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AN AB INITIO PREDICTION OF STRUCTURES AND VIBRATIONAL FREQUENCIES OF HIGH-ENERGY ROTAMERS OF GLYOXAL AND ACROLEIN

Ch.W. BOCK

Department of Chemistry, Philadelphia College of Textiles and Science,
Philadelphia, PA 19144, USA

Yu.N. PANCHENKO and S.V. KRASNOSHCHIOKOV

Laboratory of Molecular Spectroscopy, Department of Chemistry, M.V. Lomonosov Moscow State University,
Moscow 119 899, USSR

Complete optimizations of the structures and calculations of the harmonic force fields for glyoxal and acrolein stable forms in the ground electronic state have been carried out at the RHF/6-31G level. The high-energy conformers are found to be planar for both molecules in agreement with previous calculations. The empirical scale factors correcting the ab initio force field were computed for the trans (anti) conformer of glyoxal. The corresponding scale factors from 1,3-butadiene and the scale factors obtained for trans-glyoxal were then employed to correct the ab initio force fields of the cis (syn) conformer of glyoxal and both rotamers of acrolein. The vibrational frequencies were computed with the scaled quantum mechanical (SQM) force fields and some molecular parameters are also calculated. The assignment of some frequencies is also discussed.

1. Introduction

At present it is well established from experimental and theoretical investigations that the high-energy rotational isomers of glyoxal [1–11] and acrolein [4,5,7,12–16] possess the planar cis (syn) structures (see also references in cited works).

From the moment of experimental detection of the vibrational frequencies of the cis forms of glyoxal [1,2,17–20] and acrolein [21–27], a series of calculations of the force fields and vibrational frequencies of both conformers were performed. Such calculations were carried out using both the traditional technique of "reduction" of the force constant matrix from experimental vibrational frequencies followed by solution of the vibrational problem [28], and semi-empirical [29] and ab initio quantum mechanical methods [3,15]. However, an insufficient number of scale factors were used in the semi-empirical calculation [29]. This resulted in noticeable deviations of the calculated frequencies from the experimental ones. In ab inito calculations, recent scale factor techniques were not utilized [3,15].

In this connection it seems pertinent to perform an ab initio calculation of the geometry and vibrational frequencies of both stable forms of glyoxal and acrolein in sufficiently complete basis set and using an improved scaling procedure for the force field. This will allow us to achieve a good agreement between calculated and experimental vibrational frequencies of the trans rotamers and to predict quite exactly the observed and unobserved wavenumbers of the cis rotamers. Earlier this approach was successfully applied to the vibrational analysis of gauche 1,3-butadiene [30] and gauche-isoprene [31].

2. Method of calculation

The complete optimization of the geometry of the trans and cis forms of glyoxal and acrolein was done using the Hartree–Fock formalism at the 6-31G level and employing standard analytic gradient techniques [32]. The optimized geometrical parameters of these four molecules are given in tables 1 and 2 (see also fig. 1).

Table 1
Geometrical parameters of s-trans- and s-cis-glyoxal (ångström, degree and atomic units)

Parameter	s-trans-O=CH-CH=O				s-cis-O=CH-CH=O				
	exp. [42] a)	4-31G [8]	DZ+P [10]	6-31G this work	exp. [2] a)	[43] a)	4-31G [8]	DZ+P [10]	6-31G this work
r(C-C)	1.527±0.017	1.5129	1.521	1.494	1.505±0.015 b)	1.544 c)	1.5187	1.534	1.502
r(C=O)	1.202±0.012	1.2070	1.189	1.210	1.210±0.005	1.200	1.2055	1.185	1.208
r(C-H)	1.109±0.008	1.0820	1.092	1.081	1.115±0.010 b)	1.109	1.0835	1.096	1.082
∠O=C-C	121.15 ±0.15	120.87	121.1	120.7	123.8 ±0.04	122.5	122.58	122.7	122.7
∠H-C-C	115.5 ±3.0	115.03	115.3	116.5	115.5 ±1.5	115.3 b)	114.63	115.1	116.0
energy		-226.04811	-226.64294	-226.47596			-226.03998	-226.63361	-226.46690

a) r_0 structure.   b) Assumed bond distance.
c) Some of the original assignments of Durig et al. [1,9] in the microwave spectrum of s-cis-glyoxal were later revised by Mamleev et al. [43]. Since the rotational constants experienced substantial corrections, the structural data derived there from ref. [43] were recalculated in the present work.

