Theoretical study of the structure of the $CClF_2NO$ and CCl_2FNO molecules in the ground and lowest excited singlet and triplet electronic states

E. K. Dolgov, V. A. Bataev,★ and I. A. Godunov

Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 939 3689. E-mail: lant@phys.chem.msu.ru

The potential energy surfaces of the nitroso compounds $CClF_2NO$ and CCl_2FNO in the ground and lowest excited singlet and triplet electronic states were studied by various *ab initio* methods (including multiconfigurational methods). The equilibrium geometric parameters, vibrational frequencies, internal rotation potential functions, and rotational contours of bands in the $S_1 \leftarrow S_0$ vibronic spectrum of the $CClF_2NO$ molecule were calculated. For the molecules under consideration, the quantum-mechanical problem on torsional motion was solved. The results of calculations are, on the whole, in good agreement with experiment.

Key words: *ab initio* calculations, nitroso compounds, molecular structure, vibrational frequencies, internal rotation potentials, ground and excited electronic states.

Earlier,[1] we have calculated the structure of the CX_2YNO molecules (X and Y = F or Cl) in the ground (S_0) state by the second-order Möller—Plesset perturbation theory (MP2/6-31G*) and in the lowest excited singlet (S_1) electronic state by the configuration interaction (CI) method with single-excited configurations only (CIS/6-31G*). On the whole, these calculation methods well reproduced[1] the experimental data, in particular, the change in the CX_2Y top orientation caused by the $S_1 \leftarrow S_0$ excitation of the molecules as well as the energies of the torsional levels in the S_0 and S_1 states. This allowed us to suggest a new interpretation of the spectra of $CClF_2NO$. Recently, we have carried out a systematic theoretical study[2] of the structures of the carbonyl compounds R^1COR^2 in many of which the $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ excitations (T_1 is the lowest excited triplet state) also cause a change in the top orientation (see the review[3] and references cited therein) and demonstrated that CIS calculations sometimes gave qualitatively incorrect data for these molecules. In this case, it is necessary to use multiconfigurational *ab initio* methods.

In the present study, we calculated the structure of the CX_2YNO molecules (X and Y = F or Cl) in the S_0, S_1, and T_1 states by the complete active space self-consistent field (CASSCF) method (a version of the multiconfigurational self-consistent field method). The structure of the molecules in the T_1 state (experimental data on their structure are lacking) was also calculated by the unrestricted Hartree—Fock (UHF) method. Studies of the molecular structures of the nitroso compounds CX_2YNO in the ground and lowest excited electronic states allowed us to compare the predictive potential of different quantum-mechanical approximations.

Calculation methods

All *ab initio* calculations were carried out with the use of the GAMESS (US) program package[4] (PC GAMESS version).* Calculations by the MP2 and CIS methods were performed in the frozen-core approximation. Most of calculations were carried out with the standard 6-31G* basis set. To estimate the correctness of the results, calculations were also performed with the larger 6-311+G*(f) basis set including polarization f-functions on the Cl atoms.

The choice of the orbital active space in CASSCF calculations deserves comments. Earlier,[5] calculations of the related MeNO molecule by the CI method have demonstrated that the nonbonding AOs of nitrogen (n_N) and oxygen (n_O) overlap with each other to form MOs of the σ type denoted as n_+ and n_-. In the first approximation, the $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ electronic transitions can be interpreted as the $n_- \rightarrow \pi^*_{NO}$ excitation. Our test calculations of the electronic structure of this molecule by the CASSCF and multireference CI methods demonstrated that the wavefunctions of the electronic states under considerations can involve contributions of the $n_+ \rightarrow \pi^*_{NO}$, $\pi_{NO} \rightarrow \pi^*_{NO}$, and $\sigma_{NO} \rightarrow \pi^*_{NO}$ excitations. Hence, it is reasonable to use six MOs, *viz.*, σ_{NO}, π_{NO}, n_+, n_-, π^*_{NO}, and σ^*_{NO}, occupied by eight electrons as the active space whose orbitals are localized primarily on the atoms of the nitroso group (CASSCF(8-6) method). A larger active space, such as (10-8), which includes orbitals of the C, N, and O atoms, is formed by adding the σ_{CN} and σ^*_{CN} MOs noticeably delocalized over the CNO fragment.

Results and Discussion

Geometric parameters and harmonic frequencies. The calculated equilibrium geometries and estimates of the

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* A. A. Granovskii, http://classic.chem.msu.su/gran/gamess/index.html

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energy differences of the conformers of the CX_2YNO molecules in the S_0 state are given in Tables 1 and 2.

Theoretical[1] and experimental[6] studies showed that the $CClF_2NO$ molecule in the S_0 state occurs as two conformers (*gauche* and *cis*). The *gauche* conformer is the major one, but the difference between the energies of the ground vibrational levels of the conformers determined experimentally[1] is very small (14 cm^{-1}).

