcus Hook, PA 19061, USA

Yurii N. Panchenko and Sergei V. Krasnoshchiokov

Laboratory of Molecular Spectroscopy, Department of Chemistry, M.V. Lomonosov Moscow State University, Moscow 119899, USSR

Received 18 October 1988; in final form 1 March 1990

Results of complete geometry optimizations of the rotational isomers of oxalyl fluoride and acryloyl fluoride at a variety of computational levels are reported. These molecules are found to have planar *s*-trans (anti) and *s*-cis (syn) conformations. The RHF/6-31G//RHF/6-31G harmonic force fields of these molecules are calculated as analytical second derivatives, and the vibrational frequencies are obtained from the corresponding scaled quantum mechanical force fields. Some reassignments of fundamental frequencies are suggested.

1. Introduction

Combining quantum mechanical calculations of the vibrational force constants with an experimental scaling procedure has proved to be very successful in the interpretation of rotational isomerism. Recently, such an approach was used to analyse the structures and vibrational spectra of the *s*-trans (anti) and *s*-cis (syn) conformers of glyoxal and acrolein [1].

The rotational isomerism of the fluor derivatives of these molecules, oxalyl fluoride (ethanedioyl difluoride) and acryloyl fluoride (2-fluoro-2-propenal) (see fig. 1), has been investigated using various methods. In the case of oxalyl fluoride, two possible forms of the high energy conformer have been suggested, *cis* and *gauche* [2-11]. The experimental vibrational spectra of the rotamers has been measured [3,6,12] and an empirical vibrational analysis has also been carried out [13-19]. The most recent vibrational reassignment of the *trans* conformer of oxalyl fluoride was completed in 1985 [20].

At present it seems well established that acryloyl fluoride has two planar (*trans* and *cis*) conformers

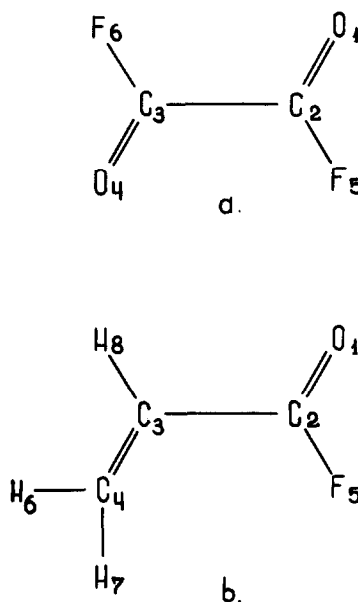


Fig. 1. Numbering of atoms: (a) oxalyl fluoride, (b) acryloyl fluoride.

[9,21–27]. This conclusion was drawn from a microwave investigation of this molecule [21]. ΔH for the rotation has been measured [21–28] and ΔE has also been predicted by ab initio calculations [9,27]. An experimental vibrational analysis of these two molecular forms has also been reported [24,26,27,29], and an empirical analysis of the vibrational spectra of the two conformers was performed in refs. [27,30]. An ab initio vibrational study of this molecule is also given in ref. [27].

This paper reports an ab initio study of the geometrical parameters and the vibrational spectra of oxalyl fluoride and acryloyl fluoride and correlates the structures of their conformers with the corresponding experimental spectra.

2. Method of calculations

Complete geometry optimizations of the two stable forms of oxalyl fluoride and acryloyl fluoride were carried out using the standard gradient method at the RHF/6-31G and RHF/6-31G* levels [31] with the GAUSSIAN 82 [32] and GAUSSIAN 86 [33] programs. Both structures of acryloyl fluoride were also optimized at the MP2/6-31G* level [34]. Cis and gauche forms of oxalyl fluoride were also investigated at the RHF/6-31G* and MP2 and MP3/6-31G//RHF/6-31G and MP2 and MP3/6-31G**/RHF/6-31G* levels. Energy differences between gauche (twisted, 30°) and s-cis (planar) oxalyl fluoride are listed in table 1. The geometrical parameters obtained are given in tables 2 and 3. The Cartesian force constants were calculated at the RHF/6-31G level using analytical differentiation. They were

Table 1
Energy differences between gauche (twisted, 30°) and s-cis (planar) oxalyl fluoride, O=CF–CF=O

Energy/geometry	$\tau_{\text{O-C-C-O}}$ (au)		ΔE (kcal/mol)
	cis (0°)	gauche (30°)	
RHF/6-31G//RHF/6-31G	–424.139667	–424.138599	0.67
MP2/6-31G//RHF/6-31G	–424.816777	–424.816051	0.46
MP3/6-31//RHF/6-31G	–424.783639	–424.782861	0.48
RHF/6-31G**/RHF/6-31G*	–424.333944	–424.333421	0.33
MP2/6-31G**/RHF/6-31G*	–425.265297	–425.264734	0.35
MP3/6-31G**/RHF/6-31G*	–425.253766	–425.253176	0.37

Table 2
Structural parameters and complete energies of s-trans and s-cis oxalyl fluorides (distances in ångström, angles in degree, and energies in atomic units)

Parameter	s-trans O=CF–CF=O			s-cis O=CF–CF=O		
	exptl. ^{a)} [42]	calc. 4-31G [2]	6-31G this work	6-31G* this work	calc. 6-31G this work	6-31G* this work
$r(\text{C–C})$	1.536(3)	1.500	1.5025	1.5248	1.5049	1.5271
$r(\text{C=O})$	1.180(1)	1.181	1.1805	1.1622	1.1803	1.1604
$r(\text{C–F})$	1.329(1)	1.338	1.3475	1.3003	1.3484	1.3049
$\angle \text{O=C–C}$	126.0(2)	145.4	126.14	125.13	124.53	123.78
$\angle \text{F–C–C}$	109.8(1)	111.8	110.90	110.57	112.65	112.13
energy		–423.72535	–424.14046	–424.33546	–424.13967	–424.33394

^{a)} r_s structure.

