# Structure of acetyl chloride molecule isotopomers $CH_3COCl$ and $CD_3COCl$ in the ground and lowest excited singlet and triplet electronic states: a quantum-mechanical study

*A. V. Kudich, V. A. Bataev,★ and I. A. Godunov*

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

The structures of isotopomers of conformationally flexible acetyl chloride molecule, $CH_3COCl$ and $CD_3COCl$, in the ground ($S_0$) and lowest excited singlet ($S_1$) and triplet ($T_1$) electronic states were calculated by the RHF, MP2, and CASSCF methods. The equilibrium geometric parameters and harmonic vibrational frequencies of the molecules in these electronic states were estimated. According to calculations, electronic excitation causes considerable conformational changes involving rotation of the $CH_3$ ($CD_3$) top and a substantial deviation of the CCOCl fragment from planarity. The results of calculations agree with experimental data. Two-dimensional torsional-inversion sections of the potential energy surface were calculated and analyzed. Vibrational problems for large-amplitude vibrations (torsional vibration in the $S_0$ state and both torsional and inversion vibrations in the $T_1$ and $S_1$ states) were solved in one- and two-dimensional approximations.

**Key words:** *ab initio* quantum-chemical calculations, carbonyl compounds, acetyl chloride, isotopomers, vibrational frequencies, potential energy surface, ground electronic state, excited electronic states.

Studies on the structures of conformationally flexible molecules in the ground and excited electronic states are of considerable importance from both practical and theoretical standpoints. The structures of stable conformers, the energy differences between them, and the heights of potential barriers to conformational transitions are responsible for a number of the most important properties of molecules and compounds.[1—3] These are the electrical and optical properties, thermodynamic characteristics, reactivity and biological activity, mechanisms of chemical (including photochemical) reactions, *etc.* Prediction of the structure and properties of such molecules first of all requires obtaining and accumulation of relevant experimental and theoretical data. Besides, of considerable interest is to elucidate (i) the physical nature of the potentials of internal rotation and inversion and (ii) conformational changes accompanying the electronic excitation of molecules (see, *e.g.*, Refs 1—5).

It was experimentally established that transitions of certain molecules of carbonyl compounds with symmetrical $CR_3$ (R = H, D, F, Cl, $CH_3$) tops from the ground state $S_0$ to the lowest excited singlet ($S_1$) and triplet ($T_1$) electronic states are accompanied by significant changes in the equilibrium geometric structures, namely, by rotation of the tops by about 60° and by pyramidalization of carbonyl fragments.[5—11]

Experimental studies of the structure of conformationally flexible molecules (especially if they are in excited electronic states) face severe difficulties, which are first of all associated with possible ambiguity of band assignment in the vibronic spectra and instability of inverse problems of the determination of potentials of internal rotation and inversion. Therefore, quantum-mechanical calculations can serve as both an additional source of structural information and a method of analysis of the nature of conformational effects.[5]

Theoretical studies[12—15] of aldehyde molecules $CX_3CHO$ (X = H, F, Cl) in the $S_0$, $S_1$, and $T_1$ states showed that the $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ electronic excitations of these molecules cause changes in the orientation of the $CX_3$ top and a pyramidal distortion of the CCHO fragment, which is planar in the $S_0$ state. The results obtained in those studies are in agreement with experimental data.

The structures of carboxylic acid haloanhydrides were studied much poorer. However, experimental studies of, *e.g.*, HFCO, HClCO, $F_2CO$, $Cl_2CO$, $CH_3COF$, and $CH_3COCl$ also revealed a pyramidal distortion of the carbonyl fragment upon electronic excitation of the molecules to the $S_1$ state.[16—18] For $CH_3COF$ and $CH_3COCl$ we showed that excitation also changes the orientation of the methyl top relative to the molecular skeleton.

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In this work we present the results of an *ab initio* quantum-chemical study of the potential energy surfaces (PES) of acetyl chloride molecule isotopomers $CH_3COCl$ (**1**) and $CD_3COCl$ (**2**) in the $S_0$, $T_1$, and $S_1$ states. Excited-state calculations and detailed analysis of anharmonic large-amplitude vibrations (torsional and inversion motions of nonplanar carbonyl fragment) were performed for the first time.

## Calculation Procedure

Based on our experience[19,20] in theoretical studies of the molecules of carbonyl compounds in the $S_0$, $T_1$, and $S_1$ electronic states, the complete active space multiconfiguration self-consistent field (CASSCF) method and a conventional basis set 6-31G(d,p) was chosen as the main computational method. Calculations in the CASSCF approximation with the active space of five MOs, which are mainly localized on the carbonyl group (we conditionally denote them as $\sigma_{CO}$, $\pi_{CO}$, $n_O$, $\pi_{CO}{}^*$ and $\sigma_{CO}{}^*$) and occupied with six electrons, allow the structure of carbonyl compounds both in the ground state and in the lowest excited electronic $n\pi^*$-states to be studied reliably at a reasonable computational cost.

Calculations of molecule **1** in the $S_1$ state (hereafter, **1**($S_1$), *etc.*) were carried out with full optimization of the second root of the multiconfiguration secular equation. In this case, the problem of variational collapse of the $S_0$ and $S_1$ states of molecule **1** (similarly to other compounds we studied earlier[19]) in the range of the geometric parameters under study did not arise when the initial approximation involved the orbitals corresponding to the symmetrical nuclear configuration in which the $S_0$ and $S_1$ states belong to different irreducible representations of the $C_s$ group.

