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Prediction of the Raman spectrum of the aqueous formate anion by a combined density functional theory and self-consistent-reaction-field study

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Abstract. Formate, HCOO\textsuperscript{--}, is a small ion that can be used as a convenient model to represent general carboxylic acids as well as the terminal side chains of glutamic and aspartic amino acids in biological systems. Several ab initio techniques (Hartree–Fock and density functional theory methods) were used to study the formate anion in aqueous solution, where the solvent was treated as an electrostatic influence by means of a self-consistent-reaction-field (SCRF) method. The comparison of calculated frequencies with Raman experimental data constitutes a good test for the solvation model employed in this work. The results showed that the application of a SCRF method not only produced smaller errors but also improved the linear correlation between predicted and experimental values. This latter characteristic enables a more efficient application of a linear scaling factor, \( \lambda \), which corrects the calculated frequencies. In fact, the application of \( \lambda \) to the values calculated for the continuum, when compared to those obtained for a vacuum, resulted in smaller root-mean-square errors of the deviations from the experimental data.

Key words: Formate anion – Density functional theory – Solvent effects – Continuum – Raman spectra

1 Introduction

In the recent past, density functional theory (DFT) became a really powerful theoretical tool for a wide range of chemical interests. Nowadays, DFT associates accuracy with low computational cost in such a way that it constitutes an attractive alternative to other post-Hartree–Fock (HF) procedures, such as the second-order Möller–Plesset (MP2) method [1].

In DFT, the total electronic energy of a molecular system, \( E_{\text{DFT}} \), can be written as a functional of the electron density, \( \rho \):

\[
E_{\text{DFT}}[\rho] = T[\rho] + E_{\text{xc}}[\rho] + J[\rho] + E_{\text{e}}[\rho],
\]

where \( T[\rho] \) is the kinetic energy, \( E_{\text{e}}[\rho] \) the attractive energy between nuclei and electrons, \( J[\rho] \) is the Coulomb term of the electron–electron interaction and \( E_{\text{xc}}[\rho] \) is the exchange–correlation functional, which includes an exchange energy, the largest contribution to \( E_{\text{xc}}[\rho] \) by far, and a correlation energy. It is usual to separate \( E_{\text{xc}}[\rho] \) into those two parts, a pure exchange and a correlation part:

\[
E_{\text{xc}}[\rho] = E_{\text{x}}[\rho] + E_{\text{c}}[\rho]
\]

Several functionals have been proposed for these energy terms, which can be classified roughly into three groups: the local density approximation (LDA) assumes that the density can be treated locally as a uniform electron gas, showing, therefore, a slowly varying function; the gradient-corrected or nonlocal energy functionals which benefit from the inclusion of density derivatives, allowing, in principle, a more correct description of atoms, molecules and their bonds; the hybrid functionals, which include combinations of exact exchange terms as given by the HF theory and DFT exchange–correlation functionals, the coefficients of combination being determined by appropriate fits to experimental data. Nowadays, a wide variety of functionals proposed for \( E_{\text{xc}}[\rho] \) may be found in the literature but well-established rules are still missing, which often makes the choice of a particular functional difficult.

Predictions of vibrational spectra are amongst the most important and current applications of DFT techniques since they have shown a good performance in the definition of molecular force fields. The implementation of analytical first and second derivatives has played a crucial role in such success [2]; however, the predicted frequencies have remained affected by errors owing, to a great extent, to anharmonicity effects. The observation that such errors occur approximately in a systematic way led several authors to propose different scaling procedures at semiempirical, HF and DFT levels of quantum
calculation [3, 4, 5, 6, 7, 8, 9]. These methodologies involving scaling have proved to be successful in reproducing vibrational spectra, especially for the selected set of molecules for which they have been calibrated. Transferability of the scaling factors is always a major problem, even for molecules exhibiting similar structural features. Besides, there is another source of errors—the inadequacy of the theoretical methods to include environmental effects such as the natural packing in the crystal structure, the presence of counterions in ionic substances and solvation effects when experimental data are obtained with solution samples. In fact, the great majority of chemical mechanisms, and, in particular, the processes with biological interest, do take place within a surrounding medium; therefore, its influence should not be neglected in a theoretical treatment if accurate results are desired. Among several theoretical methodologies proposed in the last two decades to describe the solvent effect at a quantum mechanical level, continuum models have shown flexibility and enough accuracy to become a popular tool [10, 11, 12, 13]. In these self-consistent-reaction-field (SCRF) solvation methods the solute is placed inside a cavity with appropriate shape, made in a continuous medium characterized by a dielectric constant. The electronic distribution of the solute induces a charge density at the surface of the cavity, which creates a field that modifies the energy and properties of the solute. The effect of the reaction field is solved iteratively in the SCRF method by the inclusion of a supplementary potential term in the solute Hamiltonian.

