Vibrational signature of thio-acetic acid and its oligomers

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In Short

- Tautomers of thioacetic acid
- Infrared signatures of monomers and oligomers
- Cluster size distribution of oligomers

Thioacetic acid exists as a tautomeric mixture of thiol and thion forms the former of which is more abundant at room temperature 1. In this regard it is different from the related acetic acid which has only one distinguishable tautomeric form. The two acids are similar in their potential to form hydrogen-bonded dimers, and possibly also higher oligomers. Similarly, clusters with water molecules can be envisaged in which one or more water molecules is hydrogen-bonded to one or two of the (thio-)acetic acid molecule(s). Thus, oligomers of varying size and composition can in principle exist.

Figure 1: *Tautomeric forms of thioacetic acid*

A versatile tool to discriminate the oligmers or clusters is infra-red spectroscopy, in combination with molecular simulations to facilitate the assignment of the experimentally obtained spectra. Figure 2 shows the infrared spectra, computed for the acetic acid and thioacetic acid in their monomeric and dimeric forms [1]. These spectra show, despite a large similarity between the monomers, not only remarkable differenes between the dimeric forms of the two acids, but also between the respective monomeric and dimeric forms. It can thus be anticipated that computation of solvated thioacetic acid, in its different oligomeric forms, gives insight into the actual composition of experimentally obtained spectra [2].

In contrast to acetic acid, dimers of thioacetic acid are not necessarily stable at ambient temperatures, i.e. they can dissociate, or partially dissociate into smaller, monomeric subunits. Since the vibrational signature of the monomer is different from the dimer, and likely also room a partially broken dimer, this process of dissociation, and also of reformation/oligomerisation, can be monitored by time-resolved IR spectroscopy. We will study the breaking/forming of oligomers both experimentally and computationally by molecular dynamics simulations of differently sized oligomers. These will give us insight into the probability distribution of the different oligomers in solution and the time scales associated to the dissociation process. Spectra computed from end states (e.g. intact dimer and two monomers) as well as possible intermediates (partially broken dimer) will allow the assignment of the, possibly only transiently appearing, IR bands in the experimental spectrum.

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More Information

[1] Ghazaleh Zamani Maimian. Computed vibrational spectra of thioacetic acid. Master Thesis, 2017. FU Berlin.

[2] Gerome Weiland. Wassersotffverbrückte thioessigsäuren: Aufbau und Durchführung von femtosekunden IR pump-probe messungen. Diploma Thesis, 2012. FU Berlin.

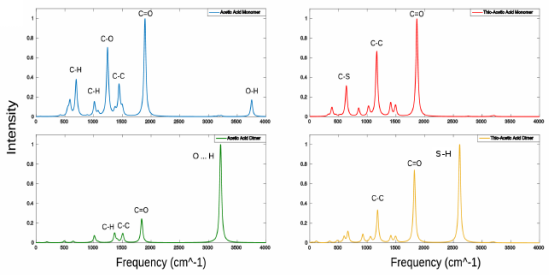

Figure 2: *Infrared spectra from acetic acid and thioacetic acid computed by a normal mode approxmation in vacuum.*