Ground-state calculations were also carried out by the RHF and MP2 methods. Perturbative calculations were also performed with the 6-311++G(f,d,p) extended basis set constructed from conventional 6-311++G(d,p) basis set augmented with *f*-functions for the Cl atoms. All quantum-chemical calculations were carried out using the GAMESS (US) program package[21] (PC GAMESS version).*

The vibrational frequencies of the molecule were calculated in the harmonic approximation. For the large-amplitude vibrations (torsional in the $S_0$ state and torsional and inversion in the $T_1$ and $S_1$ states), the one-dimensional (1D) and two-dimensional (2D) anharmonic vibrational problems were also solved by the variational method. The methods for solution of such vibrational problems were described in detail in the literature.[19,22–24] The Hamiltonian of the vibrational motion had the form

$$\hat{H}(\varphi_1, ..., \varphi_n) = -\sum_{i=1}^{n}\sum_{j=1}^{n} \frac{\partial}{\partial\varphi_i} B_{ij}(\varphi_1, ..., \varphi_n) \frac{\partial}{\partial\varphi_j} + V(\varphi_1, ..., \varphi_n), \qquad (1)$$

where $n$ is the number of the vibrational coordinates included; $B_{ij}$ are the elements of the symmetrical matrix of the kinetic parameters, which was chosen so as to provide the separation of vibrational and rotational motions of the molecule in accordance with the Eckart conditions and $V$ is the potential function. Internal rotation and inversion of the molecule were characterized by the angle of rotation of the COCl fragment and methyl group about the C—C bond ($\varphi_1$) and the angle between the C—Cl bond and the CCO plane ($\varphi_2$), respectively. To retain the symmetry of the problem, the average value of the change in three O—C—C—H(D) dihedral angles relative to the chosen conformation was taken as the $\varphi_1$ variable.

In solving the 1D vibrational problems for internal rotation, the parameters $B$ and potential function $V$ were approximated by the following expressions

$$V(\varphi_1) = \frac{1}{2}\sum_k V_k(1 - \cos k\varphi_1), \qquad (2)$$

$$B(\varphi_1) = B_0 + \sum_k B_k \cos k\varphi_1. \qquad (3)$$

When solving the vibrational problem for the inversion motion, the potential $V$ was approximated at reference points by polynomials or by the following functions

$$V(Q) = \sum_k V_k Q^k + F(Q), \qquad (4)$$

where $Q = R(\text{C—H}) \cdot \varphi_2$; $F(Q)$ is the Gauss function

$$F(Q) = A \cdot \exp(-CQ^2)$$

or the Lorentz function

$$F(Q) = A/(C + Q^2),$$

where $A$ and $C$ are constants; the function $B$ was approximated by a polynomial expansion in terms of $Q$.

In solving the 2D vibrational problems for the systems in excited electronic states the $B_{ij}(\varphi_1,\varphi_2)$ and $V(\varphi_1,\varphi_2)$ values were determined from the results of CASSCF/6-31G(d,p) calculations; the variables were changed in the ranges $0 \le \varphi_1 \le 60°$ and $0° \le \varphi_2 \le 60°$ with an increment of 10° (the remaining geometric parameters were optimized in the course of the *ab initio* calculations). Based on the values obtained, the functions $B_{ij}$ and $V$ were approximated by linear combinations of trigonometric functions

$$B_{ij}(\varphi_1,\varphi_2) = \sum_K\sum_L C_{KL}^{cc} \cos K\varphi_1 \cos L\varphi_2 + \\ + \sum_K\sum_L C_{KL}^{ss} \sin K\varphi_1 \sin L\varphi_2, \qquad (5)$$

$$V(\varphi_1,\varphi_2) = \sum_K\sum_L V_{KL}^{cc} \cos K\varphi_1 \cos L\varphi_2 + \\ + \sum_K\sum_L V_{KL}^{ss} \sin K\varphi_1 \sin L\varphi_2. \qquad (6)$$

The periodicity of the functions $B(\varphi_1)$, $V(\varphi_1)$, $B_{ij}(\varphi_1,\varphi_2)$, and $V(\varphi_1,\varphi_2)$ requires that the $k$ and $K$ subscripts in expressions (2)—(6) be a multiple of three.

The one- and two-dimensional $B$ and $V$ surfaces thus constructed were used to solve the 1D and 2D vibrational problems by the variational method with the basis set of trigonometric functions. The 1D vibrational problem for the inversion motion was solved using the basis set of harmonic oscillator functions.

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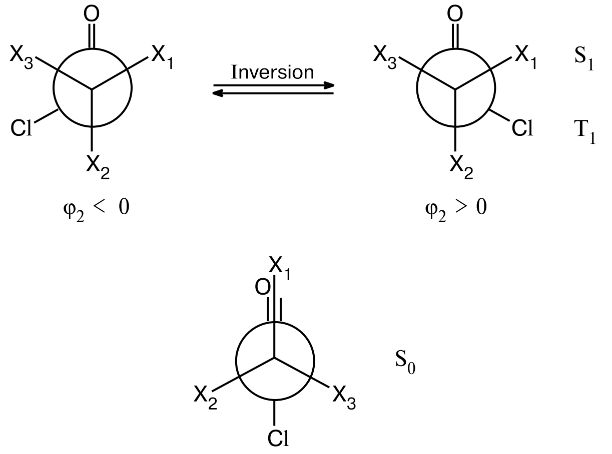

**Fig. 1.** Newman projections of the $CX_3COCl$ (X = H, D) molecules in the ground ($S_0$) and lowest excited singlet ($S_1$) and triplet ($T_1$) electronic states ($\varphi_2$ is the angle of deviation of the C—Cl bond from the CCO plane).