The analytical force fields were computed for the trans and cis optimized structures of glyoxal and acrolein. The definitions of internal local valence coordinates are given in tables 3 and 4. First, the scaled quantum mechanical (SQM) force field [34–36] was calculated for trans-glyoxal (table 5). A value of 0.8 was chosen as a starting scale factor for all coordinates. This approximation was adequate to perform the assignment of the experimental frequencies of $C_2O_2H_2$ and $C_2O_2D_2$ [37–39]. Then the starting scale factors were refined by the least-squares method controlling the potentially ill-conditioned Jacobian by the singular value decomposition method [40]. The scale factors obtained (table 6) were then transferred to the cis-glyoxal force field (table 7). Results of vibrational frequency calculations for these two forms of glyoxal and their isotopomers are summarized in table 8.

The set of scale factors for trans- and cis-acrolein was compiled from the corresponding values of glyoxal (table 6) and 1,3-butadiene [30]. The scale factors for the C–C single bond stretch and the C–C torsion were taken to be the arithmetic mean of the values for glyoxal and 1,3-butadiene. Therefore, these SQM force fields only involve experimental information about the vibrational frequencies via the scale factors transferred from related molecules. In this sense they are a priori force constants. The Coriolis constants (table 8) and mean amplitudes of vibrations of trans-glyoxal (table 9) were calculated with
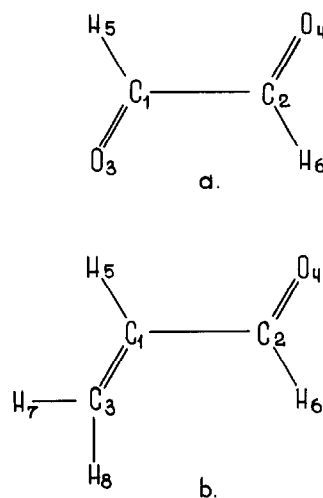
Fig. 1. Numbering of atoms of glyoxal (a) and acrolein (b).

Table 2
Structural parameters of s-trans- and s-cis-acrolein (ångström, degree and atomic units)

Parameter	s-trans-acrolein			s-cis-acrolein		
	exp. [12] [a]	6-31G this work	6-31G* [14,16]	exp. [12] [a]	6-31G this work	6-31G* [14,16]
r(C–C)	1.468	1.466	1.478	1.478	1.473	1.486
r(C=C)	1.340	1.326	1.321	1.340	1.326	1.321
r(C=O)	1.214	1.216	1.190	1.215	1.218	1.191
r(C–H) formyl	1.113	1.086	1.095	1.106	1.084	1.094
r(C–H) vinyl	1.084	1.073	1.076	1.088	1.074	1.077
r(C–H) cis	1.090	1.075	1.077	1.098	1.073	1.075
r(C–H) trans	1.080	1.072	1.075	1.081	1.073	1.075
∠C=C–C	120.4	121.7	121.2	121.5	122.1	121.5
∠O=C–C	124.0	123.6	123.9	124.2	124.3	124.4
∠C–C–H formyl	114.7	116.3	115.3	115.8	116.1	115.4
∠C=C–H vinyl	122.4	122.1	122.4	121.1	121.2	121.5
∠C=C–H cis	119.7	121.7	121.5	118.5	120.8	120.7
∠C=C–H trans	122.2	122.1	122.1	121.5	121.8	121.8
∠O=C–H formyl	121.3	120.1	120.9	120.1	119.6	120.3
∠C–C–H vinyl	117.2	116.3	116.4	117.4	116.7	117.0
∠H–C–H	118.1	116.3	116.4	120.0	117.4	117.5
energy		−190.67776	−190.76243		−190.67577	−190.75977

[a] So-called substitution structure which is close to the equilibrium parameters.

the SQM force field obtained. The trans- and cis-acrolein SQM force fields are presented in tables 10 and 11. The calculated and experimental vibrational frequencies of trans- and cis-acrolein are given in table 12. Table 13 contains the calculated values of mean amplitudes of vibrations for trans-acrolein. The calculation technique was taken from ref. [41].

It should be mentioned that the calculations of the harmonic frequencies for the 6-31G planar cis conformers of these molecules from unscaled and scaled force fields did not result in imaginary frequencies, indicating that the planar structures are energy minima.

