The structure of CX_2YNO (X, Y = F, Cl) molecules in the ground and lowest excited singlet electronic states

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Ab initio quantum-chemical calculations of equilibrium geometric parameters, vibrational frequencies, and potentials of internal rotation for $CClF_2NO$ and CCl_2FNO molecules in the ground (S_0) and lowest excited singlet (S_1) electronic states were performed. The results of calculations were compared with experimental data. A new interpretation of experimental spectra of the $CClF_2NO$ molecule was suggested.

Key words: *ab initio* quantum-chemical calculations, nitroso compounds, molecular geometry, vibrational frequencies, potentials of internal rotation, ground and excited electronic states.

Investigation of the structure and dynamics of the molecules of nitroso compounds has attracted considerable interest (see, *e.g.*, Refs. 1, 2). In particular, it has been found that excitation of molecules of nitroso compounds with C_{3v} top symmetry (CR_3, R = H, F) from the ground (S_0) to the lowest excited singlet (S_1) electronic state causes a transition from an eclipsed (with respect to R and O atoms) equilibrium conformation to a staggered one. A similar picture is also observed for the molecules of carbonyl compounds.[1,3]

Much less clear are the results obtained for the molecules of nitroso compounds with C_s top symmetry ($CClF_2$ and CCl_2F),[2] though the structure of the $CClF_2NO$ molecule has been studied in detail using several spectroscopic methods, *viz.*, IR spectroscopy,[4] UV absorption spectroscopy in the vapor phase,[5] as well as fluorescence and fluorescence excitation spectroscopy in a supersonic jet.[5] Among the facts established, the most important are the following.

1. Several similar groups of bands at intervals of 105.3, 201.8, 296.0, 384.6, and, possibly, 446.7 cm^{-1} are observed in the fluorescence excitation spectrum. They can be assigned to a torsional progression in the S_1 state of the molecule (presumably, the *gauche*-conformer). A band of medium intensity at 14187 cm^{-1} was assigned to the "origin" of the observed electronic transition (the transition between the zeroth vibrational levels of the S_0 and S_1 states).

2. Each of the intense bands of the above-mentioned torsional progression has a weak satellite shifted by 14 cm^{-1} from the main band toward the long-wavelength spectral region. An interesting feature of the satellites is that their intensities decrease as the jet temperature increases relatively and remain virtually unchanged as the temperature decreases appreciably. This rules out the assignment of such satellites to the dimers of the molecules studied or to their van der Waals complexes with the atoms of inert gases in which the band intensities should increase upon jet cooling of the molecules and, *v.v.*, decrease on raising the temperature.

3. Intense bands in the absorption and fluorescence spectrum form intervals of 72, 139, 200, and 241 cm^{-1} that can likely be assigned to a torsional progression of the major (having the lowest energy) conformer in the S_0 state.

4. An interval of 132 cm^{-1} is observed in the resonance fluorescence spectrum upon excitation of the molecules to the τ^2, τ^3, τ^4, and $\rho^1\tau^2$ levels, which is different from that of 139 cm^{-1} in the case of excitation to the τ^1, ρ^1, $\rho^1\tau^1$, and $\gamma^1\tau^1$ levels (τ, ρ and γ denote the torsional, rocking, and skeletal bending degrees of freedom, respectively, and the superscripts denote the value of the vibrational quantum number in the S_1 state). The same interval (139 cm^{-1}) is observed in the absorption spectrum. Most likely, the intervals of 132 and 139 cm^{-1} should be assigned to the different conformers in the S_0 state.

However, the interpretation of the data obtained previously[5] was rather rough and the suggested scheme of the potential functions of internal rotation for the molecule in the S_0 and S_1 states reproduces neither the experimental energies of torsional levels nor the relative intensities of electronic transitions even at a semi-quantitative level. In particular, it gives no explanation for the relatively high intensity of the band assigned to the "origin" of electronic transition for the $CClF_2NO$ molecule compared to that of the corresponding band for the CF_3NO molecule. In addition, a recent study of the IR spectrum of $CClF_2NO$ showed[2] that, in contrast

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Table 1. Parameters and extrema of the potential functions of internal rotation $V(\varphi)$ for the $CClF_2NO$ and CCl_2FNO molecules in the S_0 and S_1 states (V/cm^{-1}, φ/deg)