Table 3
Structural parameters and complete energies of *s*-trans and *s*-cis acryloyl fluorides (distances in ångström, angles in degree and energies in atomic units)

Parameter	<i>s</i> -trans O=CF-CH=CH ₂				<i>s</i> -cis O=CF-CH=CH ₂						
	exptl. [21]	[43]	3-21G [27]	6-31G this work	6-31G* [27]	MP2/6-31G* this work	exptl. [21]	3-21G [27]	6-31G this work	6-31G* [27]	MP2/6-31G* this work
r(C-O)	1.18	1.195	1.186	1.191	1.171	1.201	1.18	1.187	1.192	1.171	1.201
r(C-C)	1.49	1.470	1.463	1.461	1.475	1.470	1.48	1.464	1.468	1.477	1.474
r(C-C)	1.35	-	1.316	1.325	1.320	1.338	1.35	1.316	1.325	1.320	1.338
r(C-F)	1.35	1.350	1.360	1.376	1.325	1.366	1.35	1.355	1.373	1.323	1.365
r(C-H)t	-	1.085	1.071	1.072	1.075	1.084	-	1.071	1.072	1.074	1.084
r(C-H)c	-	1.085	1.071	1.071	1.074	1.083	-	1.073	1.073	1.074	1.085
r(C-H)	-	1.085	1.069	1.071	1.074	1.085	-	1.068	1.070	1.073	1.084
∠O=C-C	127.0	123.3	128.1	127.8	126.6	127.7	128.2	128.9	129.4	128.4	128.5
∠C=C-C	121.8	120.0	121.8	123.4	122.7	123.1	119.9	119.7	120.8	121.0	119.7
∠F-C-C	111.3	120.9	112.1	113.1	113.0	112.5	110.1	110.9	111.2	110.2	110.8
∠C-C-Ht	-	121.5	121.5	120.8	121.1	120.9	-	121.9	121.2	120.7	121.4
∠C-C-Hc	-	120.0	121.3	122.0	121.5	121.6	-	120.7	121.4	121.9	120.6
∠C-C-H	-	117.4	114.9	114.1	114.2	114.6	-	117.3	116.5	116.9	117.5
energy				-289.52413		-290.37966			-289.52373		-290.37922

Table 4
Definition and numbering of local symmetry coordinates of oxalyl fluoride

No.	Description	Definition
1	$\nu(\text{C-C})$ str.	$r(\text{C3-C2})$
2	$\nu(\text{C-O})$ str.	$r(\text{C2-O1})$
3	$\nu(\text{C-O})$ str.	$r(\text{C3-O4})$
4	$\nu(\text{C-F})$ str.	$r(\text{C2-F5})$
5	$\nu(\text{C-F})$ str.	$r(\text{C3-F6})$
6	$\delta(\text{C-C-O})$ bend.	$\angle \text{C3-C2-O1}$
7	$\delta(\text{C-C-O})$ bend.	$\angle \text{C2-C3-O4}$
8	$\rho(\text{C-F})$ rock.	$(\angle \text{F5-C2-C3} - \angle \text{F5-C2-O1})/\sqrt{2}$
9	$\rho(\text{C-F})$ rock.	$(\angle \text{F6-C3-C2} - \angle \text{F6-C3-O4})/\sqrt{2}$
10	$\chi(\text{C-F})$ wag.	F5 out of O1-C2-C3 plane
11	$\chi(\text{C-F})$ wag.	F6 out of O4-C3-C2 plane
12	$\tau(\text{C-C})$ tors.	$(\tau_{1234} + \tau_{5234} + \tau_{1236} + \tau_{5236})/2$

then transformed into local (valence) symmetry coordinates [35] (see tables 4 and 5, and fig. 1) and scaled using experimentally determined factors [36-38]. Two distinct sets of scale factors were utilized for correcting the force constants. In the first case, A, the congruent transformation of the force constant matrices were carried out using a diagonal matrix with the elements set to $0.8^{1/2}$, since ab initio calculations at the RHF/6-31G level overestimate the majority of the squares of vibrational frequencies by $\approx 20\%$. In the second case, B, the scale factors given in table 6 were used. These factors were obtained by matching the calculated and experimental values of the vibrational frequencies for glyoxal [1], buta-1,3-diene [39], and formyl fluoride by a least-squares technique [40]. The corresponding force constants (B) are listed in tables 7 and 8. The vibrational frequencies of oxalyl fluoride and acryloyl fluoride were *not* used in the refinement of their force fields, and in this

Table 6
Scale factors for force fields

Type of the coordinate	Scale factor	Type of the coordinate	Scale factor
C-C str.	0.8402	O-C-C in-plane	0.7917
C=C str.	0.7573	O-C-F in-plane	0.9021
C-O str.	0.8235	C-C (acr.)tors.	0.7584
C-H str.	0.8301	C-H, =CH ₂ wag.	0.6706
C-F str.	0.8252	C=C twist.	0.7980
$\angle \text{C=C-C}, \angle \text{C=C-H}$ (in-plane)	0.7944	C-F wag.	0.7926
		C-C (gl.)tors.	0.5189

