Ab initio study of the structure of 2,2-difluoroethanal in the ground and lowest excited triplet electronic states

V. A. Bataev, E. K. Dolgov, A. V. Abramenkov, G. M. Kuramshina, and I. A. Godunov*

Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 932 8846. E-mail: godunov@phys.chem.msu.ru

The molecular structure of 2,2-difluoroethanal (DFE) in the ground (S_0) and lowest excited triplet (T_1) electronic states was investigated by *ab initio* quantum-chemical methods. In the S_0 state, the DFE molecule exists as the only stable *cis* conformer. The $T_1 \leftarrow S_0$ electronic excitation is accompanied by the rotation of the top and the deviation of the carbonyl fragment from planarity. For the DFE molecule in the T_1 state, six minima corresponding to three pairs of enantiomers were found on the potential energy surface. Based on this potential energy surface, the problems on torsion and inversion nuclear motions were solved in the one- and two-dimensional approximations, and the interaction between these motions was revealed.

Key words: *ab initio* quantum-chemical calculations, carbonyl compounds, geometric parameters, vibration frequencies, potentials of internal rotation and inversion, ground and excited electronic states.

The structures of many conformationally flexible molecules of carbonyl compounds, which have symmetrical tops (C_{3v}), in the ground state (S_0) and in the lowest excited singlet (S_1) and triplet (T_1) electronic states have been studied. It was found that the $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ electronic excitations of these molecules are accompanied by rotations of tops and pyramidalization of carbonyl fragments (though this is not necessarily the case).[1–5] Systems with lower-symmetry tops remain poorly studied, and the data on these compounds are more ambiguous.[6] This gave impetus to our studies of the structures of RCHO molecules (R = CH_2Cl or CHF_2) in the S_0, S_1, and T_1 states by molecular spectroscopy and quantum chemistry.

In this work, we report the results of *ab initio* studies of the conformational behavior of the 2,2-difluoroethanal molecule (DFE; CHF_2CHO) in the S_0 and T_1 states. Most attention was given to large-amplitude nuclear motions, *viz.*, to torsion (in the S_0 and T_1 states) and inversion (in the T_1 state) motions, for which one- and two-dimensional vibrational problems were solved.

Taking into account our experience in investigations of molecules of carbonyl compounds in the ground and lowest excited electronic states,[6–10] we carried out calculations for the DFE molecule with the use of the restricted (RHF) and unrestricted (UHF) Hartree—Fock methods, the second-order Möller—Plesset perturbation theory (MP2), and the multiconfigurational method of the self-consistent field (the CASSCF technique) with the active space including molecular orbitals, which are close to frontier orbitals and are localized predominantly on the carbonyl fragment, *viz.*, σ_{CO}, π_{CO}, n_O, π_{CO}^*, and σ_{CO}^* (CASSCF(6e-5MO)). The principal calculations were carried out with the 6-31G** basis set. The correctness of the results was estimated by the configuration interaction method taking into account single and double excitations (CISD) and with the use of larger AO basis sets. The structure of the DFE molecule in the S_0 state was also studied by the density functional theory (DFT). The calculations were carried out with the use of the GAMESS (US)[11] (PC version*) and GAUSSIAN-94[12] program packages.

The results of studies of the DFE molecule in the S_0 state are indicative of the existence of only one stable *cis* conformer (the H atom of the top is located in the *cis* position with respect to the O atom). The calculated potential energy surface of the molecule in the T_1 state has a substantially more complex shape, *viz.*, six minima on the potential energy surface correspond to three pairs of enantiomers (Fig. 1).

The geometric parameters of the *cis* conformer of DFE in the S_0 state calculated by different methods are given in Table 1. The internuclear distance *d*(C=O) calculated by the Hartree—Fock method is somewhat underestimated compared to the results of more rigorous methods (MP2 and CASSCF). The estimates of the *d*(C=O) values are noticeably affected by the ways of taking into account the electronic correlation. The MP2 and CASSCF methods gave close values, whereas the results obtained with the use of the CISD/6-31G** technique (1.198 Å; the value is not given in Table 1) are intermediate between those obtained with the use of the above-mentioned methods and the RHF approximation.

---

* For detailed information, see http://classic.chem.msu.su/gran/gamess/index.html.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 989—995, June, 2000.