State	Parameters of the potential						Extrema of $V(\varphi)$
	V_1	V_2	V_3	V_4	V_5	V_6	
							$CClF_2NO$
S_0	256	−385	400	63	2	−1	$V_{max}(49) = 257$, $V_{min}(105) = -121$, $V_{max}(180) = 656$
S_1	493	−240	−626	73	10	1	$V_{min}(63) = -630$, $V_{max}(130) = 295$, $V_{min}(180) = -124$
							CCl_2FNO
S_0	−204	602	491	−68	7	−16	$V_{max}(71) = 891$, $V_{min}(141) = 114$, $V_{max}(180) = 297$
S_1	−414	257	−736	−55	−40	4	$V_{min}(56) = -708$, $V_{max}(112) = -160$, $V_{min}(180) = -1191$

Note. The extreme values listed are those obtained from quantum-chemical calculations. The energies V and angles φ for the *cis*-conformers were taken as the origins.

to the previous assumption,[5] it is the *gauche*-conformer rather than the *cis*-conformer of the molecule in question that has the lowest energy in the S_0 state (as was assumed earlier[5]).

The CCl_2FNO molecule has been less investigated: only IR spectra[4] and the fluorescence excitation spectrum in the jet of this compound[6] were studied.

In this work, we performed *ab initio* quantum-chemical calculations of equilibrium geometric parameters, vibrational frequencies, and potentials of internal rotation for the $CClF_2NO$ and CCl_2FNO molecules in the ground (S_0) and first excited singlet (S_1) electronic states. On the basis of calculated and experimental data, a new interpretation of the spectra[5] of the $CClF_2NO$ molecule is suggested and the reliability of calculated results obtained for the CCl_2FNO molecule was estimated.

Ab initio quantum-chemical calculations

Calculations were carried out using the second-order Møller—Plesset level of perturbation theory based on the restricted Hartree—Fock method[7] (MP2) for the S_0 state and by the method of configuration interaction with inclusion of single excited configurations[8] (CIS) for the S_1 state. The standard 6-31G* basis set of AOs was used. The frozen core approximation (the MOs, composed mainly of 1s-AOs of heavy atoms, were considered doubly occupied in all configurations) was used. All calculations* were carried out using the GAMESS program.[9]

Particular emphasis was placed on the fragment of the potential energy surface (PES) corresponding to torsional motion. The cross section of the PES along the torsional coordinate (the Cl—C—N—O and F—C—N—O dihedral angles for the $CClF_2NO$ and CCl_2FNO molecule, respectively), or the potential function of internal rotation, was studied. The energy was calculated at fixed values of the torsional coordinate in the range from 0 to 180° with an increment of 15° with optimization of all of the rest of the geometric parameters. Positions of critical points corresponding to the *gauche*-conformations having no C_s symmetry were refined separately. The set of points obtained was approximated by the function

$$V(\varphi) = \frac{1}{2} \sum_{n=1} V_n(1 - \cos n\varphi), \qquad (1)$$

where φ is the angle of internal rotation. The parameters for the *cis*-conformation were taken as the origin for the angle φ and potential energy V and n_{max} was equal to 6.

The obtained parameters of the potential functions are listed in Table 1 (their general view is shown in Fig. 1). Previously, a quantum-chemical study of these molecules in the S_0 state was carried out by the semiempirical MNDO and AM1 methods with inclusion of configuration interaction.[10] In that study, a different qualitative picture for the torsional potentials of the molecules studied in the S_0 states was obtained, *viz.*, the only minimum corresponding to the *gauche*-conformer for the $CClF_2NO$ molecule (instead of two minima for *cis*- and *gauche*-conformers) and another position of the second minimum (*trans* instead of *gauche*) for the CCl_2FNO molecule. The potential functions of internal rotation for these molecules in the S_1 states are determined for the first time.

The calculated geometric parameters for the $CClF_2NO$ molecule (Table 2) appreciably differ from experimental data (the differences amount to nearly 0.03 Å in the bond lengths and to 9° in the bond angles); however, it should be emphasized that experimental estimates of the parameters made previously[4] are rather rough. Our calculations of geometric parameters of the molecules studied with consideration for additional diffuse functions on all atoms and *f*-functions on Cl atoms slightly change the results listed in Tables 2 and 3.