As can be seen from Table 1, the RHF/6-31G* calculations gave the underestimated C—N and N=O internuclear distances. The use of the larger

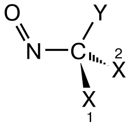

Table 1. Internuclear distances (*d*), angles (ω), and energy differences (Δ*E*) of the conformers of the $CClF_2NO$ molecule in the S_0 state calculated by different methods with the 6-31G* basis set and the corresponding experimental values

Parameter	*cis*-$CClF_2NO$					*gauche*-$CClF_2NO$				
	RHF	MP2 [a]	CASSCF		Experiment [b]	RHF	MP2 [a]	CASSCF		Experiment [b]
			(8-6)	(10-8)				(8-6)	(10-8)	
Bond					*d*/Å					
N=O	1.163	1.221	1.216	1.201	1.175(3)	1.166	1.226	1.221	1.205	1.179(3)
C—N	1.489	1.527	1.479	1.577	1.567(5)	1.487	1.521	1.478	1.571	1.561(5)
C—Cl	1.742	1.742	1.745	1.742	1.739(2)	1.748	1.750	1.750	1.746	1.741(2)
C—F(1)	1.314	1.344	1.315	1.313	1.320(2)	1.313	1.342	1.309	1.308	1.317(2)
C—F(2)	1.314	1.344	1.315	1.313	1.320(2)	1.307	1.336	1.313	1.312	1.317(2)
Angle					ω/deg					
C—N—O	115.4	113.6	114.6	114.3	110.8(12)	112.6	110.8	111.5	111.2	110.8(12)
Cl—C—N	116.1	115.9	116.6	115.5	117.5(5)	108.0	107.1	108.5	108.6	112.6(5)
F(1)—C—N	105.4	104.7	105.5	105.1	103.7(2)	106.2	105.7	112.4	111.0	106.2(2)
F(2)—C—N	105.4	104.7	105.5	105.1	103.7(2)	112.2	112.2	106.3	105.9	106.2(2)
Cl—C—N—F(1)	−122.5	−122.7	−122.5	−122.6	−123.6(14)	−118.6	−118.7	−122.5	−122.3	−122.4(2)
Cl—C—N—F(2)	122.5	122.7	122.5	122.6	123.6(14)	122.3	122.4	118.7	119.1	122.4(2)
Cl—C—N—O	0.0	0.0	0.0	0.0	0.0	106.7	104.7	99.5	104.5	104.0(10)
Energy					Δ*E*/cm^{-1}					
difference	225	121	284	110	14 [c]	0	0	0	0	0

[a] See Ref. 1.

[b] Electron diffraction.[6]

[c] Difference between the energies of the ground vibrational levels of the conformers.[1]

Table 2. Internuclear distances (*d*), angles (ω), and energy differences (Δ*E*) of the conformers of the CCl_2FNO molecule in the S_0 state calculated by different methods with the 6-31G* basis set

Parameter	*cis*-CCl_2FNO				*gauche*-CCl_2FNO			
	RHF	MP2 [1]	CASSCF		RHF	MP2 [1]	CASSCF	
			(8-6)	(10-8)			(8-6)	(10-8)
Bond				*d*/Å				
N=O	1.164	1.221	1.218	1.197	1.162	1.218	1.217	1.196
C—N	1.498	1.542	1.489	1.610	1.499	1.542	1.489	1.609
C—F	1.314	1.345	1.315	1.315	1.321	1.352	1.321	1.319
C—Cl(1)	1.751	1.750	1.753	1.747	1.754	1.755	1.755	1.751
C—Cl(2)	1.751	1.750	1.753	1.747	1.746	1.744	1.750	1.744
Angle				ω/deg				
C—N—O	112.2	110.6	111.5	110.6	114.9	113.3	113.1	113.6
F—C—N	111.5	111.1	112.1	109.4	104.6	103.8	104.9	103.6
Cl(1)—C—N	106.6	105.7	106.7	106.8	106.1	104.9	107.9	106.5
Cl(2)—C—N	106.6	105.7	106.7	106.8	114.3	114.1	113.1	113.1
F—C—N—Cl(1)	−119.7	−119.6	−119.7	−119.3	−115.5	−115.3	−116.1	−115.7
F—C—N—Cl(2)	119.7	119.6	119.7	119.3	119.7	119.9	118.6	119.2
F—C—N—O	0.0	0.0	0.0	0.0	144.1	141.4	161.5	146.2
Energy				Δ*E*/cm^{-1}				
difference	0	0	0	0	234	114	150	135

6-311+G*(f) basis set resulted in an increase in the discrepancy between the theoretical estimates of these parameters and experimental values. The C—N bond lengths calculated by the MP2 method including the electronic correlation are in better agreement with the experimental values (particularly, when the larger AO basis set was used), but this method substantially overestimated the N=O bond length. The CASSCF(8-6) method underestimated the C—N bond length and overestimated the energy differences of the conformers. The geometric parameters calculated by the CASSCF(10-8) method are in better agreement with the experimental data. The use of the 6-311+G*(f) basis set in the RHF and MP2 calculations had virtually no effect on the energy differences of the conformers (ΔE = 255 (RHF) and 122 (MP2) cm^{-1}, *cf.* Table 1), whereas an extension of the active space led to a decrease in ΔE by more than 2.5 times. The minimum value (ΔE = 110 cm^{-1}), which we obtained in the CASSCF(10-8)/6-31G* calculations differs from the experimental value (14 cm^{-1}), but the absolute error corresponds to the accuracy of the quantum-chemical approximations used.