1066-5285/00/4906-0984 $25.00

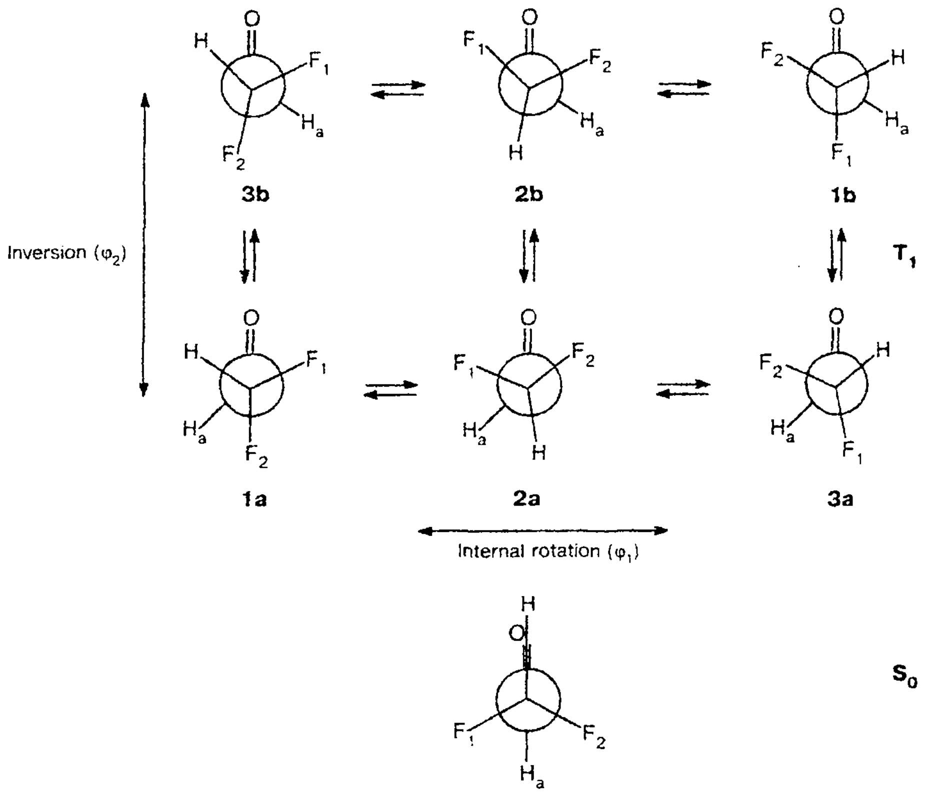

Fig. 1. Newman projections of the conformers of the DFE molecule in the S_0 and T_1 states.

Table 1. Internuclear distances (*d*), angles (φ), and relative energies (Δ*E*) of the conformers of DFE in the S_0 and T_1 states calculated with the 6-31G** basis set

Parameter	S_0 state				T_1 state					
	RHF	MP2	CASSCF	B3LYP[a]	UHF			CASSCF		
					1a	**2a**	**3a**	**1a**	**2a**	**3a**
Bond					*d*/Å					
C=O	1.183	1.220	1.221	1.207	1.336	1.334	1.336	1.365	1.363	1.365
C—C	1.516	1.516	1.509	1.531	1.497	1.493	1.494	1.496	1.491	1.492
C—H_a	1.093	1.101	1.088	1.108	1.078	1.078	1.078	1.077	1.076	1.077
C—H	1.078	1.088	1.079	1.092	1.083	1.080	1.080	1.082	1.080	1.080
C—F_1	1.340	1.368	1.340	1.372	1.340	1.346	1.345	1.340	1.346	1.346
C—F_2	1.340	1.368	1.340	1.372	1.339	1.340	1.339	1.339	1.340	1.340
Angle					φ/deg					
C—C—O	121.9	122.1	121.3	122.2	114.8	115.9	115.1	114.5	115.4	114.8
C—C—H_a	114.8	114.4	116.1	114.7	117.7	118.3	118.1	118.3	118.9	118.7
C—C—H	112.4	112.8	112.4	113.7	113.6	111.1	112.9	113.9	111.3	112.9
C—C—F_1	108.2	108.0	108.6	108.2	110.1	111.2	111.1	110.0	111.4	111.2
C—C—F_2	108.2	108.0	108.6	108.2	108.3	110.0	108.2	108.3	111.0	108.3
C—H_a[b]	0	0	0	0	−37.4	−35.4	−35.8	−37.3	−35.4	−35.7
H—C—F_1	107.7	109.9	109.8	109.4	107.8	108.2	108.0	107.7	108.1	107.9
H—C—F_2	107.7	109.9	109.8	109.4	108.5	109.1	109.1	108.3	109.0	109.1
H—C—C—O	0	0	0	0	61.0	−170.5	−48.9	62.7	−169.4	−48.2
Δ*E*/cm^{-1}	—	—	—	—	65	236	0	88	201	0

[a] Calculations with the 6-31+G* basis set.

