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$S_1 \leftarrow S_0$ vibronic spectra and structure of cyclopropanecarboxaldehyde molecule in the S_1 lowest excited singlet electronic state

I.A. Godunov*, N.N. Yakovlev, R.V. Terentiev, D.V. Maslov, V.A. Bataev, A.V. Abramenkov

Lomonosov Moscow State University, Chemistry Department, Leninskie gori, 1/3, 119991 Moscow, Russia

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ABSTRACT

The $S_1 \leftarrow S_0$ vibronic spectra of gas-phase absorption at room temperature and fluorescence excitation of jet-cooled cyclopropanecarboxaldehyde (CPCA, c-C_3H_5CHO)were obtained and analyzed. In addition, the quantum chemical calculation (CASPT2/cc-pVTZ) was carried out for CPCA in the ground (S_0) and lowest excited singlet (S_1) electronic states. As a result, it was proved that the $S_1 \leftarrow S_0$ electronic excitation of the CPCA conformers (syn and anti) causes (after geometrical relaxation) significant structural changes, namely, the carbonyl fragments become non-planar and the cyclopropyl groups rotate around the central C–C bond. As a consequence, the potential energy surface of CPCA in the S_1 state has six minima, 1ab, 2ab, and 3ab, corresponding to three pairs of mirror symmetry conformers: a and b. It was shown that vibronic bands of experimental spectra can be assigned to the $2(S_1) \leftarrow \text{syn}(S_0)$ electronic transition with the origin at 30,481 cm^{-1}. A number of fundamental vibrational frequencies for the 2 conformer of CPCA were assigned. In addition, several inversional energy levels for the 2 conformer were found and the $2a \leftrightarrow 2b$ potential function of inversion was determined. The experimental barrier to inversion and the equilibrium angle between the CH bond and the CCO plane were calculated as 570 cm^{-1} and 28°, respectively.

1. Introduction

The organic molecules with three-membered rings are very interesting objects for structural and conformational research owing to some unusual properties (see, for example, [1–3] and cited literature). In particular, it was discovered that the effect of cyclopropyl group on the molecular structure and properties in some cases is similar to the effect of alkyl group. But in other cases the effect of cyclopropyl group is more similar to the one of unsaturated ($-CH{=}CH_2$) substituent. It was interpreted within the framework of Walsh–Hoffmann model [1,2,4,5], which provides an explanation for the ability of the cyclopropyl substituent to conjugate with unsaturated moiety. There are many studies of structure and properties of these molecules but almost all of them related to the ground electronic state (S_0). Cyclopropanecarboxaldehyde (CPCA, *c*-C_3H_5CHO) is one of the simplest molecules of such type.

The gas-phase molecular geometry of CPCA was studied by electron diffraction [6] and microwave spectroscopy [7]. It was shown that CPCA exists as a mixture of two conformers having a symmetry plane: syn (the

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* Corresponding author.
E-mail addresses: godunov.msu@gmail.com (I.A. Godunov), yakovlev@phys.chem.msu.ru (N.N. Yakovlev), terentyev_ruslan@mail.ru (R.V. Terentiev), dmaslov@phys.chem.msu.ru (D.V. Maslov), v.a.bataev@gmail.com (V.A. Bataev), a.v.abramenkov@gmail.com (A.V. Abramenkov).

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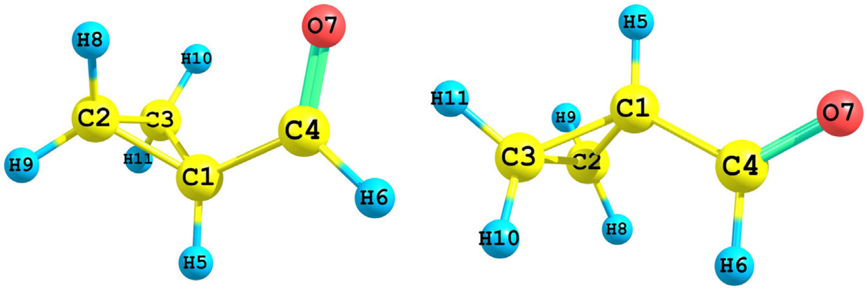

Fig. 1. Syn (on the left) and anti (on the right) conformers of CPCA (structures were built using CHEMCRAFT program, version 1.8, G.A. Andrienko, I.N. Senchenya et al., see http://chemcraftprog.com).

dihedral angle H_5–C_1–C_4–H_6 is equal to 0°) and anti (the same angle is 180°), see Fig. 1, with almost equal content in the gas phase. These conformers resemble the trans and cis conformers of acroleine ($CH_2{=}CH{-}CHO$, see [8] and cited literature) but not the gauche and trans conformers of 2-methylpropanal ($(CH_3)_2CH{-}CHO$) though the structure of 2-methylpropanal resembles CPCA structure most closely [9].