Table 3
Definition of local symmetry coordinates of glyoxal (see fig. 1 and ref. [33])

Number	Description	Definition
1	ν (C–C) str.	r(C1–C2)
2	ν (C=O) str.	r(C1=O3)
3	ν (C=O) str.	r(C2=O4)
4	ν (C–H) str.	r(C1–H5)
5	ν (C–H) str.	r(C2–H6)
6	δ (C–C=O) bend.	∠C2–C1=O3
7	δ (C–C=O) bend.	∠C1–C2=O4
8	ρ (C–H) rock.	$(\angle H5–C1–C2 − \angle H5–C1=O3)/\sqrt{2}$
9	ρ (C–H) rock.	$(\angle H6–C2–C1 − \angle H6–C2=O4)/\sqrt{2}$
10	τ (C–C) tors.	$(\tau\,3124+\tau\,5124+\tau\,3126+\tau\,5126)/2$
11	χ (C–H) wag.	H5 out of O3=C1–C2 plane
12	χ (C–H) wag.	H6 out of O4=C2–C1 plane

Table 4
Definition of local symmetry coordinates of acrolein (see fig. 1 and ref. [33])

Number	Description [a]	Definition
1	ν (C–C) str.	r(C1–C2)
2	ν (C=C) str.	r(C1=C3)
3	ν (C=O) str.	r(C2=O4)
4	ν (C–H) str. v	r(C1–H5)
5	ν (C–H) str. f	r(C2–H6)
6	ν (=CH$_2$) str.	r(C3–H8)
7	ν (=CH$_2$) str.	r(C3–H7)
8	δ (C–C=C) bend.	$\angle$C2–C1=C3
9	δ (C–C=O) bend.	$\angle$C1–C2=O4
10	ρ (C–H) rock. v	$(\angle$H5–C1–C2 $- \angle$C3=C1–H5$)/\sqrt{2}$
11	ρ (C–H) rock. f	$(\angle$C1–C2–H6 $- \angle$O4=C2–H6$)/\sqrt{2}$
12	δ (=CH$_2$) sciss.	$(2 \angle$H7–C3–H8 $- \angle$C1=C3–H7 $- \angle$C1=C3–H8$)/\sqrt{6}$
13	ρ (=CH$_2$) rock.	$(\angle$C1=C3–H8 $- \angle$C1=C3–H7$)/\sqrt{2}$
14	τ (C–C) tors.	$(\tau 4213 + \tau 4215 + \tau 6215 + \tau 6213)/2$
15	χ (C–H) wag. v	H5 out of C2–C1=C3 plane
16	χ (C–H) wag. f	H6 out of O4=C2–C1 plane
17	χ (=CH$_2$) wag.	C1 out of H7–C3–H8 plane
18	τ (C=C) twist	$(\tau 2137 + \tau 2138 + \tau 5137 + \tau 5138)/2$

[a] v stands for vinyl, f stands for formyl.

Table 5
Scaled quantum mechanical force field of s-trans-glyoxal (mdyn/Å, mdyn, mdyn Å)

	1	2	3	4	5	6	7	8	9
1	4.1764								
2	0.5064	12.2750							
3	0.5064	0.0289	12.2750						
4	0.0055	0.2838	0.0723	4.4544					
5	0.0055	0.0723	0.2838	0.0065	4.4544				
6	0.1670	0.2947	0.1474	−0.1223	−0.0339	1.2060			
7	0.1670	0.1474	0.2947	−0.0339	−0.1223	−0.3071	1.2060		
8	0.1509	−0.2945	−0.0060	0.0313	0.0149	0.0974	−0.0996	0.5421	
9	0.1509	−0.0060	−0.2945	0.0149	0.0313	−0.0996	0.0974	0.0350	0.5421

	10	11	12
10	0.0126		
11	−0.0024	0.3433	
12	−0.0024	−0.0393	0.3433

3. Discussion

3.1. Glyoxal

The calculated geometrical parameters of trans- and cis-glyoxal are juxtaposed with the experimental data (table 1) derived from analysis of the rotational structure for the bands of the H^{13}CO–OCH molecule [42,43] and the bands of the cis rotamer of the HCO–OCH molecule [43]. The results of other ab initio geometry optimizations of the trans and cis conform-