Table 5
Definition and numbering of local symmetry coordinates of acryloyl fluoride

No.	Description	Definition
1	$\nu(\text{C-C})$ str.	$r(\text{C3-C2})$
2	$\nu(\text{C=C})$ str.	$r(\text{C4-C3})$
3	$\nu(\text{C-O})$ str.	$r(\text{C2-O1})$
4	$\nu(\text{C-H})$ str.	$r(\text{C3-H8})$
5	$\nu(\text{C-F})$ str.	$r(\text{C2-F5})$
6	$\nu(\text{=CH}_2)$ str.	$r(\text{C4-H6})$
7	$\nu(\text{=CH}_2)$ str.	$r(\text{C4-H7})$
8	$\delta(\text{C-C-C})$ bend.	$\angle \text{C2-C3-C4}$
9	$\delta(\text{C-C-O})$ bend.	$\angle \text{C3-C2-O1}$
10	$\rho(\text{C-H})$ rock.	$(\angle \text{H8-C3-C2} - \angle \text{C4-C3-H8})/\sqrt{2}$
11	$\rho(\text{C-F})$ rock.	$(\angle \text{C3-C2-F5} - \angle \text{O1-C2-F5})/\sqrt{2}$
12	$\delta(\text{=CH}_2)$ sciss.	$(2\angle \text{H7-C4-H6} - \angle \text{C3-C4-H6} - \angle \text{C3-C4-H7})/\sqrt{6}$
13	$\rho(\text{=CH}_2)$ rock.	$(\angle \text{C3-C4-H6} - \angle \text{C3-C4-H7})/\sqrt{2}$
14	$\tau(\text{C-C})$ tors.	$(\tau_{1234} + \tau_{1238} + \tau_{5234} + \tau_{5238})/2$
15	$\chi(\text{C-H})$ wag.	H8 out of C4-C3-C2 plane
16	$\chi(\text{C-F})$ wag.	F5 out of O1-C2-C3 plane
17	$\chi(\text{=CH}_2)$ wag.	C3 out of H7-C4-H6 plane
18	$\tau(\text{C=C})$ twist.	$(\tau_{2346} + \tau_{2347} + \tau_{8346} + \tau_{8347})/2$

sense, they may be regarded as a priori force fields.

The vibrational frequencies for all four molecules were then predicted with both scaled quantum mechanical (SQM) force fields (A and B) (see tables 9 and 10). For s-trans oxalyl fluoride the mean amplitudes of vibrations [41] were also calculated (table 11).

3. Discussion

3.1. Oxalyl fluoride

As was mentioned in section 1 the structure of the

Table 7

Scaled quantum mechanical (SQM) force fields of *s*-trans and *s*-cis oxalyl fluorides (O=CF-FC=O) (mdyn/Å, mdyn, mdyn Å)^{a)}

<i>i, j</i>	<i>F(i, j)</i>		<i>i, j</i>	<i>F(i, j)</i>	
	trans	cis		trans	cis
1, 1	4.4224	4.4238	7, 6	0.0508	-0.0119
2, 1	0.3548	0.3881	8, 1	0.3291	0.3523
2, 2	13.6403	13.6361	8, 2	-0.3850	-0.3882
3, 2	0.0314	0.0130	8, 3	-0.0353	0.1038
4, 1	0.2140	0.1858	8, 4	-0.0430	-0.0595
4, 2	0.9645	0.9675	8, 5	0.0956	-0.0192
4, 3	0.0981	0.0533	8, 6	0.0926	0.0816
4, 4	5.9423	5.9067	8, 7	0.0164	0.0049
5, 4	0.0182	0.1374	8, 8	1.1617	1.1838
6, 1	0.1150	0.1147	9, 8	0.0586	0.1003
6, 2	0.1896	0.1922	10, 10	0.3512	0.3658
6, 3	0.1759	-0.1207	11, 10	-0.0218	0.0233
6, 4	-0.5570	-0.5512	12, 10	-0.0070	0.0052
6, 5	-0.1022	0.1559	12, 12	0.0073	0.0045
6, 6	1.2661	1.2749			

^{a)} For the definition and numbering of coordinates see table 4 and fig. 1.

second stable form of oxalyl fluoride is still being debated. In this connection we have computed energy differences between a twisted (30°) gauche form and a planar (0°) *s*-cis form of oxalyl fluoride at several different levels of computation (see table 1). The energy differences are quite small, less than 0.50 kcal/mole in most cases, indicating that the potential curve near the cis minimum is very flat. The energy difference is especially sensitive to including polarization functions in the basis set, since changing from the RHF/6-31G//RHF/6-31G level to the RHF/6-31G**/RHF/6-31G* level results in 50% decrease in ΔE . On the other hand, correlation effects play a relatively small role in this energy difference. It may be noted that this effect is associated with a low value for the scale factor for the torsional coordinate (0.5189, see table 6). This factor was transferred directly from glyoxal, for which a stable planar cis form is firmly established by a microwave study [44], and gives excellent agreement between the computed and experimental torsional frequency ν_7 of *s*-trans oxalyl fluoride (table 9).

Thus the best computational evidence to date strongly suggests that the high energy conformer of oxalyl fluoride is planar *s*-cis. Furthermore, using the available experimental data, particularly the vibrational spectra can help clarify the situation as we shall soon show.