## Results and Discussion

**Ground electronic state.** Microwave spectroscopy[25] and gas-phase electron diffraction[26] studies of acetyl chloride molecule in the $S_0$ state showed that it exists as a single conformer in which one H atom eclipses the O atom (Fig. 1). The results of the *ab initio* RHF and MP2 calculations[27,28] in the 3-21G, 3-21G(d), and 6-31G(d) basis sets are in agreement with these data, whereas the MNDO semiempirical method[27] predicts that an H atom eclipses the Cl atom in the most stable conformation.

By and large the geometric parameters of molecule **1**($S_0$), obtained both experimentally[25,26,28] and from RHF, MP2, and CASSCF calculations are in good agreement with one another and with the available calculated data[27,28] (Table 1). As should be expected,[29] the RHF calculated C=O bond length is shorter than the experimental values. MP2 and CASSCF calculations with inclusion of electron correlation effects predict a more realistic value. The C—C bond length depends only slightly on the computational methods employed; the CASSCF approximation gives the poorest results for the C—Cl bond. This can be due to the fact that the active space of orbitals contains no orbitals that are mainly localized on the Cl atom. By and large the best agreement between geometric parameters is provided by the MP2/6-311++G(f,d,p) calculations.

The harmonic and experimental[28,30] vibrational frequencies of molecules **1**($S_0$) and **2**($S_0$) are listed in Table 2. They are in reasonable agreement with experimental data. The inclusion of electron correlation leads to a typical situation where all MP2 calculated frequencies are to a variable extent underestimated compared to the results of Hartree—Fock calculations, bringing them closer to the experimental values.

Estimates of the height of the potential barrier to internal rotation in acetyl chloride molecule obtained by microwave[25,31,32] and vibronic[18] spectroscopy are in good agreement, namely, 453,[25] 472,[31] 445,[32] and 490 cm$^{-1}$.[18] The torsional frequencies calculated from these values are 136 cm$^{-1}$ for isotopomer **1** (see Ref. 30) and 100 (see Ref. 30) and 106 cm$^{-1}$ (see Ref. 18) for isotopomer **2**. However, the authors of Ref. 28 assigned a far-IR band at 162.8 cm$^{-1}$ to the torsional frequency of molecule **1** and estimated the barrier to internal rotation at 622 cm$^{-1}$. The possibility of another assignment of the band at 162.8 cm$^{-1}$ was also pointed out.[28]

**Table 1.** Calculated and experimental ground-state geometric parameters of $CH_3COCl$ ($S_0$) molecule

| Parameter | Computational method | | | | | Experiment | | |
|---|---|---|---|---|---|---|---|---|
| | RHF /6-31G(d,p) | MP2 /6-31G(d)[28] | MP2 /6-31G(d,p) | MP2 /6-311++G(f,d,p) | CASSCF /6-31G(d,p) | I[a] | II[b] | III[c] |
| Bond | | | | $d$/Å | | | | |
| C=O | 1.167 | 1.200 | 1.201 | 1.192 | 1.201 | 1.192(10) | 1.185(3) | 1.185(5) |
| C—C | 1.502 | 1.499 | 1.500 | 1.502 | 1.501 | 1.499(10) | 1.505(3) | 1.501(6) |
| C—Cl | 1.784 | 1.798 | 1.799 | 1.789 | 1.775 | 1.789(5) | 1.796(2) | 1.796(5) |
| C—H(1) | 1.081 | 1.090 | 1.086 | 1.090 | 1.081 | 1.083(5) | 1.092(5) | 1.093(2) |
| C—H(2)(H(3)) | 1.083 | 1.092 | 1.088 | 1.092 | 1.083 | 1.083(5) | 1.092(5) | 1.096(2) |
| Angle | | | | ω/deg | | | | |
| C—C—O | 127.1 | 127.4 | 127.3 | 127.5 | 126.3 | 127.08(16) | 127.2(5) | 127.4(5) |
| C—C—Cl | 112.9 | 112.0 | 112.0 | 111.7 | 113.9 | 112.67(50) | 111.6(6) | 112.2(1) |
| C—C—H(1) | 108.6 | 108.8 | 108.8 | 109.3 | 108.7 | 110.33(16) | 110.7(8) | 108.8(5) |
| C—C—H(2)(H(3)) | 109.7 | 109.7 | 109.5 | 109.2 | 109.9 | 110.33(16) | 110.7(8) | 109.4(3) |
| H(1)—C—H(2)(H(3)) | 110.4 | 110.4 | 110.5 | 110.7 | 110.2 | 109.50(20) | 108.8(8) | 109.4(3) |

[a] Obtained by microwave spectroscopy.[25]

[b] Obtained by gas-phase electron diffraction.[26]

[c] Obtained by microwave spectroscopy using the C—H bond lengths determined in the approximation of separated C—H vibrations.[28]

**Table 2.** Harmonic frequencies ($\nu_i$) of molecules **1** and **2** in the $S_0$, $T_1$, and $S_1$ states, calculated in the 6-31G(d,p) basis set

