Russian Chemical Bulletin, International Edition, Vol. 50, No. 6, pp. 945—951, June, 2001

Ab initio study of the structure and conformations of 2-fluoroethanal in the ground and lowest excited electronic states

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The structure of the conformationally flexible 2-fluoroethanal molecule (CH_2FCHO, FE) in the ground (S_0) and lowest excited triplet (T_1) and singlet (S_1) electronic states was investigated by *ab initio* quantum-chemical methods. The FE molecule in the S_0 state was found to exist as two conformers, *viz.*, as *cis* (the F—C—C—O angle is 0°) and *trans* (the F—C—C—O angle is 180°) conformers. On going both to the T_1 and S_1 states, the FE molecule undergoes substantial structural changes, in particular, the CH_2F top is rotated with respect to the core and the carbonyl CCHO fragment becomes nonplanar. The potential energy surfaces for the T_1 and S_1 states are qualitatively similar, *viz.*, six minima in each of the excited states of FE correspond to three pairs of mirror-symmetrical conformers. Based on the potential energy surfaces calculated for the FE molecule in the T_1 and S_1 states, the one-dimensional problems on the torsion and inversion nuclear motions as well as the two-dimensional torsion-inversion problems were solved.

Key words: *ab initio* quantum-chemistry calculations, carbonyl compounds, geometric parameters, vibration frequencies, potential functions of internal rotation and inversion, ground and excited electronic states, potential energy surface.

As part of our continuing experimental and theoretical studies of conformationally flexible carbonyl compounds in the ground and excited electronic states (see Refs. 1—3 and references cited therein), in the present work we investigated the structure and conformations of the 2-fluoroethanal molecule (CH_2FCHO, FE) in the ground (S_0) and lowest excited triplet (T_1) and singlet (S_1) electronic states. Particular attention was given to large-amplitude nuclear motions, *viz.*, to the torsion (in the S_0, T_1, and S_1 states) and inversion (in the T_1 and S_1 states) motions for which the vibrational problems were solved in the one- and two-dimensional approximations. Experimental data on the conformational behavior of the FE molecule are lacking. Detailed theoretical analysis of internal large-amplitude motions has not been performed previously for the FE molecule even in the S_0 state.

Taking into account experience accumulated in studies of carbonyl compounds in different electronic states,[2] we carried out calculations for the FE molecule in the S_0 state using the restricted Hartree—Fock (RHF) method and the second-order Möller—Plesset perturbation theory (MP2). In the case of the T_1 and S_1 states, we employed the multiconfigurational complete active space self-consistent field (CASSCF) method, which has previously[2,4] given the reliable data for the related carbonyl compounds in the lowest excited electronic states. It was found[2] that the active space consisting of five molecular orbitals (MO), *viz.*, σ_{CO}, π_{CO}, n_O, π_{CO}^*, and σ_{CO}^*, occupied by six electrons and the double-zeta basis set supplemented with the polarization functions on all atoms (the 6-31G** type) are sufficient for the correct description of such systems.

The calculations for the excited singlet state were carried out with full optimization of the second root of the eigenvalue problem. In the region of the potential energy surface (PES) under study, the problem of variational collapse of the ground and excited states was eliminated with the use of MOs that correspond to the symmetrical nuclear configuration in which the S_1 state is symmetry-separated from the ground state as the initial approximation. The correctness of the results obtained in the studies of the excited states of carbonyl compounds by different quantum-chemical methods was estimated based on calculations by the unrestricted Hartree—Fock (UHF) method for the T_1 state and by the configuration interaction methods (in the frozen-core approximation) taking into account only single (CIS) or single and double (CISD) excitations for the S_1 state. All calculations were carried out with the use of the GAMESS (US) program package[5] (the PC GAMESS version).★

The results of calculations for the FE molecule in the S_0 state are indicative of the existence of two conformers, *viz.*, *cis* and *trans* (Fig. 1), which agrees with the data from the earlier calculations by the *ab initio* method[6,7] with the 3-21G, 4-21G, and 6-31G*

★ For more detailed information, see http://classic.chem.msu.su/gran/gamess/index.html (A. A. Granovsky).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 906—912, June, 2001.

