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Potential functions of inversion of R_2CO (R = H, F, Cl) molecules in the lowest excited electronic states

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The inversion potentials of R_2CO (R = H, F, Cl) molecules in the lowest excited electronic states were determined from experimental data using various model potential functions and approximations for the kinetic energy operator of inversion motion. The estimates of the heights of the barriers to inversion and the equilibrium values of the inversion coordinate for the H_2CO molecule in the S_1 and T_1 states are fairly stable. The results for the F_2CO and Cl_2CO molecules are strongly dependent on the approximation used; for these molecules, the most reliable parameters of the potential functions were chosen. The problem of qualitative characteristics of the shape of inversion potentials is discussed using the results of *ab initio* quantum-chemical calculations of the molecules under study.

Key words: carbonyl compounds, excited electronic states, potential functions of inversion of molecules, calculations.

The study of the structure of conformationally nonrigid molecules in excited electronic states is of importance at least for two reasons. First, photophysical and photochemical properties of the molecules are to a great extent determined by conformational effects. Second, elucidation of the nature of hindering potentials of internal rotation and inversion of molecules in different electronic states, as well as the reasons for conformational changes caused by electronic excitation of the molecules, are of theoretical and practical interest.

In this work we studied the structure of the simplest molecules of carbonyl compounds with general formula R_2CO (R = H, F, Cl) in the lowest excited S_1 singlet states; the structure of the H_2CO molecule in the triplet T_1 state was also studied.

Previously,[1,2] it has been established experimentally that the H_2CO molecule has a planar structure in the S_0 ground electronic state and a pyramidal structure in the S_1 and T_1 states and the potential functions of inversion of the molecule in these states have been determined from experimental data (energy levels of inversion vibrations). A great deal of studies were dedicated to the determination of the potential barriers to inversion and the equilibrium values of the angles of the C=O bond deviation from the HCH plane of the H_2CO molecule in the S_1 and T_1 states using *ab initio* quantum-chemical calculations.[3–7]

The F_2CO and Cl_2CO molecules have been much less studied. Nevertheless, analysis of vibronic spectra[8,9] corresponding to the $S_1 \leftarrow S_0$ transitions showed that both

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molecules also have a pyramidal structure in the S_1 state. The potential functions of inversion of these molecules have been determined from experimental data; however, it was pointed out[8] that the reliability of the inversion potential of the F_2CO molecule is somewhat doubtful. Quantum-chemical calculations of the structure of the F_2CO molecule in the S_1 state have been reported.[10]

Our analysis[11] of the problems arose when determination of the potential functions of inversion of molecules from experimental data showed that the inversion potentials of the F_2CO and Cl_2CO molecules are strongly dependent on the type of the model functions used in the approximation.

In the present study we consider this problem in detail and report the results of *ab initio* quantum-chemical calculations of the structure and inversion potentials of R_2CO (R = H, F, Cl) molecules in the S_1 state and the H_2CO molecule in the T_1 state.

Determination of the potential functions of inversion of R_2CO (R = H, F, Cl) molecules from experimental data

Let us consider a method for the determination of the potential functions of inversion using experimental data (for a detailed description of this approach, see Refs. 11 and 12).

In the one-dimensional approximation the inversion motion of R_2CO molecules can be described by a Hamiltonian of the form

$$\hat{H}(x) = -\frac{1}{2}\frac{d}{dx}g_{44}(x)\frac{d}{dx} + V(x), \qquad (1)$$

where x is the inversion coordinate defined as

$$x = R_{CO}\cdot\theta, \qquad (2)$$

where R_{CO} is the C=O bond length and θ is the angle of deviation of the C=O bond from the RCR plane.

The function $g_{44}(x)$ in the kinetic energy operator of the Hamiltonian (1) is the reciprocal reduced mass, which is calculated as the corresponding diagonal element of the kinetic energy matrix of dimension 4×4 in the momentum representation, where the three coordinates describe the rotation of the molecule as a whole and the fourth coordinate describes the inversion motion. In the most rough approximation the dependence of the g_{44} function on the inversion coordinate is ignored:

$$g_{44}(x) = g_{44}(0) = \text{const.} \qquad (3)$$

A more accurate model implies taking into account the dependence of the g_{44} function on x, which is usually approximated by polynomials (see, *e.g.*, Refs. 11 and 12). In this study we used the following approximation:

$$g_{44}(x) = g_{44}^{(0)} + g_{44}^{(2)}x^2 + g_{44}^{(4)}x^4 + g_{44}^{(6)}x^6 + g_{44}^{(8)}x^8, \qquad (4)$$

where the $g_{44}^{(i)}$ coefficients were determined by the least squares method using a set of the g_{44} values calculated at different x corresponding to changes in the θ angle in the range from −120° to +120° (Fig. 1).