It is noteworthy that in the S_0 states the corresponding geometric parameters of the CX_2Y tops (X, Y = F, Cl) of different conformers of the molecules differ to

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* The results of calculations will be published elsewhere.

a greater extent than in the S_1 states (see Tables 2 and 3). This may indicate that in the S_1 states the molecules studied are more rigid than in the S_0 states. Appreciable increase in the C—N—O angles (by ~10°) and considerable decrease in the C—N and N—O bond lengths is observed upon $S_1 \leftarrow S_0$ electronic excitation of the molecules. For the related CF_3NO molecule, changes in the C—N—O angle and N—O bond length were estimated[11] at +6.5° and +0.05 Å, respectively. Currently, the reasons for opposite changes in the N—O bond length in the CX_2YNO and CF_3NO molecules remain unclear and further investigations are required.

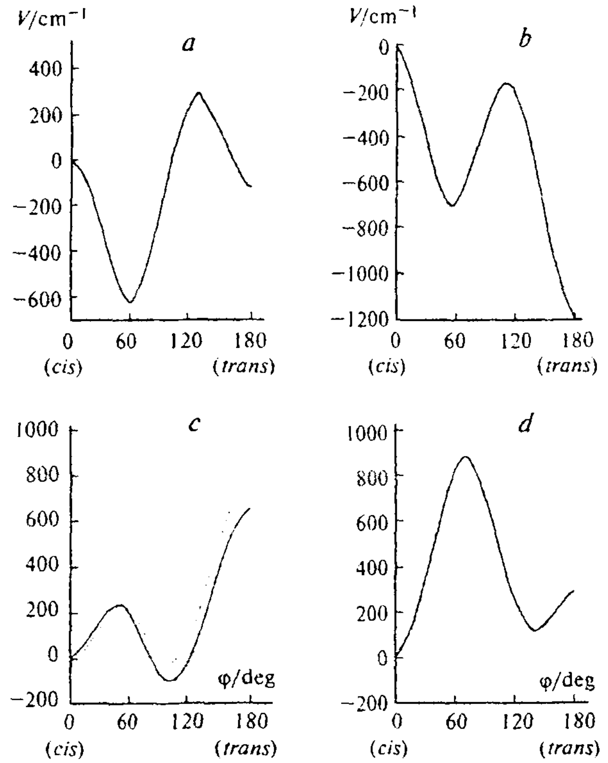

Fig. 1. Potential functions of internal rotation for the $CClF_2NO$ (*a*, *c*) and CCl_2FNO (*b*, *d*) molecules in the S_1 (*a*, *b*) and S_0 states (*c*, *d*): solid and dashed lines correspond to the results of quantum-chemical calculations and to those obtained from experimental data, respectively.

Table 2. Calculated and experimental internuclear distances (*d*) and angles (ω) for the $CClF_2NO$ molecule in the ground (S_0) and the lowest excited singlet (S_1) electronic states

Parameter	Calculated values				Experiment[4] for the S_0 state
	S_0 state		S_1 state		
	gauche	*cis*	*gauche*	*trans*	
Bond			*d*/Å		
NO	1.226	1.221	1.187	1.189	1.195
CN	1.521	1.527	1.441	1.446	1.51
CCl	1.750	1.742	1.758	1.740	1.726
CF(1)	1.342	1.344	1.306	1.315	1.324
CF(2)	1.336	1.344	1.315	1.315	1.324
Angle			ω/deg		
CNO	110.8	113.6	123.2	121.3	112.4
ClCN	107.1	115.9	112.1	109.1	113.9
F(1)CN	105.8	104.7	107.0	109.7	113.9
F(2)CN	112.2	104.7	109.9	109.7	113.9
F(1)CNO	−136.6	−122.7	−176.6	58.9	−120*
F(2)CNO	−17.7	122.7	−58.4	−58.9	120*
ClCNO	104.7	0	62.9	180.0	0

* Accepted.