1066-5285/01/5006-945 $25.00

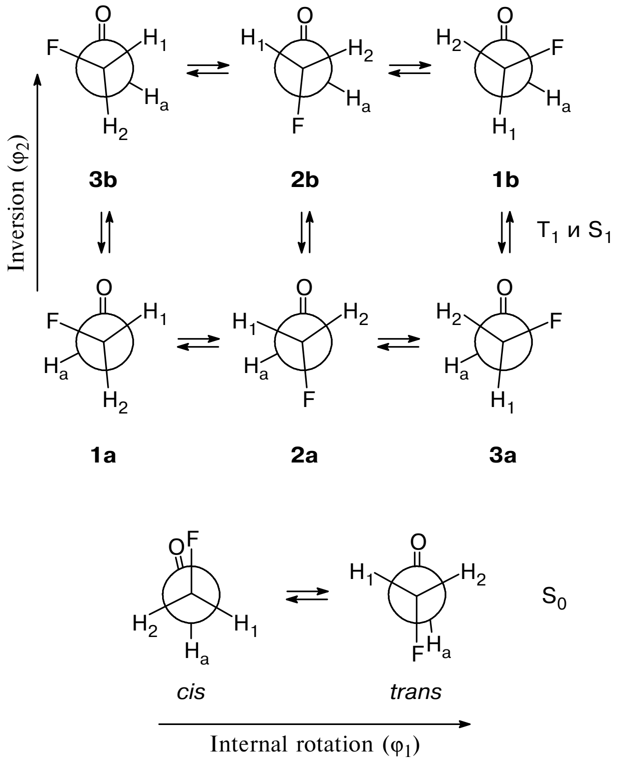

Fig. 1. Newman projections for the conformers of the FE molecule in the S_0, T_1, and S_1 states.

basis sets and by the semiempirical CNDO/2 method.[8] The geometric parameters and the relative energies of the *cis* and *trans* conformers of the FE molecule in the S_0 state are given in Table 1. The corresponding parameters obtained by different methods (RHF, MP2, and CASSCF) have rather close values. Noticeable differences are observed only for the C=O and C—F bond lengths. The known drawback of the RHF method is an underestimation of the lengths of strongly polar bonds.[9] The latter are increased approaching the experimental values with allowance for the electronic correlation (for example, according to the perturbation theory). Apparently, the similarity of the *d*(C—F) values obtained in the RHF and CASSCF approximations is attributable to the fact that the calculations by the CASSCF method were performed with the active space consisting of the orbitals almost completely localized on the carbonyl group. From the data of Table 1 it also follows that the inclusion of the polarization functions on the H atoms (on going from the 6-31G* to 6-31G** basis set) had virtually no effect on the results of calculations.

Our calculations demonstrated that the $T_1 \leftarrow S_0$ and $S_1 \leftarrow S_0$ excitations of the molecule are accompanied by substantial changes in its geometrical configuration (see Fig. 1 and Table 2). Six minima corresponding to six different conformers are observed on the potential energy surface of the FE molecule in the T_1 and S_1 states (see Fig. 1). The geometric parameters of three conformers (**1a**, **2a**, and **3a**, see Fig. 1) are given in Table 2. The remaining three conformers are the enantiomers of the former (**1b**, **2b**, and **3b**, see Fig. 1). Therefore, it can be seen from Fig. 1 and Table 2 that the $T_1 \leftarrow S_0$ and $S_1 \leftarrow S_0$ excitations of the FE molecule lead to rotation of the CH_2F group and pyramidalization of the carbonyl fragment. In addition, the internuclear distance *d*(C=O) is substantially increased and the C—C—O angle is decreased, which are typical of $n \to \pi^*$ excitations of carbonyl compounds.

A comparison of the geometric parameters and the relative energies of the same conformers of the FE molecule in the T_1 state (Table 2) calculated by the UHF and CASSCF methods shows that they have close

Table 1. Internuclear distances, angles, and relative energies (Δ*E*) of the conformers of the FE molecule in the S_0 state calculated with the 6-31G** basis set, unless otherwise stated

Parameter	RHF		MP2		MP2/6-31G*[7]		CASSCF	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
Bond/Å								
C=O	1.183	1.186	1.219	1.224	1.218	1.220	1.219	1.222
C—C	1.506	1.510	1.509	1.513	1.508	1.511	1.505	1.508
C—H_a	1.098	1.094	1.106	1.103	1.110	1.107	1.092	1.089
C—F	1.351	1.364	1.378	1.390	1.378	1.390	1.354	1.365
C—$H_{1,2}$	1.086	1.083	1.094	1.091	1.098	1.094	1.086	1.083
Angle/deg								
C—C—O	124.5	122.1	124.0	122.2	124.0	122.2	123.8	121.6
C—C—H_a	113.7	115.3	113.8	115.0	114.0	115.2	115.0	116.4
C—C—F	111.3	109.3	110.9	109.3	110.8	109.2	111.1	109.1
C—C—$H_{1,2}$	109.1	109.8	109.1	109.8	109.3	109.9	109.4	110.2
C—H_a*	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F—C—$H_{1,2}$	109.6	109.3	109.9	109.5	109.7	109.4	109.4	109.1
F—C—C—O	0.0	180.0	0.0	180.0	0.0	180.0	0.0	180.0
Δ*E*/cm^{-1}	849.0	0.0	551.0	0.0	591.0	0.0	774.0	0.0

* The angle of deviation of the C—H_a bond from the CCO plane.

