Theoretical study of structures of the X_2CO and XYCO molecules (X and Y = H, F, or Cl) in the ground and lowest excited triplet electronic states

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Systematic calculations of the structures of the H_2CO, F_2CO, Cl_2CO, HClCO, HFCO, and FClCO molecules in the S_0 and T_1 states were performed using the B3LYP and MP2 methods with different AO basis sets and also at the CCSD(T)/cc-pV(T+d)Z level of theory. The saturation of the correlation consistent sequence of basis sets cc-pV(N+d)Z (N = D, T, Q, and 5) and aug-cc-pV(N+d)Z (N = D, T, and Q) was studied. Recommendations for choosing the calculation method are given. The relativistic corrections were estimated. The influence of the number and type of halogen atoms on the geometric parameters of the molecules in the S_0 and T_1 states and the heights of inversion barriers in the T_1 state was investigated.

Key words: quantum-chemical calculations, systematic basis sets, structures of molecules in excited electronic states, inversion motion, formaldehyde, halogen-substituted formaldehydes.

Experimental studies of vibronic spectra of carbonyl compounds demonstrated that the carbonyl fragment in particular compounds becomes nonplanar upon excitation from the ground (S_0) to the lowest triplet (T_1) and singlet (S_1) electronic states due to which a large-amplitude internal motion, *viz.*, the inversion of the nonplanar carbonyl fragment, can occur.[1]

The molecules of formaldehyde (H_2CO) and its halogen-substituted derivatives are the simplest representatives of carbonyl compounds and serve as convenient models for studying the structural features of this class of molecules. Many of these compounds have found use in industry as chemicals for organic synthesis (for example, phosgene Cl_2CO is used as the starting material in the production of dyes, polycarbonates, urea and its derivatives, pesticides, drugs, solvents, *etc.*). Some of them are generated upon photolysis and oxidation of fluoro and chloro derivatives of hydrocarbons, including freons, in the troposphere and stratosphere; it is supposed that these compounds catalyze ozone decomposition.[2—5] Hence, the physical and chemical properties of these compounds are of considerable interest.

Earlier, the molecules of halogen-substituted formaldehydes have been studied primarily in the ground electronic state by vibrational spectroscopy and gas electron diffraction.[6—10] The structure of the H_2CO molecule in the S_0 state has been investigated in depth by microwave and rovibrational spectroscopy.[11] Analysis of the rovibronic spectra provided information[11] on the structures of these molecules in the S_1 and (only for formaldehyde) T_1 states. We performed theoretical study of the structures and vibrational dynamics of formaldehyde and its halogen-substituted derivatives in the S_0 and T_1 states. Our investigation included two steps. In the first step, we estimated the reliability of different methods for solving the electronic Schroedinger equation. In the second step, the chosen methods were used for studying the potential energy surface (PES) in the region, where vibrational wavefunctions are localized, and solved the nuclear Schroedinger equation. Since the inversion of the nonplanar carbonyl fragment belongs to large-amplitude vibrations, this region would be expected to be rather large. Hence, in the first step, it was necessary to find not only a reliable approach to the solution of the electronic Schroedinger equation but also methods, which would allow us to efficiently investigate large regions of potential energy surfaces.

In the present study, we report the results obtained in the first step. Only one theoretical study devoted to systematic calculations of the structures of all fluoro and chloro derivatives of formaldehyde in the T_1 electronic state by the ROHF method with the minimum basis set has been published so far.[12] Systematic calculations of the structure of the F_2CO molecule in the S_0, T_1, and S_1 states were carried out by the UMP2, QCISD, and CASSCF methods.[13] The structures of the H_2CO, F_2CO,

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and Cl_2CO molecules in the S_0, T_1, and S_1 states were calculated at the CASSCF(6-5)/6-31G** level.[14] In the T_1 electronic state, all these molecules have[12—14] a pyramidal structure. However, these data are insufficient for solving the problem of nuclear vibrations. In the present study, we performed calculations of the structures of the X_2CO and XYCO molecules (X and Y = H, F, or Cl) by high-level methods, including those with relativistic corrections, and found a combination of a method and a basis set optimal for investigating large PES regions.

Calculation procedures

Each chosen approach (combination of a method for solving the electronic equation and a one-electron AO basis set) was used to calculate the geometric parameters corresponding to minima on the potential energy surfaces of the X_2CO and XYCO molecules in the S_0 and T_1 electronic states and to saddle points on the potential energy surfaces of these molecules in the T_1 state, which characterize the inversion barriers. The total energies at these points were used to estimate the inversion barriers (as the difference between the total energies of the saddle point and the minimum on the PES of the molecules in the T_1 state) and the adiabatic energies of electronic transitions (as the difference between the total energies of the minima on the PES of the molecules in the T_1 and S_0 states).

Nowadays, the B3LYP and MP2 methods (or the UB3LYP and UMP2 methods for open-shell systems) seem to offer the most reasonable compromise between the computational efficiency (which is of particular importance in studies of large PES regions) and the reliability. We carried out calculations by these methods with the following basis sets: Pople's triple zeta basis sets[15] 6-311G(d), 6-311G(2d), and 6-311++G(d) and Dunning's correlation consistent basis sets[16,17] cc-pVNZ (N = D, T, Q, or 5) and aug-cc-pVNZ (N = D, T, or Q). Recently,[18] a new modification of correlation consistent basis sets for third row atoms, cc-pV(N+d)Z and aug-cc-pV(N+d)Z, which have a more systematic character, have been constructed. We used these basis sets for the Cl atom instead of the original basis sets employed in the study.[16] For first- and second row atoms, the cc-pVNZ and cc-pV(N+d)Z basis sets are identical.

In addition, we calculated the equilibrium geometric parameters of the X_2CO and XYCO molecules in the S_0 and T_1 electronic states, the inversion barriers, and the adiabatic energies of the electronic transition using the more resource-consuming (and more reliable[15] than MP2 and B3LYP) CCSD(T) (or UCCSD(T) for open-shell systems) method with the cc-pV(T+d)Z AO basis sets; calculations for the H_2CO and F_2CO molecules were carried out with the cc-pVQZ basis set.