| Symmetry of vibrations[a] | $\nu_i$ /cm$^{-1}$ | Approximate assignment[b] of vibrations | $S_0$ | | | | $T_1$ | | $S_1$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | MP2 | MP2[c] | CASSCF | Experiment[28] [d] | UHF | CASSCF | CASSCF | Experiment[18] [d] |
| | | | | | $CH_3COCl$ (**1**) | | | | | |
| a′ | $\nu_1$ | $\nu^{as}(CH_3)$ | 3275 | 3211 | 3316 | 3027 | 3296 | 3295 | 3295 | — |
| | $\nu_2$ | $\nu^{s}(CH_3)$ | 3149 | 3092 | 3290 | 2948 | 3187 | 3192 | 3190 | — |
| | $\nu_3$ | $\nu(CO)$ | 1863 | 1835 | 1846 | 1818 | 1384 | 1318 | 1294 | 1223 |
| | $\nu_4$ | $\delta^{as}(CH_3)$ | 1523 | 1485 | 1592 | 1417[e] | 1601 | 1602 | 1602 | — |
| | $\nu_5$ | $\delta^{s}(CH_3)$ | 1441 | 1406 | 1540 | 1368 | 1541 | 1544 | 1545 | — |
| | $\nu_6$ | $\rho(CH_3)$ | 1157 | 1139 | 1218 | 1108 | 1032 | 1005 | 992 | — |
| | $\nu_7$ | $\nu(CC)$ | 997 | 981 | 1054 | 956 | 1179 | 1183 | 1199 | 922 |
| | $\nu_8$ | $\delta(COCl)$ | 626 | 629 | 670 | 607 | 372 | 366 | 376 | — |
| | $\nu_9$ | $\nu(CCl)$ | 454 | 462 | 489 | 444 | 693 | 700 | 706 | 690 |
| | $\nu_{10}$ | $\rho(COCl)$ | 354 | 350 | 368 | 348 | 330 | 329 | 330 | 298 |
| a″ | $\nu_{11}$ | $\nu^{as}(CH_3)$ | 3249 | 3186 | 3213 | 2990[e] | 3263 | 3265 | 3263 | — |
| | $\nu_{12}$ | $\delta^{as}(CH_3)$ | 1527 | 1485 | 1602 | 1431 | 1607 | 1609 | 1607 | — |
| | $\nu_{13}$ | $\delta(CH_3)$ | 1075 | 1046 | 1139 | 1032 | 1154 | 1153 | 1184 | — |
| | $\nu_{14}$ | Inversion[f] | 523 | 519 | 537 | 514 | 451 | 439 | 427 | 452 |
| | $\nu_{15}$ | Torsional | 145 | 134 | 155 | 163 (136[g]) | 205 | 205 | 205 | 148 |
| | | | | | $CD_3COCl$ (**2**) | | | | | |
| a′ | $\nu_1$ | $\nu^{as}(CD_3)$ | 2431 | 2383 | 2462 | 2266 | 2444 | 2442 | 2443 | — |
| | $\nu_2$ | $\nu^{s}(CD_3)$ | 2262 | 2220 | 2309 | 2138 | 2292 | 2295 | 2294 | — |
| | $\nu_3$ | $\nu(CO)$ | 1860 | 1832 | 1841 | 1821 | 1372 | 1223 | 1203 | 1222 |
| | $\nu_4$ | $\delta^{as}(CD_3)$ | 1194 | 1170 | 1268 | 1027[e] | 1155 | 1156 | 1151 | — |
| | $\nu_5$ | $\delta^{s}(CD_3)$ | 1095 | 1066 | 1148 | 1138 | 1059 | 1064 | 1074 | — |
| | $\nu_6$ | $\rho(CD_3)$ | 1006 | 991 | 1063 | 819 | 855 | 841 | 839 | — |
| | $\nu_7$ | $\nu(CC)$ | 849 | 831 | 893 | 960 | 1245 | 1316 | 1313 | 877 |
| | $\nu_8$ | $\delta(COCl)$ | 579 | 583 | 623 | 559 | 362 | 357 | 367 | — |
| | $\nu_9$ | $\nu(CCl)$ | 451 | 458 | 483 | 441 | 652 | 659 | 663 | 609 |
| | $\nu_{10}$ | $\rho(COCl)$ | 317 | 314 | 331 | 314 | 297 | 297 | 298 | — |
| a″ | $\nu_{11}$ | $\nu^{as}(CD_3)$ | 2406 | 2358 | 2437 | 2247[e] | 2417 | 2420 | 2417 | — |
| | $\nu_{12}$ | $\delta^{as}(CD_3)$ | 1101 | 1070 | 1154 | 1041[e] | 1152 | 1153 | 1155 | — |
| | $\nu_{13}$ | $\delta(CD_3)$ | 902 | 883 | 947 | 872[e] | 947 | 947 | 944 | — |
| | $\nu_{14}$ | Inversion[f] | 463 | 458 | 481 | 451[e] | 418 | 407 | 395 | — |
| | $\nu_{15}$ | Torsional | 104 | 97 | 113 | 106[18] (100[g]) | 147 | 148 | 148 | 128 |

[a] Only for the $S_0$ state.

[b] Notations: $\nu$ is stretching, $\delta$ is bending, and $\rho$ is rocking vibration.

[c] Calculated with the 6-311++G(p,d,f) basis set.

[d] These experimental frequencies were obtained in the gas phase unless otherwise specified.

[e] Solid phase.

[f] In the $S_0$ state, the out-of-plane CCl vibration.

[g] See Ref. 30 (calculated using the published[31] height of potential barrier to internal rotation).

Table 3 lists the results of solution to the 1D torsional problem for molecules **1**($S_0$) and **2**($S_0$) by the CASSCF, RHF, and MP2 methods in the 6-31G(d,p) basis set and by the MP2/6-311++G(f,d,p) method. The estimates of the barriers to internal rotation (coefficient $V_3$ in expression (2)) differ insignificantly. The calculated energies of torsional levels are by and large close to the experimental values.[18,25,31,32]

**Excited electronic states.** According to our calculations of acetyl chloride molecule in the $S_1$ and $T_1$ states, the global minimum on the PES corresponds to a conformation with nonplanar CCOCl fragment and a rotated top (Table 4, Fig. 1). Earlier,[18] a pyramidal structure of this fragment was established in an experimental study of the $S_1 \leftarrow S_0$ vibronic spectra of molecules **1** and **2**. In that study the estimate of the equilibrium value of the angle, $\theta_m$, between the C=O bond and the CCCl plane was obtained by fitting the calculated and experimental rotational contours of the $0_0^0$ band in the vibronic spectrum of molecule **1**, which gave $\theta_m = 45°$. The solution to the inverse spectral problem for the inversion motion gives $\theta_m = 37$ or $40°$ depending on the shape of the model potential.[16] Our CASSCF/6-31G(d,p) calculations predict $\theta_m = 42°$. Note that pyramidalization of the CCHO