One of the most important agents in biological processes is the carboxylate group, which rules the interactions established by the side chains of glutamic and aspartic acids. The formate anion has been the subject of many experimental and theoretical studies, and it has also been used as a very convenient model for those terminal side chains, enabling, therefore, the theoretical study of their chemical properties [14].

As mentioned previously, the solvent affects the solute properties to a variable extent, which is not easy to quantify without the use of accurate calculations. In the present work, the solvation models employed only take into account electrostatic effects of the solvent, which are the most important interactions to be considered for a charged molecular system such as the formate anion.

The performance of several DFT functionals in reproducing Raman vibrational spectra of the formate anion in aqueous solution was evaluated in this work. The solvent effect was modeled by two SCRF solvation methods and the influence of the basis set was also considered.

2 Methods

All the calculations were based on HF and DFT methods as implemented in Gaussian98 [15]. The post-HF Møller–Plesset (MPn) methods were used also at the second, third, and fourth order of perturbation, as a reference to evaluate the ability of DFT functionals to include electronic correlation effects. As far as DFT methods are concerned, the exchange functionals, $E_x$, used in this study include Slater’s LDA [16] (abbreviated S) with an exchange scaling factor of 2/3, the $X_a$ functional, which is an older version developed by Slater (XA) [16, 17] with a different value for the exchange scale factor, Becke’s functional (B) [18], which includes a gradient correction, the functional proposed by Perdew and Wang in 1991 (PW91) [19] and the corresponding version of Adamo and Barone (MPW) [20], and finally the recent functional of Gill (G96) [21]. The correlation functionals, $E_{c}[\rho]$, considered here are the local spin density form of Vosko, Wilk and Nusair (VWN) [22], the gradient-corrected functional of Lee, Yang and Parr (LYP) [23], the local (non-gradient-corrected) functional of Perdew (PL) [24] and Perdew’s functionals with gradient corrections – versions from 1986 (P86) [25] and from 1991 with Wang (PW91) [19]. These functionals were combined to give 33 different methods: S—null, B—null and XA—null, respectively, Slater. Becke and Xa, which include only exchange functional terms to $E_x[\rho]$; and 30 exchange-plus-correlation functionals, $E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$, which were the result of the association of six exchange components S, B, Xa, PW91, MPW and G96 with five correlation terms VWN, LYP, PL, P86 and PW91. Additionally, seven hybrid methods were also tested: one using equal contributions of HF exchange and Slater exchange functional without correlation (BHandH) [26]; the same as before but with LYP correlation added (BHandHLYP) [23]; Becke’s three-parameter exchange-correlation functional with nonlocal correlation corrections provided by three different terms: Perdew’s expression (B3P86) [27], the LYP expression (B3LYP) [23, 27] and the Perdew–Wang expression (B3PW91) [25, 27]; the version proposed by Adamo and Barone of Becke’s one-parameter functional with the LYP correlation term (B1LYP) [20, 28] and their version of Becke’s one-parameter functional with modified Perdew–Wang exchange and correlation terms (MPW91PW91) [20].

The SCRF methods employed here to model the electrostatic influence of the solvent were the conductor-like solvation model approach of the polarizable continuum model (COSMO–PCM) [29] and the integral equation formulation of the PCM model (IEF–PCM [11, 13]). Therefore, the formate anion was inserted in a cavity with a shape based on interlocking spheres centered on heavy atoms C and O, as defined by the united atom model for HF [30]. This cavity was formed in a continuous medium characterized by a dielectric constant of 78.39 in order to simulate the electrostatic influence of water bulk. The SCRF methods were used at the same HF and DFT levels of those calculations previously performed for a vacuum.

The energy minimizations, both for a vacuum and for a continuum, were performed under the C2v symmetry constraints. The geometrical parameters which were allowed to be optimized are shown in Fig. 1.

The basis sets of atomic functions employed throughout this work were the split-valence 3-21G and the expanded basis set 6-311 + + G(d,p), where valence orbitals are split into three functions and a complete set of diffusion and polarization functions are added to hydrogens (s and p types) and also to other atoms (p and d types). Previous calculations made by Pope et al. [31] at the HF level have shown that good predictions of vibrational frequencies were obtained with the smaller basis set, 3-21G, for a reasonable set of neutral molecules. The authors concluded that expansion of the basis set to 6-31G(d) did not show an improvement in the calcu-

![Fig. 1. Geometrical parameters of the formate anion which were allowed to be optimized](image-url)