Calculations by the B3LYP and MP2 methods with the cc-pVQZ and smaller basis sets were performed using the GAMESS(US) program package.[19] Calculations by the CCSD(T) method with all basis sets and by the MP2 method with the aug-cc-pVQZ and cc-pV5Z basis sets were carried out using the NWChem program package.[20,21] The basis sets were obtained through the Internet from the Basis Set Database maintained by the Environmental Molecular Sciences Laboratory (EMSL).[22]

All calculations by the MP2 and CCSD(T) methods were performed in the frozen-core approximation. In the calculations with the 6-31G(d) basis set, the Cartesian components of the d-type functions (a total of six functions) were used. In all other cases, spherical harmonic functions (five components for the d-type functions, seven components for the f-type functions, *etc.*) were used.

Results and Discussion

The coupled-cluster method CCSD(T) combined with a saturated basis set is supposed to be reliable for systems consisting of light atoms and having an electronic wavefunction with one dominant configuration.[23,24] Calculations[13,14] of the structures of the symmetrical H_2CO, F_2CO, and Cl_2CO molecules by the CASSCF method have demonstrated that these systems do satisfy the above requirements. Hence, in the first step we calculated the structures of the molecules by the CCSD(T) method. The calculated first-order cluster amplitudes were rather small, which is additional indirect evidence that the wavefunctions of all molecules are, to a large extent, single-configuration functions. Table 1 gives the geometric parameters of the molecules in the S_0 and T_1 states, the inversion barriers in the T_1 state, and the adiabatic energies of the transition $T_1 \leftarrow S_0$ calculated at the CCSD(T)/cc-pV(T+d)Z level of theory along with the available experimental data.[6—11]

The geometric parameters of all molecules in the S_0 state calculated by the CCSD(T)/cc-pV(T+d)Z method agree well with the experimental data (see Table 1). The experimental data on the structures in the T_1 state were obtained only for the H_2CO molecule, and the results of calculations at the CCSD(T)/cc-pV(T+d)Z level of theory are also in good agreement with the these data.

It was of interest to elucidate whether the results can be further refined. The main drawbacks of the above-described calculations are the basis set incompleteness error (BSIE) and the fact that the zero-point energy correction and relativistic corrections (for Cl-containing molecules) are ignored. The estimation of the zero-point energies is related to the solution of the nuclear problem, and these results will be published elsewhere.

The basis set incompleteness error can be estimated by studying the saturation of the results of calculations with the use of the systematic cc-pV(N+d)Z or aug-cc-pV(N+d)Z basis sets. However, it is impossible to use extended basis sets ($N > 4$) simultaneously with the CCSD(T) method because such calculations require significant computational resources. Because of this, we performed analysis with the use of the less resource-consuming MP2 method, which is known[24] to exhibit the asymptotic behavior upon saturation of the basis set analogous to that of the CCSD(T) method (and other high-level methods). Since the results of calculations will be used for

Table 1. Calculated (I) and experimental (II) geometric parameters and the inversion barriers (V_i) of the X_2CO and XYCO molecules (X and Y = F or Cl) in the T_1 and S_0 electronic states (in square brackets) and the adiabatic energies of the electronic transition $T_1 \leftarrow S_0$[a]

Parameter	H_2CO		F_2CO		Cl_2CO		HFCO		HClCO		FClCO	
	I	II[11]	I	II[6]	I	II[7]	I	II[8]	I	II[9]	I	II[10]
Bond length/Å												
C—O	1.316	1.307	1.359	—	1.320	—	1.349	—	1.324	—	1.332	—
	[1.209]	[1.203]	[1.176]	[1.174]	[1.182]	[1.180]	[1.183]	[1.181]	[1.187]	[1.182]	[1.179]	[1.173]
C—X	1.095	1.084	1.326	—	1.751	—	1.344	—	1.753	—	1.331	—
	[1.103]	[1.101]	[1.313]	[1.312]	[1.748]	[1.742]	[1.340]	[1.338]	[1.771]	[1.762]	[1.325]	[1.334]
C—Y	1.095	1.084	1.326	—	1.751	—	1.095	—	1.094	—	1.759	—
	[1.103]	[1.101]	[1.313]	[1.312]	[1.748]	[1.742]	[1.092]	[1.095]	[1.094]	[1.092]	[1.732]	[1.725]
Angle/deg												
X—C—Y	115.5	121.8	112.4	—	118.0	—	113.7	—	114.1	—	115.1	—
	[116.2]	[116.3]	[107.8]	[108.0]	[111.9]	[111.8]	[109.5]	[109.9]	[110.1]	[110.4]	[109.5]	[108.8]
X—C—O	113.6	—	110.1	—	110.4	—	111.9	—	111.7	—	113.5	—
	[121.9]	—	[126.1]	—	[124.0]	—	[123.0]	[122.8]	[123.7]	[123.3]	[124.1]	[123.7]
Y—C—O	113.6	—	110.1	—	110.4	—	111.0	—	113.4	—	105.8	—
ρ^b	41.5	41.1	51.8	—	47.4	—	48.0	—	45.2	—	50.9	—
V_i/cm^{-1}	663.6	775.6	10187.6	—	3247.8	—	2916.6	—	1596.6	—	5996.3	—
E_{ad}/cm^{-1}	25641.9	25194.3	36033.9	—	31389.6	—	35045.5	—	30558.4	—	34076.6	—

[a] Calculations by the CCSD(T)/cc-pV(T+d)Z method.

[b] The angle of deviation of the C=O bond from the CXY plane.

the solution of the problem of nuclear vibrations, including the analysis of rather large PES regions, it was of interest to find a method more efficient than CCSD(T)/cc-pV(T+d)Z (for example, the choice of the optimal basis set for the MP2 method or the use of density functional theory at the B3LYP level). For this purpose, we examined rather small basis sets, such as 6-311G(d), 6-311G(2d), and 6-311++G(d), and performed calculations by the B3LYP method using different basis sets. Since, when solving the problem of nuclear vibrations, it is important to know the precise positions of the stationary points on potential energy surfaces, we optimized the geometric parameters for each combination (method for solving the electronic equation/a one-electron AO basis set). It should be noted that this approach is somewhat different from that described in the literature,[24] where only the saturation of the estimates of various parameters is investigated at a fixed molecular geometry.

