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# The vibrational properties of formic acid as monomer and dimer: a DFT study

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## Abstract

The vibrational wavenumbers and force constants were calculated for the formic acid as monomer, cyclic dimer and open dimer, using DFT techniques. The existing experimental data and assignments for the monomer and cyclic dimer were confirmed by the theoretical results. These data were subsequently used in the definition of scaled quantum mechanics force fields for the three chemical species.
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*Keywords:* Formic acid; Formic acid dimers; DFT calculations; Force constants

## 1. Introduction

The vibrational properties of formic acid and of its cyclic dimer were studied many times, either experimentally [1–6] or theoretically [7–10].

As part of a series of studies on hydrogen-bonded systems, which comprised fluorosulfonic acid [11] and formamide [12], formic acid in its monomeric and associated forms was now studied using Density Functional Theory (DFT) techniques. The open dimer was included in the present study after observing some evidence about its existence in dilute solutions of formic acid in $CCl_4$ [13]. The purpose of this study is to obtain a force field for these species based on a well-founded set of experimental vibrational wavenumbers. Besides, the calculations served to check the proposed assignments for the bands observed in infrared and Raman spectra, and specially those originating in the intermonomer modes of the cyclic dimer.

## 2. Calculations

Geometry optimizations, harmonic wavenumbers for the normal modes of vibration and force fields in cartesian coordinates were calculated using the B3LYP [14,15] functional together with the 6-31G(d,p) basis set. Such combination is being used with good results for organic molecules [16] and hydrogen-bonded systems [12,17], and represent a good compromise between economy of computational resources, accuracy and applicability to many-atoms molecules. All the calculations were made with the Gaussian 98 set of programs [18].

No correction for basis set superposition error (BSSE) was applied in the calculations made for dimers. Such effect is important in the calculation of interaction energies, but seem to have no influence in the calculation of vibrational

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properties. An interesting discussion about the BSSE corrections in such calculations was made by Williams and Lowrey [7].

The harmonic force field given by the theoretical calculation was transformed to a set of natural (local symmetry) coordinates [19] through the corresponding B matrix [20], calculated with a standard program. The resulting force field was subsequently scaled using the scheme of Pulay et al. [21], in which the diagonal force constants are multiplied by scale factors $f_i$, $f_j$ and so on, and the corresponding interaction constants are multiplied by $(f_i f_j)^{1/2}$, adjusting the scale factors by means of a least squares procedure to reproduce as well as possible the experimental wavenumbers. The potential energy distribution was calculated with the resulting SQM force field.

The force field transformation, scaling and P.E.D. calculation were performed with the program FCARTP [22]. The atomic displacements given by the Gaussian 98 programs for each vibrational mode served to understand qualitatively the nature of the molecular vibrations; for that purpose, the corresponding data were represented graphically by means of the program Moldraw [23].

Atomic charges and Wiberg bond indexes [24] of the studied molecules were calculated by means of the Natural Bond Orbitals (NBO) approach [25], as implemented in the Gaussian 98 package, using also the B3LYP/6-31G(d,p) combination.

## 3. Results

### 3.1. Calculated structures

Only the trans rotamer (considering the relative location of the CH and OH bonds) of monomeric formic acid was considered in the present work, as the cis rotamer exists in a very low concentration in the gas phase. In fact, the cis/trans population ratio amounts to only $1.2 \times 10^{-3}$ [26].

Seven stable cyclic dimer structures were shown to be theoretically possible for formic acid, which include the formation of O−H···O and C−H···O hydrogen bonds [9]. However, only the cyclic dimer having two O−H···O=C hydrogen bonds was considered in the present work, as it was recognized as the most stable in experimental and theoretical studies, and the only one whose geometrical parameters were measured in the gas phase [27].

The optimized structures resulting from the calculations appear in Fig. 1, whereas the corresponding geometrical parameters are gathered in Table 1. Planar structures are predicted for the monomer and the cyclic dimer, in agreement with experiment [27]. After comparison with the experimental structural data, it can be seen that the geometrical parameters of the monomer and cyclic dimer are reasonably well reproduced, although the results are not better than those obtained with the MP2 procedure using the 6-31+G(d,p) basis set [10].

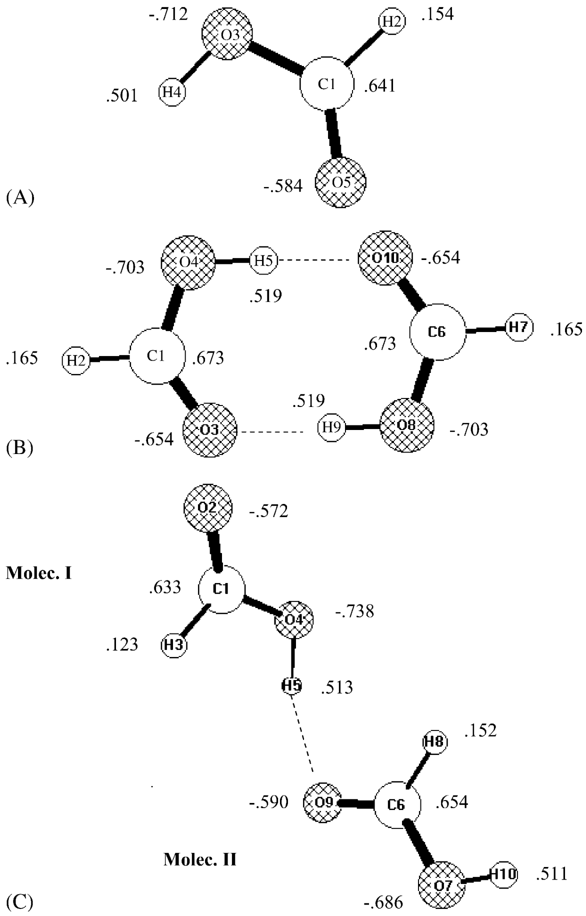

Fig. 1. The molecular structure and atomic charges of the formic acid species: (A) monomer; (B) cyclic dimer; (C) open dimer. Dashed lines represent hydrogen bonds.

The expected bond distance changes resulting from the formation of hydrogen bonds upon dimerization are clearly shown by the calculations which, for the cyclic dimer, reproduces better than in previous calculations [10] the increase of the OH distance and O−C=O angle and the decrease of the single C–O bond length. The increase of the C–O–H angle, however, is not well reproduced. The value predicted for the O···O distance is between those given by the HF and MP2 calculations in [10].

No stable dimers of formic acid having only one O−H···O hydrogen bond (open dimers) were found when each single molecule is in the trans configuration [9]. Such result was confirmed by our own calculations, which converged always to a cyclic dimer. However, similar calculations made with cis rotamers lead to a stable open dimer, as shown in Fig. 1C.

Both molecules conserve practically their planarity in the open dimer, with the respective single C–O bonds forming an angle of 141.1°. The predicted O–H (molecule I, donor) and C–O (molecule II, acceptor) bond length changes caused by hydrogen bond formation are about a fourth of the changes calculated for the cyclic dimer, showing a considerably weaker interaction. In fact, the

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