Table 2. Internuclear distances, angles, and relative energies (ΔE) of the conformers of the FE molecule in the T_1 and S_1 states calculated with the 6-31G** basis set

Parameter	T_1 state						S_1 state				
	UHF			CASSCF			CASSCF			CIS	CISD
	1a	**2a**	**3a**	**1a**	**2a**	**3a**	**1a**	**2a**	**3a**		
Bond/Å											
C=O	1.338	1.342	1.340	1.366	1.370	1.368	1.388	1.392	1.388	1.256	1.319
C—C	1.491	1.502	1.495	1.490	1.501	1.495	1.489	1.489	1.493	1.509	1.492
C—H_a	1.078	1.080	1.080	1.077	1.079	1.078	1.076	1.078	1.077	1.086	1.081
C—F	1.374	1.365	1.367	1.374	1.365	1.368	1.373	1.365	1.367	1.371	1.378
C—H_1	1.082	1.086	1.082	1.083	1.086	1.082	1.083	1.086	1.083	1.080	1.082
C—H_2	1.082	1.083	1.086	1.082	1.083	1.086	1.082	1.084	1.086	1.081	1.081
Angle/deg											
C—C—O	115.8	114.3	115.6	115.4	114.0	115.3	115.3	113.6	114.9	119.7	118.0
C—C—H_a	120.0	118.3	118.8	120.6	118.9	119.3	121.0	119.3	119.6	118.5	120.8
C—C—F	111.4	108.2	110.3	111.6	108.3	110.3	111.2	108.4	110.1	112.5	111.4
C—C—H_1	110.7	111.7	109.4	110.7	112.0	109.3	110.6	111.6	109.7	109.8	110.4
C—C—H_2	109.4	110.9	111.5	109.5	110.8	111.8	109.7	110.9	111.4	108.1	109.0
C—H_a*	−33.7	−37.8	−36.2	−33.8	−37.7	−36.2	−32.5	−36.7	−35.2	−23.9	−24.6
F—C—H_1	107.9	108.3	108.8	107.9	108.1	108.7	107.9	108.3	108.8	107.9	107.9
F—C—H_2	108.1	108.9	107.6	108.0	108.9	107.5	108.1	108.9	107.6	108.1	110.1
F—C—C—O	75.7	−172.7	−64.1	75.8	−170.0	−64.2	74.6	−173.8	−62.8	78.3	79.3
ΔE/cm^{-1}	0.0	439.0	372.0	0.0	512.0	416.0	0.0	272.0	291.0	—	—

* The angle of deviation of the C—H_a bond from the CCO plane.

values except for the distance d(C=O) for which the CASSCF method gave the noticeably larger value. At the same time, the geometric parameters for these conformers in the T_1 and S_1 states except for d(C=O) calculated by the CASSCF method differ only insignificantly.

The results of calculations for the FE molecule in the S_1 state by the configuration interaction methods (CIS and CISD) are also indicative of pyramidalization of the carbonyl fragment and a change in the orientation of the CH_2F top. However, these methods predicted the existence of only one stable conformer. Its

Table 3. Harmonic frequencies (ν) for the conformers of the FE molecule in the S_0, T_1, and S_1 states calculated with the 6-31G** basis set

Vibration type approximate		ν/cm^{-1}							
		S_0 (MP2)		T_1 (CASSCF)			S_1 (CASSCF)		
		cis	*trans*	**1a**	**2a**	**3a**	**1a**	**2a**	**3a**
a′	CH_2 str	3113	3144	3238	3203	3208	3290	3202	3206
a′	CH_a str	3003	3050	3333	3312	3324	3342	3327	3332
a′	CO str	1808	1796	967	1118	1163	947	1106	948
a′	CH_2 sciss	1542	1540	1641	1655	1642	1642	1652	1642
a′	CH_2 wag	1458	1447	1549	1571	1553	1552	1572	1555
a′	H_aCO bend	1441	1389	1475	1394	1452	1469	1388	1446
a′	CF str	1170	1127	1160	1198	1224	1155	1199	1222
a′	CC str	900	1088	1217	1098	961	1208	1102	1099
a′	CCO bend	754	537	328	312	326	321	306	322
a′	CCF bend	258	319	486	484	524	489	484	517
a″	CH_2 str	3171	3211	3291	3260	3273	3237	3259	3272
a″	CH_2 twist	1286	1270	1368	1351	1383	1367	1347	1385
a″	CH_a o.o.p.*	1146	1130	765	732	753	760	727	764
a″	CH_2 rock	749	747	1127	1199	1107	1131	1184	1158
a″	tors	177	86	131	96	107	123	107	114

