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Modeling the antisymmetric and symmetric stretching vibrational modes of aqueous carboxylate anions



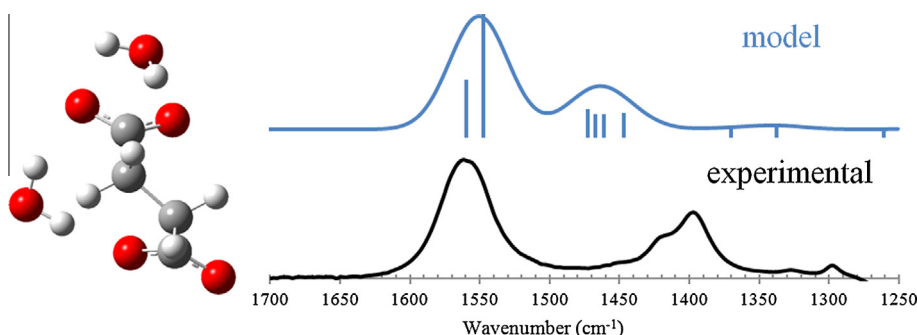
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HIGHLIGHTS

- Infrared spectra are calculated for aqueous carboxylate ions using DFT.
- Spectra for six anions from 1700 to 1250 cm^{-1} are compared with experimental data.
- Use of a continuum solvent model improves over calculations performed in vacuum.
- The effect of molecular conformation is examined and is found to be minor.
- Explicit water molecules do not significantly change the simulated spectra.

GRAPHICAL ABSTRACT



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ABSTRACT

The infrared spectra of six aqueous carboxylate anions have been calculated at the M05-2X/cc-pVTZ level of theory with the SMD solvent model, and validated against experimental data from the literature over the region of 1700 cm^{-1} to 1250 cm^{-1} ; this region corresponds to the stretching modes of the carboxylate group, and is often interrogated when probing bonding of carboxylates to other species and surfaces. The anions studied here were formate, acetate, oxalate, succinate, glutarate and citrate. For the lowest energy conformer of each anion, the carboxylate moiety antisymmetric stretching peak was predicted with a mean signed error of only 4 cm^{-1} using the SMD solvent model, while the symmetric peak was slightly overestimated. Performing calculations in vacuum and scaling was found to generally over-predict the antisymmetric vibrational frequencies and under predict the symmetric peak. Different conformers of the same anion were found to have only slightly different spectra in the studied region and the inclusion of explicit water molecules was not found to significantly change the calculated spectra when the implicit solvent model is used. Overall, the use of density functional theory in conjunction with an implicit solvent model was found to result in infra-red spectra that are the best reproduction of the features found experimentally for the aqueous carboxylate ions in the important 1700 cm^{-1} to 1250 cm^{-1} region. The development of validated model chemistries for simulating the stretching modes of aqueous carboxylate ions will be valuable for future studies that investigate how carboxylate anions complex with multivalent metal cations and related species in solution.

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Introduction

Carboxylate anions are encountered in a diverse range of situations including biological systems and pharmaceuticals, as well as in materials science and minerals processing. Carboxylate anions

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exhibit characteristic vibrational spectra in the infrared (IR) which typically includes an intense peak due to symmetric stretching of the -COO^- functional group as well as a peak due to antisymmetric stretching. When carboxylates complex with metal cations [1–4] or become adsorbed onto a surface [5–11] it has been observed that these peaks undergo shifts. Understanding these vibrational modes and how they change upon bonding can provide insight into the type of bonding that occurs. In order to model how the vibrational spectra of aqueous carboxylates change in the presence of cations or surfaces, we first require reliable means of describing the vibrational frequencies of the carboxylate anions on their own.

The theoretical determination of vibrational frequencies is a long established area of interest. In the gas phase it is common to scale theoretically calculated frequencies so as to more accurately reflect experimental results, and this approach has also been extended to solution-phase studies [12,13]. Scaling is typically achieved via the use of a fixed model chemistry dependent scaling factor [14–19], although results can also be scaled linearly with frequency [20,21] or individual modes can be scaled separately [22,23]. When extending vibrational frequency calculations to aqueous species, continuum solvation models can be incorporated [20,24–36]. As well as being sensitive to the choice of solvent description, vibrational frequencies will also be affected by the molecular conformation, which can change upon moving from the gas-phase to solution, as well as with the inclusion of explicit solvent molecules [29,33]. To our knowledge there have been few efforts to determine appropriate model chemistries for predicting vibrational frequencies of aqueous carboxylate anions taking into account the various approaches available to model the solvent.

This work investigates the vibrational spectra of six carboxylate anions modeled using both scaled gas phase calculations as well as with the SMD solvent model and validated against experimental results in the literature. The effect of different conformations and the inclusion of explicit water molecules on the calculated spectra are also examined.

Computational details

The equilibrium geometries and harmonic vibrational frequencies of six carboxylate anions were computed using density functional theory (DFT), at the M05-2X/cc-pVTZ level of theory. This model chemistry incorporates both a modern meta-GGA functional and a large (triple zeta) basis set; it was used in parameterising the SMD solvent model [37] and has been previously shown to accurately model the dissociation of aqueous carboxylic acids [38]. The anions studied here are formate, acetate, oxalate, succinate, glutarate and citrate. In order to identify different molecular conformations, systematic relaxed internal rotor scans were performed. Calculations were performed in the gas phase as well as with the SMD solvent model [37]; in both cases the anions were examined alone and in the presence of up to n explicit water molecules, where n is the number of carboxylate groups in the anion. Harmonic vibrational frequencies for the gas phase calculations are scaled by a factor of 0.9483 [15]. All vibrational modes above 1000 cm^{-1} were used to simulate IR spectra, which are presented here as both individual modes and as Gaussian convolutions with full width at half maximum of 20 cm^{-1} . This region corresponds to the location of the COO^- group antisymmetric

Formate			
	F1		
Acetate			
	A1	A2	
SMD relative Gibbs energy	0 kJ/mol	0.1 kJ/mol	
Gas phase relative Gibbs energy	0 kJ/mol	-	
Oxalate			
	O1	O4	
SMD relative Gibbs energy	0 kJ/mol	-	
Gas phase relative Gibbs energy	-	0 kJ/mol	
Succinate			
	S1	S2	S3
SMD relative Gibbs energy	0 kJ/mol	5.6 kJ/mol	11.0 kJ/mol
Gas phase relative Gibbs energy	-	0 kJ/mol	-
Glutarate			
	G1	G2	
SMD relative Gibbs energy	0 kJ/mol	6.9 kJ/mol	
Gas phase relative Gibbs energy	16.9 kJ/mol	0 kJ/mol	
Citrate			
	C1	C2	C3
SMD relative Gibbs energy	0 kJ/mol	0.3 kJ/mol	3.5 kJ/mol
Citrate			
	C4	C5	C6
Gas phase relative Gibbs energy	0 kJ/mol	8.0 kJ/mol	8.8 kJ/mol

Fig. 1. Conformations and relative energies of the carboxylates without explicit water molecules. Illustrations are from the SMD calculations, unless the conformation is only present in the gas phase.

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