The potential function of inversion $V(x)$ in the Hamiltonian (1) was approximated using the following model functions:

$$V(x) = A_2x^2 + A_4x^4, \qquad (5)$$

$$V(x) = A_2x^2 + A_4x^4 + A_6x^6, \qquad (6)$$

$$V(x) = A_2x^2 + B\exp(-Cx^2), \qquad (7)$$

$$V(x) = A_4x^4 + B\exp(-Cx^2), \qquad (8)$$

$$V(x) = A_2x^2 + \frac{B}{C + x^2}, \qquad (9)$$

$$V(x) = A_4x^4 + \frac{B}{C + x^2}, \qquad (10)$$

which hereafter are respectively denoted as the 2-4, 2-4-6, 2-G, 4-G, 2-L, and 4-L functions. The figures in the notations indicate the degrees of the polynomial terms and the letters G and L indicate the presence of the Gaussian or Lorentzian components, respectively.

Each of the model potentials contains the terms describing the shape of outer branches of the potential curve and those describing the shape of the barrier between two potential wells. The shape of outer branches

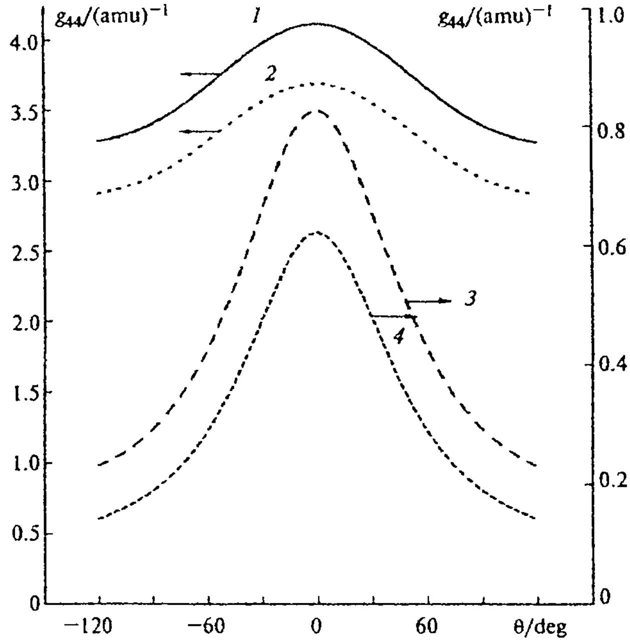

Fig. 1. Dependence of the g_{44} function on the inversion coordinate (θ) for R_2CO molecules: *1*, H_2CO (T_1); *2*, H_2CO (S_1); *3*, F_2CO (S_1); and *4*, Cl_2CO (S_1).

is described mostly by using a harmonic or quartic potential (possibly, with addition of terms of higher degrees in x, as in the case of the 2-4-6 function), whereas the shape of the barrier can be described by quadratic (2-4, 2-4-6), Gaussian (2-G, 4-G), or Lorentzian (2-L, 4-L) functions. It is assumed that in the purely polynomial 2-4 and 2-4-6 functions the A_2 coefficients are negative, while the A_4 coefficients are positive. Depending on the sign of the A_6 coefficient, the 2-4-6 function behaves differently: at $A_6 > 0$, the steepness of the outer branches increases; however, the shape of the potential remains qualitatively unchanged; at $A_6 < 0$, the shape of the potential barrier is corrected and maxima simultaneously appear on the outer branches, thus changing their shape. Thus, at large x the potential function becomes qualitatively incorrect, which presents considerable difficulties in solving the vibrational problem. Recently,[11] a more detailed consideration of this issue has been reported. The case $A_6 < 0$ is more commonly used in practice.

The procedure for the determination of the potential function $V(x)$ using experimental data consists in solving the Scrödinger equation using the Hamiltonian (1); in this case the coefficients in the expression for the $V(x)$ function are varied until the best coincidence between the calculated and experimental frequencies (transition energies) is achieved.