Note. Vibrations are denoted as follows: str, stretching; bend, bending; sciss, scissoring; wag, wagging; twist, twisting; o.o.p, out-of-plane; rock, rocking; tors, torsional. The classification of the vibrations by symmetry refers only to the S_0 state.

* In the S_0 state, the out-of-plane vibration of the CHO group; in the T_1 and S_1 states, the inversion vibration.

geometric parameters are for the most part close to those obtained by the CASSCF method for conformer **1**, except for the CO bond lengths and the angle of deviation of the CH_a bond from the CCO plane. When analyzing the results of calculations, it should be taken into account that the configuration interaction methods give less reliable data on the shape of the potential energy surfaces of carbonyl compounds in the excited states than those obtained by the CASSCF method.[2,10] Hence, we also considered the results obtained for the FE molecule in the S_1 state by the CIS and CISD methods as less reliable.

The estimates of the harmonic vibration frequencies of FE in the electronic states under study are given in Table 3. For the *cis* and *trans* conformers of the FE molecule in the S_0 state, the noticeable differences are observed only in the frequencies of the CC stretching vibrations, the CCO bending vibrations, and the torsional vibrations (qualitatively similar results have also been obtained[7] in the RHF/3-21G approximation). The calculations predicted a decrease in the CO stretching, CO in-plane, and CHO out-of-plane vibrations both in the T_1 and S_1 excited electronic states, which is consistent with the experimental data obtained for other carbonyl compounds.[1] In addition, the frequencies of a number of skeletal vibrations are increased upon these electronic excitations. From the data of Table 3 it also follows that the vibration frequencies for the same conformers in the excited states generally differ insignificantly. The frequencies of the same vibration types for different conformers are also similar; the exceptions are the CC and CO stretching vibrations and the torsional vibrations. However, it should be taken into account that the difference in the CC and CO stretching vibrations is attributable to the fact that the assignment of the complex vibrations was made rather arbitrarily.

The vibration frequencies given in Table 3 were determined within the framework of the harmonic model, which can be used, strictly speaking, only in the case of small-amplitude vibrations. Since torsion and inversion vibrations belong to large-amplitude nuclear motions, we considered the corresponding models in the one- and two-dimensional approximations.

Procedures for the solution of the problems on large-amplitude vibrations have been described previously.[2,11–13] The following Hamiltonian of the vibrational motion was considered:

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

where n is the number of vibrational coordinates taken into account, B_{ij} are elements of the symmetrical matrix of the kinetic parameters chosen so that the vibrational and rotational motions are separated according to the Eckart conditions, and V is the potential function. The internal rotation and inversion of the FE molecule are described by the φ_1 (the angle of the relative rotation of the aldehyde and CHF_2 groups; the O—C—C—F dihedral angle) and φ_2 (the angle characterizing deviation of the CH_a bond from the CCO plane) variables, respectively.

In the one-dimensional approximation for the internal rotation, the angle of inversion φ_2 was not fixed, but was determined in the course of geometry optimization depending on the φ_1 angle; the same is true for the one-dimensional inversion model. Because of this, the one-dimensional internal rotation or the one-dimensional inversion have curvilinear trajectories on the two-dimensional surface.

The B parameters and the V potential functions in the one-dimensional approximations were approximated by the following equations:

for internal rotation

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

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

for inversion

$$B(Q) = \sum_{k=0}^{N}B_kQ^k = \frac{\hbar^2}{2}\sum_{k=0}^{N}g_{44}^{(k)}Q^k, \quad (3a)$$

$$V(Q) = \sum_{k=0}^{M}V_kQ^k, \quad (3b)$$

where $Q = R_{CHa}\cdot\varphi_2$. In the two-dimensional approximation, the B_{ij} and V functions were approximated by