The results of calculations of the structures of the X_2CO and XYCO molecules (X and Y = H, F, or Cl) by the MP2 and B3LYP methods are presented in Figs 1—6 as plots of the relative deviations Δ, which were determined by the equation

$$\Delta = \frac{x - x_0}{x_0} \cdot 100\%, \qquad (1)$$

where x is the result of calculations and x_0 is the value relative to which the deviation is calculated. The mean-average of the absolute value of Δ for each geometric parameter (three bond lengths, three bonds angles, and the angle ρ characterizing the deviation of the C=O bond from the CXY plane) was taken as the deviation of the estimates of the geometric parameters:

$$\Delta = \frac{1}{7}\sum_{i=1}^{7}\frac{|x^i - x_0^i|}{x_0^i} \cdot 100\%. \qquad (2)$$

We used the experimental data for the H_2CO molecule and the results of calculations at the CCSD(T)/cc-pV(T+d)Z level for other molecules as the parameters x_0. It should be noted that we chose these x_0 exclusively because it was necessary to use the common reference points for the molecules, which have been insufficiently characterized by experimental data. We do not report the results of calculations of the structure of the FClCO molecule at the B3LYP level of theory because the structure of this molecule in the T_1 state is, apparently, inadequately described by this method (calculations with the 6-311G-type basis sets revealed no minima on the potential energy surface of this system; calculations with the use of other AO basis sets gave Δ as high as 15% due primarily to the incorrect description of the C=O bond length).

The data presented in Figs 1—6 are consistent with the results of quantum-chemical calculations.[23] For example, the deviations of the estimates of the geometric parameters are substantially smaller in absolute value and are more rapidly saturated with increasing size of the AO

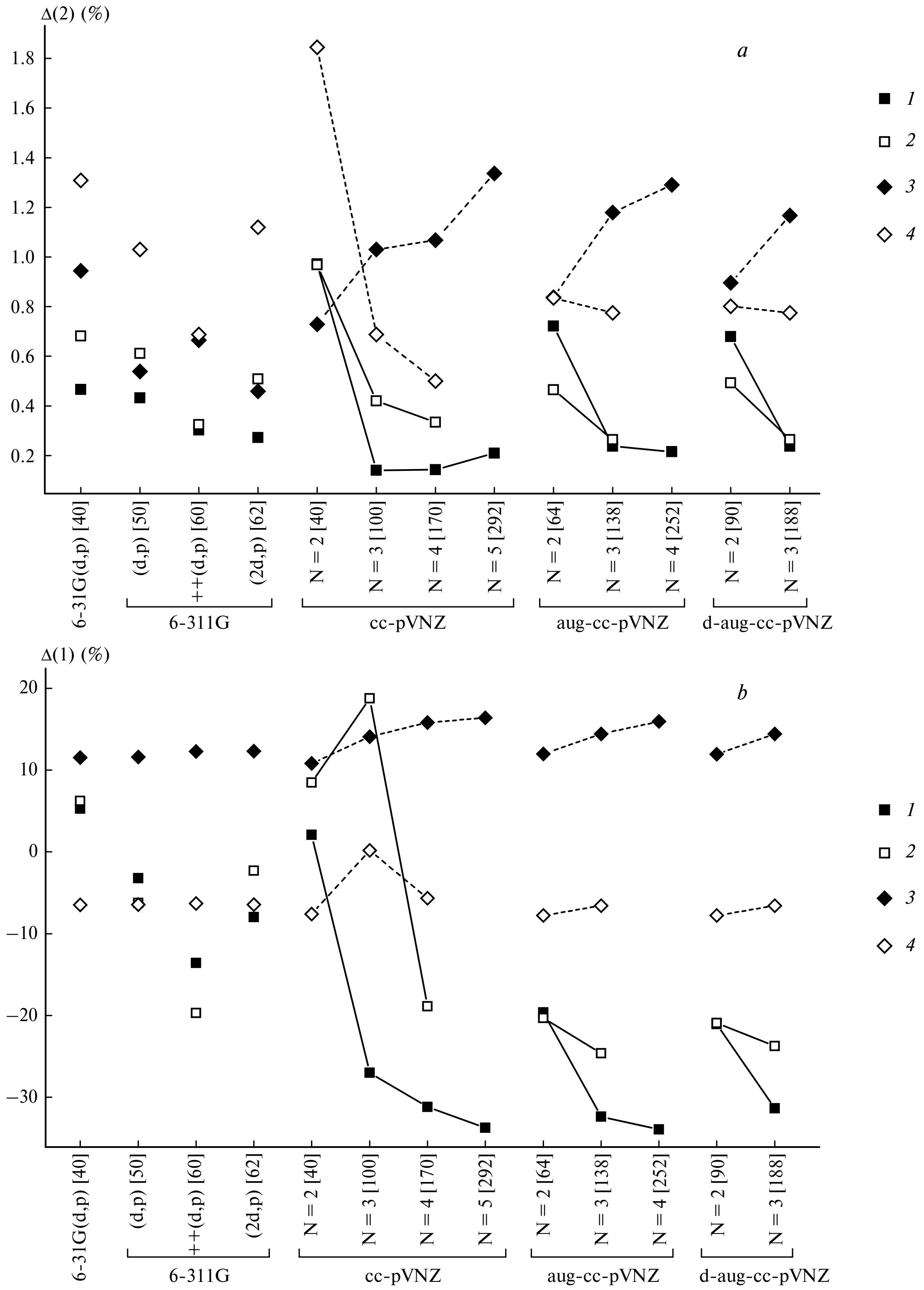

Fig. 1. Deviations of the geometric parameters (*a*) of the H_2CO molecule in the S_0 (*1*, *2*) and T_1 (*3*, *4*) states and the energy parameters (*b*), *viz*., the inversion barriers (*1*, *2*) and the energies of the electronic transition $T_1 \leftarrow S_0$ (*3*, *4*), calculated by the MP2 (*1*, *3*) and B3LYP (*2*, *4*) methods with different AO basis sets from the corresponding experimental values; see Eqs (1) and (2) in the text. The numbers in square brackets indicate the numbers of basis functions. The points corresponding to systematic sequences of basis sets are connected by lines.