The results of determination of the potential functions of inversion of R_2CO (R = H, F, Cl) molecules from experimental data are shown below. From Table 1 it can be seen that all types of the model potentials (except for the 2-4 potential) give nicely consistent parameters of the shape of the potential function for the H_2CO molecule in the S_1 state, *viz.*, the values of the equilibrium angle θ_{min} of the C=O bond deviation from the HCH plane and the barrier heights V_0, irrespective of the type of the g_{44} approximation used. Nevertheless, the best agreement between the calculated and experimental inversion levels is attained when using the model functions (7)—(9), where the barrier shape is described by the Gaussian (2-G, 4-G) or Lorentzian (2-L) functions and the shape of outer branches of the potential is described by quadratic (2-G, 2-L) or quartic (4-G) terms.

Table 1. Experimental[1,2] and calculated energies of inversion transitions (E), calculated potential barriers to inversion (V_0), and the equilibrium values of the deviation angle (θ_{min}) (Eq. (2)) for the H_2CO molecule in the S_1 singlet electronic state

Type of approximation	$E_{calc} - E_{exp}$/cm^{-1}				σ	V_0 /cm^{-1}	θ_{min} /deg
	$0\to1^a$	$0\to2^b$	$0\to3^c$	$0\to4^d$			
(2-4)*	7.1	−20.8	−5.7	10.6	12.5	285	36
(2-4)**	5.5	−17.9	−4.8	9.1	10.7	299	36
(2-4-6)*	−0.6	−2.0	2.4	−0.8	1.7	355	35
(2-4-6)**	−0.5	−1.5	1.9	−0.7	1.3	357	34
(2-G)*	−0.3	−0.6	1.0	−0.4	0.6	356	34
(2-G)**	−0.3	−0.5	0.9	−0.4	0.5	357	34
(4-G)*	0.4	0.5	−1.3	0.7	0.8	355	34
(4-G)**	0.3	0.3	−0.8	0.4	0.5	357	34
(2-L)*	−0.1	−0.2	0.5	−0.2	0.3	356	34
(2-L)**	−0.2	−0.3	0.5	−0.2	0.3	357	34
(4-L)*	1.0	0.6	−3.1	1.7	1.9	354	34
(4-L)**	0.7	0.6	−2.2	1.2	1.3	356	34

Note. Calculation versions are denoted by the model function used; g_{44} = const = 3.689740 in the versions marked by an asterisk and $g_{44}(x) = 3.689740 - 0.299639x^2 + 0.056094x^4 - 0.007854x^6 + 0.000718x^8$ in the versions marked by two asterisks (the g_{44} values (in amu^{-1}) were calculated using the reported geometric parameters[1,2]); and σ is the RMS deviation.

[a] E_{exp} = 124.6 cm^{-1}. [b] E_{exp} = 542.3 cm^{-1}. [c] E_{exp} = 947.9 cm^{-1}. [d] E_{exp} = 1429.3 cm^{-1}.

The model functions (5)—(10) (in cm^{-1}) for the H_2CO molecule in the S_1 state obtained using the $g_{44}(x)$ function approximated by formula (4) (the x coordinate is given in Å) have the form:

$$V(x) = -883x^2 + 653x^4, \tag{5'}$$

$$V(x) = -1182x^2 + 1062x^4 - 134x^6, \tag{6'}$$

$$V(x) = 2449x^2 + 5615\exp(-0.656x^2), \tag{7'}$$

$$V(x) = 382x^4 + 771\exp(-1.709x^2), \tag{8'}$$

$$V(x) = 3409x^2 + 62265/(3.655 + x^2), \tag{9'}$$

$$V(x) = 409x^4 + 1079/(0.873 + x^2). \tag{10'}$$

Comparison of the results of calculations performed, on the one hand, using the 2-4, 2-4-6, 4-G, and 4-L functions and, on the other hand, using the 2-G and 2-L functions shows that the potential including the A_2x^2 term reproduces the shape of outer branches of the potential function of inversion somewhat better than that including the A_4x^4 term, though a combination of the A_4x^4 potential and a Gaussian barrier (the 4-G potential) is also quite satisfactory.

Analogously, the 2-4 model function gives the worst results for the H_2CO molecule in the T_1 state (Table 2), whereas the best agreement between the calculated and experimental inversion energy levels was obtained using the 2-G and 2-L functions in which the outer branches of the inversion potential are described by a quadratic term rather than by a quartic term. As to the model 2-4-6 functions, the negative values of the V_6 coefficients obtained in the course of determination of the parameters of the potential lead to the appearance of maxima on the outer branches at rather low energies, comparable with the energy of the highest inversion level observed in the experiment. Hence, a reliable determination of this type of potential function is impossible.