The calculated geometrical parameters (table 2) reproduce quite well the unique features of the experimental structure of trans oxalyl fluoride as measured in the electron diffraction study [42]. It is interesting to note that the value of the O=C-C angle decreases in going from the trans to the cis conformer. This is contrary to the case of glyoxal [1] and may suggest some F...F interaction. It should be mentioned that the value of the O=C-C angle calculated in ref. [2] deviates sharply from the experimental value and the values computed using the 6-31G and 6-31G* basis sets.

The vibrational frequencies computed with both force fields A and B are quite close (table 9), and it is possible to carry out the assignments of the experimental bands, generally speaking, with force field A.

The present calculations support the reassignments of the 513 cm⁻¹ band of trans OCF-FCO to the symmetrical bending of the O=C-C angle (ν_4) as was suggested in ref. [20]. However, the most significant reassignment which follows from our calculation is connected with vibrational modes ν_2 and ν_3 . In all previous analyses the band at 1278 cm⁻¹ was assigned to the C-F bond stretch [3,6,12-19]. The vibrational forms of ν_2 and ν_3 are highly "mixed". In order to avoid this difficulty the vibrational problems were solved for isotopomers with ¹³C. The iso-

Table 8

Scaled quantum mechanical (SQM) force fields of s-trans and s-cis acryloyl fluorides (mdyn/Å, mdyn, mdyn Å)^{a)}

	1	2	3	4	5	6	7	8	9
s-trans									
1	5.0969								
2	0.3419	8.6323							
3	0.4981	-0.0917	12.8051						
4	0.0173	0.0558	0.0241	5.2746					
5	0.3194	-0.0135	1.0401	0.0047	5.0199				
6	-0.0001	0.0329	0.0164	0.0097	-0.0043	5.2594			
7	-0.0368	0.0280	-0.0073	-0.0078	0.0204	0.0133	5.2984		
8	0.3374	0.2555	0.1035	-0.1288	0.0040	0.0402	-0.1057	1.2258	
9	0.0955	0.0296	0.2073	-0.0489	-0.6511	0.0063	0.0343	0.0627	1.3119
10	0.1852	-0.1776	-0.0037	0.0215	0.0578	0.0093	-0.0198	-0.0066	-0.0705
11	0.3377	0.0181	-0.3733	0.0262	-0.0077	0.0048	-0.0446	0.1131	0.0741
12	-0.0108	-0.2005	0.0004	-0.0040	-0.0227	0.0514	0.0454	-0.0188	-0.0150
13	0.0171	-0.0059	0.0279	-0.0272	-0.0196	0.0904	-0.0842	0.0439	0.0309
	10	11	12	13	14	15	16	17	18
10	0.5101								
11	0.0521	1.3116							
12	0.0153	0.0	0.4444						
13	0.0388	-0.0280	0.0036	0.5359					
14					0.0238				
15					-0.0112	0.2176			
16					-0.0048	-0.0136	0.3906		
17					-0.0011	0.0219	-0.0105	0.2650	
18					0.0087	-0.0031	0.0204	-0.0005	0.1284
	1	2	3	4	5	6	7	8	9
s-cis									
1	5.0442								
2	0.3381	8.6080							
3	0.5602	-0.1293	12.6070						
4	0.0066	0.0524	0.0064	5.3072					
5	0.2778	-0.0186	1.0430	0.0280	5.1806				
6	0.0	0.0319	-0.0035	0.0095	0.0127	5.2662			
7	-0.0159	0.0486	0.0171	-0.0076	-0.0030	0.0126	5.2449		
8	0.2622	0.2314	-0.0078	-0.1214	0.0885	0.0389	-0.0608	1.1092	
9	0.1926	-0.0681	0.1888	0.0623	-0.6442	-0.0032	-0.0228	-0.0488	1.3397
10	0.1983	-0.1766	0.0479	0.0102	0.0057	0.0088	0.0192	-0.0076	0.0747
11	0.2623	0.0405	-0.3704	-0.0352	0.0112	0.0084	0.0044	0.0795	0.1263
12	-0.0018	-0.1956	-0.0157	-0.0042	0.0013	0.0508	0.0352	-0.0049	0.0197
13	0.0327	-0.0007	-0.0073	-0.0265	0.0358	0.908	-0.1024	0.0771	-0.0112
	10	11	12	13	14	15	16	17	18
10	0.5083								
11	-0.0138	1.2264							
12	0.0149	-0.0097	0.4416						
13	0.0393	0.0114	0.0045	0.5272					
14					0.0169				
15					-0.0025	0.2318			
16					-0.0015	0.0169	0.3812		
17					-0.0011	0.0209	0.0109	0.2633	
18					0.0007	-0.0103	-0.0207	0.0020	0.1277

^{a)} For the definition and numbering of coordinates see table 5 and fig. 1.