Table 6
Scale factors for glyoxal and acrolein

Coordinate	Glyoxal (optimized scale factors)	Acrolein (transferred scale factors)
C–C stretch	0.8290	0.8402 [a]
C=O stretch	0.8235	0.8235
C=C stretch		0.7573 [b]
C–C stretch	0.7535	0.7535
C=C–C, C=C–H in plane		0.7944 [b]
C–C–H, O=C–C in plane	0.7917	0.7917
C–C torsion	0.5189	0.7584 [a]
C–H stretch		0.8301 [b]
C–H, =CH$_2$ wag.		0.6706 [b]
C–H wag.	0.7805	0.7805
C=C twist		0.7980 [b]

[a] Arithmetic mean of corresponding values for glyoxal and 1,3-butadiene [30].
[b] Transferred from 1,3-butadiene [30].

Table 7
Scaled quantum mechanical force field of s-cis-glyoxal (mdyn/Å, mdyn, mdyn Å)

	1	2	3	4	5	6	7	8	9
1	4.0980								
2	0.5119	12.3037							
3	0.5119	0.0163	12.3037						
4	0.0185	0.3375	0.0501	4.3742					
5	0.0185	0.0501	0.3375	0.0258	4.3742				
6	0.2508	0.1795	−0.1323	−0.1326	0.0393	1.2289			
7	0.2508	−0.1323	0.1795	0.0393	−0.1326	−0.1596	1.2289		
8	0.1664	−0.3240	0.0427	0.0174	0.0199	0.0901	0.0829	0.5844	
9	0.1664	0.0427	−0.3240	0.0199	0.0174	0.0829	0.0901	−0.0090	0.5844

	10	11	12
10	0.0034		
11	−0.0024	0.3423	
12	−0.0024	0.0391	0.3423

ers at the Hartree–Fock level using various basis sets with and without polarization functions on the hydrogens and heavy atoms [8,10] are also included in table 1.

Comparison of the calculated results with the experimental data shows that in the case of trans-glyoxal the values calculated in ref. [10] agree better with the experimental geometrical parameters, due to the more complete basis set used in ref. [10].

The energy difference 5.7 kcal/mol obtained in the present calculation, as well as the value calculated

with a more complete basis set [10], is higher than the experimental value $\Delta H = 3.2$ kcal/mol [18]. This discrepancy is discussed in detail by Osamura and Schaefer [10].

In the case of cis-glyoxal the results of calculations are compared with data of two experimental studies [2,43]. However, some values of the geometrical parameters (e.g. C–C and C–H bond) were assumed in both investigations (table 1). It should be noted that both calculations, as expected, demonstrate the increase of the C–C bond length while from the exper-

Table 8
Experimental and calculated vibrational frequencies of trans- and cis-glyoxal (cm⁻¹)

ν	Species	Assignment	Trans-OCHCHO		Trans-OCDCDO		Species	Trans-OCHCDO		Species	Cis-OCHCHO	
			exp. [37]	calc.	exp. [37,38]	calc.		exp. [37,38]	calc.		exp. [1,2,17–20]	calc.
1	a$_g$	ν(C–H) str.	2843 a)	2848	2138	2121	a′	2835	2849	a$_1$	–	2834
2		ν(C=O) str.	1746	1764	1722	1740		1735	1754		1746	1739
3		δ(C–H) bend.	1338	1336	932	930		1335	1327		–	1375
4		ν(C–C) str.	1065	1074	1131 b)	1096		1116 b)	1084		827	891
5		δ(O=C–C) bend.	551	564	537	552		542	559		286	291
6	a$_u$	χ(C–H) wag.	801	803	630	632	a″	999	999	a$_2$	1050	1066
7		τ(C–C) tors.	127	127	118	116		123	122		91	89
8	b$_g$	χ(C–H) wag.	1048	1048	911	908	a′	688	697	b$_2$	–	775
9	b$_u$	ν(C–H) str.	2835	2851	2130	2120		2130	2121	b$_1$	–	2809
10		ν(C=O) str.	1732	1719	1710	1691		1717	1702		–	1752
11		δ(C–H) bend.	1312	1317	1010	1005		972	968		–	1367
12		δ(O=C–C) bend.	339	340	311	316		324	328		–	787
		$\zeta^A_{12,7}$	0.79±0.05	0.83	0.78±0.05	0.77		0.76±0.05	0.79			

a) Recently measured vibrational frequencies are as follows: $\nu_1 = 2840$ cm⁻¹, $\nu_2 = 1742.5$ cm⁻¹ and $\nu_3 = 1353.5$ cm⁻¹ [39].
b) Vibrational frequencies measured in the crystalline phase [38].