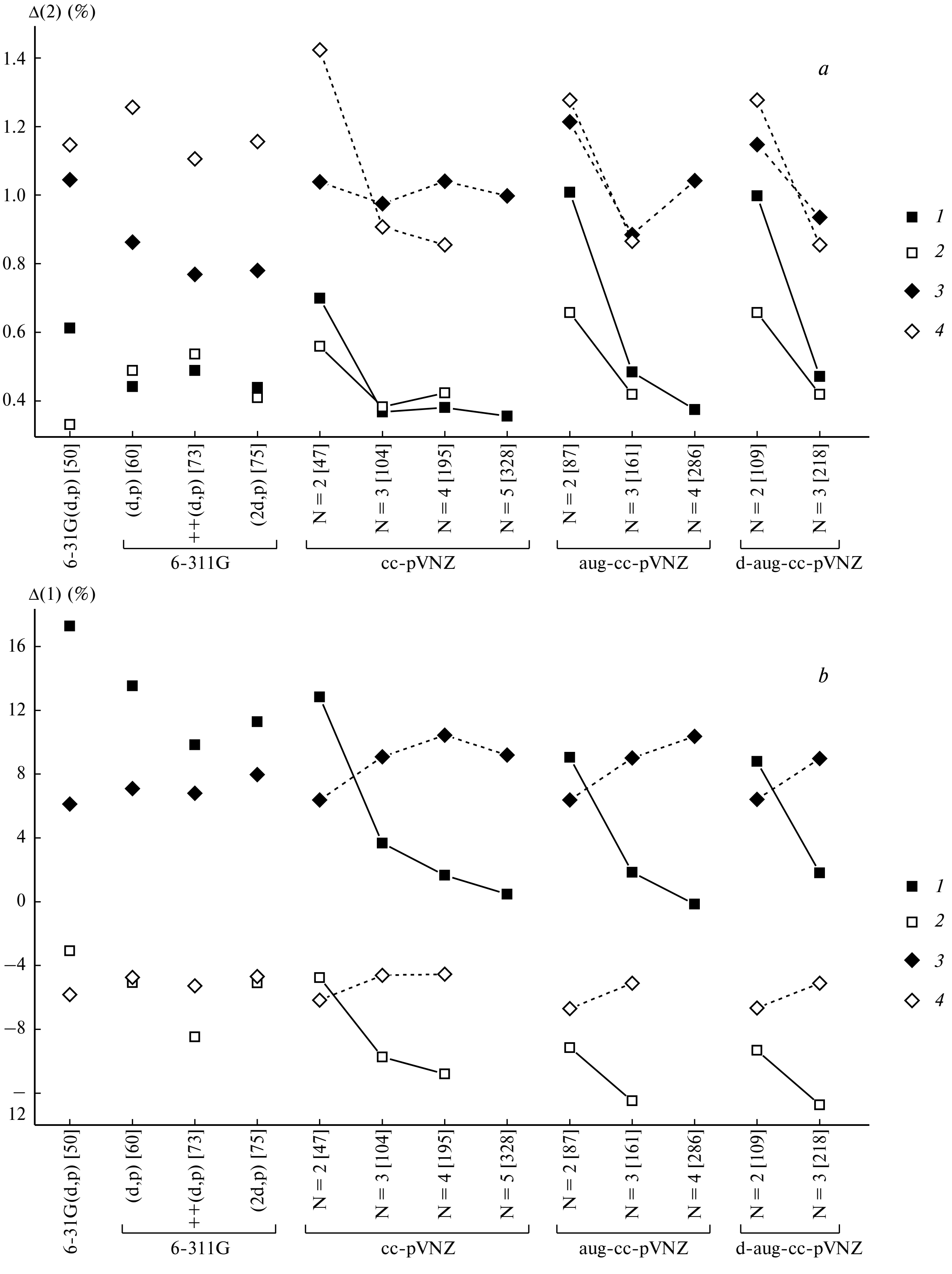

Fig. 2. Deviations of the geometric parameters (*a*) of the HFCO molecule in the S_0 (*1*, *2*) and T_1 (*3*, *4*) states and the energy parameters (*b*), *viz*., the inversion barriers (*1*, *2*) and the energies of the electronic transition $T_1 \leftarrow S_0$ (*3*, *4*), calculated by the MP2 (*1*, *3*) and B3LYP (*2*, *4*) methods with different AO basis sets from the corresponding values estimated at the CCSD(T)/cc-pVTZ level. See also the caption for Fig. 1.