Calculations of the CCl_2FNO molecule in the S_0 state by different methods demonstrated that this molecule also exists as two stable conformers (*cis* and *gauche*). However, the *cis* conformer of this molecule is the major one (see Table 2). As in the case of $CClF_2NO$, the C—N and N=O bond lengths predicted by the RHF method are smaller than those calculated by the MP2 method. The CASSCF(8-6) method substantially underestimated the C—N bond length compared to those calculated by the CASSCF(10-8) and MP2 methods. The MP2 and CASSCF methods gave similar energy differences of the conformers. Calculations at the RHF/6-31G* level gave a higher estimate (ΔE = 234 cm^{-1}), whereas the use of a larger basis set in MP2 calculations led to a decrease in this value (ΔE = 31 cm^{-1}).

A comparison of the geometric parameters of the molecules calculated by the CASSCF method with different active spaces, *viz.*, (8-6) and (10-8), clearly demonstrated that the inclusion of the electron correlation in the calculation scheme employed has a selective effect on the results. Thus, the CASSCF and RHF methods gave results, which differ only in the geometric parameters relating to the positions of the atoms on which MOs of the active space are localized. Because of this fact in combination with ambiguity of the choice of active-space orbitals and the commonly occurring instability and poor convergence of the self-consistent procedure, it is unreasonable to apply the CASSCF method to the study of only the S_0 state of the CX_2YNO molecules. In this case, it is more appropriate to use the MP2 method, which better reflects the trends in changes in the geometric parameters compared to the RHF method. However, perturbative calculations of molecules in the excited states (particularly, in the S_1 state) present a complicated problem. In this case, it is more reasonable to employ multiconfigurational methods, such as MRCI, which often invoke the results of calculations by the CASSCF method as the zero approximation. Nevertheless, as can be seen from Table 1, the geometric parameters of the $CClF_2NO$ molecule in the S_0 state calculated with the use of different versions of the CASSCF method agree well with experiment. There is reason to believe that calculations by the CASSCF method also adequately reflect the structure of the CCl_2FNO molecule.

The vibrational frequencies of the conformers of the CX_2YNO molecules in the S_0 state calculated by the CASSCF method in the harmonic approximation are, on the whole, in good agreement with the experimental values[1,7] (Tables 3 and 4). It should be noted that the CN and CCl stretching vibrations and the CF_2, CCl_2, and NCF bending vibrations have rather complex shapes even for the conformers with a symmetry plane. Hence, the assignments made in these cases are arbitrary.

The calculated geometric parameters and harmonic frequencies of the conformers of the $CClF_2NO$ and CCl_2FNO molecules in the T_1 and S_1 states are given in Tables 3—6. The minima on the corresponding potential energy surfaces (PES) correspond to the *gauche* and *trans* conformers. It should be noted that the lower energies correspond to the *gauche* conformer of the $CClF_2NO$ molecule and the *trans* conformer of the CCl_2FNO molecule.

A comparison of the geometric parameters of the molecules in different electronic states calculated by the CASSCF method (see Tables 3—6) showed that the $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ electronic excitations cause changes in the orientations of the CX_2Y tops of both conformers relative to the frame. In addition, the C—N—O angle slightly increases (by several degrees), the N=O bond lengths increase by 0.05—0.06 Å (S_1) and 0.03—0.04 Å (T_1), and the C—N bond lengths decrease. These results are consistent with an increase in the C—N—O angle by 6.5° and an increase in the N=O bond length by 0.05 Å, which were estimated experimentally[10] for the related CF_3NO molecule upon its excitation from the S_0 state to the S_1 state. (In our earlier study,[1] where the geometric parameters of the $CClF_2NO$ molecule in the S_0 and S_1 states were calculated by the MP2 and CIS methods, respectively, we have not achieved such an agreement.)

The N=O bond lengths calculated by the CASSCF method with the (8-6) and (10-8) active spaces have close values, which are somewhat larger than those calculated by the UHF and CIS methods (see Tables 5 and 6). The CIS, UHF, and CASSCF(8-6) methods gave similar estimates of the C—N bond length, whereas calculations by the CASSCF(10-8) method predicted (as in the case of the S_0 state) a much larger value.

As can be seen from Tables 3 and 4, the CASSCF method predicted only a slight decrease in the NO stretch-

Table 3. Vibrational frequencies (cm^{-1}) of the conformers of the $CClF_2NO$ molecule in the S_0, T_1, and S_1 states calculated by different methods with the 6-31G* basis set and the corresponding experimental values