Table 9
Mean amplitudes of vibrations for s-trans-glyoxal (ångström)

Pair of atoms	Experimental [47]	Calculated	
		0 K	298 K
C–C	0.0546 ± 0.0041	0.0500	0.0507
C=O	0.0371 ± 0.0030	0.0377	0.0377
C–H	0.057 ± 0.010	0.0798	0.0798
C...O	0.0599 ± 0.0037	0.0575	0.0628
O...O	0.0602 ± 0.0040	0.0541	0.0573

Table 10
Scaled quantum mechanical force field of s-trans-acrolein (mdyn/Å, mdyn, mdyn Å)

	1	2	3	4	5	6	7	8
1	4.8510							
2	0.2769	8.5820						
3	0.6328	−0.0936	11.7696					
4	0.0256	0.0476	0.0385	5.1965				
5	0.0589	0.0294	0.3538	0.0044	4.2649			
6	−0.0077	0.0397	0.0133	0.0113	0.0000	5.2478		
7	−0.0091	0.0691	0.0045	−0.0041	0.0112	0.0220	5.1392	
8	0.2081	0.2014	0.0786	−0.1383	−0.0259	0.0373	−0.0553	1.0333
9	0.1902	0.0869	0.2378	−0.0609	−0.1478	0.0150	−0.0001	0.2155
10	0.1470	−0.1738	−0.0069	0.0160	0.0203	0.0088	−0.0234	0.0160
11	0.1793	−0.0113	−0.3143	0.0193	0.0171	−0.0038	0.0112	−0.0443
12	−0.0046	−0.1939	−0.0026	−0.0046	−0.0082	0.0557	0.0536	−0.0189
13	0.0294	0.0079	0.0313	−0.0262	−0.0032	0.0916	−0.1051	0.0816

	9	10	11	12	13
9	1.2724				
10	−0.0937	0.4849			
11	0.0778	0.0347	0.6013		
12	−0.0156	0.0139	−0.0024	0.4490	
13	0.0122	0.0384	−0.0007	0.0080	0.5244

	14	15	16	17	18
14	0.0246				
15	−0.0080	0.2278			
16	0.0007	−0.0192	0.3703		
17	−0.0033	0.0216	−0.0074	0.2568	
18	0.0084	−0.0001	0.0211	0.0015	0.1263

imental study [2] it would seem that this bond decreases.

The theoretical increase of the C–C=O angles in going from the trans to the cis conformer is correlated with the experimental one.

The differences in values of the geometrical parameters obtained in the present calculation and in ref. [10] should not affect significantly the calculated vibrational frequencies since these are computed from empirically scaled force fields (tables 5 and 7).

Comparison of the SQM force fields of the trans and cis conformers shows in some cases a change in sign and/or order of magnitude for the off-diagonal

Table 11
Scaled quantum mechanical force field of s-cis-acrolein (mdyn/Å, mdyn, mdyn Å)

	1	2	3	4	5	6	7	8
1	4.8072							
2	0.3271	8.5304						
3	0.6941	−0.1225	11.5286					
4	0.0171	0.0633	0.0235	5.1489				
5	0.0626	0.0062	0.3484	0.0202	4.3205			
6	−0.0028	0.0415	−0.0022	0.0123	0.0052	5.2244		
7	−0.0318	0.0610	0.0212	−0.0033	0.0005	0.0152	5.2352	
8	0.2821	0.1927	−0.0021	−0.1461	0.0382	0.0432	−0.0650	1.0783
9	0.3011	−0.0873	0.1868	0.0570	−0.1427	−0.0084	−0.0286	−0.0497
10	0.1707	−0.1877	0.0322	0.0000	0.0087	0.0094	−0.0210	0.0048
11	0.1758	0.0388	−0.3120	0.0006	0.0152	0.0076	0.0007	0.0647
12	0.0023	−0.1904	−0.0175	−0.0064	−0.0011	0.0545	0.0342	0.0032
13	0.0233	0.0063	−0.0023	−0.0317	0.0125	0.0938	−0.1075	0.0818

	9	10	11	12	13
9	1.3867				
10	0.0817	0.5130			
11	0.0790	−0.0094	0.6093		
12	0.0223	0.0160	−0.0050	0.4384	
13	−0.0216	0.0431	0.0103	0.0008	0.5234

	14	15	16	17	18
14	0.0137				
15	−0.0057	0.2293			
16	0.0055	0.0169	0.3812		
17	−0.0012	0.0191	0.0091	0.2573	
18	0.0010	−0.0038	−0.0172	0.0054	0.1273

force constants when going from the trans to the cis rotamer. For the out-of-plane coordinates the diagonal force constant of the torsional vibration decreases sharply, and the off-diagonal force constant of the waging coordinate changes its sign.