Table 3. Calculated internuclear distances (*d*) and bond angles (ω) for the CCl_2FNO molecule in the ground (S_0) and lowest excited singlet (S_1) electronic states

Parameter	S_0 state		S_1 state	
	gauche	*cis*	*gauche*	*trans*
Bond		*d*/Å		
NO	1.218	1.221	1.187	1.185
CN	1.542	1.542	1.444	1.440
CF	1.352	1.345	1.324	1.314
CCl(1)	1.744	1.750	1.766	1.765
CCl(2)	1.755	1.750	1.746	1.765
Angle		ω/deg		
CNO	113.3	110.6	122.6	124.7
FCN	103.8	111.1	108.9	106.1
Cl(1)CN	114.1	105.7	110.9	111.0
Cl(2)CN	104.9	105.7	108.0	111.0
Cl(1)CNO	21.5	−119.6	−62.9	61.8
Cl(2)CNO	−103.2	119.6	174.3	−61.8
FCNO	141.4	0	55.6	180.0

The calculated vibrational frequencies of CX_2YNO molecules are, on the whole, in good agreement with the corresponding experimental data for both the S_0 and S_1 states. Therefore the assignment of frequencies presents no difficulties, though the vibrations are, as a rule, coupled more strongly than indicated in Tables 4 and 5.

It is noteworthy that the calculated and experimental torsional frequencies for both molecules in the S_0 and S_1 states are in rather good agreement. The frequencies of the stretching NO vibrations appreciably increase, while those of bending CNO vibrations substantially decrease, upon $S_1 \leftarrow S_0$ electronic excitation of the molecules studied.

Band assignment in the $S_1 \leftarrow S_0$ vibronic spectra of $CClF_2NO$

According to calculations, the *gauche*-conformers of the $CClF_2NO$ molecule have lower energies in both the S_0 and S_1 state. Therefore, a group of intense bands starting with a band at 14187 cm⁻¹ and forming a torsional progression with bands at 105.3, 201.8, 296.0, and 384.6 cm⁻¹ in the fluorescence excitation spectrum of supersonically cooled molecules[5] was assigned to the *gauche*←*gauche* transitions of the conformer (this is in agreement with the reported data[2] and, at the same time, contradicts the conclusion drawn by the authors of the experimental study[5]), while the band at 14187 cm^{-1} was assigned to the "origin" of corresponding electronic transition (Table 6).

Table 4. Calculated and experimental vibrational frequencies (cm^{-1}) for the $CClF_2NO$ molecule in the ground (S_0) and lowest excited singlet (S_1) electronic states

Vibra-tion	Vibration mode	Calculations				Experiment	
		S_0		S_1		S_0	S_1
		cis	*gauche*	*trans*	*gauche*	(*gauche*)[a]	(*gauche*)[b]
1	NO str	1547	1525	1942	1962	1600	
2	CF_2 str. as	1232	1298	1354	1411	1244	
3	CF_2 str. s	1214	1195	1280	1287	1168	
4	CN str	1049	976*	1127	1077	925 or 932	
5	CNO bend	683	797	240	252	768 or 774	227.3
6	CCl str	661	452*	513	506	410–453[c]	
7	CF_2 wag	449	473*	848*	794*		
8	CF_2 twist	443	363*	576	668*	353 or 361	
9	CF_2 sciss	424	639	619	551	644	
10	CF_2 rock	352	313*	379	385	283	
11	NCCl bend	243	294	394	419	225	342.9
12	tors	74	78	106	113	70.7[d]	105.3

Note. The following notations were used: str is stretching, bend is skeletal bending, wag is wagging, twist is twisting, sciss is scissoring, rock is rocking, tors is torsional, s is symmetric, and as is antisymmetric mode. Approximate descriptions of vibration modes calculated in this work for the *cis*-conformer in the S_0 state are given. Strongly coupled vibrations are asterisked.

[a] See Ref. 4.

[b] See Ref. 5.

[c] Five bands of medium intensity are observed in this spectral region.

[d] See Ref. 2.