[b] The deviation of the CH_a bond from the CCO plane.

The geometric parameters of three conformers of the DFE molecule in the T_1 state (**1a**, **2a**, and **3a** in Fig. 1) are also given in Table 1. The other three forms are their enantiomers (**1b**, **2b**, and **3b** in Fig. 1). When the electronic correlation was taken into account both for the T_1 and S_0 states by the CASSCF method, the internuclear distance d(C=O) increased, while other geometric parameters changed only slightly compared to those calculated in the UHF approximation. From Fig. 1 and Table 1 it follows that the $T_1 \leftarrow S_0$ excitation of the DFE molecule is accompanied by rotation of the CHF_2 group and pyramidalization of the carbonyl fragment. In addition, a substantial increase in the internuclear distance d(C=O) and a decrease in the C—C—O angle are observed. These changes are typical of the $n \rightarrow \pi^*$ excitation of carbonyl compounds.

The estimates of harmonic vibration frequencies of the DFE conformers in the S_0 and T_1 states are given in Table 2. It can be seen that the calculated and experimental frequencies of DFE in the S_0 state are in reasonable agreement. The stretching (C=O) and bending (CCO) vibration frequencies of the conformers of DFE are sharply decreased upon $T_1 \leftarrow S_0$ electronic excitation of the *cis* conformer, which is consistent with the data for other carbonyl compounds.[2]

The frequencies given in Table 2 were determined within the framework of the classical harmonic model. This model makes it possible to adequately describe only small-amplitude vibrations. Taking into account that the torsion and inversion (of the nonplanar carbonyl fragment of DFE in the T_1 state) vibrations are large-amplitude nuclear motions, we examined the corresponding one- and two-dimensional quantum-mechanical models for these vibrations.

Methods for the solution of problems on large-amplitude vibrations have been described in detail previously.[6,13–15] Let us briefly consider the calculation procedure. The following Hamiltonian of the vibrational motion is considered:

$$\hat{H}(\varphi_1,\ldots,\varphi_n) = \\ = -\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\partial}{\partial\varphi_i}B_{ij}(\varphi_1,\ldots,\varphi_n)\frac{\partial}{\partial\varphi_j} + V(\varphi_1,\ldots,\varphi_n). \quad (1)$$

Here, n is the number of vibrational coordinates taken into account, B_{ij} are elements of the symmetrical matrix of the kinetic parameters, and V is the potential function. The internal rotation and the inversion of the DFE molecule are described by the variables φ_1 (the angle of the relative rotation of the aldehyde and CHF_2 groups) and φ_2 (the angle characterizing the deviation of the CH_a bond from the CCO plane), respectively.

In the two-dimensional approximation, the $B_{ij}(\varphi_1,\varphi_2)$ and $V(\varphi_1,\varphi_2)$ functions were calculated from the geometric parameters and the total energies for a series of points, which were obtained by varying the φ_1 and φ_2 values in the ranges $0 \le \varphi_1 \le 180°$ and $-60° \le \varphi_2 \le 60°$ with steps of 15° and 10°, respectively. The remaining geometric parameters were optimized. In the one-dimensional approximation for the internal rotation, the angle of inversion φ_2 was also determined in the course of geometry optimization as the φ_1 angle changed. Analogously, the values of the φ_1 angle were calculated for the one-dimensional model of inversion. Because of this, the one-dimensional internal rotation or the one-dimensional inversion have curvilinear trajectories on the two-dimensional surface.

Table 2. Experimental and calculated (with the 6-31G** basis set) harmonic frequencies (v/cm^{-1}) for the conformers of DFE in the S_0 and T_1 states

Approximate type of vibrations	S_0 state				T_1 state					
	RHF	MP2	B3LYP[a]	Experiment[b]	UHF			CASSCF(6e-5MO)		
					1a	**2a**	**3a**	**1a**	**2a**	**3a**
a' CH str	3330	3214	3149	2988	3324	3301	3301	3348	3303	3301
a' CH_a str	3188	3076	2986	2844	3262	3327	3324	3267	3349	3346
a' CO str	2061	1797	1839	1770	1214	1212	1233	1164	1175	1125
a' H_aCO bend	1556	1451	1418	1390	1424	1507	1411	1408	1470	1384
a' CCH bend	1462	1367	1332	1314	1546	1560	1593	1550	1567	1589
a' CC str	1266	1172	1093	946	1086	981	1134	1090	977	1239
a' CF_2 str	1210	1138	1118	1095	1269	1299	1237	1258	1290	1206
a' CF_2 sciss	663	611	596	605	623	801	618	620	798	620
a' CF_2 wag	353	427	418	—	529	562	485	534	561	485
a' CCO bend	412	374	377	—	267	253	269	261	251	267
a'' CH o.o.p.	1526	1424	1366	1350	1566	1528	1530	1560	1529	1532
a'' CF_2 str	1261	1157	1083	1126	1296	1225	1273	1290	1224	1257
a'' CH_a o.o.p.	1094	990	967	850	807	778	798	818	776	799
a'' CF_2 twist	466	322	318	—	467	402	471	463	404	468
a'' tors	85	69	77	—	99	92	102	96	99	104