Quite good agreement was achieved for the calculated and experimental vibrational frequencies of three isotopomers of trans-glyoxal (table 8). Some greater deviations from the mean value are observed for the stretch vibrational mode of the C–C single bond of the $C_2O_2D_2$ and C_2O_2HD molecules. However, it should be noted that these frequencies were measured in the crystalline phase and underwent a crystal field shift. Such shifts for organic compounds are usually equal to 10–20 cm^{-1}. The other interesting feature of these vibrations is their inverse isotopic shift (see, e.g., ref. [44]). Indeed, when taking into account the possible crystalline shift, the exper-

imental value of ν_4 of the $C_2O_2D_2$ molecule is shifted in comparison with $C_2O_2H_2$ by approximately 50 cm^{-1} in the direction of higher frequencies. For the C_2O_2HD molecule this shift is equal to 30 cm^{-1}. The calculated values of the vibrational frequencies are also shifted in the direction of higher vibrational frequencies (table 8). However, the calculated shifts are lower than the experimental ones. Perhaps, this is connected with the fact that these frequencies of the skeletal vibrations for these molecules are simulated, in general, a little worse by these force fields. The manifestation of the inverse isotopic shift is corroborated by the calculation of the vibrational frequencies of the $D^{13}CO-O^{13}CD$ and $H^{13}CO-O^{13}CD$ isotopomers. It is well known [44] that the inverse isotopic shift manifests itself for vibrational frequencies (in this case ν_4) of moieties attached at the functional group (e.g., the C–H group) when a light atom

Table 12
Experimental and calculated vibrational frequencies of trans- and cis-acrolein (cm^{-1})

ν	Species	Assignment [a]	Trans-CH2CHCHO exp. IR gas [27]	Trans-CH2CHCHO calc.	Trans-CH2CHCDO exp. UV gas [21-24]	Trans-CH2CHCDO calc.	Cis-CH2=CH-CH=O exp. UV gas [21-24]	Cis-CH2=CH-CH=O exp. IR gas [27]	Cis-CH2=CH-CH=O exp. IR cryst. [25]	Cis-CH2=CH-CH=O exp. IR matr. [26] [b]	Cis-CH2=CH-CH=O calc.	Cis-CH2CHCDO exp. UV gas [21-24]	Cis-CH2CHCDO calc.
1	a'	ν(=CH2) as. str.	3103	3121	3101	3121	–	–	–	–	3131	–	3131
2		ν(C-H) str. v	3069	3077	–	3077	–	–	–	–	3065	–	3065
3		ν(=CH2) sym. str.	2998	3032	2988	3032	–	–	–	2838	3041	–	3041
4		ν(C-H) str. f	2800	2783	2060	2063	–	–	–	–	2801	–	2077
5		ν(C=O) str.	1724	1728	1709	1710	1722	–	–	1709	1711	1709	1688
6		ν(C=C) str.	1625	1619	1621	1617	1624	–	1616	1612	1616	1616	1615
7		δ(=CH2) sc.	1420	1432	1403	1422	1403	–	1402	1402	1420	–	1418
8		δ(C-H) bend. f	1360	1365	–	1048	–	–	–	–	1393	–	1112
9		δ(C-H) bend. v	1275	1278	1275	1277	1285	1288	–	1285	1293	–	1296
10		ν(C-C) str.	1158	1167	1153	1158	919	919	918	935	928	846	857
11		ρ(=CH2) rock.	912	918	877	881	–	–	–	1056	1068	–	1041
12		δ(O=C-C) bend.	564	556	561	554	–	–	–	669	672	–	665
13		δ(C=C-C) bend.	324	316	313	308	(276)	–	–	284	282	–	281
14	a"	χ(C-H) wag. v	993	995	993	996	1005	989	995	990	989	991	991
15		χ(C-H) wag. f	972	1007	846	869	988	–	–	–	1017	879	883
16		χ(=CH2) wag.	959	951	959	957	970	968	970	978	972	972	974
17		τ(=CH2) twist.	593	579	556	545	544	542	547	550	545	521	522
18		τ(C-C) tors.	158	159	151	152	138	–	–	–	162	129	146

[a] v stands for vinyl, f stands for formyl.
[b] The values of these frequencies were measured from fig. 1 of ref. [26].