The 2-G and 2-L model functions (in cm^{-1}) calculated for the H_2CO molecule in the T_1 state using the approximation (4) for the $g_{44}(x)$ function (the x coordinate is given in Å) are given below:

$$V(x) = 888x^2 + 2216\exp(-1.389x^2)$$

$$V(x) = 1229x^2 + 5638/(1.249 + x^2)$$

In Fig. 2, the 2-G potential functions for the S_1 and T_1 states of the H_2CO molecule are shown and the experimental inversion levels used in the determination of the parameters of the model potentials are indicated.

A much less definite picture is observed for the inversion potential of the F_2CO molecule in the S_1 state (Table 3). In this case none of the model functions (5)—(7) can satisfactorily reproduce both the experimentally observed splitting of 0.3 cm^{-1} between the eighth and ninth inversion levels and the energies of other inversion levels simultaneously, irrespective of the type of approximation ((3) or (4)) of the g_{44} function. Because of this, these functions are not listed in Table 3. Using the model functions (8)—(10), one can more or less satisfactorily describe all available experimental data[8] (Fig. 3); however, the results obtained are strongly dependent on how rigid the requirements imposing on the accuracy of reproduction of the 8 → 9 splitting are and which type of approximation of the $g_{44}(x)$ function is used (the agreement between the calculated and experimental splitting was controlled by varying the corresponding weighting factors for the deviations).

Table 2. Experimental[1,2] and calculated energies of inversion transitions (E), calculated potential barriers to inversion (V_0), and the equilibrium values of the deviation angle (θ_{min}) (Eq. (2)) for the H_2CO molecule in the T_1 triplet electronic state

Type of approximation	$E_{calc} - E_{exp}/cm^{-1}$				σ	V_0 /cm^{-1}	θ_{min} /deg
	0→1[a]	0→2[b]	0→3[c]	0→4[d]			
(2-4)*	−17.8	−3.4	−1.8	26.7	11.1	843	51
(2-4)**	−16.6	−3.4	−1.8	26.4	10.5	839	50
(2-4-6)*	0.2	0.0	−0.5	3.4	0.7	782	45
(2-4-6)**	−1.0	−0.4	−0.1	2.0	0.7	772	43
(2-G)*	0.5	0.1	−0.7	3.8	0.9	779	42
(2-G)**	0.6	0.1	−0.8	4.0	0.9	782	42
(4-G)*	−0.5	−0.9	−3.3	22.8	4.6	784	42
(4-G)**	−0.1	−0.7	−3.1	20.9	4.2	785	42
(2-L)*	0.8	−0.2	−2.2	13.2	2.7	782	42
(2-L)**	0.8	−0.1	−2.0	12.1	2.5	784	41
(4-L)*	−3.6	−2.2	−4.2	33.9	7.0	798	44
(4-L)**	−2.9	−2.0	−4.0	31.5	6.4	798	43

Note. The notations of the calculation variants are given in the Note to Table 1. Here the g_{44} function was approximated by the expressions g_{44} = const = 4.119774 and $g_{44}(x) = 4.119760 - 0.336525x^2 + 0.064520x^4 - 0.008738x^6 + 0.000703x^8$ (the g_{44} values (in amu^{-1}) were calculated using the reported geometric parameters[1,2]), and σ is the RMS deviation.
[a] E_{exp} = 36.0 cm^{-1}. [b] E_{exp} = 538.2 cm^{-1}. [c] E_{exp} = 777.2 cm^{-1}. [d] E_{exp} = 1175.0 cm^{-1}.

Previously,[8] the potential function of inversion for the F_2CO molecule has been determined using the 2-L model function. The dependence of the reciprocal reduced mass on the angle of the C=O bond deviation from the FCF plane was taken into account using a procedure somewhat different from that used in this work and the values obtained for the 8 → 9 splitting, the potential barrier to inversion, and the equilibrium angle of the C=O bond deviation from the FCF plane were 0.11 cm^{-1}, V_0 = 8200 cm^{-1}, and θ_{min} = 32°, respectively. It was pointed out[8] that, in a physical sense, the potential function of inversion found in this case, with a high barrier and relatively small θ_{min} value, seems to be not quite realistic. Indeed, the inversion potential[8] is rather close to that listed in Table 3 (the (2-L)*A potential).