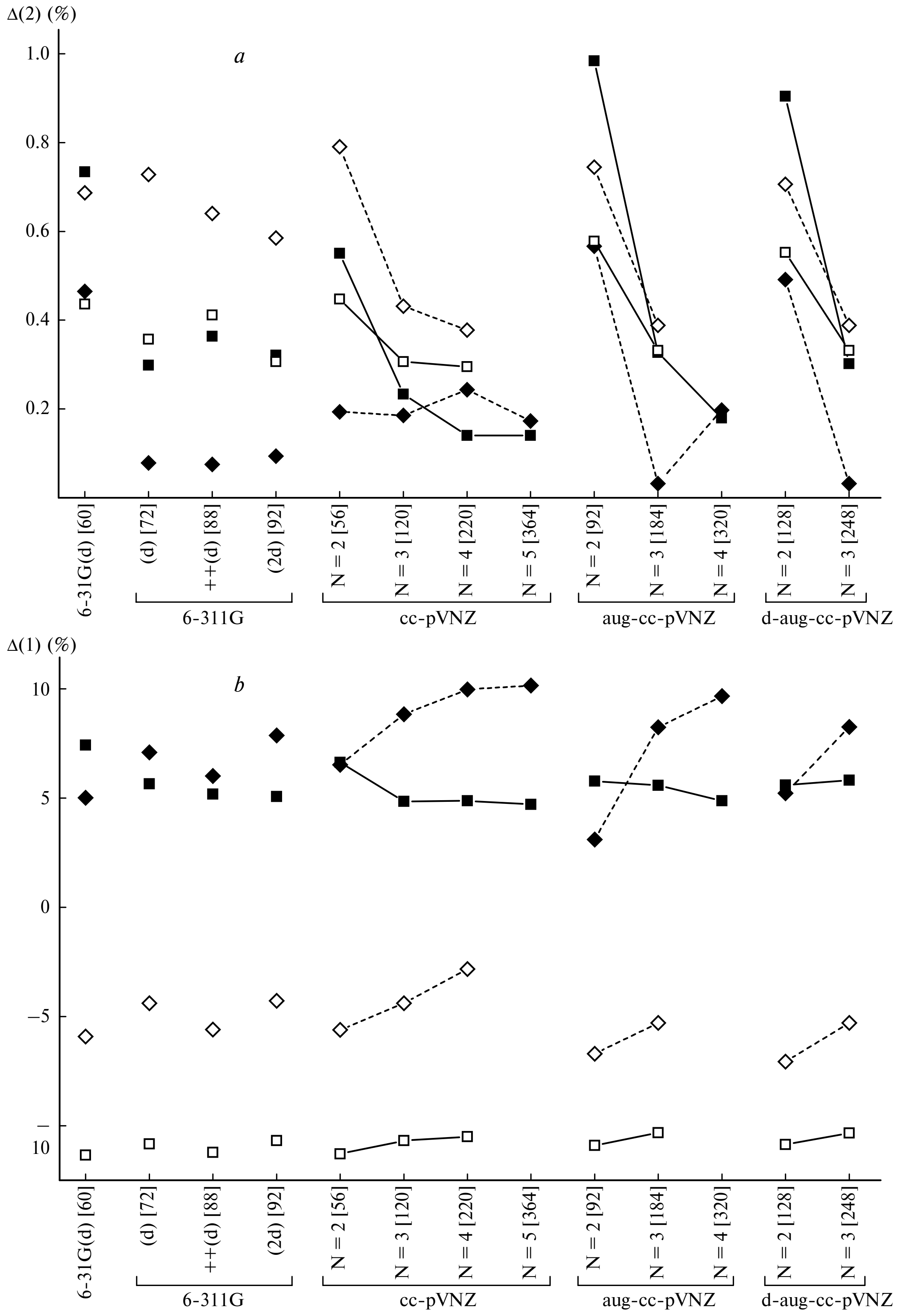

Fig. 3. Deviations of the geometric parameters (*a*) of the F_2CO molecule in the S_0 (*1*, *2*) and T_1 (*3*, *4*) states and the energy parameters (*b*), *viz.*, the inversion barriers (*1*, *2*) and the energies of the electronic transition $T_1 \leftarrow S_0$ (*3*, *4*), calculated by the MP2 (*1*, *3*) and B3LYP (*2*, *4*) methods with different AO basis sets from the corresponding values estimated at the CCSD(T)/cc-pVTZ level. See also the caption for Fig. 1.

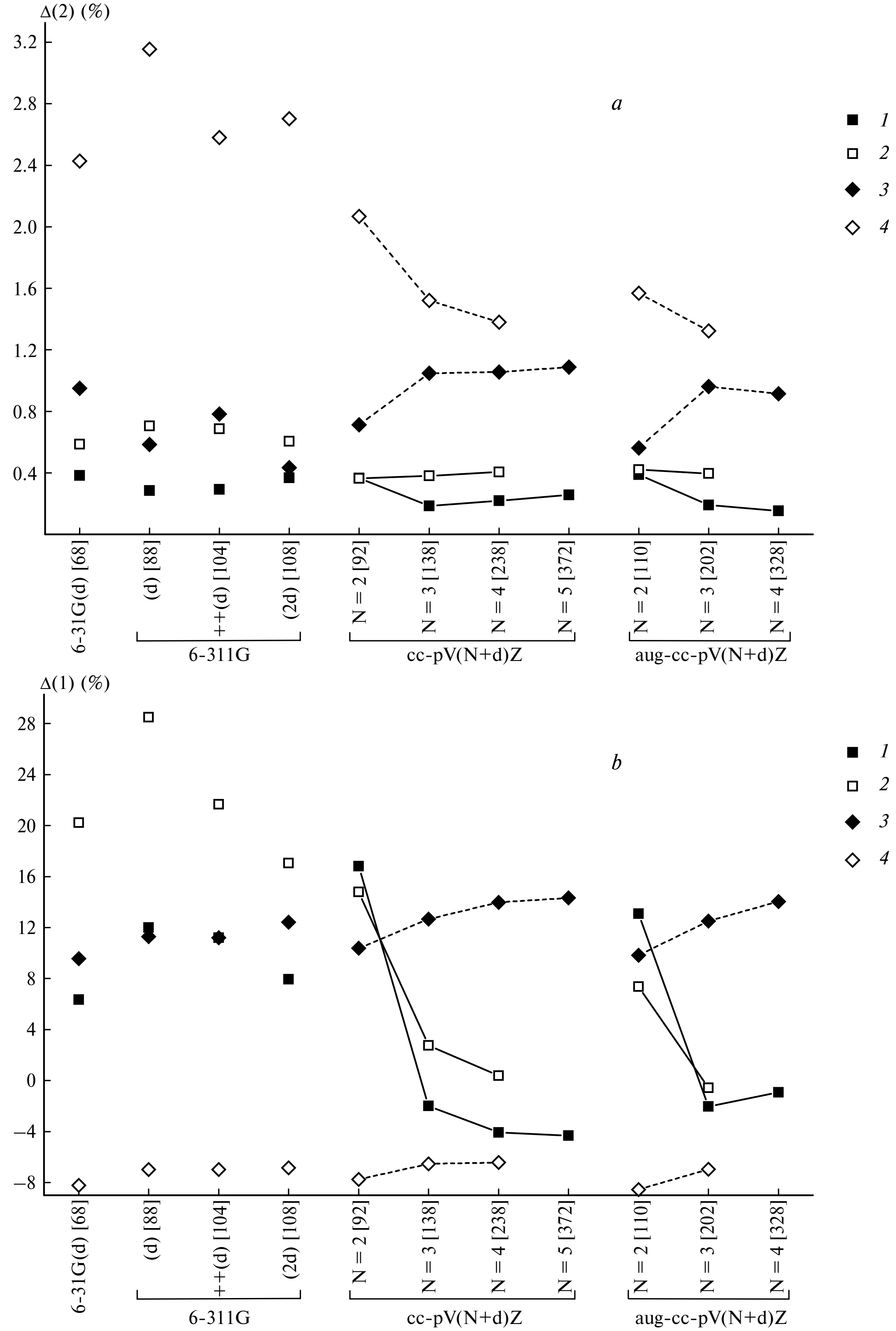

Fig. 4. Deviations of the geometric parameters (*a*) of the Cl_2CO molecule in the S_0 (*1*, *2*) and T_1 (*3*, *4*) states and the energy parameters (*b*), *viz.*, the inversion barriers (*1*, *2*) and the energies of the electronic transition $T_1 \leftarrow S_0$ (*3*, *4*), calculated by the MP2 (*1*, *3*) and B3LYP (*2*, *4*) methods with different AO basis sets from the corresponding values estimated at the CCSD(T)/cc-pV(T+d)Z level. See also the caption for Fig. 1.