Table 5. Calculated and experimental vibrational frequencies (ν/cm^{-1}) for the CCl_2FNO molecule in the ground (S_0) and lowest excited singlet (S_1) electronic states

Vibra-tion	Vibration mode	Calculations				Experiment	
		S_0		S_1		S_0	S_1
		cis	*gauche*	*trans*	*gauche*	(*gauche*)[a]	(*gauche*)[b]
1	NO str	1535	1549	1963	1942	1614	
2	CF str	1218	1189	1131	1265	1140	
3	CCl_2 str. as	915	972	952	987	865 or 916	
4	CN str	887*	878*	1034	1067	823 or 829	
5	CNO bend	787	661	231*	231*	754 or 756 or 759	198.8
6	CCl_2 str. s	494	553	656	734	481 or 485	
7	CCl_2 twist	414	401	462	518*	391 or 399	
8	CCl_2 wag	387*	323*	603*	439*	362	
9	NCF bend	324	418	465	483	306	319.0
10	CCl_2 rock	308	279*	374	386*	260	
11	CF_2 sciss	248	236*	312	289	232	
12	tors	76	76	119	115	71.3[b]	108.4

Note. For the notations, see note to Table 4. Approximate descriptions of vibration modes calculated in this work for the *cis*-conformer in the S_0 state are given. Strongly coupled vibrations are asterisked.

[a] See Ref. 4.

[b] See Ref. 2.

The above dependence of the "satellite" band intensities on temperature can be explained only if this group of bands starting with the band at 14173 cm^{-1} (*i.e.*, 14187 cm^{-1} – 14 cm^{-1}) is assigned to the transitions of the *cis*-conformer of the $CClF_2NO$ molecule from the zeroth vibrational level in the S_0 state to the zeroth and higher torsional levels of the *gauche*-conformer of this molecule in the S_1 state. In this case, the energy of the "origin" of the corresponding electronic transition is 14173 cm^{-1} and the energy difference between the zeroth vibrational levels of $CClF_2NO$ conformers in the S_0 state is 14 cm^{-1}.

A weak band at 13966 cm^{-1} in the absorption spectrum (see Table 6) was assigned to the 11_1^0 (*gauche*←*gauche*) transition, whereas in the S_0 state $\upsilon_{11}''(gauche)$ = 221 cm^{-1} (225 cm^{-1} in the IR spectrum[4]); transitions of the type $11_1^0 12_{\upsilon''}^{\upsilon'}$ are also observed in the spectrum (see Table 6). In the spectral region above 14389 cm^{-1} our assignment coincides with the suggested one[5] (the notations of the ρ and χ vibrations in Ref. 5 correspond to vibrations Nos. 5 and 11, respectively, see Table 4); therefore only the wave numbers of the bands of the $12_0^{\upsilon'}$ torsional progression are listed in Table 6 for this region.

The interval 132 cm^{-1} observed in the resonance fluorescence spectrum[5] (see above) and measured from the 0_0^0 (*gauche*←*cis*) band is 118 cm^{-1} (132 cm^{-1} – 14 cm^{-1}); initially, it was assigned to a torsional overtone of the *cis*-conformer in the S_0 state.

Using the energy of the second torsional level of the *cis*-conformer 118 cm^{-1}, those of the four torsional levels of the *gauche*-conformer (72, 139, 200, and 241 cm^{-1}), and the energy difference between the conformers (14 cm^{-1}), we calculated the potential function of internal rotation of the $CClF_2NO$ molecule in the S_0 state.

To this end, we numerically solved the one-dimensional Schrödinger equation[12] with the following Hamiltonian:

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

The function $F(\varphi)$ that appears in the kinetic energy operator was determined from the experimental geometric parameters of the molecule[4] (see Table 2) in the form

$$F(\varphi) = \sum_{k=0}^{5} F_k \cos k\varphi . \qquad (3)$$

where $F = h/(8\pi^2 c I_{red})$ (I_{red} is the reduced moment of inertia).

The potential function of internal rotation $V(\varphi)$ was represented in form (1).

For the found function of internal rotation, we calculated the energies of the first and third torsional levels of the *cis*-conformer (62 and 166 cm^{-1}, respectively).

