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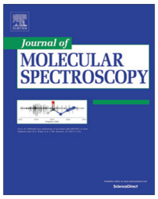

Molecular structure and ring tunneling of phenyl formate as observed by microwave spectroscopy and quantum chemistry

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ABSTRACT

Phenyl formate has been investigated by molecular jet Fourier-transform microwave spectroscopy in the frequency range from 2 to 26.5 GHz. Quantum chemical calculations at the MP2/6-311++G(d,p) level of theory indicate that this molecule does not have a plane of symmetry at equilibrium, and that the phenyl ring performs a large amplitude tunneling motion from one side of the C_s configuration to the other. The tilt angle of the ring out of the H—(C═O)O plane is ±70° and the calculated tunneling barrier is only 28 cm^{-1}. The two lowest torsional states $v_t = 0$ and 1 are assigned in the experimental spectrum and fitted using the program *SPFIT/SPCAT*. The Coriolis splitting ΔE between these states is 46.2231(25) GHz, very close to the value of 48.24 GHz calculated using a simple two-top torsional Hamiltonian of the formate group and the phenyl ring.

1. Introduction

Phenyl formate (formic acid phenyl ester), $H(C{=}O)OC_6H_5$, with the structure illustrated in Fig. 1, is a molecule of chemical, biological, quantum chemical, and spectroscopic interest.

Chemically, phenyl formate belongs to the class of small esters, which are widely used in organic chemistry as a reagent for the formylation of amines [1]. In addition, small esters contain a number of common odorant molecules. Many of these have been the object of our microwave studies, e.g. in Refs. [2–4], with a view toward determining dynamical and/or conformational properties that might correlate with processes involved in the sense of smell. Phenyl formate itself has a typical aromatic smell. It has been suggested in the process of olfaction that odorants may be carried by transport proteins, so-called odorant binding proteins, which can contain aromatic amino acids in their binding pocket such as tryptophan, phenylanaline, and tyrosine [5]. These amino acids could bind molecules such as phenyl formate and other aromatic odorants via π-π interactions [6]. Although under physiological conditions, conformations of aromatic compounds could be totally unrelated to the gas phase, it is important to understand the structure and dynamic of the isolated ligand without any influences from the environment. This is helpful to improve and develop force fields which can then be used to study the molecular dynamics of biological processes at a molecular scale.

Quantum chemically, the relatively small empirical formula of $C_7H_6O_2$ and the well-known planarity of the phenyl ring [7] and the formate group [8–10] suggest that structure optimizations carried out for phenyl formate are within the capabilities of our computational resources. Because it is not always possible to determine microwave spectroscopic structures using the traditional method by isotopic substitutions, the support of quantum chemistry is indispensable, as *ab initio* structures can be taken as references for a comparison of the experimental and calculated molecular parameters. As mentioned above, the orientation of the phenyl group is important in many biological processes, but it is difficult to predict. Whenever possible, we tend to assume a plane of symmetry, i.e. the phenyl group is located in the plane formed by the heavy atoms of the formate group. This is the situation found for many phenyl ring containing molecules investigated by microwave spectroscopy so far, such as anisole [11], phenetole [12], acetophenone [13], benzoyl fluoride [14], and benzaldehyde [15]. On the other hand, in some cases phenyl rings are reported to tilt out of the plane spanned by its neighboring heavy atoms, e.g. in *cis*-formanilide [16,17] and acetanilide [18]. Such tilt angle of a molecule fragment is not always easy to believe when it is based on the rather modest quantum chemistry calculations carried out in experimental spectroscopic laboratories, as e.g. in our investigations on allyl acetate [19]. As the present study shows,

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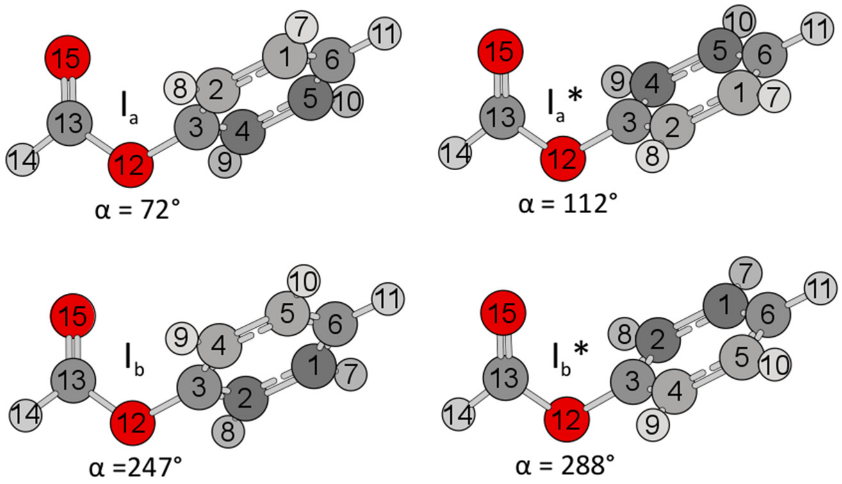

Fig. 1. Four energetically equivalent minima of the most stable *trans* conformer I of phenyl formate. The structures were optimized at the MP2/6-311++G(d,p) level of theory. The dihedral angles $\alpha = \angle(C_{13}, O_{12}, C_3, C_2)$ are given. Note that the pairs I_a/I_a^* and I_b/I_b^* are enantiomers, while I_a and I_b as well as I_a^* and I_b^* can be transformed into each other by a rotation of 180° of the phenyl ring.

the phenyl group is also tilted out of the $H(C{=}O)O$ plane in phenyl formate.