Vibration	Assignment[a]	S_0 State				T_1 State				S_1 State	
		cis,	*gauche*			*gauche*		*trans*		*gauche*,[b]	*trans*,
		CASSCF[c]	CASSCF[c]	MP2[d]	Experiment[e]	UHF	CASSCF[c]	UHF	CASSCF[c]	CASSCF[c]	CASSCF[c]
1	NO str	1633	1613	1525	1600	1501	1578	1490	1561	1408	1403
		(1663)	(1647)				(1533)		(1518)	(1319)	(1517)
2	CF_2 str. as	1367	1430	1298	1244	1397	1401	1355	1367	1402	1358
		(1371)	(1425)				(1404)		(1370)	(1413)	(1369)
3	CF_2 str. s	1340	1344	1195	1168	1312	1312	1292	1298	1296	1276
		(1321)	(1298)				(1294)		(1294)	(1276)	(1293)
4	CN str	1221	1122	976	925, 932	789	801	839	860	796	848
		(1061)	(1003)				(759)		(806)	(727)	(804)
5	CNO bend	712	860	797	768, 774	244	247	232	228	247	237
		(670)	(801)				(236)		(227)	(238)	(225)
6	CCl str	475	490	452		498	505	509	503	501	509
		(471)	(481)		410—		(496)		(504)	(491)	(503)
7	CF_2 wag	500	540	473	—453	1115	1136	1170	1164	1105	1155
		(415)	(456)				(1055)		(1093)	(977)	(1086)
8	CF_2 twist	507	343	363	353, 361	553	551	543	563	551	554
		(452)	(375)				(524)		(534)	(620)	(534)
9	CF_2 sciss	763	703	639	644	651	662	607	606	653	614
		(717)	(679)				(645)		(607)	(509)	(605)
10	CF_2 rock	387	393	313	283	376	383	377	365	379	377
		(364)	(310)				(377)		(375)	(388)	(375)
11	NCCl bend	270	335	294	225	399	410	388	386	400	387
		(237)	(299)				(399)		(378)	(361)	(378)
12	tors	62	74	78	70.7[f]	122	117	97	110	118	105
		(70)	(70)				(106)		(103)	(108)	(99)

[a] The approximate assignments of the vibrational frequencies calculated for the *cis* conformer are given. The following notations are used: str, stretching; bend, bending; wag, wagging; twist, twisting; sciss, scissoring; rock, rocking; tors, torsional; s, symmetrical; as, asymmetrical.

[b] For *gauche*-$CClF_2NO$ (S_1), the following vibrational frequencies were determined experimentally:[8] 342.9 (NCCl bend), 227.3 (CNO bend), and 105.3 cm^{-1} (tors).

[c] The vibrational frequencies were calculated in the CASSCF(8-6) and CASSCF(10-8) approximations (values in parentheses).

[d] See Ref. 1.

[e] See Refs. 1 and 7.

[f] See Ref. 8.

ing frequencies upon the $T_1 \leftarrow S_0$ electronic excitation of the molecules under study, whereas the CNO bending frequencies decrease substantially. A much more substantial decrease in the NO stretching frequency was predicted in the case of the $S_1 \leftarrow S_0$ excitation.

Calculations of the rotational contours of the bands in the $S_1 \leftarrow S_0$ vibronic spectrum of the $CClF_2NO$ molecule. Earlier,[8,9] it has been noted that each intense band in the fluorescence excitation spectrum of the $CClF_2NO$ molecule measured at low temperature is accompanied by a weak band (satellite), which is shifted from the main band to the long-wavelength region by 14 cm^{-1}. We have assigned[1] the intense bands and satellites to the S_1(*gauche*) $\leftarrow$ S_0(*gauche*) and S_1(*gauche*) $\leftarrow$ S_0(*cis*) electronic transitions, respectively.

In the present study, we calculated the rotational contours of the bands in the $S_1 \leftarrow S_0$ vibronic spectrum of the $CClF_2NO$ molecule. The experimental contours of the 0_0^0(*gauche* $\leftarrow$ *gauche*) (*a*) and 0_0^0(*gauche* $\leftarrow$ *cis*) (*b*) bands in the $S_1 \leftarrow S_0$ vibronic spectrum of the $CClF_2NO$ molecule[9] and the corresponding contours calculated with the use of the program analogous to that described earlier[11] are shown in Fig. 1.* We used the experimental[6] geometric parameters of the conformers of the molecule in the ground electronic state (denoted as $q(S_0)$). The

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* Fragments of the experimental fluorescence excitation spectrum in a supersonic jet (see Fig. 1, *a*, *b*) are reproduced from the paper[9] with the permission of the Elsevier Science Publishers.

Table 4. Vibrational frequencies (cm^{-1}) of the conformers of the CCl_2FNO molecule in the S_0, T_1, and S_1 states calculated by different methods with the 6-31G* basis set and the corresponding experimental values