Table 9

Experimental and calculated vibrational frequencies of s-trans and s-cis oxalyl fluorides (cm^{-1})

No.	Description	Sym.	s-trans OCF-FCO			Sym.	s-cis OCF-FCO		
			exptl. [3,6,12]	calc. ^{a)}			exptl. [3,6,12]	calc. ^{a)}	
				A	B			A	B
1	$\nu(\text{C}=\text{O})$ str.	A_g	1867	1832	1863	A_1	1897	1840	1868
2	$\nu(\text{C}-\text{C})$ str.		1278	1267	1283		1267	1266	1290
3	$\nu(\text{C}-\text{F})$ str.		804	777	798		799	776	793
4	$\delta(\text{C}-\text{C}=\text{O})$ def.		513	513	514		249	247	251
5	$\rho(\text{C}-\text{F})$ rock.		415	398	416		420	414	427
6	$\chi(\text{C}-\text{F})$ wag.	A_u	421	432	430	A_2	-	762	758
7	$\tau(\text{C}-\text{C})$ tors.		54	59	48		-	46	37
8	$\chi(\text{C}-\text{F})$ wag.	B_g	-	755	752	B_2	-	436	434
9	$\nu(\text{C}=\text{O})$ str.	B_u	1865	1814	1841	B_1	-	1800	1827
10	$\nu(\text{C}-\text{F})$ str.		1105	1097	1118		1093	1095	1108
11	$\rho(\text{C}-\text{F})$ rock.		673	636	661		664	638	661
12	$\delta(\text{C}-\text{C}=\text{O})$ def.		257	243	246		-	492	502

^{a)} A is for the solution of the vibrational problem with the force constant matrix multiplied uniformly by 0.8 (see section 2). B is for the solution of the vibrational problem with the force constant matrix multiplied by the scale factors given in table 6.

Table 10

Experimental and calculated vibrational frequencies ν_n of s-trans and s-cis acryloyl fluorides (cm^{-1})

No.	Description	Sym.	s-trans O=CF-CH=CH ₂				s-cis O=CF-CH=CH ₂			
			exptl.		calc. ^{b)}		exptl.		calc. ^{b)}	
			[24]	[27]	A	B	[24]	[27]	A	B
1	$\nu(=\text{CH}_2)$ a str.	A'	3125	3126	3089	3146	3120	-	3084	3141
2	$\nu(\text{C}-\text{H})$ str.		3057	3084	3046	3102	3049	3090	3054	3111
3	$\nu(=\text{CH}_2)$ s str.		3005	3058	3002	3057	3005	-	2996	3050
4	$\nu(\text{C}=\text{O})$ str.		1839.5 ^{a)}	1803 ^{a)}	1782	1810	1835 ^{a)}	1813 ^{a)}	1765	1794
5	$\nu(\text{C}-\text{C})$ str.		1636	1630 ^{a)}	1649	1622	1634	1623 ^{a)}	1653	1626
6	$\delta(=\text{CH}_2)$ sci.		1409.9	1413	1430	1424	1412.0	1409	1430	1425
7	$\delta(\text{C}-\text{H})$ def.		1298.0	1298	1302	1293	1296.0	1285	1309	1299
8	$\nu(\text{C}-\text{C})$ str.		1226	1225	1226	1239	1125.0	1125	1138	1156
9	$\rho(=\text{CH}_2)$ rock.		1002.9 ^{a)}	980	1013	1016	1115 ^{a)}	-	1084	1083
10	$\nu(\text{C}-\text{F})$ str.		811 ^{a)}	826	789	803	830	810	812	825
11	$\delta(\text{C}-\text{F})$ def.		606.2	606	579	602	495	510 ^{a)}	484	487
12	$\delta(\text{C}-\text{C}=\text{O})$ def.		526.0	527	523	524	626.3	627	609	616
13	$\delta(\text{C}-\text{C}=\text{C})$ def.		277	283	270	272	262	276	263	263
14	$\chi(\text{C}-\text{H})$ wag.	A''	999.8 ^{a)}	990	1016	994	990.0	988	1011	992
15	$\chi(=\text{CH}_2)$ wag.		986.0	986	1079	978	977.4	977	1079	977
16	$\chi(\text{C}-\text{F})$ wag.		804	800	794	773	800.2	805	797	775
17	$\tau(=\text{CH}_2)$ tw.		485.3	476	482	467	485.3	486	484	468
18	$\tau(\text{C}-\text{C})$ tors.		115	117	133	129	109	101	117	114

^{a)} Crystal phase. ^{b)} See footnote a to table 9.

Table 11
Mean amplitudes of vibrations of s-trans and s-cis oxalyl fluoride (ångström)

	Parameter	Exptl. [42]	Calc.		
			0 K	298 K	298 K [17]
1	$l(\text{C}-\text{C})$	0.053(4)	0.0485	0.0495	0.0475
2	$l(\text{C}-\text{O})$	0.042(2)	0.0367	0.0367	0.0380
3	$l(\text{C}-\text{F})$	0.050(2)	0.0443	0.0446	0.0530
4	$l(\text{O}\dots\text{F})$	0.055(3)	0.0497	0.0516	0.0537
5	$l(\text{C}\dots\text{F})$	0.065(3)	0.0570	0.0634	0.0633
6	$l(\text{C}\dots\text{O})$	0.056(3)	0.0544	0.0592	0.0635