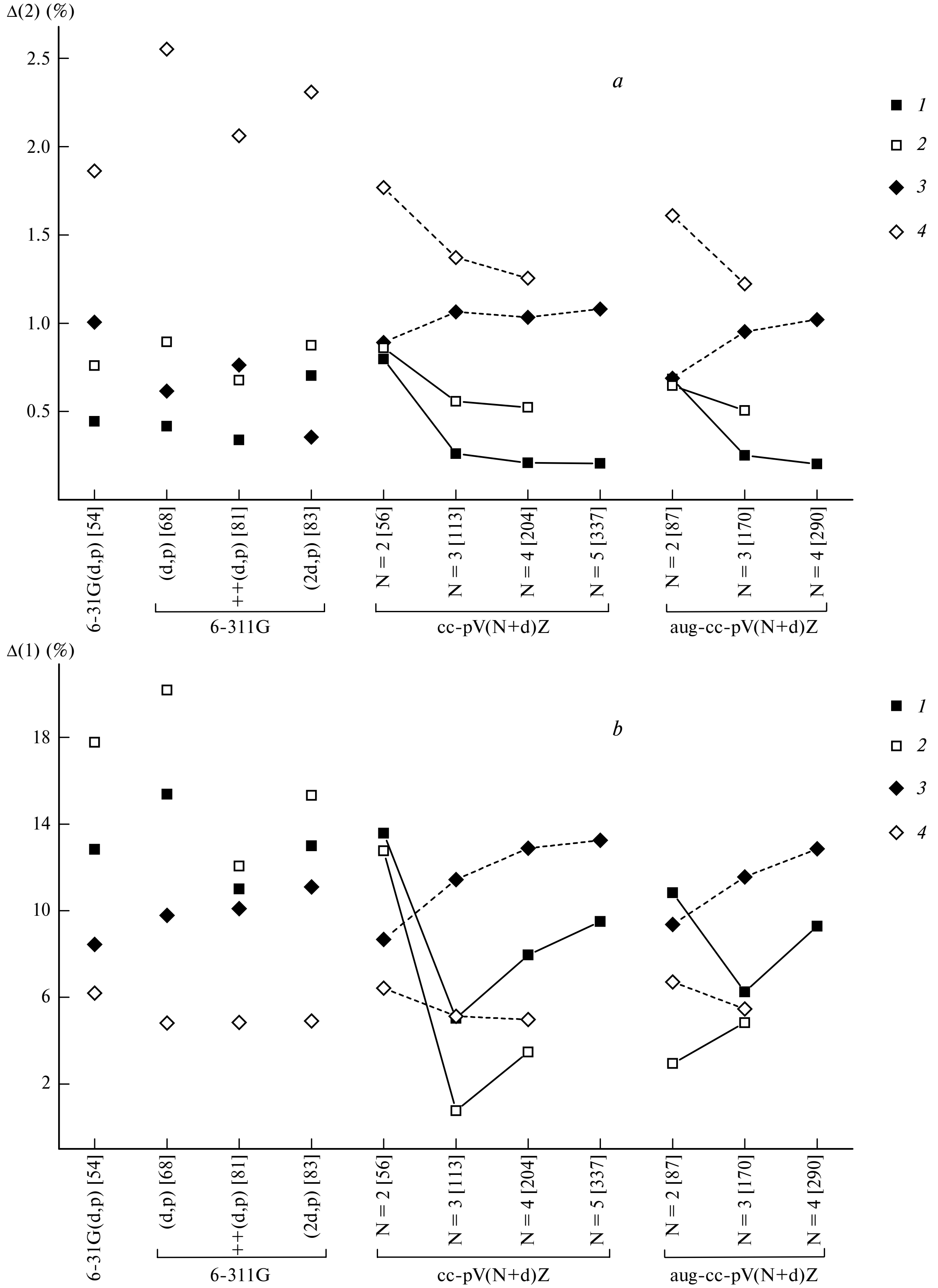

Fig. 5. Deviations of the geometric parameters (*a*) of the HClCO molecule in the S_0 (*1*, *2*) and T_1 (*3*, *4*) states and the energy parameters (*b*), *viz.*, the inversion barriers (*1*, *2*) and the energies of the electronic transition $T_1 \leftarrow S_0$ (*3*, *4*), calculated by the MP2 (*1*, *3*) and B3LYP (*2*, *4*) methods with different AO basis sets from the corresponding values estimated at the CCSD(T)/cc-pV(T+d)Z level. See also the caption for Fig. 1.