Table 4. Parameters of the one-dimensional kinetic energy function (B) (Eq. (2a)) and the one-dimensional potential function (V) of internal rotation (Eq. (2b)) for the FE molecule in the S_0 state and the standard deviations (σ/cm^{-1})

k	B_k^e		V_k^e	
	RHF	MP2	RHF	MP2
0	3.2099	3.0539	—	—
1	0.6200	0.5818	−1260.8	−927.4
2	0.4015	0.4003	1313.3	1169.5
3	0.1308	0.1356	428.7	392.8
4	0.0289	0.0289	36.1	53.8
5	0.0088	0.0087	−16.9	−16.1
6	0.0021	0.0023	−11.8	−16.4
σ	0.0005	0.0005	0.2	0.1

Note. In this approximation, the barriers to the *cis→trans* transition (cm^{-1}) are 1160 (RHF) and 1114 (MP2) and the differences between the energies of the conformers are 849 (RHF) and 551 (MP2).

Table 5. Parameters (cm^{-1}) of the one-dimensional kinetic energy functions (Eqs. (2a) and (3a)) and the one-dimensional potential functions (Eqs. (2b) and (3b)) of internal rotation and inversion for the FE molecule in the T_1 and S_1 states and the standard deviations (σ/cm^{-1}) calculated by the CASSCF/6-31G** method

k	Internal rotation								Inversion **1a** $\rightleftharpoons$ **3b**			
	T_1				S_1				T_1		S_1	
	$B_k{}^e$	$B_k{}^o$	$V_k{}^e$	$V_k{}^o$	$B_k{}^e$	$B_k{}^o$	$V_k{}^e$	$V_k{}^o$	$g_{44}{}^{(k)}$	V_k	$g_{44}{}^{(k)}$*	V_k
0	2.5623	—	—	—	2.5178	—	—	—	1.1351	690.4	1.1333	616.5
1	0.4661	0.0055	−319.5	186.4	0.4651	0.0048	−402.6	139.0	−0.0173	741.2	−0.0173	623.9
2	0.2647	0.0221	−698.0	136.0	0.2664	0.0201	−537.8	74.5	−0.0864	−2239.8	−0.0791	−2376.8
3	0.0807	0.0147	−637.4	−271.3	0.0870	0.0104	−676.7	−232.8	0.0366	−1406.3	0.0439	−1399.7
4	0.0362	0.0078	−8.2	−15.7	0.0377	0.0066	−11.1	−12.0	0.1106	2592.1	0.0945	3225.8
5	0.0081	0.0034	−47.5	18.0	0.0086	0.0031	−42.1	17.9	−0.0235	1126.3	−0.0362	1214.5
6	0.0027	−0.0002	−1.2	−3.8	0.0027	−0.0001	−1.1	−3.6	−0.0988	146.3	−0.0824	−478.9
7	0.0007	−0.0003	3.3	2.6	0.0007	−0.0003	3.8	1.9	0.0059	−336.9	0.0114	−387.1
8	−0.0001	−0.0004	−2.2	−0.1	−0.0001	−0.0003	−1.7	0.2	0.0333	−252.0	0.0273	−41.0
σ	0.0001		0.2		0.0002		0.2		0.0003	2.7	0.0002	3.5

Note. In these approximations, the barriers to conformational transitions **1a**→**2a**→**3a**→**1a**→**3b** for the T_1 states are 933 (757), 237 (406), 1130 (1117), and 748 (655) cm^{-1}, respectively; the energy differences of conformers **2** and **3** calculated from the potential functions of internal rotation are 512 (272) and 416 (291) cm^{-1}; the energy differences of conformers **1** and **3** calculated based on the inversion potential is 417 (292) cm^{-1}; the values for the S_1 state are given in parentheses.

* The values $g_{44}{}^{(k)}$ are given in (a.m.u.)$^{-1}$ · E^{-k}.

linear combinations of trigonometric functions using the least-squares method

$$B(\varphi_1,\varphi_2) = \sum_K\sum_L C^{cc}_{KL}\cos K\varphi_1\cos L\varphi_2 + {}$$
$$+ \sum_K\sum_L C^{ss}_{KL}\sin K\varphi_1\sin L\varphi_2\,, \qquad (4a)$$

$$V(\varphi_1,\varphi_2) = \sum_K\sum_L V^{cc}_{KL}\cos K\varphi_1\cos L\varphi_2 + {}$$
$$+ \sum_K\sum_L V^{ss}_{KL}\sin K\varphi_1\sin L\varphi_2\,. \qquad (4b)$$

In this case, the φ_1 and φ_2 angles were varied 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 course of the *ab initio* calculation.