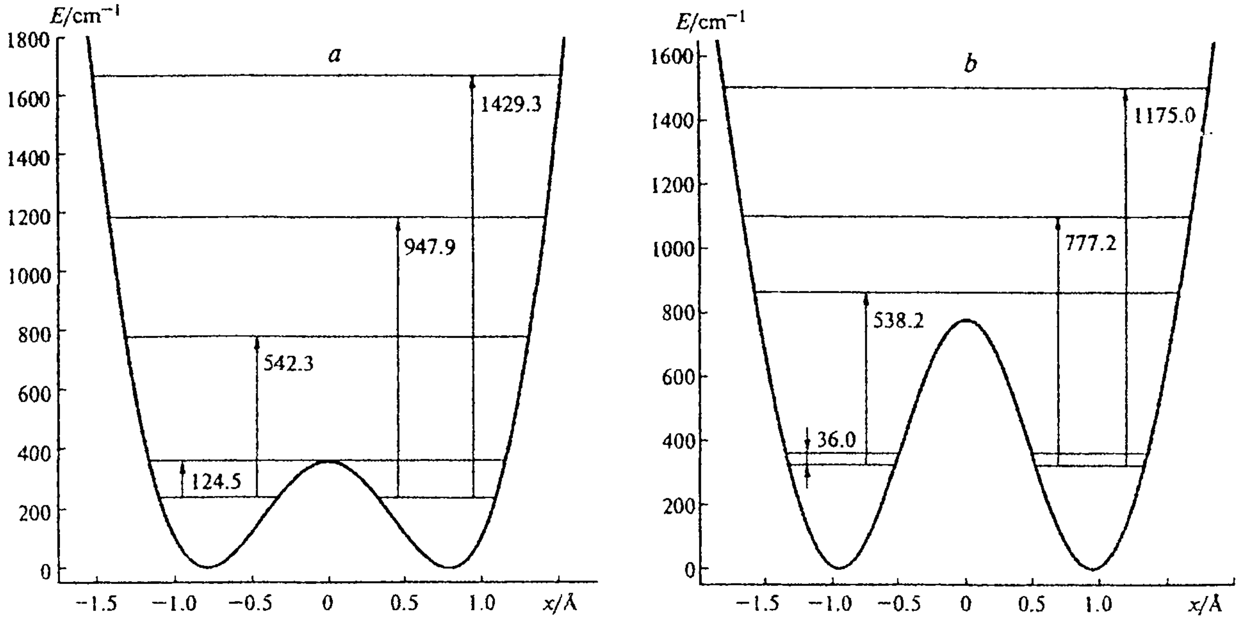

Fig. 2. The 2-G model potentials for the H_2CO molecule in the S_1 (*a*) and T_1 (*b*) excited electronic states and the experimental inversion energy levels used in the calculations; $x = R_{CO} \cdot \theta$.

Table 3. Experimental[8] and calculated energies of inversion transitions (E), calculated potential barriers to inversion (V_0), and the equilibrium values of the deviation angle (θ_{min}) (Eq. (2)) for the F_2CO molecule in the S_1 singlet electronic state

Type of approximation	Variant	$E_{calc} - E_{exp}$/cm^{-1}						σ	V_0 /cm^{-1}	θ_{min} /deg
		(0,1)→(2,3)[a]	(2,3)→(4,5)[b]	(4,5)→(6,7)[c]	(6,7)→8[d]	8→9[e]	9→10[f]			
(4-G)*	A	−0.6	0.3	2.2	0.3	−0.17	−8.0	2.6	5314	38
	B	−0.8	0.5	2.5	0.3	0.00	−9.9	3.2	5104	37
(4-G)**	A	0.4	−0.9	1.4	1.7	0.03	−2.8	1.2	5746	30
	B	0.5	−0.9	1.4	1.7	0.00	−2.6	1.1	5782	30
(2-L)*	A	0.1	−0.6	0.5	0.5	−0.15	−1.6	0.6	8043	29
	B	0.1	−0.6	0.6	0.5	0.00	−1.8	0.6	7874	27
(2-L)**	A	13.2	1.6	−7.6	−17.5	−0.15	−29.0	11.8	6712	30
	B	13.7	1.6	−7.9	−18.2	−0.01	−30.2	12.2	6628	29
(4-L)*	A	−1.6	0.5	2.3	−0.3	−0.20	−10.1	3.3	5157	43
	B	−2.1	0.7	2.8	−0.2	0.00	−12.6	4.1	4914	41
(4-L)**	A	−1.2	0.2	1.9	−0.1	−0.16	8.0	2.6	5372	37
	B	−1.5	0.4	2.2	−0.1	0.00	−9.4	3.1	5176	36

Note. The notations of the calculation versions are given in the Note to Table 1. Variants A and B correspond to different accuracies of reproducing the splitting between the eighth and ninth inversion levels. Here the g_{44} function was approximated by the expressions g_{44} = const = 0.823192 and $g_{44}(x) = 0.812769 - 0.301436x^2 + 0.073287x^4 - 0.008557x^6 + 0.000371x^8$, and σ is the RMS deviation.