Table 13
Experimental and calculated mean amplitudes of vibrations of s-trans-acrolein (ångström)

Pair of atoms [a]	Experimental		Calculated	
	[48]	[47]	0 K	298 K
C1–H5	0.070±0.006	0.0776	0.0768	0.0768
C2–H6		0.0790 [b]	0.0807	0.0807
C2=O4	0.0360±0.0045	0.0382	0.0381	0.0381
C1–C3	0.0477±0.0038	0.0439	0.0423	0.0424
C1–C2	0.0422±0.0032	0.0548	0.0484	0.0489
O4...H6		0.1000 [b]	0.0945	0.0947
C1...H8		0.1000 [b]	0.0967	0.0981
C1...H6		0.1000 [b]	0.1019	0.1028
C2...H5		0.1000 [b]	0.1023	0.1038
C1...O4	0.0494±0.0037	0.0636	0.0555	0.0596
C2...C3	0.075±0.09	0.0787	0.0594	0.0656
C3...H6		0.1400 [b]	0.1329	0.1455
C2...H8		0.1600 [b]	0.1360	0.1471
O4...H5		0.1375 [b]	0.1336	0.1436
C2...H7		0.1000 [b]	0.0950	0.0969
O4...C3	0.065±0.06	0.0722	0.0570	0.0605
O4...H8		0.1300 [b]	0.1344	0.1449
O4...H7		0.1200 [b]	0.1013	0.1036

[a] See fig. 1.   [b] Assumed values.

is substituted by a heavy one. This functional group itself must also undergo the usual isotopic shift. In the case of ^{13}C molecules, the usual isotopic shift is expected for the ν_4 frequencies of the ^{13}C–^{13}C bond stretching vibrations. That is why when going from $C_2O_2D_2$ and C_2O_2HD to molecules with ^{13}C atoms the usual isotopic shifts of the calculated vibrational frequencies ν_4 up to 1070 and 1056 cm^{-1} were obtained for the di- and monodeutero derivatives, respectively.

The calculated values of the Coriolis constants $\zeta_{12,7}$ for the trans conformers of glyoxal and its isotopomers (table 8) are within the limits of the experimentally measured values [37].

Good agreement was achieved for calculated and experimental values of the mean amplitudes of vibrations for trans-glyoxal, see table 9.

The set of force constants obtained for the cis conformer simulates the experimental vibrational frequencies quite well (table 8). It should only be mentioned that the greater deviation is observed again for the vibrational frequency ν_4 of cis-glyoxal. It is especially noteworthy that the calculated and experimental values of ν_5 agree well. This means that the

calculations reproduce the characteristic changes in the vibrational spectrum of glyoxal on going to the high-energy rotamer.

3.2. Acrolein

The calculations of geometrical parameters of trans- and cis-acrolein at the HF/6-31G level (this work) and HF/6-31G* [14,16] are in good agreement, in general, with the microwave data [12] (table 2). Here the expected increase of the C–C single bond length was reproduced quite well on going from the trans to the cis conformer. As for the C=C–C and O–C–C angles the calculated data indicate a greater change of the latter while the experimental results give the greater increase for the C=C–C angle. Some disagreement was also observed for the C=C–H angle attached at the formyl group. In other instances the calculated data simulate correctly the trend in changes of the geometrical parameters when going from the trans to the cis conformer.

In the case of acrolein, the energy difference calculations at the 6-31G (this work) and the 6-31G* [14,16] levels give values of 1.2 and 1.7 kcal/mol,

respectively. The latter one is in good agreement with the experimental values of 1.9 kcal/mol (UV spectroscopy [21–23] and 2.1 kcal/mol (ultrasonic study [45]).

