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

I. A. Godunov,* A. V. Abramenko, V. A. Bataev, and V. I. Pupyshev

Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 932 8846. E-mail: godunov@phys.chem.msu.ru

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.

Previously, 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 $S_1 \leftrightarrow S_0$ transitions showed that both...
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 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.

Our analysis 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

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

where $x$ is the inversion coordinate defined as

$$
x = R_{CO}\cdot\theta,
$$

where $R_{CO}$ is the C=O bond length and $\theta$ 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 4x4 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:

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

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:

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

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 $\theta$ angle in the range from $-120^\circ$ to $+120^\circ$ (Fig. 1).

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

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

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

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

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

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

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

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