Note. Vibrations are denoted as follows: str, stretching; bend, bending; sciss, scissoring; wag, wagging; o.o.p., out-of-plane; twist, twisting; tors, torsional.

[a] Calculations with the 6-31+G* basis set.

[b] The IR spectrum in the gaseous phase.

Based on the calculated sets of values, the B and V functions were fitted by the least-squares method according to the following equations:

for the internal rotation in the one-dimensional approximation,

$$B(\varphi_1) = B_0 + \sum_{k=1}^{N} B_k^{\mathrm{e}} \cos k\varphi_1 + \sum_{k=1}^{P} B_k^{\mathrm{o}} \sin k\varphi_1, \tag{2a}$$

$$V(\varphi_1) = V_0 + \frac{1}{2}\sum_{k=1}^{M} V_k^{\mathrm{e}}(1 - \cos k\varphi_1) + \frac{1}{2}\sum_{k=1}^{L} V_k^{\mathrm{o}}(1 - \sin k\varphi_1), \tag{2b}$$

where B_k^{e} and B_k^{o} are the coefficients at the even (e) and odd (o) components;

and for the inversion in the one-dimensional approximation,

$$B(Q) = \sum_{k=0}^{N} B_k Q^k, \tag{3a}$$

$$V(Q) = \sum_{k=0}^{M} V_k Q^k + F(Q), \tag{3b}$$

where $Q = d(\mathrm{C{-}H_a}) \cdot \varphi_2$ and $F(Q)$ is the Gaussian function ($F(Q) = B\exp(-CQ^2)$) describing the shape of the potential barrier (the purely polynomial approximation ($F(Q) \equiv 0$) can also be used).

For the two-dimensional torsion-inversion motion, the equations take the following forms:

$$\begin{aligned} B(\varphi_1,\varphi_2) &\approx \sum_K\sum_L C^{cc}_{KL} \cos K\varphi_1 \cos L\varphi_2 + \\ &+ \sum_K\sum_L C^{ss}_{KL} \sin K\varphi_1 \sin L\varphi_2, \end{aligned} \tag{4a}$$

$$\begin{aligned} V(\varphi_1,\varphi_2) &\approx \sum_K\sum_L V^{cc}_{KL} \cos K\varphi_1 \cos L\varphi_2 + \\ &+ \sum_K\sum_L V^{ss}_{KL} \sin K\varphi_1 \sin L\varphi_2. \end{aligned} \tag{4b}$$

The coefficients of approximating functions (2)—(4) and the standard deviations σ are given in Tables 3—7. The one-dimensional potential curves for the internal rotation of the DFE molecule in the S_0 state are shown in Fig. 2. These curves have a deep minimum and a high maximum corresponding to the *cis* and *trans* positions, respectively. At $\varphi \approx 65$—90°, the potentials change only slightly, forming a sort of plateau. A comparison of the curves constructed by the RHF and MP2 methods demonstrates that if the electronic correlation is taken into account according to the perturbation theory, the barrier decreases by ~400 cm^{-1}; the use of the extended basis set (6-311++G**) gives the same result.

The torsion-inversion potential energy surface for the DFE molecule in the T_1 state is displayed in Fig. 3, where particular conformers to which the potential wells correspond are shown (see also Fig. 1). The relation between the torsion and inversion motions for the DFE molecule in the T_1 state (for example, the inversion is accompanied by the rotation of the top) can be seen from Figs. 1 and 3.