Vibration	Assignment[a]	S_0 State				T_1 State				S_1 State	
		cis, CASSCF[c]	*gauche*			*gauche*		*trans*		*gauche*,[b] CASSCF[c]	*trans*, CASSCF[c]
			CASSCF[c]	MP2[d]	Experiment[e]	UHF	CASSCF[c]	UHF	CASSCF[c]		
1	NO str	1615 (1665)	1617 (1673)	1549	1614	1461	1559 (1512)	1483	1579 (1529)	1359 (1279)	1385 (1284)
2	CF str	1354 (1338)	1329 (1321)	1189	1140	1276	1282 (1284)	1322	1337 (1318)	1279 (1291)	1323 (1342)
3	CCl_2 str. as	978 (979)	972 (1006)	972	865, 916	992	1013 (1023)	954	964 (974)	1001 (1018)	1040 (979)
4	CN str	1085 (904)	1139 (883)	878	823, 829	1113	1120 (966)	1095	1139 (977)	1089 (849)	1079 (834)
5	CNO bend	872 (753)	697 (684)	661	754, 756, 759	228	231 (218)	222	215 (217)	254 (224)	209 (217)
6	CCl_2 str. s	526 (549)	635 (579)	553	481, 485	717	743 (694)	659	668 (622)	735 (615)	674 (581)
7	CCl_2 twist	450 (434)	335 (322)	401	391, 399	508	511 (511)	454	474 (450)	515 (445)	466 (442)
8	CCl_2 wag	436 (366)	444 (426)	323	306	434	439 (422)	575	597 (576)	447 (403)	577 (553)
9	NCF bend	354 (324)	465 (407)	418	362	462	477 (460)	466	455 (455)	467 (506)	467 (448)
10	CCl_2 rock	347 (303)	304 (285)	279	260	378	383 (375)	352	368 (352)	385 (363)	361 (330)
11	CCl_2 sciss	270 (252)	250 (228)	236	232	286	289 (286)	307	299 (309)	280 (282)	287 (307)
12	tors	72 (69)	58 (75)	76	71.3[f]	120	125 (109)	127	141 (112)	135 (104)	126 (118)

[a] The approximate assignments of the vibrational frequencies calculated for the *cis* conformer are given. For notations, see Table 3. Compared to the earlier study,[1] the assignments of the CCl_2 wag and NCF bend vibrations are changed.

[b] For *gauche*-CCl_2FNO (S_1), the following vibrational frequencies were determined experimentally:[9] 319 (NCF bend), 198.8 (CNO bend), and 108.4 cm^{-1} (tors).

[c] The vibrational frequencies were calculated in the CASSCF(8-6) and CASSCF(10-8) approximations (values in parentheses).

[d] See Ref. 1.

[e] See Refs. 1 and 7. In the earlier study,[1] the opposite assignment of the frequencies 306 and 362 cm^{-1} was proposed.

[f] IR spectrum.[9]

geometric parameters of the *gauche* conformer of the molecule in the S_1 state (denoted as $q(S_1)$) were calculated by the formula $q(S_1) = q(S_0) + \Delta q$, where Δq is the difference between the corresponding geometric parameters of the conformers in the S_1 and S_0 states calculated by the CASSCF method.

Since the *gauche* conformers of the $CClF_2NO$ molecule in the S_0 and S_1 states have no symmetry elements, the spectrum should, generally speaking, have A + B + C hybrid bands. Because of this, we carried out calculations by varying contributions of the bands of different types. It was demonstrated that the contours of the bands of the B + C type (1 : 1), which were determined from the results of calculations by the CASSCF(10-8) method, gave the best fit to the experimental 0_0^0-transition bands (see Fig. 1). The rotational contours, which were determined either based on only the calculated geometric parameters without employing the experimental data $q(S_0)$ or with the use of methods other than CASSCF(10-8), are in poorer agreement with experiment.

Internal rotation potential functions and torsional energy levels. For the CX_2YNO molecules in all three electronic states, we constructed one-dimensional cross-sections of the full PES along a torsional coordinate (so-called internal rotation potential functions). The Cl—C—N—O and F—C—N—O dihedral angles were taken as the torsional coordinate (φ) for the $CClF_2NO$ and CCl_2FNO molecules, respectively. *Ab initio* calculations were carried out for fixed values of the torsional coordinate in the range of 0—180° with a step of 15° with optimization of

Table 5. Internuclear distances (d), angles (ω), and energy differences (ΔE) of the conformers of the $CClF_2NO$ molecule in the T_1 and S_1 states calculated by different methods with the 6-31G* basis set

Parameter	T_1 State						S_1 State					
	gauche			*trans*			*gauche*			*trans*		
	UHF	CASSCF		UHF	CASSCF		CIS [1]	CASSCF		CIS [1]	CASSCF	
		(8-6)	(10-8)		(8-6)	(10-8)		(8-6)	(10-8)		(8-6)	(10-8)
Bond						d/Å						
N=O	1.220	1.245	1.239	1.221	1.247	1.242	1.187	1.271	1.264	1.189	1.273	1.267
C—N	1.435	1.428	1.477	1.439	1.430	1.479	1.441	1.435	1.510	1.446	1.438	1.516
C—Cl	1.758	1.757	1.752	1.745	1.746	1.742	1.758	1.758	1.749	1.740	1.744	1.739
C—F(1)	1.310	1.310	1.308	1.317	1.316	1.314	1.306	1.309	1.306	1.315	1.316	1.312
C—F(2)	1.316	1.315	1.313	1.317	1.316	1.314	1.315	1.316	1.311	1.315	1.316	1.312
Angle						ω/deg						
C—N—O	117.4	120.1	120.1	116.0	118.7	118.5	123.2	116.3	114.5	121.3	114.8	112.6
Cl—C—N	112.0	112.3	112.0	109.3	109.1	109.0	112.1	112.2	111.8	109.1	109.0	108.5
F(1)—C—N	107.1	107.0	106.5	110.0	110.1	109.5	107.0	106.9	105.9	109.7	110.0	109.2
F(2)—C—N	110.2	110.1	109.5	110.0	110.1	109.5	109.9	110.2	109.4	109.7	110.0	109.2
Cl—C—N—F(1)	−120.1	−120.2	−120.4	−120.7	−120.7	−120.8	−120.6	−120.1	−120.2	−121.1	−120.7	−120.8
Cl—C—N—F(2)	122.0	121.9	121.9	120.7	120.7	120.8	121.3	122.0	122.3	121.1	120.7	120.8
Cl—C—N—O	67.1	65.2	64.9	180.0	180.0	180.0	62.9	67.0	67.0	180.0	180.0	180.0
Energy						ΔE/cm^{-1}						
difference	0	0	0	416	288	280	0	0	0	506	355	336