Vibrational spectra of CPCA were studied in works [10–12]. The analysis of earlier studies of the structure of CPCA in the S_0 state was presented in review [1]. But fewer works were devoted to investigations of this molecule in the excited electronic states.

More than twenty years ago one of us (IAG) studied experimentally the electronic absorption spectrum of gas-phase CPCA [13,14]. This spectrum was attributed to the singlet-singlet ($S_1 \leftarrow S_0$) and singlet-triplet ($T_1 \leftarrow S_0$) electronic transitions of the anti (trans) and syn (cis) conformers (S_1 and T_1 are the lowest excited singlet and triplet electronic states, respectively). The analysis of this spectrum suggested that the both conformers in the S_1 and T_1 states retain the structure with the symmetry plane (as in the S_0 state).

But later [15] we carried out the quantum chemical calculations using the multiconfigurational method CASPT2/aug-cc-pVDZ and determined geometric parameters, sections of potential energy surface (PES), and vibrational frequencies in the harmonic approximation for CPCA molecule in the S_0, S_1 and T_1 states. In contradiction to the experimental suggestions [13,14], the theoretical results demonstrated that excitation of the CPCA conformers to the T_1 and S_1 electronic states causes significant structural changes, namely, the carbonyl fragments CCHO become nonplanar, and the cyclopropyl groups rotate around the C-C bond changing the relative position of the carbonyl and cyclopropyl groups.

Thus, the effect of the cyclopropyl group on the structure of CPCA molecule in the S_0 state is similar to the effect of unsaturated substituent, but according to our calculations [15], one in the lowest excited electronic states (S_1 and T_1) is similar to molecules with saturated substituent, for example CX_2YCHO [16,17], where X, Y=H, F, Cl, CH_3.

To clarify this issue we have reinvestigated the $S_1 \leftarrow S_0$ electronic absorption spectrum of gas-phase CPCA and obtained and analyzed the $S_1 \leftarrow S_0$ fluorescence excitation spectrum of jet-cooled CPCA. In addition, we have calculated geometric parameters and harmonic vibrational frequencies of CPCA conformers in the S_0 and S_1 states and the two-dimensional (2D) section of PES in the S_1 state (along internal rotation and inversional coordinates) using the CASPT2/cc-pVTZ method. At last, the 2D vibrational problem has been solved and energies of torsional and inversional levels for CPCA conformers in the S_1 state have been determined. These results are presented below.

2. Methods of investigation

2.1. Experimental

The sample of CPCA was obtained from “Aldrich” Co., 98% purity, and was additionally purified by trap-to-trap distillation under vacuum.

The fluorescence excitation spectrum of jet-cooled CPCA in the region of 30,475–32,530 cm^{-1} was obtained using an experimental setup described previously [18]. The sample vapor was degassed and buffered by argon; CPCA/argon 1:10 mixture under a stagnation pressure of 3.5 atm was injected into a vacuum chamber during the spectra recording. Spectral bandwidth of laser radiation was 10 cm^{-1}, accuracy of wavelength setting -4 to 5 cm^{-1}. The fluorescence excitation spectrum of CPCA in the region of 30,475–31,730 cm^{-1} is presented in Fig. 2a).

The gas-phase absorption spectrum of CPCA in the region of 29,280–33,500 cm^{-1} was obtained at room temperature using a White-type multipass optical cell with an absorption path length from 20 to 100 m at vapor pressures from 0.5 to 24 T.

The spectrum was photographed using a DFS-452 spectrograph in the first order of a 2400 lines/mm grating with a 120,000 theoretical resolving power. The slit width was 20 μm. The spectrum from lamp with a hollow Fe-Ne cathode was used as a reference. The spectrum obtained on photographic plates was scanned using an Epson 4870 Photo scanner with a maximum optical resolution of 4800 dpi. The digitization and processing of the data and the determination of vibronic band vacuum wavenumbers were performed using a special program developed for this purpose. The part of spectrum in the region of 30,440–31,740 cm^{-1} is presented in Fig. 2b).

The list of wavenumbers with the assignments of vibronic bands measured in the $S_1 \leftarrow S_0$ gas-phase