Table 3. Parameters of the kinetic energy function (Eq. (2a)) and the one-dimensional potential function of internal rotation (2b) for the DFE molecule in the S_0 state (calculations with the 6-31G** basis set) and the standard deviations (σ/cm^{-1})[a]

k	B_k^{e}			k	V_k^{e}		
	RHF	MP2	B3LYP[b]		RHF	MP2	B3LYP[b]
0	2.2204	2.1008	2.1795	Barrier[c]	1827	1428	1539
1	0.0184	0.0033	−0.0159	1	1364.4	1042.1	1153.6
2	−0.1618	−0.1602	−0.1768	2	−343.4	−257.0	−157.3
3	0.0312	0.0031	0.0479	3	443.7	371.1	371.1
4	0.0101	0.0101	0.0013	4	−25.9	−32.7	−39.3
5	−0.0040	−0.0038	0.0022	5	18.0	14.0	12.2
6	−0.0015	−0.0014	−0.0014	6	−14.2	−18.7	−15.8
7	0.0005	0.0003	0.0008	7	1.1	1.2	2.2
8	0.0004	0.0002	−0.0003	8	−0.5	−0.7	−3.3
σ	0.0006	0.0010	0.0004	σ	0.12	0.24	0.65

[a] By symmetry, all V_i^{o} and B_i^{o} are equal to zero.

[b] Calculations with the 6-31+G* basis set.

[c] The barriers to internal rotation, which were determined by approximation of the potential, are given. The direct use of the results of quantum-chemical calculations gave the following values (cm^{-1}): 1827 (RHF/6-31G**), 1539 (B3LYP/6-31+G*), 1784 (RHF/6-311++G**), 1362 (MP2/6-311++G**), 1653 (CASSCF(6e-5MO)/6-31G**), 1617 (CISD/6-31G**), 1490 (MP3//MP2/6-31G**), and 1359 (MP4-STDQ//MP2/6-31G**).

Table 4. Parameters of the kinetic energy function (Eq. (2a)) and the one-dimensional potential function of internal rotation (2b) for the DFE molecule in the T_1 state and the standard deviations (σ/cm^{-1})

k	UHF/6-31G**			
	B_k^{e}	B_k^{o}	V_k^{e}	V_k^{o}
0	1.7363	—	—	—
1	0.0005	−0.0034	433.9	60.1
2	−0.1155	0.0088	149.6	−57.2
3	0.0244	−0.0032	−658.8	263.1
4	0.0025	0.0009	10.5	−18.9
5	0.0012	−0.0018	22.7	6.2
6	−0.0003	0.0008	−4.0	7.3
7	−0.0005	−0.0001	−1.2	−1.6
8	0.0000	0.0000	1.4	−0.1
9	0.0002	−0.0002	0.02	−0.0
10	−0.0003	0.0002	—	—
11	0.0000	−0.0002	—	—
12	0.0001	0.0000	—	—
σ		0.0000		0.16

Note. In this approximation, the energies of conformers **1** and **2** relative to that of conformer **3** are 65 and 236 cm^{-1}. The potential barriers to conformational transitions **1a**→**2a**→**3a**→**1a** are 951, 694, and 512 cm^{-1}, respectively.

The energy levels and the wave functions of the model Hamiltonian (1) were determined by the variational method with the use of the one- and two-dimensional B and V functions constructed according to the above-mentioned procedure.

The energies of the torsion levels of the *cis* conformer of DFE in the S_0 state calculated in the one-dimensional

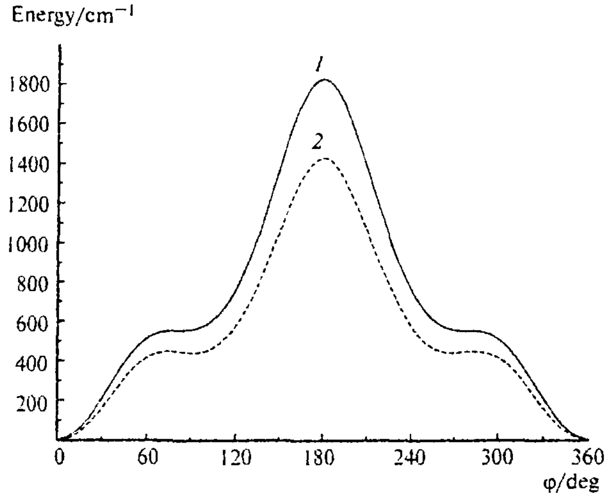

Fig. 2. One-dimensional potential functions of internal rotation of the DFE molecule in the S_0 state: *1*, RHF/6-31G**; *2*, MP2/6-31G**.

approximation are given in Table 8. The torsion-inversion energy levels of the conformers of DFE in the T_1 state, which were found by solving the two-dimensional