The coefficients in expansions (2)—(4) for the FE molecule in the S_0, T_1, and S_1 states and the standard deviations characterizing the accuracy of reproduction of the kinetic parameters and the potentials at the control points are given in Tables 4—7. The one- and two-dimensional surfaces of the *B* and *V* functions thus constructed were used for the solution of the corresponding vibrational problems by the variational method with the trigonometric function basis set.

The one-dimensional potential of internal rotation of the FE molecule in the S_0 state is shown in Fig. 2. It should be noted that the potential function of internal rotation for the related CH_2ClCHO molecule studied previously has a somewhat more complex shape, *viz*., a planar and broad minimum in the vicinity of the point corresponding to the major *trans* conformer with a small "hump" at the Cl—C—C—O angle of 180° (see Ref. 14 and references cited therein). The energies of the torsional transitions calculated based on the determined potentials are given in Table 8. It can be seen that the energies of the 0→1 transitions agree well with the

Table 6. Coefficients for approximation of the kinetic parameters B_{11}, B_{12}, and B_{22} (in cm^{-1}) in Eq. (4a) and the standard deviations (σ/cm^{-1}) according to the data of the CASSCF/6-31G** calculations

K	L	T_1 state			S_1 state		
		B_{11}	B_{12}	B_{22}	B_{11}	B_{12}	B_{22}
		$C_{KL}{}^{cc}$ coefficient					
0	0	4.0475	3.9019	20.2617	3.7177	3.6025	20.1922
0	1	−1.6628	−2.1199	−3.0619	−1.2951	−1.8029	−3.0500
0	2	0.7973	1.4527	3.1201	0.6891	1.3594	3.0948
0	6	0.0186	0.0397	0.0882	0.0216	0.0424	0.0888
1	0	0.6313	0.4646	−0.0381	0.6184	0.4664	−0.0250
1	2	0.0592	0.1762	−0.0452	0.0756	0.1851	−0.0474
1	4	0.0385	0.0278	−0.0151	0.0335	0.0244	−0.0145
2	0	0.4128	0.4827	0.6985	0.4021	0.4623	0.6827
2	2	0.0468	0.2135	0.5004	0.0561	0.2174	0.4979
2	4	0.0256	0.0533	0.1345	0.0200	0.0479	0.1299
3	0	0.1176	0.0981	0.0640	0.1224	0.1053	0.0716
3	2	0.0104	0.0408	0.0310	0.0202	0.0533	0.0392
4	0	0.0582	0.0633	0.0776	0.0598	0.0629	0.0764
4	2	0.0132	0.0360	0.0734	0.0133	0.0351	0.0724
6	0	0.0061	0.0077	0.0105	0.0069	0.0080	0.0102
		$C_{KL}{}^{ss}$ coefficient					
1	2	0.0017	−0.0634	−0.1799	0.0031	−0.0670	−0.1808
1	4	−0.0171	0.0269	−0.0005	−0.0178	0.0260	−0.0020
2	2	0.0073	0.1003	0.2666	0.0085	0.0962	0.2574
2	4	−0.0097	−0.0089	0.0346	−0.0086	−0.0049	−0.0335
3	2	−0.0248	−0.0179	−0.0308	−0.0197	−0.0111	−0.0229
σ		0.016	0.018	0.024	0.017	0.019	0.024

Table 7. Coefficients for approximation of the potential function (V/cm^{-1}) in Eq. (4b) and the standard deviations (σ/cm^{-1}) according to the data of the CASSCF/6-31G** calculations

K	L	State	
		T_1	S_1
		V_{KL}^{cc} coefficient	
0	0	16672.8	19343.6
0	1	−22145.8	−26156.4
0	2	6634.6	7883.2
0	4	113.4	6.4
0	6	17.4	30.2
1	0	165.1	206.6
1	2	−31.6	−31.0
2	0	398.6	331.9
2	2	96.0	40.6
2	4	108.5	114.7
3	0	384.0	410.7
3	2	−233.3	−226.5
3	6	−17.9	−17.9
4	0	10.4	9.8
5	0	13.4	13.4
		V_{KL}^{ss} coefficient	
1	1	345.6	244.1
1	2	−137.2	−88.8
1	4	41.3	27.9
2	2	9.4	−38.7
2	4	89.7	−99.9
3	1	468.5	425.3
3	2	−442.3	−392.2
3	6	−13.4	−16.8
4	2	−12.1	−8.4
4	4	14.3	11.0
	σ	8.6	7.9

Note. In this approximation for the FE molecule in the T_1 and S_1 states, the energies of conformers **2** and **3** relative to **1** are 509 (268) and 416 (290) cm^{-1}, respectively; the potential barriers to conformational transitions **1a**→**2a**→**3a**→**1a**→**3b** and **2a**→**2b** are 922 (748), 236 (408), 1134 (1119), 747 (654), and 1176 (981) cm^{-1}, respectively; the values for the S_1 state are given in parentheses.

harmonic estimates of the torsional vibrations (see Table 3) for both conformers.