The character of the changes of some force constants in going from the trans to the cis conformer (tables 10 and 11) is practically the same as for glyoxal. The transfer of the scale factors from glyoxal and 1,3-butadiene allows us to obtain sets of force constants, which in the majority of cases, simulate quite well the experimental vibrational frequencies of the two rotamers of acrolein (table 12). Some systematic deviations are observed only for the out-of-plane wagging vibration ν_{15} of the C–H bond attached at the formyl group. As for the torsional vibration ν_{18} of the cis rotamer, the treatment of the corresponding UV band may have been performed incorrectly, or the features may be connected with the definition of the torsional coordinate in molecules without axial symmetry. In ref. [27], the assignment of the out-of-plane vibrations ν_{14} and ν_{17} of trans-C_3OH_4 was mutually interchanged. It should be noted in this connection that the interpretation of the vibrational spectrum must take into account not only the potential energy distribution terms but also the isotopic shifts. In the case of the ν_{14} and ν_{17} frequencies the vibration eigenvectors are "mixed" and cannot be unambiguously assigned. This is the reason why the frequencies of the out-of-plane vibrations of the $CD_2=CH–CH=O$ and $CH_2=CD–CH=O$ molecules were calculated. In the case of $CD_2=CH–CH=O$ the calculated value of 995 cm^{-1} of the ν_{14} vibration decreased to 924 cm^{-1} and the wavenumber at 579 cm^{-1} (ν_{17}) decreased to 468 cm^{-1}. For $CH_2=CD–CH=O$ the corresponding decreases were as follows: the frequency at 995 cm^{-1} transformed into 839 cm^{-1} and the value of 579 cm^{-1} transformed into 547 cm^{-1}. Hence, it follows obviously that the 995 cm^{-1} frequency belongs to the C–H structural fragment and the vibrational frequency at 579 cm^{-1} characterizes the =CH_2 structural fragment of the vinyl group. The analogous analysis was carried out earlier for the vinyl group of 1,3-butadiene [29,46] and isoprene [31].

As in the case of glyoxal the frequencies of the stretch vibration of the C–C single bond (ν_{10}) and the deformation skeletal vibrations (ν_{12} and ν_{13}) underwent the greatest changes on going to the cis

form. The frequency ν_{11} (rocking vibration of the =CH_2 group) also changes. It is of interest to note here that the positions of the ν_{10} bands in the spectra of the trans forms of the C_3OH_4 and C_3OH_3D molecules (table 12) are approximately the same. However, for the cis conformers of these two isotopomers the ν_{10} vibration undergoes a sharp decrease of its frequency under deuteration.

The appearance of the first overtone $2\nu_{16}$ is characteristic of the vinyl group [46]. Indeed, the band at 1935 cm^{-1} was observed in the argon matrix spectrum of cis-acrolein [26].

It should be mentioned that the calculated values of the vibrational frequencies ν_8, ν_{12} and ν_{13} of cis-acrolein are underestimated in ref. [28] (1266, 629 and 234 cm^{-1}, respectively).

The calculated values of the mean amplitudes of vibrations (table 13) agree quite well with the experimental data [47,48].

It should also be noted that the bands belonging to the s-cis forms of glyoxal and acrolein were detected, as a rule, in the crystalline samples or in matrices where the corresponding intensities differ sharply from their values in gas spectra. In this connection it seems reasonable that the calculation of band intensities for the gas phase does not improve the reliability of the suggested assignment for the vibrational spectra of s-cis rotamers of glyoxal and acrolein.

4. Conclusion

The present calculations corroborate the planar structure of the high-energy rotamers of glyoxal and acrolein. It should be mentioned that in ref. [49] from an analysis of the inertial defect of the high-energy rotamer of glyoxal the conclusion was reached that its structure was not planar in the ground electronic state. Results of the analysis given in the present paper evidently demonstrate that this conclusion was incorrect. Besides, recently performed calculations [50] of the energies and structures of glyoxal in the lowest triplet states show that this molecule exists in the form of planar trans conformer. Rotational analysis of some vibronic bands of glyoxal [51–53] and investigation of its two-photon spectra [54] resulted also in the predominant planar trans structure for the first excited singlet and first excited triplet states.

The SQM force fields calculated for the trans and cis structures of these molecules simulate all the peculiarities of their vibrational spectra as well as a set of other molecular parameters including the Coriolis constants and the mean amplitudes of vibrations. The predicted values of unobserved frequencies of the cis conformers may now facilitate their experimental detection.

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