Table 5. Parameters of the kinetic energy function (Eq. (3a)) and the one-dimensional potential function of inversion (3b) for the DFE molecule in the T_1 state and the standard deviations (σ/cm^{-1}) calculated in the UHF/6-31G** approximation

k	**1a** ⇌ **3b** or **1b** ⇌ **3a**		**2a** ⇌ **2b***
	B_k	V_k	B_k
0	1.1382	744.8	1.0652
1	0.3934	−359.8	—
2	0.5114	−3788.6	−0.018
3	−0.6647	1256.0	—
4	0.2462	5874.2	0.0103
5	0.7571	−1438.3	—
6	—	−2465.8	−0.0054
7	—	554.5	—
8	—	834.6	—
σ	0.019	10.5	—

Note. In this approximation, the energy of conformer **1** relative to that of conformer **3** is 63 cm^{-1}. The potential barriers to conformational transitions **1a**→**3b** and **2a**→**2b** are 691 and 658 cm^{-1}, respectively.

* The inversion potential was approximated by the following equation:

$$V = -148.0 - 911.6Q^2 + 2146.8Q^4 + 805.5\exp(-3.88Q^2).$$

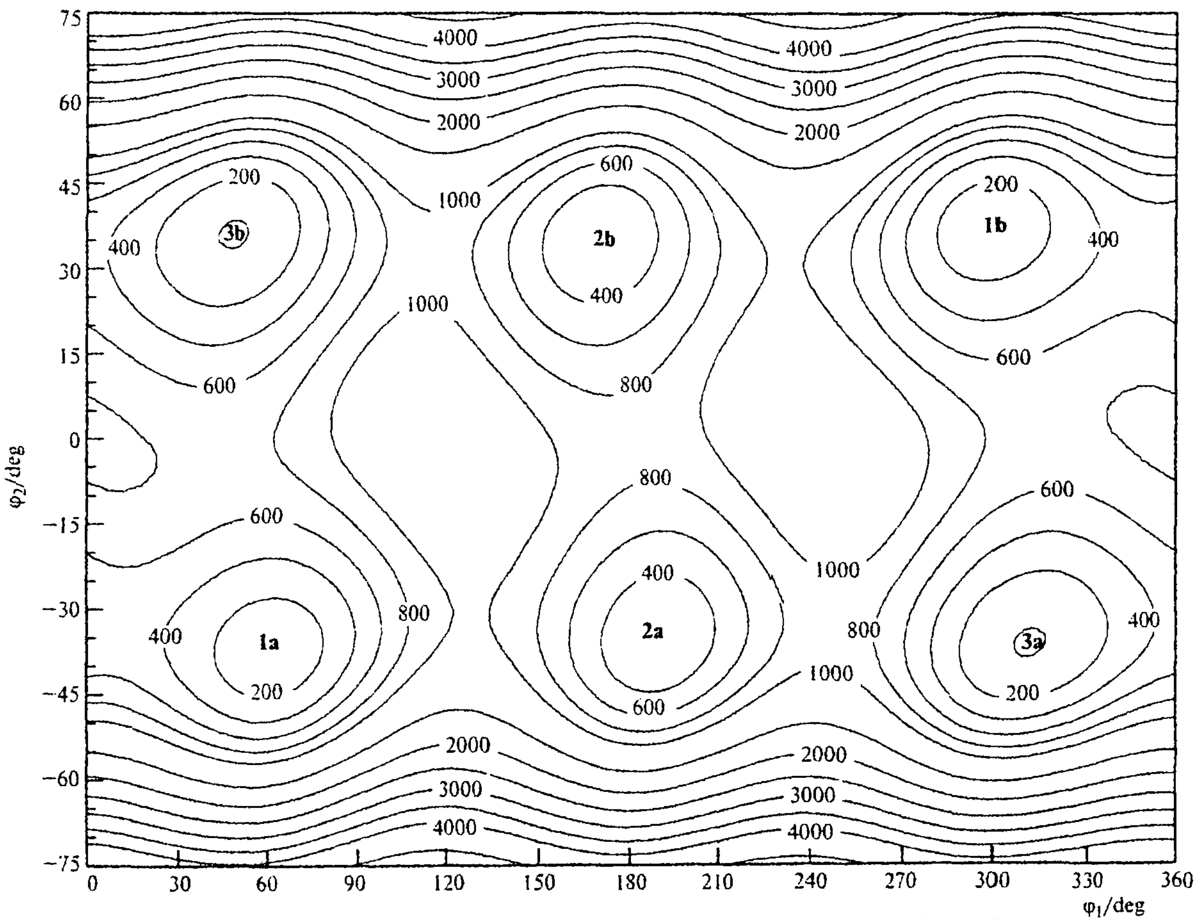

Fig. 3. Two-dimensional potential energy surface for the DFE molecule in the T_1 state (UHF/6-31G**).