topic shifts of the calculated frequencies 1283 cm^{-1} (ν_2) and 798 cm^{-1} (ν_3) of the parent oxalyl fluoride on going to trans- $^{13}\text{C}_2$ -oxalyl fluoride turned out to be -43 and -7 cm^{-1} , respectively. Nearly the same isotopic shifts were also obtained for the cis- $^{13}\text{C}_2$ -conformer, viz. -44 and -6 cm^{-1} . Therefore, the experimental bands at 1278 and 1267 cm^{-1} were assigned as the stretch modes of the single C-C bonds and the bands at 804 and 799 cm^{-1} were attributed to the symmetrical stretch modes of the C-F bonds of the trans and cis conformers, respectively. The experimental Raman spectra of these conformers do not allow an unambiguous assignment of these frequencies since the corresponding bands are intense and manifest a high degree of depolarization [3]. Transition from the trans to the cis form results primarily in a change of the bending modes of the O=C-C angles ν_4 and $\nu_{1,2}$, while in the case of glyoxal the stretch vibration of the single C-C bond is also involved [1]. It should be mentioned that the calculated value of the torsional frequency for the cis conformer was found to be about 40 cm^{-1} . In refs. [7,8,10] this magnitude was measured in the UV spectrum of oxalyl fluoride and found to be 5.6 cm^{-1} in the ground electronic state. This very low value of the torsional frequency led to a prediction of a gauche structure (about 15° from planar cis form) of the high energy conformer [10]. Earlier the gauche structure was predicted by ab initio calculations at the minimal RHF/STO-3G level [9].

An experimental argument for the realization of the planar rather than gauche structure of the high energy rotational isomer of oxalyl fluoride can be based, in general, on the appearance in the Raman spectrum of the bands of the ν_6 and ν_7 vibrations and their ab-

sence in the IR spectrum of this rotamer (see table 9). Indeed, in the case of an s-cis conformation these vibrations must belong to the A_2 symmetry type and be forbidden in the IR spectrum and active in the Raman spectrum (see table 9). However, these bands were not observed either in the IR or Raman spectra. This may be explained by the very low intensity of these out-of-plane bands in the Raman spectrum which is a characteristic for these vibrations. This explanation is supported by the absence of the out-of-plane vibration ν_8 in the experimental Raman spectrum of trans oxalyl fluoride. On the other hand, these vibrations would be active in the IR spectrum in the case of a non-planar gauche structure and the intensities of these bands would be very high and they would most certainly be detected experimentally. Therefore, the absence of the ν_6 and ν_7 bands in the IR spectrum is supporting evidence for a planar structure for the minor rotamer of oxalyl fluoride. Of course, a detailed analysis of the vibrational spectra from a low temperature matrix study of oxalyl is desirable.

Another argument which favors the planar structure is the very good prediction of the ν_4 vibration of s-cis OCF-FCO. The value of this frequency ν_4 is very sensitive to the angle of internal rotation in oxalyl fluoride, since it changes from 513 to 249 cm^{-1} in going from the trans to the cis conformer. This suggests that the possible deviation from the planar structure of the high energy conformer should result in the marked deviation of the calculated wave number from the experimental value. However, the excellent agreement between the theoretical and experimental values of ν_4 , demonstrates the realization of the planar s-cis structure.

The reassignment of some fundamentals of trans oxalyl fluoride affected the mean amplitudes of vibrations, see table 11. The erroneous assignments of ν_{11} and ν_{12} in ref. [17] resulted in an overestimated value of the mean amplitude $l(\text{C}\cdots\text{O})$.

3.2. Acryloyl fluoride

The calculated changes in the structure of acryloyl fluoride in going from the trans to the cis conformer, parallel the experimental changes found in studying the microwave spectrum of this molecule [21]. Indeed, the calculated values of the O=C-C, C=C-C, and F-C-C angles of the two conformers agree well with the observed experimental changes. The computed lengths of all the bonds are nearly the same in the two conformers in accordance with the experimental results [21]. As expected, the values of most of the calculated geometrical parameters at the MP2/6-31G* level agree better with the experimental values since correlation effects have been included. The values of the O=C-C and F-C-C angles calculated from the moments of inertia in ref. [43] deviate markedly from the present calculation and the results of ref. [21].

All the experimental frequencies of the trans and cis conformers of acryloyl fluoride (table 10) were taken from the studies of Redington [24] and Durig et al. [27]. The experimental value of 109 cm^{-1} for ν_{18} was also measured in the UV spectrum [29]. While assigning the experimental vibrational spectrum of a mixture of the two rotamers, all the criteria used in refs. [24,27] to separate the frequencies of these conformers were explicitly taken into consideration.

For the in-plane vibrations of the trans and cis forms of acryloyl fluoride, the assignments obtained in the present work coincide, in general, with those of ref. [27]. They corroborate the reassignments of the experimental vibrational frequencies [24,26,29] performed in ref. [27]. Exceptions are the ν_9 and ν_{12} modes of the trans and cis conformers. In ref. [27] the frequencies of the in-plane vibrations $\rho(=\text{CH}_2)$ rock. and $\delta(\text{C-F})\text{def.}$ are assigned as wagging vibrations of the $=\text{CH}_2$ and O=C-F moieties. It should be noted that the wagging notations are usually used for the out-of-plane vibrations in planar molecular frag-

ments. Furthermore, in ref. [27] the band at 999 cm^{-1} is assigned as ν_9 for cis acryloyl fluoride. However, the region of 1000 cm^{-1} is overcrowded by very intense out-of-plane bands (ν_{14} and ν_{15} of both conformers). In the same region there is also a band associated with the rocking vibration of the $=\text{CH}_2$ moiety of the trans conformer. Therefore, it is very difficult to identify an additional band ν_9 of the cis conformer in this spectral region. Our calculated value of this frequency is 1083 cm^{-1} which is quite close to the experimental value of 1115 cm^{-1} (crystal phase). The band at 1115 cm^{-1} is overlapped in the gas phase by the more intense band at 1125.0 cm^{-1} and is observed only in the crystal phase [24]. In general, factor group splitting (Davydov splitting) may take place here. Indeed, the corresponding band ν_8 of the s-trans rotamer is split in the Raman spectrum of the solid [27]. However, the appearance of Davydov splitting depends not only on the symmetry of a molecule but also on the structure of the crystal.