Table 6. Wave numbers (ν)[5] and band assignment in the low-frequency region of the S_1(*gauche*)←S_0(*gauche*)-spectra of $CClF_2NO$

ν/cm^{-1}	$\Delta\nu$/cm^{-1}	Assignment	ν/cm^{-1}	$\Delta\nu$/cm^{-1}	Assignment
13945 s	−241	12_4^0	14189 w	2	12_3^2, $11_1^0 12_1^3$
13966 w	−221	11_1^0	14217 s	30	12_1^1, $5_0^1 12_3^0$
13990 vs	−197	12_3^0	14260 w	73	12_2^2, $11_1^0 12_0^3$
14010 sh	−177	—[a]	14280 m	93	12_3^3, $5_0^1 12_2^0$
14047 s	−140	12_2^0	14291.8 vs[b]	105.3	12_0^1
14069 m	−118	11_1^0, 12_0^1	14317 m	130	12_1^2
14091 w	−96	12_3^1, $11_1^0 12_1^2$	14349 m	162	12_2^3, $5_0^1 12_0^1$
14110 m	−76	12_1^0	14388.3 s[b]	201.8	12_0^2
14128 w	−58	$11_1^0 12_2^3$	14389 m	202	$5_0^1 12_2^1$
14152 m	−34	12_2^1	14482.5 s[b]	296.0	12_0^3
14186.5 m[b]	0	0_0^0	14571.1 m[b]	384.6	12_0^4

Note. Listed are the wave numbers of the bands in the vapor-phase absorption spectrum, if otherwise not indicated. Conventional notations of vibronic transitions are used, *viz.*, $N_{\upsilon''}^{\upsilon'}$, where N is the number of the vibration (see Table 3), υ' and υ'' are the vibrational quantum numbers for the S_1 and S_0 states, respectively. The "origin" of electronic transition is denoted as 0_0^0. The notations of band intensities: vs is very strong, s is strong, m is medium, w is weak, and sh is shoulder.

[a] Assigned to the 12_3^0 (*gauche*←*cis*)-transition, see text.

[b] Bands of the fluorescence excitation spectrum.

The intervals of 72 (76) and 180 (177) cm^{-1} measured from the bands corresponding to the "origin" and "pseudo-origins" of the *gauche*←*gauche*-transition are observed in the resonance fluorescence and absorption spectra. The first of them was assigned to the torsional frequency of the *gauche*-conformer in the S_0 state (see Table 6), whereas the second has no reliable assignment. We believe that the transition 12_1^0 (*gauche*←*cis*) is possibly masked by a more intense 12_1^0 (*gauche*←*gauche*) transition, while the interval 180 cm^{-1} measured from the band 0_0^0 (*gauche*←*cis*) transition (180 cm^{-1} − 14 cm^{-1} = 166 cm^{-1}) corresponds to the energy of the third torsional level of the *cis*-conformer.

The energy of the third torsional level of the *cis*-conformer was also used in final calculations of the potential function of internal rotation for the $CClF_2NO$ molecule in the S_0 state. (The described calculations of the potential of internal rotation from experimental data will be denoted below as calculations I.) In addition, the energies of torsional levels for the conformers of CX_2YNO (X, Y = F, Cl) molecules were calculated by the equation with the Hamiltonian (2) using the potential functions of internal rotation obtained from quantum-chemical calculations (see Table 1) and geometric parameters (see Table 2 and 3) (hereafter, calculations II).

The results of calculations I and II and experimental energies of torsional levels for the CCl_2FNO molecule in the S_0 state are listed in Table 7. As can be seen, the calculated and experimental data are in good agreement.

The coefficients F_k in expression (3) were found to be F_0 = 1.7066, F_1 = 0.0195, F_2 = 0.1218, F_4 = 0.0054, and F_5 = 0.0003 cm^{-1}. The potential function of internal rotation V was described by expression (1) with the following parameters V_n: V_1 = 421, V_2 = −362, V_3 = 362, V_4 = 34, V_5 = 0 (accepted), and V_6 = −12 cm^{-1}. For the angle and energy, the parameters for the *cis*-conformer were taken as the origin; other extrema are characterized by the following values: $V_{max}(53°)$ = 233 cm^{-1}, $V_{min}(102°)$ = −20 cm^{-1}, and $V_{max}(180°)$ = 783 cm^{-1}. The energy differences between the zeroth vibrational levels of the conformers obtained from calculations I and II are 14 and 121 cm^{-1}, respectively (ΔE_{exp} = 14 cm^{-1}).