Table 6. Coefficients for approximation of the kinetic parameters B_{11}, B_{12}, and B_{22} by Eq. (4a) and the standard deviations (σ/cm^{-1})

K	L	B_{11}	B_{12}	B_{22}
		Coefficients C_{KL}^{cc}		
0	0	3.1455	−3.7166	19.6964
0	1	−1.6412	2.1935	−2.9732
0	2	0.7060	−1.2480	2.5109
1	0	−0.0044	0.0226	−0.0826
2	0	−0.1933	0.3300	−0.5325
2	2	−0.0423	0.1499	−0.4194
3	0	0.0300	−0.0363	0.0517
3	2	0.0056	−0.0144	0.0056
4	0	0.0092	−0.0198	0.0371
4	2	0.0078	−0.0190	0.0468
		Coefficients C_{KL}^{ss}		
1	1	0.0210	−0.1110	0.1929
2	2	−0.0018	0.0734	−0.2446
3	1	−0.0825	0.0964	−0.0669
3	2	0.0424	−0.0503	0.0210
σ		0.0102	0.0168	0.0392

Table 7. Coefficients for approximation of the potential function (V/cm^{-1}) for the DFE molecule by Eq. (4b) and the standard deviations (σ/cm^{-1})

K	L	V_{KL}^{cc}	K	L	V_{KL}^{cc}
0	0	11822.1	4	4	11.7
0	1	−14782.9	5	0	−9.0
0	2	2935.5	6	0	5.1
0	3	997.8	K	L	V_{KL}^{ss}
1	1	−353.0	1	1	−63.7
1	2	184.3	2	1	94.2
2	0	−101.1	2	3	−23.6
3	1	569.9	3	1	26.5
3	2	−405.5	3	3	−156.1
2	4	−28.5	4	3	8.2
4	0	−3.9	σ		9.06

Table 8. Energies of the torsion levels for the *cis*-DFE molecule in the S_0 state

υ_t	Energy/cm^{-1}		
	RHF/6-31G**	MP2/6-31G**	B3LYP/6-31+G*
1	83	70	76
2	163	138	151
3	239	203	224
4	310	260	293

problem, are listed in Table 9. In this table, the corresponding values estimated within the framework of the one-dimensional models are also given for comparison. Based on the analysis of the structures of nodal surfaces and regions of localization of the calculated wave functions, the low-lying energy levels, which were determined by solving the two-dimensional problem, were assigned to particular conformers and the vibrational quantum numbers for the internal rotation and inversion were obtained.

Table 9. Energies of the torsion, inversion, and torsion-inversion levels of the conformers of DFE in the T_1 state calculated in the UHF/6-31G** approximation

Energy/cm^{-1}		Assignment[c]	Energy/cm^{-1}		Assignment[c]
$n = 2$[a]	$n = 1$[b]	(υ_t, υ_i)	$n = 2$[a]	$n = 1$[b]	(υ_t, υ_i)
0.0	0.0	**3** (0,0)+	330.6	344.2	**1** (3,0)−
0.0		**3** (0,0)−	331.2		**1** (3,0)+
78.1	67.0	**1** (0,0)−	368.9	419.3	**3** (5,0)+
78.1		**1** (0,0)+	389.0		**3** (5,0)−
87.9	94.4	**3** (1,0)+	395.9	419.3	**1** (4,0)−
87.9		**3** (1,0)−	401.2		**1** (4,0)+
169.1	165.2	**1** (1,0)−	407.4	430.0	**2** (2,0)+
169.1		**1** (1,0)+	415.1	449.4	**2** (2,0)−
171.4	184.7	**3** (2,0)+	432.8	424.6	**3** (6,0)+
171.5		**3** (2,0)−	440.5	424.6	**1** (5,0)−
217.3	237.9	**2** (0,0)+	470.3	424.6	**3** (6,0)−
234.2	257.3	**2** (0,0)−	470.7	424.6	**1** (5,0)+
249.2	270.5	**3** (3,0)+	476.3	493.7	**1,3** (0,1)−
249.7		**3** (3,0)−	476.3		**1,3** (0,1)+
254.0	258.0	**1** (2,0)−	495.6	521.0	**2** (3,0)−
254.0		**1** (2,0)+	501.3	540.4	**2** (3,0)+
314.6	335.5	**2** (1,0)−	507.8	474.9	**1** (6,0)−
316.2	350.6	**3** (4,0)+	510.3	474.9	**3** (7,0)+
322.4		**3** (4,0)−	546.0	474.9	**1** (6,0)+
325.9	354.9	**2** (1,0)+	551.3	474.9	**3** (7,0)−

[a] The energy levels determined by solving the two-dimensional torsion-inversion problem.