The corresponding value of this vibration in ref. [27], calculated from the scaled ab initio force field, is 1040 cm^{-1} . This variation in the computed values is likely due to the different scaling techniques employed. In the case of ref. [27] the scaling was carried out only for the diagonal elements of the quantum mechanical force field from the experimental frequencies of the trans and cis conformers with prescribed assignments. Besides, the corresponding force field for the cis conformer was computed at the 3-21G level, while the force field of the trans conformer was obtained at the 6-31G* level. The present scaled force fields of both the trans and cis rotamers were obtained from the quantum mechanical force fields calculated at the same RHF/6-31G level. This was followed by correcting all the force constants with scale factors transferred from related small molecules. Therefore, they are nearly a priori force fields, and the calculated frequencies can be considered as predicted.

From the two bands at 495 and 485.3 cm^{-1} of cis acryloyl fluoride (see table 10) the last one shows a C-type contour [24] and may be assigned as the out-of-plane vibration. Durig et al. [27] also assigned the bands at 510 and 486 cm^{-1} (see table 10) as fundamentals. According to our calculations the bands at 510 and 627 cm^{-1} should be assigned as $\delta(\text{C-F})\text{def.}$ and $\delta(\text{C-C=O})\text{def.}$, respectively.

Table 12
Experimental ΔH and calculated ab initio ΔE values of rotational isomers of acryloyl fluoride (cal/mole)^{a)}

Experimental		Calculated	
method	ΔH	theoret. level	ΔE
MW [21]	90 ± 100	3-21G [27]	91
IR, Raman [22]	99 ± 15	4-21G [9]	400
UV [23]	114 ± 86	6-31G this work	246
IR [26]	150 ± 100	6-31G* [27]	226
IR [24]	251	MP2/6-31G* this work	276
NMR [28]	253 ± 67		
NMR [25]	800 ± 250		
Raman ^{b)} [27]	-266 ± 94		

^{a)} In harmonic approximation $\Delta H = \Delta E + \frac{1}{2}(\omega_{\text{cis}} - \omega_{\text{trans}})$.

^{b)} From temperature studies of the Raman spectra of the gas the cis conformer was calculated to be more stable.

Our assignments of the out-of-plane vibrations are at variance with results of ref. [27]. In ref. [27] the ν_{15} , ν_{16} , and ν_{17} vibrations are attributed to rocking and bending vibrations which are characteristics of the in-plane vibrations. However, the values of the experimental frequencies for trans and cis acryloyl fluoride interpreted in the present work as the out-of-plane vibrations coincide with the corresponding experimental wave numbers in ref. [27]. An exception is the band at 486 cm^{-1} (ν_{17}) of cis acryloyl fluoride mentioned above. It should be noted that the assignments suggested here are based on the isotopic shifts as was done in the case of acrolein (see details in ref. [1]). The difference of energies of two conformers obtained in the present calculation, $\Delta E = 246$ cal/mole (RHF/6-31G) and $\Delta E = 276$ cal/mole (MP2/6-31G*), correlates quite well with values ΔH reported in previous studies [24,27,28] and corroborates that the population of the cis conformer is quite high (table 12). The variations in values of ΔH are explained in ref. [27] by solvent effects.

4. Conclusion

All the calculations performed in this paper predict that both conformers of oxalyl fluoride and acryloyl fluoride in the ground electronic state are planar s-trans (anti) and s-cis (syn) structures. All the experimental vibrational frequencies of these compounds may be attributed to these planar rotamers. The approach of transferring the scale factors from related

molecules, as applied in the present work, is clearly reasonable, since it allows the prediction of the vibrational assignments which agree with experiment and also do not contradict the results on isotopic shifts.

Acknowledgement

The authors would like to thank the Computer Center of the Philadelphia College of Textiles and Science for a generous grant of computer time. Many of the calculations were carried out on a Multiflow Trace 7/200 at the American Research Institute and the Cray Y/MP at the Pittsburgh Supercomputer Center.

References

- [1] C.W. Bock, Yu.N. Panchenko and S.V. Krasnoshchiokov, Chem. Phys. 125 (1988) 63.
- [2] J. Tyrrell, J. Am. Chem. Soc. 98 (1976) 5456.
- [3] J. Goubeau and M. Adelheim, Spectrochim. Acta 28 A (1972) 2471.
- [4] D.C. Frost, C.A. McDowell, G. Pouzard and N.C.P. Westwood, J. Electron Spectry. 10 (1977) 273.
- [5] W. von Niessen, G.H.F. Diercksen and L.S. Cederbaum, J. Am. Chem. Soc. 100 (1978) 6374.
- [6] J.R. Durig, S.C. Brown and S.E. Hannum, J. Chem. Phys. 54 (1971) 4428.
- [7] I.A. Godunov and V.I. Tyulin, Deposited Document, VINITI, N 5472-81 (1981).
- [8] I.A. Godunov and V.I. Tyulin, Deposited Document, VINITI, N 5473-81 (1981).