It is impossible to determine the potential function of internal rotation for the $CClF_2NO$ molecule in the S_1 state with full details from experimental data, since no information on vibronic transitions of the *trans*-conformer are available. However, the calculated (calculations II) energies of torsional levels are in very good agreement with corresponding experimental energies

Table 7. Parameters of the potential functions of internal rotation (1) for the $CClF_2NO$ molecule in the S_0 state determined from experimental data and experimental and calculated energies of torsional levels for the conformers (cm^{-1})

υ[a] (*gauche*)	Energy: Experiment[b]	Energy: Calculations I	Energy: Calculations II	υ[a] (*cis*)	Energy: Experiment[b]	Energy: Calculations I	Energy: Calculations II
1±	72	72	75	1	(62)[c]	62	72
2±	139	139	147	2	118	118	135
3±	200	197	215	3	166	166	188
4±	241	241	277				

[a] The number of the torsional level. For the *gauche*-conformer, the torsional levels are doubly degenerate (±).

[b] Data of resonance fluorescence spectra and absorption spectra.[5]

[c] Not used in the determination of $V(\varphi)$, see text.

Table 8. Calculated and experimental energies of torsional levels for the *gauche*-conformers of $CClF_2NO$ and CCl_2FNO molecules in the S_1 states

v^a	Energy/cm^{-1}			
	$CClF_2NO$		CCl_2FNO	
	Calculations II	Experiment[b]	Calculations II	Experiment[c]
1±	109	105.3	108	108.4[d]
2±	213	201.8	210	—
3±	313	296.0	305	332
4±	405	384.6	393	446
5+, 5−			466, 469	559
6+, 6−			522, 538	673

[a] The number of the torsional level.

[b] See Ref. 5.

[c] See Ref. 6.

[d] See Ref. 2.

(Table 8). Therefore, it is hoped that our calculations describe the structure of the $CClF_2NO$ molecule in the S_1 state fairly well.

Vibronic spectrum and the potential function of internal rotation for the CCl_2FNO molecule in the S_0 and S_1 states

Previously, experimental studies of the vibrational spectrum[4] and fluorescence excitation spectrum[2,6] of the CCl_2FNO molecule were carried out. However, the assignment of bands to conformers was not considered in the first case. The band intensity distribution in the fluorescence excitation spectrum[2,6] indicates that a transition from the eclipsed conformation to the staggered one occurs upon electronic excitation of the molecule ($S_1 \leftarrow S_0$); no transitions for the second conformer were found in the spectrum.

Our calculations of the potential functions of internal rotation for the CCl_2FNO molecule in the S_0 and S_1 states (see Fig. 1) confirm that the torsional progression starting with 14522 cm^{-1} ($0_0{}^0$-transition) found under jet-cooling conditions[2,6] should be assigned to the *gauche*(S_1)←*cis*(S_0) vibronic transitions. The absence of experimental data on the second conformers of CCl_2FNO in the S_0 and S_1 states makes it impossible to determine the potential functions of internal rotation for this molecule by performing calculations I. However, as can be seen in Table 8, the use of calculations II makes it possible to obtain energies of torsional levels for the *gauche*-conformer in the S_1 state which are in good agreement with corresponding experimental data.

Taking into account that the calculated harmonic frequency for *cis*-CCl_2FNO in the S_0 state is also in good agreement with its experimental value (see Table 5), it can be expected that the potential functions of internal rotation for the CCl_2FNO molecule in the S_1 and S_0 states obtained from quantum-chemical calculations are rather reliable.

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Thus, our *ab initio* quantum-chemical calculations of the $CClF_2NO$ and CCl_2FNO molecules in the S_0 and S_1 states made it possible to determine the geometric parameters, vibrational frequencies, and potential functions of internal rotation and suggest a new interpretation of experimental vibrational and vibronic spectra of these molecules.

The results obtained from calculations are in good agreement with all available experimental data. In particular, a substantial decrease in the intensities of the bands corresponding to the $0_0{}^0$-transitions in the $S_1 \leftarrow S_0$-spectra in the series $CClF_2NO$ (*gauche*←*gauche*), CCl_2FNO (*gauche*←*cis*), and CF_3NO (staggered conformation ← eclipsed conformation)[2] is explained (in accordance with the Franck—Condon principle) by the increased shift of the minimum on the potential surface in the S_1 state with respect to the minimum in the S_0 state along the torsional coordinate, *viz.*, 42°, 56° (see Table 1), and 60°, respectively.

The results obtained indicate that quantum-chemical methods employed in this work can be used for the description of fine conformational effects in the molecules of nitroso compounds in the ground and lowest excited electronic states.

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