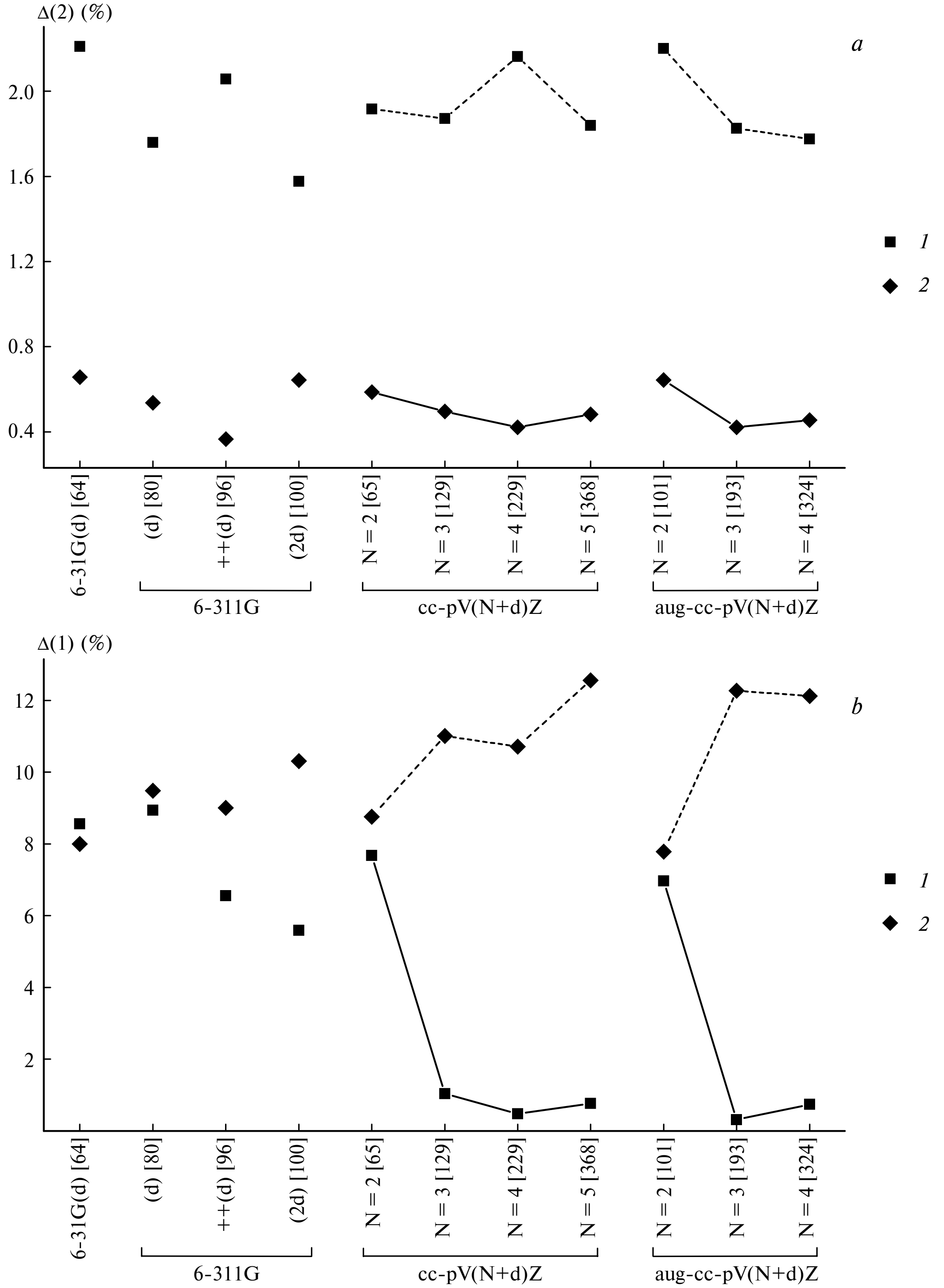

Fig. 6. Deviations of the geometric parameters (*a*) of the FClCO molecule in the T_1 (*1*) and S_0 (*2*) states calculated by the MP2 method with different AO basis sets and of the energy parameters (*b*), *viz.*, the inversion barriers (*1*) and the energies of the electronic transition $T_1 \leftarrow S_0$ (*2*), from the corresponding values estimated at the CCSD(T)/cc-pV(T+d)Z level. See also the caption for Fig. 1.

basis set than the deviations of the estimates of the energy parameters (energies of electronic transitions and inversion barriers). Nevertheless, unlike the conventional approach,[24] the saturation generally occurs nonsystematically and even nonmonotonically. Apparently, this is attributed to the fact that all calculations were carried out with geometry optimization. The effect of the addition of diffusion functions can sometimes serve as a criterion of the basis set saturation (see Figs 1—6). Actually, the addition of diffusion functions to the double zeta basis set cc-pVDZ for the H_2CO, HFCO, and F_2CO molecules leads to substantial changes in the calculation results. The influence of the diffusion functions on the results obtained with the use of the triple zeta basis sets 6-311G(d) and cc-pVTZ is less significant, whereas calculations with the cc-pVQZ and aug-cc-pVQZ basis sets give nearly the same results. This effect, which has been described in the literature,[25] was attributed to the possible involvement of the diffusion functions in valence splitting, although they are not intended for this purpose. However, this is not always true for Cl-containing molecules.

Therefore, the double zeta basis sets 6-31G(d) and cc-pVDZ are suitable only for qualitative estimations. In most cases, the results, which are closer to saturation, can be obtained with the use of the cc-pVTZ or aug-cc-pVTZ basis sets. To obtain more quantitative estimates, the cc-pVQZ and larger basis sets should be used. The Pople triple zeta basis sets 6-311G(d,p) and 6-311G(2d) combined with the MP2 method seem to offer a reasonable compromise between the computational time and the reliability of calculations. On the whole, the errors associated with BSIE can be as high as 30% of the estimated value. This is primarily true for estimations of the energy characteristics of the molecules with the use of double zeta basis sets.

We also estimated the error that occurs when relativistic corrections are ignored. It is known[23,24] that one-electron relativistic corrections for small molecules containing first, second, and third row atoms depend only slightly on the calculation method but require a specialized basis set. As an example, we estimated these corrections only by the MP2 method at the second-order Douglas—Kroll (DK2) level[26] with the use of the cc-pVQZ-DK basis set. The values calculated at the MP2/cc-pVQZ-DK level are given in Table 2; the results of calculations by the MP2/cc-pVQZ method without the inclusion of relativistic effects are presented for comparison. Table 2 also gives the results of calculations of the structures of the H_2CO and F_2CO molecules by the CCSD(T)/cc-pVQZ method without the inclusion of relativistic effects. On the one hand, the errors related to BSIE can be more adequately estimated taking into account the results of calculations at the CCSD(T)/cc-pVTZ level (see Table 1). On the other hand, a comparison of the values calculated by the MP2/cc-pVQZ-DK and MP2/cc-pVQZ methods (see Table 2) shows that, in most cases, the relativistic corrections are an order of magnitude smaller than those related to BSIE. The only exceptions are the corrections to the estimates of the inversion barriers in Cl-containing molecules.

The above-considered data show that the values obtained at the CCSD(T)/cc-pV(T+d)Z level of theory can

Table 2. Geometric parameters and the inversion barriers (V_i) of the X_2CO and XYCO molecules (X and Y = F or Cl) in the T_1 and S_0 electronic states (in square brackets) and the adiabatic energies of the electronic transition $T_1 \leftarrow S_0$ calculated by different methods without correction for relativistic effects (cc-pVQZ basis set) and with relativistic corrections (cc-pVQZ-DK basis set, printed in bold type)