Table 6. Internuclear distances (d), angles (ω), and energy differences (ΔE) of the conformers of the CCl_2FNO molecule in the T_1 and S_1 states calculated by different methods with the 6-31G* basis set

Parameter	T_1 State						S_1 State					
	gauche			*trans*			*gauche*			*trans*		
	UHF	CASSCF		UHF	CASSCF		CIS [1]	CASSCF		CIS [1]	CASSCF	
		(8-6)	(10-8)		(8-6)	(10-8)		(8-6)	(10-8)		(8-6)	(10-8)
Bond						d/Å						
N=O	1.222	1.246	1.240	1.219	1.244	1.237	1.187	1.273	1.264	1.185	1.270	1.261
C—N	1.439	1.431	1.486	1.435	1.430	1.486	1.444	1.439	1.531	1.440	1.435	1.527
C—F	1.325	1.325	1.322	1.319	1.319	1.317	1.324	1.325	1.319	1.314	1.318	1.314
C—Cl(1)	1.751	1.752	1.748	1.763	1.763	1.756	1.746	1.750	1.744	1.765	1.763	1.752
C—Cl(2)	1.764	1.763	1.757	1.763	1.763	1.756	1.766	1.764	1.753	1.765	1.763	1.752
Angle						ω/deg						
C—N—O	116.6	119.7	119.5	118.8	121.4	121.5	122.6	115.5	113.2	124.7	117.6	115.8
F—C—N	109.5	109.2	108.4	106.0	105.9	105.2	108.9	109.4	108.2	106.1	105.8	104.3
Cl(1)—C—N	108.1	107.9	107.6	111.1	111.3	110.8	108.0	107.8	107.0	111.0	111.3	110.6
Cl(2)—C—N	110.6	111.2	110.7	111.1	111.3	110.8	110.9	111.0	110.3	111.0	111.3	110.6
F—C—N—Cl(1)	−118.5	−118.4	−118.2	−117.7	−117.8	−117.8	−118.7	−118.4	−118.1	−118.2	−117.7	−117.5
F—C—N—Cl(2)	119.3	119.2	119.1	117.7	117.8	117.8	118.5	119.3	119.4	118.2	117.7	117.5
F—C—N—O	50.6	54.4	54.3	180.0	180.0	180.0	55.6	51.6	51.4	180.0	180.0	180.0
Energy						ΔE/cm^{-1}						
difference	376	236	245	0	0	0	483	317	315	0	0	0

the remaining geometric parameters. The set of points thus obtained was approximated by the function

$$V(\varphi) = 0.5\sum_{n=1} V_n[1 - \cos(n\varphi)]. \qquad (1)$$

The general view of the functions $V(\varphi)$ are shown in Fig. 2. Calculations by different methods gave qualitatively similar internal rotation potential functions for the same molecular system (see Fig. 2). Generally, CASSCF(8-6)