The two-dimensional potential energy surface for the T_1 state is shown in Fig. 3. This surface is similar in shape to that of the S_1 state and is qualitatively similar to the two-dimensional potential energy surface obtained previously for the CH_2ClCHO molecule in the T_1 state.[4] It can also be seen from Fig. 3 that the torsional and inversion motions are coupled. Thus, the inversion is accompanied by a rotation of the CH_2F top.

The results of calculations in the one- and two-dimensional approximations for a series of low-lying vibrational states of the FE molecule in the T_1 and S_1 states are given in Tables 9 and 10, respectively. The assignment of the low-lying energy levels to different conformers and the determination of the vibrational quantum numbers υ_t and υ_i for two constituent motions (internal rotation and inversion, respectively) were performed based on analysis of the regions of localization and the structures of the nodal surfaces of the calculated wave functions. This assignment presents no problems if the vibrational wave functions are localized primarily in potential wells corresponding to individual conformers.

Table 8. Energies of the torsional transitions (cm^{-1}) for the *cis* and *trans* conformers of the FE molecule in the S_0 state calculated with the 6-31G** basis set

Transition	Energy/cm^{-1}			
	cis		*trans*	
	RHF	MP2	RHF	MP2
0→1	174.9	166.5	97.7	88.5
1→2	166.4	158.7	98.4	89.3
2→3	157.1	150.0	98.7	89.5
3→4	147.0	140.5	98.7	89.2

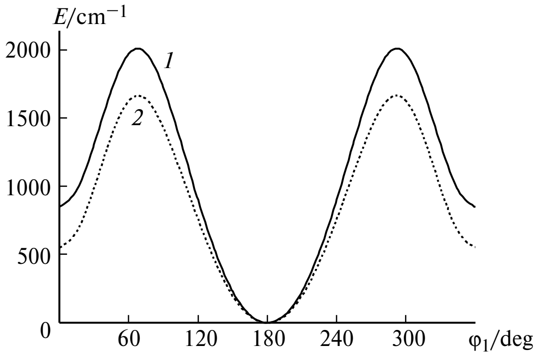

Fig. 2. One-dimensional potential functions of internal rotation calculated for the FE molecule in the S_0 state by the RHF/6-31G** (*1*) and MP2/6-31G** (*2*) methods.

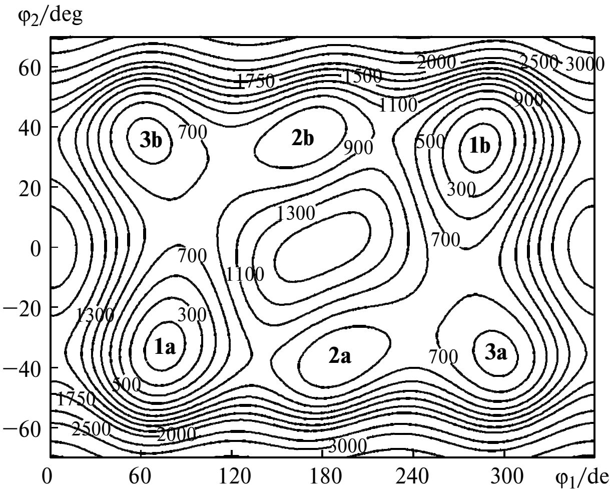

Fig. 3. Two-dimensional potential energy surface for the FE molecule in the T_1 state (CASSCF/6-31G**). Since the calculated potential energy surface for FE in the S_1 state is similar in shape, it is not presented. Angles φ_1 and φ_2 are coordinates of internal rotation and inversion, respectively.