[a] E_{exp} = 669.1 cm^{-1}. [b] E_{exp} = 668.2 cm^{-1}. [c] E_{exp} = 665.2 cm^{-1}. [d] E_{exp} = 663.1 cm^{-1}. [e] E_{exp} = 0.3 cm^{-1}. [f] E_{exp} = 662.5 cm^{-1}.

However, this solution is unstable and V_0 changes substantially when using a higher level of approximation for the $g_{44}(x)$ function (*cf.* the data of the (2-L)**A version). The results listed in Table 3 show that V_0 values lying in the range from 5000 to 6000 cm^{-1} and θ_{min} lying in the interval from 30 to 40° are the most probable. The 4-G and 4-L model functions (see Table 3, version B) determined for the F_2CO molecule in the S_1 state using the $g_{44}(x)$ function approximated by formula (4) have the form:

$$V(x) = 1009x^4 + 6290\exp(-6.229x^2),$$

$$V(x) = 1369x^4 + 3097/(0.355 + x^2).$$

The first of these functions is shown in Fig. 3. It is of interest to note that both functions describe the outer branches of the inversion potential by a quartic term in x rather than by a quadratic term; however, more accurate or additional experimental data are required for a more reliable determination of the inversion potential of the F_2CO molecule.*

Previously,[9] the 2-L potential function of inversion of the Cl_2CO molecule in the S_1 state, characterized by a V_0 value of 3170 cm^{-1} and a θ_{min} value of 32.5°, has been determined from experimental data using the same procedure for taking into account the dependence of reciprocal reduced mass on the angle of the C=O bond deviation from the Cl_2C plane as that used in the case of the F_2CO molecule.[8] Our calculations showed that the results are strongly dependent on both the type of the model function and the type of $g_{44}(x)$ approximation. The inversion potential found[9] is close to that we obtained using the same 2-L model function assuming that g_{44} = const; however, on going to a higher level of approximation for the $g_{44}(x)$ function the results change appreciably, *viz.*, the barrier height increases by 1500 cm^{-1} and the angle of the C=O bond deviation from the Cl_2C plane increases

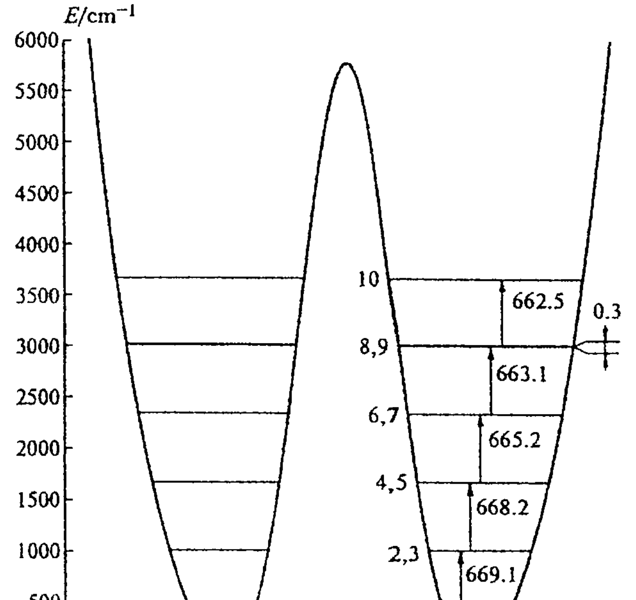

Fig. 3. The 4-G model potential for the F_2CO molecule in the S_1 excited electronic state and the experimental inversion energy levels used in the calculations; $x = R_{CO} \cdot \theta$.

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* We also approximated the inversion potential of the F_2CO molecule by model functions of the types (8) and (10) in which the A_6x^6 term was used instead of the A_4x^4 term. However, the description of the highest inversion level using the values obtained ($V_0 \approx$ 4800 cm^{-1} and $\theta_{min} \approx$ 40°) is deteriorated.