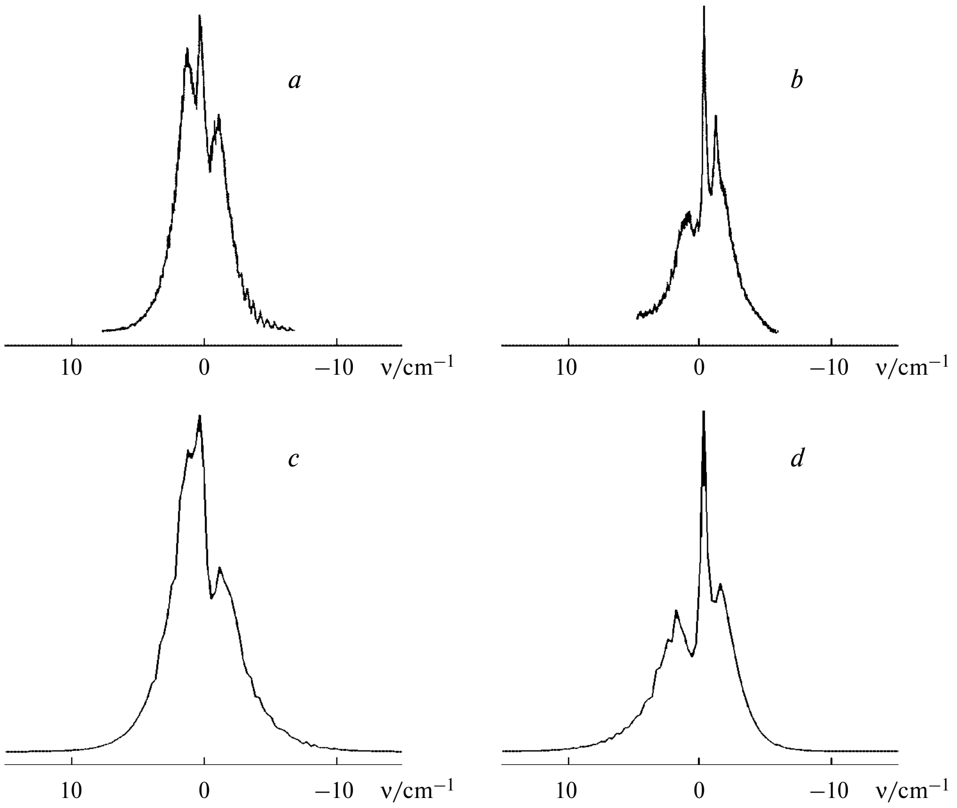

Fig. 1. Experimental (*a*, *b*) and calculated (*c*, *d*) rotational contours of the 0_0^0(*gauche* ← *gauche*) (*a*, *c*) and 0_0^0(*gauche* ← *cis*) (*b*, *d*) bands in the $S_1 \leftarrow S_0$ vibronic spectrum of the $CClF_2NO$ molecule. The calculated (see the text) rotational constants (in cm^{-1}): *c*, *gauche*-$CClF_2NO$ (S_0 state), A = 0.142121, B = 0.083502, C = 0.071979 and *gauche*-$CClF_2NO$ (S_1 state), A = 0.127647, B = 0.091632, C = 0.073453; *d*, *cis*-$CClF_2NO$ (S_0 state), A = 0.115271, B = 0.101047, C = 0.074471 and *gauche*-$CClF_2NO$ (S_1 state), A = 0.126828, B = 0.094843, C = 0.074087. The slit width was 0.3 cm^{-1}, the temperature was 20.0 K.

calculations give higher estimates of the torsional barriers than CASSCF(10-8).

The calculated internal rotation potential functions $V(\varphi)$ described by Eq. (1) were used for solving the one-dimensional Schrödinger equation with the Hamiltonian[12]

$$\hat{H}(\varphi) = -\frac{d}{d\varphi}F(\varphi)\frac{d}{d\varphi} + V(\varphi). \qquad (2)$$

The function $F(\varphi)$ included in the kinetic energy operator was determined from the calculated geometric parameters of the molecules:

$$F(\varphi) = \sum_{k=1} F_k \cos(k\varphi). \qquad (3)$$

The energies of the torsional levels calculated in this approximation are given in Tables 7 and 8. The energies of high torsional levels of the CCl_2FNO molecule in the S_1 state calculated by the CASSCF(10-8) method are noticeably lower than the corresponding experimental values. However, the experimental data are, on the whole, in satisfactory agreement with the calculated values.

Table 7. Torsional energy levels of the $CClF_2NO$ molecule in the S_0 state

Torsional level	Energy/cm^{-1}				
	Experiment		Calculation		
	I[a]	II[b]	MP2[c]	CASSCF	
				(8-6)	(10-8)
			gauche Conformer		
1±	72	72	75	66	66
2±	139	139	147	130	130
3±	200	197	215	192	188
4±	241	241	277	250	240, 241
			cis Conformer		
1	62	62	72	44	64
2	118	118	135	91[d]	117
3	166	166	188	128[d]	173[d]

[a] Absorption and resonance fluorescence spectra.[8]

[b] The levels calculated with the use of the internal rotation potential functions determined from the experimental data.[1]

[c] See Ref. 1.

[d] The levels are higher than the *cis—gauche* potential barrier.