**Table 3.** Parameters $V_3$ and $V_6$ 1D potential functions internal rotation and energy torsional transitions for molecules **1**($S_0$) and **2**($S_0$)

| Computational method | $V_3$ | $V_6$ | 1e←0e | 2e←1e | 3e←1e | 4e←1e |
|---|---|---|---|---|---|---|
| | $cm^{-1}$ | | | | | |
| | | | $CH_3COCl$ (**1**) | | | |
| RHF/6-31G(d,p) | 456.1 | −10.5 | 133 | 121 | 213 | 321 |
| MP2/6-31G(d,p) | 418.6 | −14.1 | 125 | 114 | 198 | 306 |
| MP2/6-311++G(f,d,p) | 421.2 | −26.8 | 120 | 113 | 201 | 308 |
| CASSCF/6-31G(d,p) | 497.1 | −11.4 | 140 | 128 | 228 | 337 |
| | | | $CD_3COCl$ (**2**) | | | |
| RHF/6-31G(d,p) | 456.1 | −10.5 | 99 | 93 | 177 | 254 |
| MP2/6-31G(d,p) | 418.6 | −14.1 | 92 | 87 | 166 | 239 |
| MP2/6-311++G(f,d,p) | 421.2 | −26.8 | 88 | 85 | 165 | 239 |
| CASSCF/6-31G(d,p) | 497.1 | −11.4 | 103 | 97 | 187 | 269 |
| Experiment[18] | 490 | — | — | 97 | 184 | 265 |

*Note*. The potential barriers to internal rotation of acetyl chloride molecule, determined by microwave and vibronic spectroscopy, lie in the interval 445—490 $cm^{-1}$ (see text).

**Table 4.** Geometric parameters of $CH_3COCl$ molecule (**1**) in the excited electronic states $S_1$ and $T_1$, calculated in the 6-31G(d,p) basis set

| Parameter | $S_1$ | $T_1$ | |
|---|---|---|---|
| | CASSCF | UHF | CASSCF |
| Bond | | $d$/Å | |
| C=O | 1.392 | 1.344 | 1.374 |
| C—C | 1.496 | 1.500 | 1.500 |
| C—Cl | 1.737 | 1.747 | 1.745 |
| C—H(1) | 1.084 | 1.084 | 1.084 |
| C—H(2) | 1.082 | 1.082 | 1.082 |
| C—H(3) | 1.086 | 1.086 | 1.086 |
| Angle | | ω/deg | |
| C—C—O | 114.2 | 114.0 | 113.9 |
| C—C—Cl | 118.9 | 117.8 | 118.1 |
| C—C—H(1) | 109.3 | 109.3 | 109.4 |
| C—C—H(2) | 110.0 | 109.6 | 109.6 |
| C—C—H(3) | 110.8 | 111.1 | 111.2 |
| C—Cl* | 40.3 | 41.0 | 41.1 |
| H(1)—C—H(2) | 108.7 | 108.8 | 108.7 |
| H(1)—C—H(3) | 108.7 | 108.9 | 108.9 |
| H(1)—C—C—O | 52.2 | 51.8 | 50.7 |

* Angle of deviation of the C—Cl bond from the CCO plane ($\varphi_2$).

fragment on electronic excitation was also experimentally observed[5,15,33] for related $CX_3CHO$ (X = H, F, Cl) molecules; here, the angle of deviation of the C—H bond from the CCO plane lies in the interval 35—37°.

Electronic excitation of acetyl chloride molecule to the $T_1$ and $S_1$ states causes a significant lengthening of the C=O bond and a decrease in the C—C—O angle (see Tables 1 and 4); this is characteristic of the molecules of carbonyl compounds.[5,19,20] Experimental[18] estimates of elongation of the C=O bond and of the decrease in the C—C—O angle on $S_1 \leftarrow S_0$ electronic excitation of molecule **1** are 0.20 Å and 18° (*cf.* 0.19 Å and 12°, respectively, obtained from CASSCF/6-31G(d,p) calculations). Changes in the remaining geometric parameters are not so large. UHF/6-31G(d,p) calculations of acetyl chloride molecule in the $T_1$ state predict a somewhat smaller C=O bond length compared to the CASSCF method, but the remaining geometric parameters determined by these methods differ only slightly.

Harmonic vibrational frequencies of molecules **1** and **2** in the $S_1$ and $T_1$ states and the experimental[18] frequencies of these molecules in the $S_1$ state are listed in Table 2. By and large the experimental and calculated results are in reasonable agreement. Excitation of the molecules to the $S_1$ state causes an appreciable decrease in the C=O stretching frequency, which is typical of $n\pi^*$-electronic excitations of the molecules of carbonyl compounds. The frequency of the in-plane deformation vibration of the COCl fragment ($\nu_8$) also decreases. Analogous changes were also observed in the case of $T_1 \leftarrow S_0$ electronic excitation. Note that the UHF and CASSCF calculated vibrational frequencies of both molecules in the $T_1$ state differ insignificantly.

The potential energy distribution (PED) for the normal vibrations corresponding to large-amplitude motions was analyzed using the results of the CASSCF calculations. It was found that the torsional motion makes a nearly 100% contribution to the corresponding normal vibrations of molecules **1** and **2** in the $T_1$ and $S_1$ states. This suggests quite a high degree of separation (in the harmonic approximation) of the torsional vibration from other molecular vibrations. The inversion vibration is much stronger coupled, namely, the contribution of the motion corresponding to the C—Cl bond deviation from the CCO plane is 60% for **1** ($S_1$, $T_1$) and 50% for **2** ($S_1$, $T_1$).