- [9] A.J.P. Devaquet, R.E. Townshend and W.J. Hehre, *J. Am. Chem. Soc.* 98 (1976) 4068.
- [10] I.A. Godunov, A.V. Abramnikov and V.I. Tyulin, *Zh. Strukt. Khim.* 24 (1983) 31.
- [11] Yu.N. Panchenko, V.I. Mochalov and Yu.A. Pentin, *Moscow Univ. Chem. Bull.* 38 (1983) N4, 51 (English pagination).
- [12] J.L. Hencher and G.W. King, *J. Mol. Spectry.* 16 (1965) 168.
- [13] R. Ramasamy, *Indian J. Pure Appl. Phys.* 16 (1978) 866.
- [14] G. Fleury, *Compt. Rend. Acad. Sci. (Paris)* 268 B (1969) 1489.
- [15] J.G. Contreras and J.O. Machuca, *An. Quim. A* 77 (1981) 370.
- [16] J.G. Contreras and J.O. Machuca, *An. Quim. A* 78 (1982) 35.
- [17] J.G. Contreras and J.O. Machuca, *An. Quim. A* 78 (1982) 321.
- [18] G. Fleury and L. Bardet, *J. Mol. Struct.* 2 (1968) 67.
- [19] K. Venkatesvarlu and P. Bhamambal, *Indian J. Pure Appl. Phys.* 8 (1970) 180.
- [20] G. Moller and D.S. Tinti, *Mol. Phys.* 54 (1985) 541.
- [21] J.J. Keirns and R.F. Curl Jr., *J. Chem. Phys.* 48 (1968) 3773.
- [22] J.R. Durig, J.S. Church and D.A.C. Compton, *J. Chem. Phys.* 71 (1979) 1175.
- [23] L.A. Glebova, L.N. Margolin, Yu.A. Pentin and V.I. Tyulin, *Zh. Strukt. Khim* 17 (1976) 703 (English pagination).
- [24] R.L. Redington, *J. Chem. Phys.* 62 (1975) 4927.
- [25] D.F. Koster, *J. Am. Chem. Soc.* 88 (1966) 5067.
- [26] G.L. Carlson, W.G. Fately and R.W. Witkowski, *J. Am. Chem. Soc.* 89 (1967) 6437.
- [27] J.R. Durig, R.J. Berry and P. Groner, *J. Chem. Phys.* 87 (1987) 6303.
- [28] F.F.S. Lin and H.L. Servis, *J. Am. Chem. Soc.* 94 (1972) 5794.
- [29] L.A. Glebova, L.N. Margolin and V.I. Tyulin, *Moscow Univ. Chem. Bull.* 32 (1977) N 2, 170 (English pagination).
- [30] L.N. Bazhenova, G.S. Koptev and V.I. Tyulin, *Moscow Univ. Chem. Bull.* 40 (1985) N 1, 20 (English pagination).
- [31] W.H. Hehre, R. Ditchfield and J.A. Pople, *J. Chem. Phys.* 56 (1972) 2257.
- [32] J.S. Binkley, M.J. Frisch, D.J. DeFrees, K. Raghavachari, R.A. Whiteside, H.B. Schlegel, E.M. Fluder and J.A. Pople, *GAUSSIAN 82*, Carnegie-Mellon University, Pittsburgh, PA, USA (1983).
- [33] M.S. Frisch, J.S. Binkley, H.B. Schlegel, K. Raghavachari, C.F. Melius, R.L. Martin, J.J.P. Stewart, F.W. Bobrowicz, C.M. Rohlfing, L.R. Kahn, D.J. DeFrees, R. Seeger, R.A. Whiteside, D.J. Fox, E.M. Fluder and J.A. Pople, *GAUSSIAN 86*, Carnegie-Mellon University Pittsburgh, PA, USA (1984).
- [34] C. Møller and M.S. Plesset, *Phys. Rev.* 46 (1934) 618.
- [35] P. Pulay, G. Fogarasi, F. Pang and J.E. Boggs, *J. Am. Chem. Soc.* 101 (1979) 2550.
- [36] P. Pulay, in: *Applications of Electronic Structure Theory*, ed. H.F. Schaefer III (Plenum Press, New York, 1977) p. 153.
- [37] G. Fogarasi and P. Pulay, *Ann. Rev. Phys. Chem.* 35 (1984) 191.
- [38] G. Fogarasi and P. Pulay, in: *Vibrational Spectra and Structure*, Vol. 14, ed. J.R. Durig (Elsevier, Amsterdam, 1984).
- [39] C.W. Bock, Yu.N. Panchenko, S.V. Krasnoshchiokov and V.I. Pupyshev, *J. Mol. Struct.* 129 (1985) 57.
- [40] S.V. Krasnoshchiokov, A.V. Abramnikov and Yu.N. Panchenko, *Moscow Univ. Chem. Bull.* 40 (1985) N 1, 31 (English pagination).
- [41] S.J. Cyvin, *Molecular Vibrations and Mean Square Amplitudes* (Elsevier, Amsterdam, 1968).
- [42] D.T. Frisen, *Diss. Abstr. Int.* 41B (1981) N 9, 3458.
- [43] A.A. Zenkin, L.N. Margolin, Yu.A. Pentin and V.I. Tyulin, *J. Mol. Struct.* 29 (1975) 65.
- [44] M. Rodler, M. Oldani, G. Grassi and A. Bauder, *J. Chem. Phys.* 86 (1987) 5365.