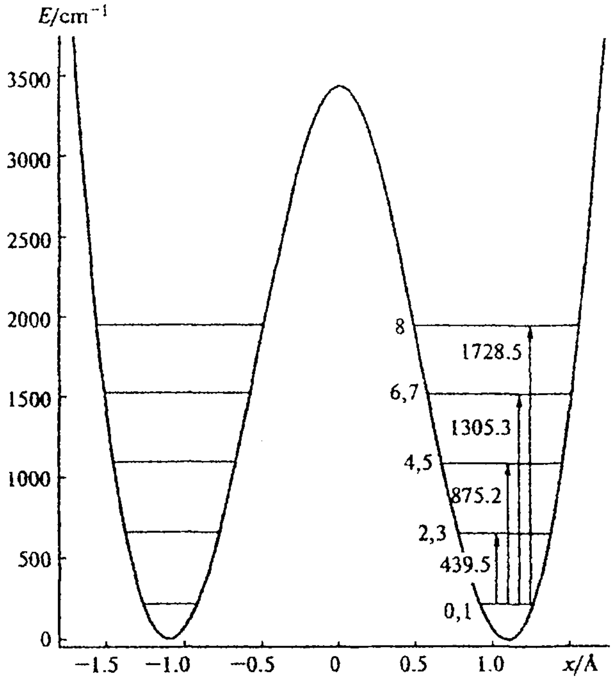

Fig. 4. The 4-L model potential for the Cl_2CO molecule in the S_1 excited electronic state and the experimental inversion energy levels used in the calculations; $x = R_{CO} \cdot \theta$.

by 14°. As in the case of the F_2CO molecule, the model functions (5)—(7) can likely be excluded from consideration since their use leads to strong overestimation of the angle of the out-of-plane deviation (up to 80—100°) and the barrier height (more than 7000 cm^{-1}). For the functions (8)—(10) the characteristics of the potential shape vary over a rather wide range: from 34 to 51° for θ_{min} and from 3200 to 4700 cm^{-1} for the barrier height. Based on the stability of the results, a θ_{min} value of 42° and a barrier height of 3440 cm^{-1} obtained using the 4-L function and the $g_{44}(x)$ function approximated by formula (4) seem to be the most probable. These $g_{44}(x)$ functions calculated using the geometric parameters reported in Ref. 9 and $V(x)$ given in cm^{-1} have the form:

$$g_{44}(x) = 0.610078 - 0.238948x^2 + 0.056480x^4 - $$
$$- 0.006259x^6 + 0.000254x^8,$$

$$V(x) = 774x^4 + 10695/(1.182 + x^2).$$

This potential function is shown in Fig. 4. Thus, as in the case of the F_2CO molecule, the function with outer branches of the inversion potential described by the A_4x^4 potentials appears to be preferred.

It should be noted that the results obtained for the Cl_2CO molecule are less reliable than those obtained for the F_2CO molecule because of two reasons related to the available experimental data. First, only the frequencies of four transitions (compared to six frequencies for the F_2CO molecule) were measured for the Cl_2CO molecule. Second, the splitting between the eighth and ninth inversion levels observed experimentally for the F_2CO molecule indicates that the energies of these levels lie near the top of the potential barrier. This makes it possible to estimate the barrier height for the F_2CO molecule more reliably than in the case of the Cl_2CO molecule, for which no data on the splitting of inversion levels are available. Obtaining new experimental data for the S_1 state of the Cl_2CO molecule could help in drawing more definite conclusions concerning the shape of the inversion potential of this molecule.

Ab initio quantum-chemical calculations

The potential surface can be independently described explicitly by *ab initio* calculations only. Keeping in mind that quantum-chemical calculations make it possible to take into account changes in different contributions to the energy, which occur as the geometric configuration of the nuclei changes, in a rather balanced manner, *i.e.*, to obtain estimates of the energy correlated in a certain way, we performed a series of calculations of the effective potential functions of inversion of R_2CO molecules in the singlet and triplet excited states using the GAMESS program suite.[13]

The results of our *ab initio* study will be reported in more detail elsewhere; here we consider only those aspects of the problem that are of interest for the choice of the shape of the potential. The AO basis sets used for calculations of excited states can have a rather strong effect on the shape of the potential surface of the excited states; however, trial calculations showed that diffuse orbitals can be ignored when calculating the lowest singlet and triplet states, so we dwelt on the 6-31G** type of basis sets. The calculations were mostly performed by the multiconfigurational complete active space self-consistent field (CAS SCF) method, involving all configurations obtained by localization of six electrons on the valence MOs, which are of prime importance for the description of excitation effects (σ_{CO}, π_{CO}, n_O, π_{CO}^*, and σ_{CO}^*), into the active space. Attempts to extend this system of MOs and include correlation effects by the CISD method change little the estimates of the characteristics of the potential surface.