**Table 5.** Coefficients of approximation ($V^{cc}_{KL}$ and $V^{ss}_{KL}$) of the potential functions $V$ using expression (6) for molecule **1** in the $S_1$ and $T_1$ states

| $K$ | $L$ | $S_1$ | $T_1$ |
|---|---|---|---|
| | | Coefficients $V^{cc}_{KL}$ | |
| 0 | 0 | 23491.7 | 25374.5 |
| 0 | 1 | −31773.9 | −34778.9 |
| 0 | 2 | 9894.4 | 11404.0 |
| 0 | 4 | 507.4 | 275.4 |
| 0 | 6 | — | 97.6 |
| 0 | 8 | 21.8 | — |
| 0 | 12 | −1.2 | 2.2 |
| 3 | 0 | 402.7 | 365.3 |
| 3 | 2 | −348.5 | −336.1 |
| 3 | 4 | −40.4 | −61.6 |
| 3 | 6 | — | 14.3 |
| 3 | 8 | −16.1 | −22.5 |
| 3 | 12 | −0.8 | — |
| 6 | 0 | −9.0 | — |
| 6 | 2 | 15.7 | — |
| 6 | 4 | −3.3 | 7.6 |
| 6 | 6 | — | −4.6 |
| 6 | 8 | — | 1.8 |
| | | Coefficients $V^{ss}_{KL}$ | |
| 3 | 1 | 158.4 | 460.8 |
| 3 | 3 | −306.2 | −801.0 |
| 3 | 4 | — | 381.8 |
| 3 | 6 | 19.7 | −79.9 |
| 3 | 8 | −26.2 | — |
| 3 | 10 | — | −4.3 |
| 6 | 1 | −107.6 | −23.4 |
| 6 | 2 | 82.2 | — |
| 6 | 3 | — | 32.4 |
| 6 | 4 | −13.8 | −18.0 |
| 6 | 8 | 1.0 | 0.9 |

**Table 6.** Barriers to conformational transitions for internal rotation ($V_t$) and inversion ($V_i$) and the standard deviations of approximation (6) ($\sigma$) for molecule **1** in the $S_1$ and $T_1$ states

| State | $V_t$ | $V_i$ | $\sigma$ |
|---|---|---|---|
| | $cm^{-1}$ | | |
| $S_1$ | 792 | 2140* | 0.65 |
| $T_1$ | 791 | 2340 | 1.87 |

*Note.* The values obtained by vibronic spectroscopy are as follows: $V_t$ = 520 $cm^{-1}$ and $V_i$ = 1720 $cm^{-1}$ for **1**($S_1$) and $V_t$ = 695 $cm^{-1}$ for **2**($S_1$).

* An approximate estimate (see text).

The results of calculations listed in Table 2 were obtained in the small vibration approximation, which is generally inapplicable to the description of large-amplitude motions. In these cases, anharmonic problems with the Hamoltonian (1) were solved.

Table 5 lists the CASSCF/6-31G(d,p) calculated coefficients for approximation of the 2D torsional-inversion sections of the PES of molecule **1** ($S_1$, $T_1$) by expression (6). The map of the 2D section of the PES of system **1**($S_1$) is presented in Fig. 2. The calculated PES of molecule **1**($T_1$) is qualitatively similar and therefore not shown here. The barriers to conformational transitions in the case of internal rotation ($V_t$) and inversion ($V_i$)* are listed in Table 6. It should be noted that in spite of quite a high degree of separation of torsional motions from other molecular vibrations in the harmonic approximations, the $V_t$ values for molecules **1** and **2** determined independently from the experimental torsional energy levels are appreciably different (520 and 695 $cm^{-1}$, respectively, see Ref. 18).

The PES shown in Fig. 2 has six equivalent minima, because it corresponds to the molecular symmetry group $G_6$, which is isomorphic to the $D_3$ group (see, *e.g.*, Ref. 34). Aldehyde molecules $CX_3CHO$ (X = H, F, Cl) in excited electronic states are also characterized by similar PES.[19] Such PES exhibit two valleys with three minima in each valley; transitions between the minima occur by the torsional motion. Minima lying in the same valley are labeled identically, "*a*" or "*b*" (see Fig. 2). Transitions from one valley to the other correspond to inversion of the carbonyl fragment. It should be noted that for all compounds mentioned above minima in different valleys are markedly shifted relative to one another along the $\varphi_1$ coordinate. Therefore, if the torsional motion can in principle occur independently of inversion (all three minima in the same valley have the same coordinate $\varphi_2$), a "pure" inversion transition between two minima *a* and *b* is impossible.

In spite of qualitative similarity, the shape of the PES of the aldehyde $CX_3CHO$ (X = H, F, Cl) and haloanhydride $CH_3COY$ (Y = F, Cl) molecules in the $S_1$ and $T_1$ states exhibit significant differences. Because of this, interrelation between the torsional and inversion motions for these groups of molecules manifests itself in different manner. The PES of the aldehyde molecules are characterized[19] by relatively low barriers to inversion (less than 1000 $cm^{-1}$) and clearly defined valleys connecting pairs of minima *a* and *b*, the curvature of the 1D minimum energy paths for the torsional and inversion motions being low. In this case the torsional-inversion interaction must mainly involve tunneling between valleys. The PES

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* The estimates of the parameter $V_i$ obtained[16] in studies of stability of the 1D inverse spectral problem for **1**($S_0$) using different model potentials are very close, namely, 1740 and 1760 $cm^{-1}$.