Table 9. Energies of the torsion, inversion (n = 1), and torsion-inversion (n = 2) levels of the conformers of the FE molecule in the T_1 state calculated by the CASSCF/6-31G** method

Energy/cm^{-1}		Assignment	Energy/cm^{-1}		Assignment
n = 2	n = 1		n = 2	n = 1	
0.0	0.0	**1** (0,0)+	549.5	490.2	**2** (0,0)+
0.0		**1** (0,0)−	550.8		**2** (0,0)−
130.8	131.3	**1** (1,0)−	554.8	489.7	**1,3** (0,2)−
130.8		**1** (1,0)+	554.9		**1,3** (0,2)+
257.6	259.3	**1** (2,0)+	602.4	618.4	**1** (5,0)+
257.6		**1** (2,0)−	602.5		**1** (5,0)−
375.8	375.4^a	**1,3** (0,1)+^{c}	617.0	646.8^a	**3** (3,0)+
375.8	405.1^b	**1,3** (0,1)−^{c}	617.0		**3** (3,0)−
382.5	383.7	**1** (3,0)+	622.8	576.1	**2** (1,0)+
382.5		**1** (3,0)−	624.6		**2** (1,0)−
445.0	479.8	**3** (1,0)+	650.2	621.0^d	**1,3** (1,2)+
445.0		**3** (1,0)−	650.4	594.1^e	**1,3** (1,2)−
497.3	503.7	**1** (4,0)+	678.1	650.2	**2** (2,0)+
497.3		**1** (4,0)−	678.9		**2** (2,0)−
527.0	571.9^a	**3** (2,0)−	706.8	711.3	**3,2** (4,0)+
527.0	601.7^b	**3** (2,0)+	707.0		**3,2** (4,0)−

Note. In the two-dimensional torsional-inversion model, the doubly approximately degenerate levels correspond to the pairs of the mirror-symmetrical conformers (Fig. 1, **a** and **b**). The torsional (υ_t) and inversion (υ_i) quantum numbers are given in parentheses; the numbers of the conformers are given in front of the parentheses; the symmetrical and antisymmetrical components of inversion degeneration/splitting are denoted by the plus and minus signs, respectively. The assignment to different conformers is indicative of delocalization of the wave function in the corresponding regions.

[a,b] The origin of the energy was determined based on the system of the inversion[a] and torsional[b] levels.

[c] Simultaneously, it is the zero level of conformer **3**.

[d,e] The torsional levels of conformers **1** [d] and **3** [e] were used.

Table 10. Energies of the torsion, inversion (n = 1), and torsion-inversion (n = 2) levels of the conformers of the FE molecule in the S_1 state calculated in the CASSCF/6-31G** approximation

Energy/cm^{-1}		Assignment	Energy/cm^{-1}		Assignment
n = 2	n = 1		n = 2	n = 1	
0.0	0.0	**1** (0,0)+	444.5	486.1^a	**3,1** (2,0)−
0.0		**1** (0,0)−	444.5	500.0^b	**3,1** (2,0)+
122.9	124.0	**1** (1,0)−	462.4	471.4	**1** (4,0)+
122.9		**1** (1,0)+	462.5		**1** (4,0)−
240.4	244.4	**1** (2,0)+	496.5	449.0	**2** (2,0)−
240.4		**1** (2,0)−	498.7		**2** (2,0)+
279.4	273.2^a	**3,1** (0,1)+^{c}	516.3	581.5^d	**1,3** (0,2)−
279.4	287.1^b	**3,1** (0,1)−^{c}	516.4	569.3^e	**1,3** (0,2)+
322.2	259.7	**2** (0,0)+	531.7	571.1^a	**3** (3,0)−
326.9		**2** (0,0)−	531.8	585.0^b	**3** (3,0)+
352.7	360.6	**1** (3,0)+	550.6	575.0	**1,2,3** (5,0)−
352.7		**1** (3,0)−	551.6		**1,2,3** (5,0)+
367.3	385.0^a	**3,1** (1,0)+	572.8	530.8	**2,1** (3,0)+
367.4	398.9^b	**3,1** (1,0)−	573.5		**2,1** (3,0)−
415.8	358.0	**2** (1,0)+	594.7	631.1^a	**3,2,1** (4,0)−
418.7		**2** (1,0)−	595.1	654.0^b	**3,2,1** (4,0)+

For *Notes*, see Table 9.

However, the wave functions are rather rapidly delocalized as the torsional and inversion quantum numbers are increased and in some cases the assignment of vibrational levels (in particular, the high-lying torsional-inversion levels) involves difficulties.

From the data of Tables 9 and 10 it follows that the energies of the low-lying torsional levels calculated for the conformers of FE in the one- and two-dimensional approximations are in good agreement with each other, but the difference between these energies increases as the torsional quantum number increases. The poorer agreement is observed for the inversion levels. Apparently, the correct description of the dynamic behavior of the FE molecule in the T_1 and S_1 states calls for solution of the multidimensional problem.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 98-03-33233a and 00-15-97346).

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Received November 16, 2000;
in revised form January 26, 2001