The calculated values of barriers to inversion (619, 717, 10012, and 2703 cm^{-1} for the H_2CO (S_1), H_2CO (T_1), F_2CO, and Cl_2CO molecules, respectively) are, on the whole, in poor agreement with experimental estimates, in particular, for the F_2CO and Cl_2CO molecules. However, it is of interest to consider the shape of the curves on the qualitative level. The results of approximation of the effective potential curves of inversion using the functions (6)—(10), the values of the RMS errors of the approximations used (σ), and those of maximum deviations (α) of calculated points from experimental ones are listed in Table 4.

Table 4. Comparison of the quantum-chemical methods for description of the inversion potentials of R_2CO molecules in the lowest excited states

Molecule	Method of calculation	Potential	σ^a	α^b
H_2CO (S_1)	CAS SCF (6e-5MO)/6-31G**	2-4-6	3.6	7.5
		2-G	18.4	39.2
		4-G	71.7	167.0
		2-L	19.8	33.6
		4-L	62.3	104.3
H_2CO (S_1)	CISD/6-31G**	2-4-6	8.7	17.4
		2-G	39.4	73.7
		4-G	156.9	390.7
		2-L	49.4	97.7
		4-L	163.6	392.6
H_2CO (T_1)	CAS SCF (6e-5MO)/6-31G**	2-4-6	3.8	6.6
		2-G	16.2	32.1
		4-G	56.8	82.0
		2-L	18.1	28.7
		4-L	52.8	86.4
F_2CO (S_1)	CAS SCF (6e-5MO)/6-31G*	2-4-6	394.5	671.4
		2-G	200.7	365.0
		4-G	107.4	209.7
		2-L	134.3	253.0
		4-L	39.3	61.9
Cl_2CO (S_1)	CAS SCF (6e-5MO)/6-31G*	2-4-6	95.4	155.0
		2-G	38.8	65.6
		4-G	65.2	146.0
		2-L	23.5	44.1
		4-L	105.6	217.3
Cl_2CO (S_1)	CAS SCF (6e-5MO)/DH+*	2-4-6	108.0	197.4
		2-G	42.7	73.8
		4-G	75.6	165.0
		2-L	43.0	79.8
		4-L	118.5	239.5
Cl_2CO (S_1)	CAS SCF (6e-5MO)/DH+*(*f*)	2-4-6	113.2	203.6
		2-G	43.7	80.9
		4-G	80.8	160.5
		2-L	24.9	43.8
		4-L	125.0	214.2

[a] RMS deviation. [b] Maximum deviation of calculated points from approximated data (cm^{-1}).

Judging by the α- and σ-criteria, the 2-4-6 polynomial approximation, whose drawbacks have already been discussed above, is the best for the H_2CO molecule. Using the σ-criterion, the 2-G and 2-L approximations can be chosen for the singlet and triplet state, respectively. It should be noted that the results obtained in the 4-G approximation are characterized by the largest deviations from those calculated for the equilibrium nuclear configuration.

Based on the results of *ab initio* calculations and processing of experimental data, the approximations based on the quartic potential are the most appropriate in the case of the F_2CO molecule, which reflects its considerably larger rigidity as compared to that of the H_2CO molecule. On the contrary, quadratic approximations are preferred for the Cl_2CO molecule. The results of calculations of the H_2CO molecule in the S_1 state by the CISD method listed in Table 4 as well as the use of more extended basis sets (the Dunning—Hay basis sets[14] augmented with diffuse and polarization functions, DH+*, and those augmented with *f*-functions, DH+*(*f*)) in CAS SCF calculations of the Cl_2CO molecule do not change qualitative conclusions concerning the best types of approximations of the potentials.

Thus, it seems likely that using the results of *ab initio* estimates of the potential energy surfaces one can make assumptions on the physically well-founded shape of the inversion potential of R_2CO molecules. However, for the sake of justice, it should be noted that calculations of vibrational levels performed using these data showed their weak dependence on the choice of the approximation function. In this case there is still a doubt in reliability of the "experimental" V_0 and θ_{min} values and, hence, the question arises as to whether the calculated V_0 values for the F_2CO and Cl_2CO molecules are closer to the true ones. However, it should be noted that calculations of R_2CO (R = F, Cl) molecules reproduce poorly the experimental frequencies of inversion transitions and, in particular, do not reproduce a splitting of 0.3 cm^{-1} for the F_2CO molecule.

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