Spectroscopically, phenyl formate is a derivative of formic acid, where the proton in the acid group has been replaced by the much heavier phenyl group. When starting this work, we expected the spectrum of phenyl formate to be essentially that of a rigid-rotor with centrifugal distortion correction. However, as we shall see below, this simple rigid-rotor expectation turned out to be completely incorrect.

2. Quantum chemical calculations

All calculations were carried out at the MP2/6-311++G(d,p) level of theory with the *GAUSSIAN 09* program package [20]. For a conformational analysis, we varied the dihedral angles $\alpha = \angle(C_{13}, O_{12}, C_3, C_2)$ and $\beta = \angle(H_{14}, C_{13}, O_{12}, C_3)$ in a grid of 10° (for atom numbering see Fig. 1), corresponding to the rotation of the phenyl ring about the O_{12}—C_3 bond and the rotation of the formyl group $HC{=}O$ about the C_{13}—O_{12} bond, respectively. The two-dimensional potential energy surface (2D-PES) depending on α and β revealed two stable conformers; each of which appears as four equivalent minima. Because of the planarity of both, the phenyl ring and the formyl group, the geometries represented by (α, β), $(\alpha + 180°, \beta)$, $(-\alpha, -\beta)$, and $(180 - \alpha, -\beta)$ have the same potential energy, and only a quarter of the full 2D-PES calculations are necessary. The calculated energies were parameterized using a 2D Fourier expansion based on terms with the correct symmetry of the angles α and β. The coefficients from this parameterization are given in Table S-1 in the supplementary material. Using these Fourier coefficients, the 2D-PES was drawn as a contour plot illustrated in Fig. 2.

If α is increased from 0° to 360° along the vertical lines at β = 0° or 180°, a series of four minima is found lying alternating slightly above and below the α = 90° and α = 270° lines. The *trans* conformer (conformer I), lying close to the β = 180° line, can be found in four different versions, I_a ($\alpha = 70.3°$, $\beta = 180.5°$), I_a^* ($\alpha = 109.7°$, $\beta = 179.5°$), I_b ($\alpha = 250.3°$, $\beta = 180.5°$), and I_b^* ($\alpha = 289.7°$, $\beta = 179.5°$) on the PES. The closer lying adjacent minima (I_a/I_a^* and I_b/I_b^* with $\Delta\alpha = 39.4°$) are enantiomers, which are separated by a lower barrier of about 28 cm^{-1}, while the minima I_a/I_b and I_a^*/I_b^* with $\Delta\alpha = 180°$ arising from the 180° rotation of the phenyl ring are separated by a higher barrier of 726 cm^{-1}. This situation is depicted in Fig. 3, where a one-dimensional "cut" along β = 180° of the PES is plotted. This cut is

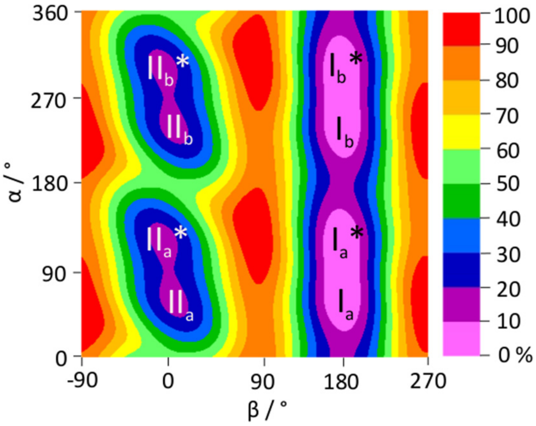

Fig. 2. The potential energy surface of phenyl formate calculated at the MP2/6-311++G(d,p) level of theory depending on the dihedral angles $\alpha = \angle(C_{13}, O_{12}, C_3, C_2)$ and $\beta = \angle(H_{14}, C_{13}, O_{12}, C_3)$. The color code indicates the energy (in per cent) relative to the energetically lowest conformations with $E_{min} = -419.7514621$ Hartree (0%). The energy maximum (100%) is $E_{max} = -419.7327553$ Hartree.

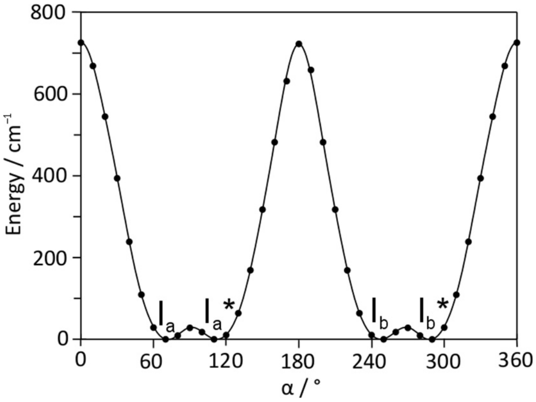

Fig. 3. A one-dimensional "cut" of the potential surface in Fig. 2 along the vertical line at β = 180° calculated by varying the dihedral angle α from 0° to 360° at a starting value of β = 180°. All molecular geometry parameters including β are optimized at the MP2/6-311++G(d,p) level of theory. The closer lying adjacent minima (with $\Delta\alpha \approx 40°$) are separated by a lower barrier of about 28 cm^{-1}, while the minima I_a/I_b and I_a^*/I_b^* (with $\Delta\alpha = 180°$) arising from the 180° rotation of the phenyl ring are separated by a higher barrier of 726 cm^{-1}.

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