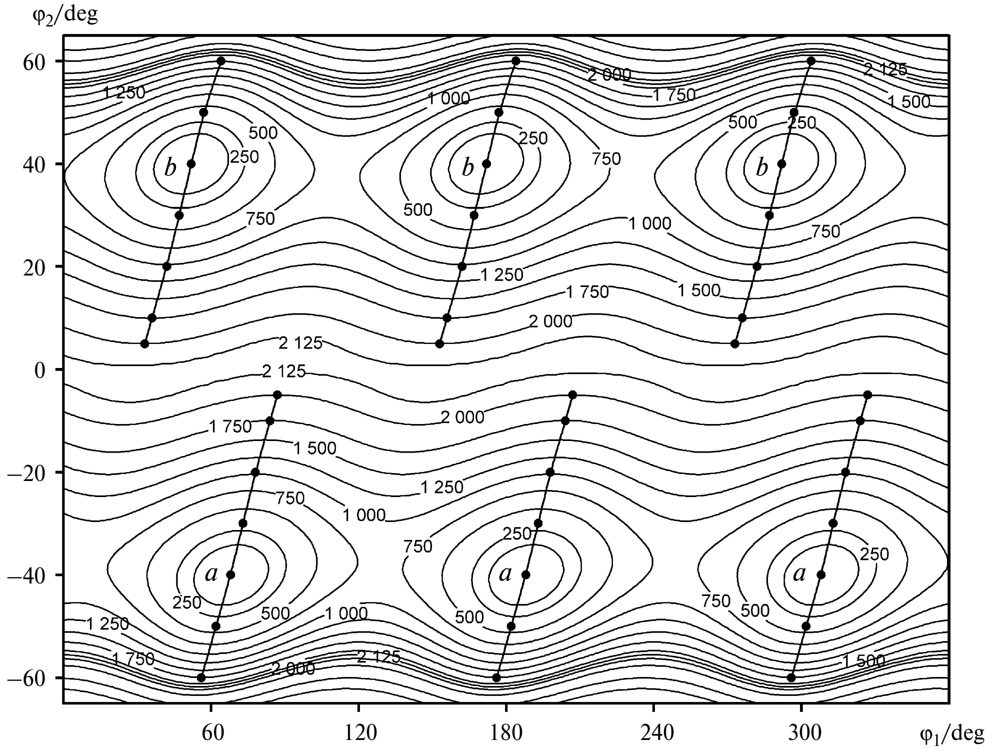

**Fig. 2.** Map of the 2D section of the PES of molecule **1** in the $S_1$ state ($\varphi_1$ is the torsional coordinate and $\varphi_2$ is the inversion coordinate). Shown are also fragments of the 1D minimum energy paths ($cm^{-1}$) for the inversion motion. Minima lying in the same valley are labeled identically (*a* or *b*).

of the haloanhydride molecules (data for Y = F were taken from Ref. 35) are characterized by high barriers (~2000 $cm^{-1}$ for **1** and ~4000 $cm^{-1}$ for $CH_3COF$) between valleys, tunneling through which in the case of low-lying vibrational levels is hindered. This allows the motion in both valleys to be considered to some extent independently. In this case the torsional-inversion interaction is mainly due to anharmonicity of the potential in the valley and can be evaluated from the curvature of the 1D minimum energy paths.

Mention may also be made that the shape of the PES of molecule **1**($S_1$) precludes unambiguous construction of the 1D path of inversion transition (at least in the coordinates used in this work). Continuous fragments of these paths are shown in Fig. 2. Near $\varphi_2 = 0$, the 2D PES has a nearly flat region and the inversion reaction pathway is bifurcated. In such cases the 1D approximation can provide an inadequate description of upper-lying inversion states. This conclusion can also be drawn by analyzing the shape of the 2D torsional-inversion wave functions for the states lying near the barrier to inversion. An example of such a wave function is shown in Fig. 3.

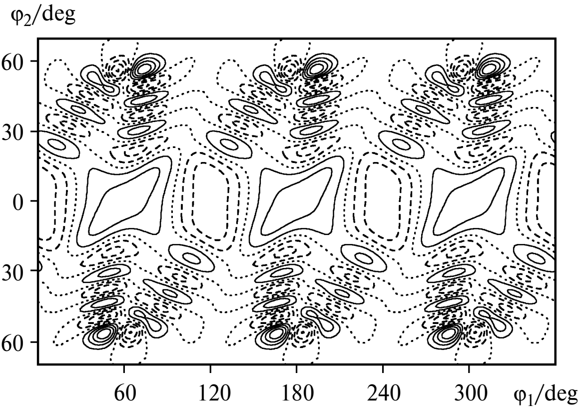

**Fig. 3.** Map of the vibrational wave function corresponding to the torsional-inversion level of molecule **1** in the $S_1$ state with energy $E = 1935$ $cm^{-1}$ (for $\varphi_1$ and $\varphi_2$ see caption to Fig. 2).

Yet another problem posed in solving the vibrational problems is as follows: the shape of the PES of molecule **1** in the $S_1$ and $T_1$ states makes the description of high-lying states difficult. The large equilibrium value of $\varphi_2$ requires calculations of highly distorted structures with $\varphi_2 > 70°$ in order to provide a correct description of the outer walls of the potential; however, in this case one can not expect localization of electronic excitation only on the C=O fragment, and the MO active space employed in this work may appear to be inappropriate. With allowance for this fact in constructing the PES we did not include the points with $\varphi_2 > 65°$ for the $S_1$ state and with $\varphi_2 > 70°$ for the $T_1$ state.