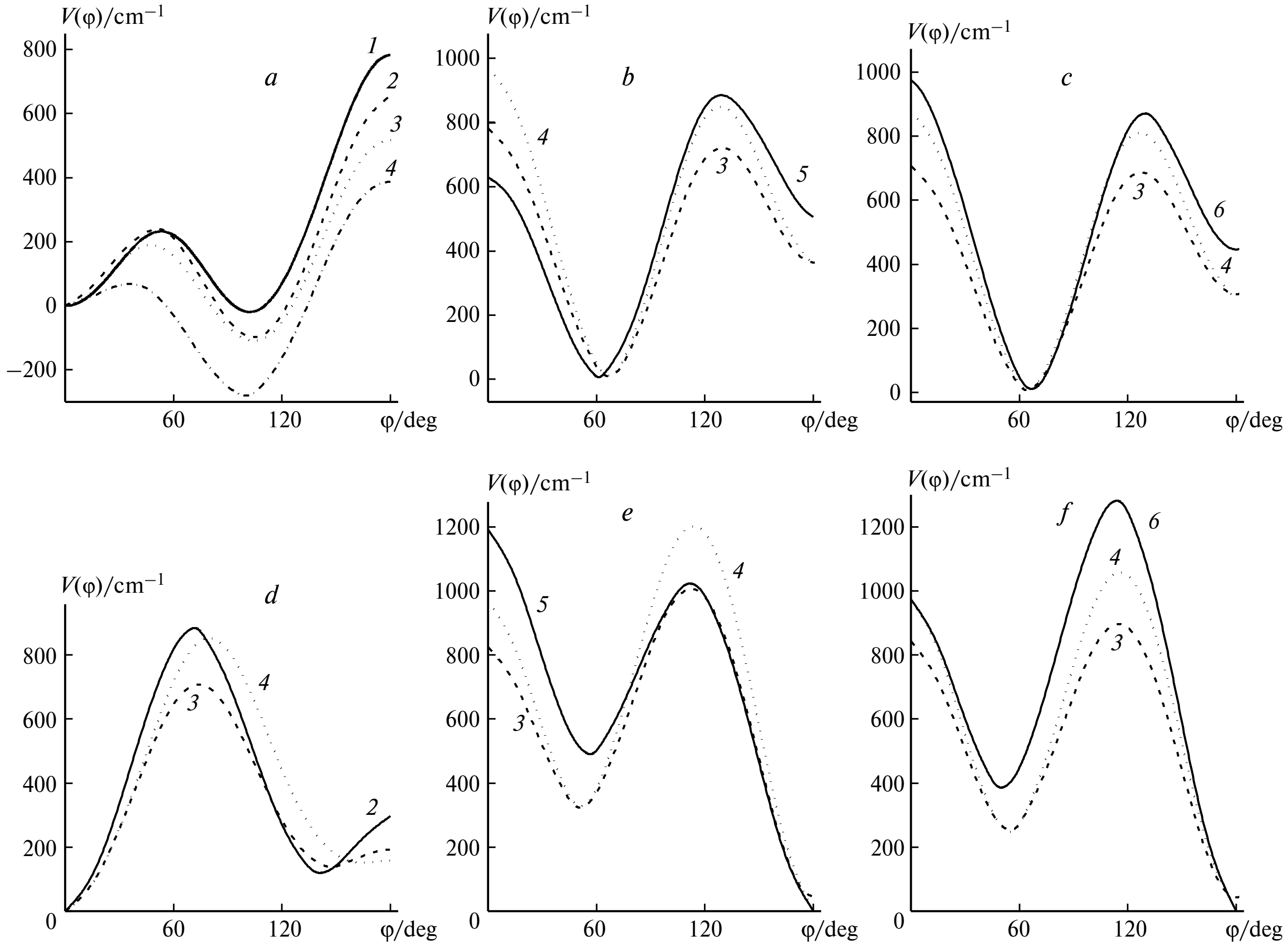

Fig. 2. Internal rotation potential functions $V(\varphi)$ of the $CClF_2NO$ (*a—c*) and CCl_2FNO (*d—f*) molecules in the S_0 (*a*, *d*), S_1 (*b*, *e*), and T_1 (*c*,*f*) states calculated by different methods: by fitting the experimental data[1] (*1*), MP2/6-31G* (*2*), CASSCF(10-8)/6-31G* (*3*), CASSCF(8-6)/6-31G* (*4*), CIS/6-31G* (*5*), and UHF/6-31G* (*6*).

Table 8. Torsional energy levels of the *gauche* conformers of the $CClF_2NO$ and CCl_2FNO molecules in the S_1 state

Torsional level	Energy/cm^{-1}			
	Experiment[a]	Calculation		
		CIS[b]	CASSCF	
			(8-6)	(10-8)
		$CClF_2NO$		
1±	105.3	109	108	97
2±	201.8	213	212	190
3±	296.0	313	312	278
4±	384.6	405	408	363
		CCl_2FNO		
1±	108.4	108	106	93
2±	—	210	207	182
3±	332	305	302	265
4±	446	393	394	342
5+, 5–	559	466, 469	477, 478	410, 411
6+, 6–	673	522, 538	551, 556	463, 479

[a] Experimental values for $CClF_2NO$ [8] and CCl_2FNO.[13]

[b] See Ref. 1.

All quantum-chemical methods (RHF, UHF, and CASSCF) used for studying PES of the CX_2YNO molecules (X and Y = F or Cl) in the S_0, S_1, and T_1 electronic states gave results, which are in satisfactory agreement with experiment.

The theoretical predictions of the changes in the molecular geometries caused by the $S_1 \leftarrow S_0$ electronic excitations, which were obtained in the calculations of the CX_2YNO molecules in the S_0 and S_1 states by the same method (CASSCF), are qualitatively analogous to the experimental estimates obtained for the related CF_3NO molecule.

A comparison of the active spaces (8-6) and (10-8) showed that the multiconfigurational method CASSCF(10-8) gave somewhat better results (geometric parameters, in particular, the N=O and C—N bond lengths, the energy differences of the conformers of the $CClF_2NO$ molecule, and vibrational frequencies). This conclusion was also confirmed by the calculations of the rotational contours of the bands in the $S_1 \leftarrow S_0$ vibronic spectrum of the $CClF_2NO$ molecule. However, the use of a rather large number of orbitals in the active space (10-8) is of doubtful value in the subsequent application of the methods, such as MRCI. This problem calls for further investigation, which we plan to carry out in the future.

* * *

The results of the present study provide evidence that the quantum-chemical methods used are applicable to the description of fine conformational effects in molecules of nitroso compounds in the ground and lowest excited electronic states. Taking into account that it is desirable to compare information on the molecular structure in different electronic states within the same method and to have a possibility of obtaining subsequent electronic correlation corrections, it can be concluded that CASSCF is the method of choice.

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