[b] The energy levels determined by solving the one-dimensional torsion and inversion problems.

[c] The number of the conformer; the torsion (υ_t) and inversion (υ_i) quantum numbers are given in parentheses; the components of degeneration/splitting (for the pairs of conformers **a** and **b**, Fig. 1) described by the symmetrical and antisymmetrical torsion-inversion wave functions are denoted by the plus and minus signs, respectively.

It follows from Table 9 that the energy levels of the conformers of DFE in the T_1 state determined in one- and two-dimensional approximations are somewhat different. The larger the torsion and inversion quantum numbers, the more substantial this difference. The wave functions of the lower torsion-inversion states are located in potential wells corresponding to the conformers; however, the wave functions are rapidly delocalized as the torsion and inversion quantum numbers increase (because the potential barriers separating the conformers are no higher than 1000 cm^{-1}). To describe higher electronic states, it is necessary to solve a multidimensional problem.

To summarize, the *ab initio* calculations for the DFE molecule in the S_0 and T_1 states demonstrated that the molecule in the S_0 state exists as one stable *cis* conformer. The $T_1 \leftarrow S_0$ electronic excitation is accompanied by rotation of the top and deviation of the carbonyl group from planarity. In this case, the potential energy surface has six minima corresponding to three pairs of enantiomers. For the conformers of DFE in the T_1 state, interaction between the large-amplitude vibrations is observed, *viz.*, the inversion nuclear motion is accompanied by rotation of the top. As the quantum numbers corresponding to torsion and inversion nuclear motions increase, the vibrational wave functions are rapidly delocalized.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 96-15-97469 and 98-03-33233a).

References

1. D. J. Clouthier and D. C. Moule, *Topics in Current Chemistry*, 1989, **150**, 167.
2. I. A. Godunov and N. N. Yakovlev, *Zh. Strukt. Khim.*, 1995, **36**, 269 [*Russ. J. Struct. Chem.*, 1995, **36**, 238 (Engl. Transl.)].
3. I. A. Godunov, N. N. Yakovlev, and E. B. Averina, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 294 [*Russ. Chem. Bull.*, 1998, **47**, 287 (Engl. Transl.)].
4. I. A. Godunov and N. N. Yakovlev, *Zh. Fiz. Khim.*, 1998, **72**, 1087 [*Russ. J. Phys. Chem.*, 1998, **72**, 969 (Engl. Transl.)].
5. N. N. Yakovlev, M. N. Mikhailov, and I. A. Godunov, *Zh. Strukt. Khim.*, 1998, **39**, 507 [*Russ. J. Struct. Chem.*, 1998, **39** (Engl. Transl.)].
6. V. A. Bataev, V. I. Pupyshev, A. V. Abramenkov, and I. A. Godunov, *Zh. Fiz. Khim.*, 2000, **74**, in press [*Russ. J. Phys. Chem.*, 2000, **74**, in press (Engl. Transl.)].
7. V. A. Bataev, V. I. Pupyshev, and I. A. Godunov, *J. Mol. Struct.*, 1999, **480—481**, 263.
8. V. A. Bataev, V. I. Pupyshev, and I. A. Godunov, *Zh. Fiz. Khim.*, 1999, **73**, 1614 [*Russ. J. Phys. Chem.*, 1999, **73** (Engl. Transl.)].
9. V. A. Bataev and I. A. Godunov, *Zh. Fiz. Khim.*, 2000, **74**, 103 [*Russ. J. Phys. Chem.*, 2000, **74**, in press (Engl. Transl.)].
10. V. A. Bataev, V. I. Pupyshev, and I. A. Godunov, *Zh. Strukt. Khim.*, 1998, **39**, 510 [*Russ. J. Struct. Chem.*, 1998, **39** (Engl. Transl.)].
11. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
12. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *Gaussian 94 (Revision D.1)*, Gaussian, Inc., Pittsburgh, PA, 1995.
13. A. Niño, C. Muñoz-Caro, and D. C. Moule, *J. Phys. Chem.*, 1994, **98**, 1519.
14. A. V. Abramenkov, *Zh. Fiz. Khim.*, 1995, **69**, 1048 [*Russ. J. Phys. Chem.*, 1996, **69** (Engl. Transl.)].
15. I. A. Godunov, A. V. Abramenkov, and N. N. Yakovlev, *Zh. Strukt. Khim.*, 1998, **39**, 947 [*J. Struct. Chem.*, 1998, **39** (Engl. Transl.)].

Received December 30, 1999