**Table 7.** Energies (in $cm^{-1}$) of torsional-inversion levels of molecules **1**($S_1$) and **2**($S_1$): experimental[18] and calculated for one-dimensional (1D) and two-dimensional (2D) problems

| **1**($S_1$) | | | **2**($S_1$) | | Assignment* |
|---|---|---|---|---|---|
| 2D | 1D | Experiment | 2D | 1D | |
| 0 | 0 | 0 | 0 | 0 | (0, 0) a, e |
| 192 | 190 | 148 | 142** | 140** | (1, 0) a, e |
| 367 | 362 | 281 | 274 | 272 | (2, 0) a |
| 367 | 362 | — | 274 | 272 | (2, 0) e |
| 528 | 514 | 382 | 397 | 394 | (3, 0) e |
| 530 | 518 | — | 397 | 394 | (3, 0) a |
| 626 | 628 | — | 509 | 507 | (4, 0) a |
| 648 | 648 | — | 509 | 507 | (4, 0) e |
| 323 | 292 | 452 | 321 | 272 | (0, 1) a,e |
| 642 | 581 | 870 | 639 | 540 | (0, 2) e |
| 644 | 581 | 870 | 639 | 540 | (0, 2) a |
| 956 | 864 | 1227 | 952 | 803 | (0, 3) e |
| 961 | 864 | 1227 | 952 | 803 | (0, 3) $a_1$ |
| 961 | 864 | 1244 | 952 | 803 | (0, 3) $a_2$ |
| 1271 | 1142 | 1510 | 1258 | 1060 | (0, 4) $a_1$, e |
| 1271 | 1142 | 1586 | 1258 | 1060 | (0, 4) $a_2$, e |
| 1573 | 1411 | 1708 | 1554 | 1310 | (0, 5) $a_1$, e |
| 1569 | 1412 | — | 1554 | 1311 | (0, 5) e |
| 1569 | 1412 | — | 1555 | 1311 | (0, 5) $a_2$ |

* For notations ($\upsilon_1$, $\upsilon_2$) of the symmetry types of energy levels, see text.

** Experimental values is 128 $cm^{-1}$.[18]

**Table 8.** Energies (in $cm^{-1}$) of torsional-inversion levels of molecules **1**($T_1$) and **2**($T_1$) calculated for one-dimensional (1D) and two-dimensional (2D) problems

| **1**($T_1$) | | **2**($T_1$) | | Assignment* |
|---|---|---|---|---|
| 2D | 1D | 2D | 1D | |
| 0 | 0 | 0.0 | 0.0 | (0, 0) a, e |
| 192 | 191 | 142 | 141 | (1, 0) a, e |
| 366 | 364 | 274 | 273 | (2, 0) a |
| 367 | 364 | 274 | 273 | (2, 0) e |
| 509 | 516 | 397 | 397 | (3, 0) e |
| 511 | 520 | 397 | 397 | (3, 0) a |
| 627 | 631 | 509 | 509 | (4, 0) a |
| 646 | 650 | 509 | 509 | (4, 0) e |
| 331 | 298 | 329 | 277 | (0, 1) a, e |
| 660 | 592 | 654 | 550 | (0, 2) a, e |
| 984 | 881 | 975 | 818 | (0, 3) a |
| 986 | 881 | 975 | 818 | (0, 3) e |

* For notations ($\upsilon_1$, $\upsilon_2$) of the symmetry types of energy levels, see text.

The energies of a number of low-lying vibrational levels molecules of **1** and **2** in the $T_1$ and $S_1$ states, obtained in solving the 1D and 2D vibrational problems are listed in Tables 7 and 8. The corresponding states were assigned based on the results of analysis of the wave function localization regions and the structure of the nodal surfaces of the vibrational wave functions. The notations ($\upsilon_1$, $\upsilon_2$) in Tables 7 and 8 correspond to conditional assignment of the vibrational state in the approximation of separated torsional ($\upsilon_1$) and inversion ($\upsilon_2$) motions. For the 2D problem, the assignment of states can be done with ease provided that the wave functions are well localized. Since symmetry of the PES corresponds to the $D_3$ group, the torsional-inversion states are denoted using traditional notations of irreducible representations, *viz*., $a_1$, $a_2$, and e. Tables 7 and 8 list the results of separately solved 1D vibrational problems for the inversion motion and internal rotation. Table 7 also lists the experimental values of the energies of torsional and inversion levels of molecule **1**($S_1$).

A feature of the systems under study is degeneration of the low-lying levels $a_1$ and $a_2$ (degenerate levels are denoted as a in Tables 7 and 8) and two pairs of the e type levels. It is associated with a relatively high barrier to inversion in the $S_1$ and $T_1$ electronic states and, therefore, with a very small tunneling splitting, which also depends on the mass of the particles involved in the vibrations.

The energies of the lowest torsional levels of molecules **1** and **2** in the $T_1$ and $S_1$ states, obtained in solving the 1D and 2D vibrational problems, are very close (see Tables 7 and 8). At the same time the energies of the inversion and, hence, torsional-inversion levels calculated for the 1D and 2D problems, differ appreciably, the differences increasing with the increase in the inversion quantum number. This is quite natural because of the peculiarities of the PES shape.

Thus, the results obtained show that the use of the CASSCF method and 6-31G(d,p) AO basis set in studies of the structure of molecules **1** and **2** in the ground ($S_0$) and lowest excited electronic states ($S_1$ and $T_1$) leads by and large to good agreement between the calculated equilibrium geometric parameters and harmonic vibrational frequencies and experimental data. In particular, the experimentally observed pyramidalization of the CCOCl fragment and rotation of the methyl top as a result of $S_1 \leftarrow S_0$ electronic excitations of the molecule are reproduced correctly.

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