Parameter	CCSD(T)/cc-pVQZ		MP2/cc-pVQZ-DK					
	H_2CO	F_2CO	H_2CO	F_2CO	Cl_2CO	HFCO	HClCO	FClCO
Bond length/Å								
C—O	1.310	1.355	1.310, **1.310**	1.353, **1.353**	1.323, **1.322**	1.343, **1.343**	1.322, **1.322**	1.337, **1.336**
	[1.207]	[1.173]	[1.208, **1.208**]	[1.174, **1.174**]	[1.181, **1.181**]	[1.181, **1.181**]	[1.186, **1.186**]	[1.177, **1.177**]
C—X	1.095	1.324	1.086, **1.086**	1.322, **1.322**	1.728, **1.728**	1.339, **1.339**	1.728, **1.724**	1.328, **1.327**
	[1.102]	[1.311]	[1.099, **1.099**]	[1.313, **1.313**]	[1.737, **1.737**]	[1.343, **1.343**]	[1.764, **1.760**]	[1.326, **1.326**]
C—Y	1.095	1.324	1.086, **1.086**	1.322, **1.322**	1.728, **1.728**	1.089, **1.089**	1.087, **1.087**	1.731, **1.731**
	[1.102]	[1.311]	[1.099, **1.099**]	[1.313, **1.313**]	[1.737, **1.737**]	[1.089, **1.089**]	[1.091, **1.091**]	[1.722, **1.721**]
Angle/deg								
X—C—Y	115.3	112.3	117.4, **117.5**	112.5, **112.5**	118.2, **118.1**	114.1, **114.1**	115.4, **115.4**	115.4, **115.4**
	[116.4]	[107.8]	[116.4, **116.4**]	[107.6, **107.6**]	[111.6, **111.5**]	[109.1, **109.1**]	[109.9, **109.9**]	[109.3, **109.2**]
X—C—O	113.6	110.1	113.4, **113.6**	110.2, **110.2**	110.8, **110.8**	111.5, **111.5**	112.0, **112.0**	111.7, **111.7**
	[121.8]	[126.1]	[121.8, **121.8**]	[126.2, **126.2**]	[124.2, **124.2**]	[122.9, **122.9**]	[123.6, **123.6**]	[124.2, **124.2**]
Y—C—O	113.6	110.1	113.4, **113.6**	110.2, **110.2**	110.8, **110.8**	111.5, **111.5**	113.3, **113.2**	108.8, **108.7**
ρ*	41.4	52.0	40.1, **39.6**	51.6, **51.6**	46.3, **46.4**	47.6, **47.6**	44.0, **44.0**	49.6, **49.7**
V_i/cm^{-1}	648.5	10249.4	533.7, **536.5**	10685.0, **10718.2**	3248.6, **3310.6**	2964.9, **2976.8**	1515.8, **1512.9**	6083.3, **6138.6**
E_{ad}/cm^{-1}	25937.6	36354.8	29180.8, **29168.8**	39629.6, **39601.3**	35822.3, **35812.3**	38676.7, **38696.2**	34543.6, **34553.4**	38265.8, **38239.7**

* See the note[b] in Table 1.

be considered as reliable. The calculations by this method (see Table 1) predicted that all the molecules under study are planar in the ground state. The average C=O bond length is 1.17—1.18 Å. Upon electronic excitation, the molecules in the T_1 state have nonplanar structures. The angle of deviation of the C=O bond from the CXY plane $\rho \approx 41$—51°, the C=O bond is elongated (on the average, by 0.10—0.18 Å), and the X—C—Y angle increases (by 5—7°).

The results of calculations and experimental data demonstrate that the C=O bonds in the molecules of halogen-substituted formaldehydes are shorter, on the average, by 0.03 Å compared to that in the H_2CO molecule (S_0). It is commonly supposed that this is due to an electron density shift. However, the opposite tendency is observed in the excited T_1 state. The shortest C=O bond was found in the H_2CO molecule, whereas the longest bond is present in the F_2CO molecule (according to calculations by the CCSD(T)/cc-pV(T+d)Z method, the bond lengths in the series F_2CO, Cl_2CO, and H_2CO are 1.359, 1.320, and 1.316 Å, respectively; the bond lengths in HFCO, HClCO, and H_2CO are 1.349, 1.324, and 1.316 Å, respectively; see Table 1). Therefore, electronic excitation causes the largest elongation of the C=O bond in the F_2CO molecule, for which the most substantial decrease in the stretching frequency ν(CO) would be expected.

The calculations also predicted (see Table 1) that the height of the inversion barrier depends substantially on the nature of the molecule (it varies from 664 cm^{-1} for H_2CO to 10188 cm^{-1} for F_2CO). Consequently, the inversion tunneling would not be observed experimentally for molecules characterized by a relatively high inversion barrier (F_2CO and FClCO). There is also an interesting tendency in the change in the inversion barrier upon the replacement of the H atom with halogen atoms. The following three characteristic series of molecules can be distinguished (formulas are written in the form, in which the systematic features are easily seen): (HCO)H, (HCO)Cl, (HCO)F; (ClCO)H, (ClCO)Cl, (ClCO)F; (FCO)H, (FCO)Cl, and (FCO)F. In essence, these series describe the replacement of the H atoms with halogens in order of increasing electronegativity of the halogen atoms. According to the calculations (see Table 1), the inversion barrier increases by a factor of approximately two on going from one molecule to the next one in each series. Taking into account that some members in these series are identical, the above-described tendency describes the increase in the height of the inversion barrier in the following series: H_2CO < HClCO < HFCO ~ Cl_2CO < < FClCO < F_2CO. The same tendency would be expected to occur in other series of carbonyl compounds. For example, according to calculations[27—29] by the CASSCF(6-5)/6-31G* method, the series (CH_3CO)H, (CH_3CO)Cl, and (CH_3CO)F also follows this rule. Nevertheless, it can easily be seen that bromo and iodo derivatives are lacking in this scheme, although the Br and I atoms should be present in the series arranged in order of increasing electronegativity between the Cl and H atoms.

To summarize, we performed systematic calculations of the structures of the H_2CO, F_2CO, Cl_2CO, HClCO, HFCO, and FClCO molecules in the S_0 and T_1 states by different quantum-chemical methods. The MP2 method combined with Pople's triple zeta basis sets seems to offer a reasonable compromise between the computational time and the reliability of calculations. The AO basis set cc-pVTZ can be considered as rather saturated for these molecules. The relativistic corrections estimated at the second-order Douglas—Kroll level with the cc-pVQZ-DK basis set are, as a rule, an order of magnitude smaller than the basis set incompleteness errors. The B3LYP method inadequately describes the structure of the FClCO molecule in the T_1 state. Calculations with the use of this method and Pople's triple zeta basis sets revealed no minima on the potential energy surface of the FClCO molecule, which is contradictory to the results of other approaches.

It was found that the CCSD(T)/cc-pV(T+d)Z method allows one to evaluate the inversion barriers and the energies of the transition $T_1 \leftarrow S_0$, which are in good agreement with the available experimental data. Calculations by this method predicted that electronic excitation of all the molecules under study leads to a pyramidal distortion of the molecular geometry and elongation of the C=O bond. In addition, data on the structures of the H_2CO and F_2CO molecules in the S_0 and T_1 states were obtained at the CCSD(T)/cc-pVQZ level of theory.

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