

# Structural Motives of Acetic Acid from Ultrafast CARS Spectroscopy of the CO Vibration

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**Abstract:** The carbonyl vibration of acetic acid is analyzed by spontaneous and ultrafast coherent anti-Stokes Raman spectroscopy. The complex band is decomposed into four contributions from different structural motives and the cyclic dimer signature is extracted.

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## 1. Introduction

The physical properties of molecules are intimately connected to their structures. Molecular structures in gaseous and crystalline phases are typically well characterized since in the first case the molecules are isolated and in the second case diffraction methods provide detailed information. In liquids the situation is more complicated due to disorder and the possible coexistence of different local structural motives. Hydrogen bonds (HBs) play a decisive role for the molecular network of many liquids. HBs are local and directed interactions which lead to the formation of complexes. Especially, if several HB donor and acceptor sites are present different structural motives can appear. Acetic acid (AA) exhibits two acceptor sites, the carbonyl and the hydroxyl oxygen, and four donor sites, the hydroxyl and methyl hydrogen atoms. The structure of liquid AA is still under debate. In detail, linear chain oligomers and cyclic dimers are discussed to be the predominate molecular aggregates. Since the carbonyl stretch vibration is involved in hydrogen bonding it is a good probe for the local structure of AA.

We report in this contribution a comparison of spontaneous Raman measurements with time and frequency resolved ultrafast coherent anti-Stokes Raman spectroscopy (CARS). Spontaneous Raman probes the static time averaged CO vibration and dephasing as well as static vibrational distributions are encoded in the line width of the Raman resonance. In CARS the pump and Stokes pulse stimulate a coherent excitation of a vibration. A time delayed probe pulse with a duration of ca. 1 ps scatters off this driven vibration. Mapping the coherence decay with the narrowband probe pulse allows the determination of dephasing times with an intrinsic spectral resolution defined by the spectral width of the probe [1]. Under these conditions strongly dephasing contributions fade out very fast and slowly dephasing vibrational modes persists longer and can be observed separated from other contributions.

## 2. CO vibration of neat acetic acid

The spontaneous Raman spectrum of CO reveals three clear features (Fig. 1a). Nakabayashi et al. assigned all components to vibrations originating from a linear chain aggregate [2]. This assignment is not intuitive at first glance since the most stable structure formed by two monomers is the cyclic dimer and not the dimer from which the

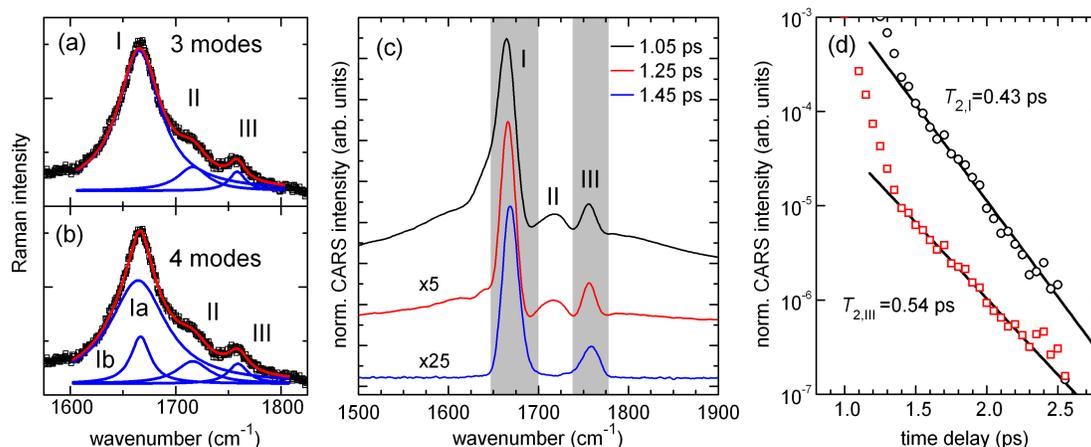


Fig. 1. Raman and CARS measurements of the carbonyl stretch vibration of neat acetic acid. Decomposition of the Raman spectrum by three and four contributions are shown in (a) and (b), respectively. (c) Selected CARS spectra showing the passage from the cross correlation region to time delays after temporal pulse overlap. The decays of the two remaining slow dephasing signals are fitted with mono exponentials (d).

linear chain can be constructed. E.g. D'Amico et al. used for analyzing the CO vibrational band an additional mode which is caused by the cyclic dimer contribution [3]. From the spontaneous Raman spectrum no clear statement can be made with respect to the number of modes, since a reconstruction with three as well as four modes mirrors the essential shape of the spectrum. Probing the carbonyl vibration with time resolved CARS gives additional insight into the interpretation of this band since it discriminates the vibrational contributions in the time domain. Sub-50 fs Stokes pulses at 570 nm and 0.7 ps long pump and probe pulses at 510 nm are focused into a 2 mm thick sample cell applying a phase matched boxcars geometry and the resulting CARS signal is spectrally dispersed detected by a CCD camera. After the cross correlation two distinct modes are observed in the CARS spectra (Fig. 1c). The higher frequency mode corresponds according to its center frequency as well as the dephasing time (Fig. 1d) to mode III in the linear Raman spectrum. The lower frequency contribution is located within the broad band I but the dephasing constant determined from the decay of the CARS signal corresponds to a line width only half as large as the Raman line width. This leads to the conclusion that band I has to be interpreted as a superposition of two independent contributions most likely originating from different aggregation structures.

### 3. CO vibration in diluted acetic acid

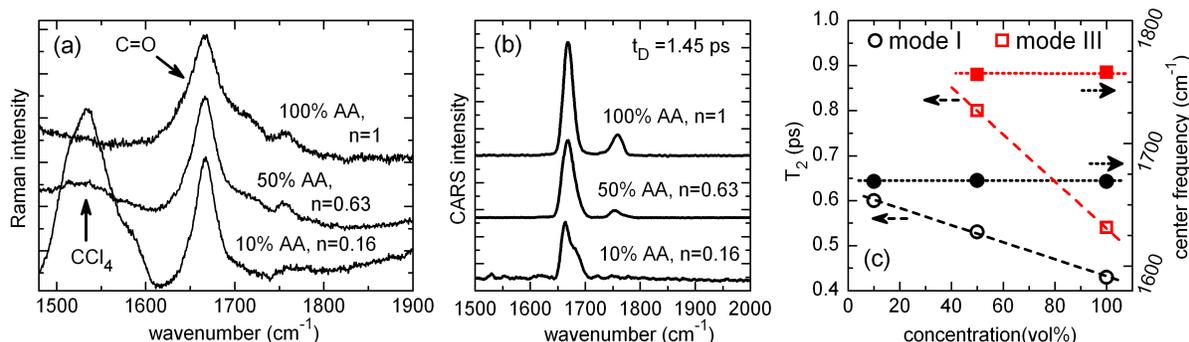


Fig. 2. (a) Raman and (b) CARS spectra after cross correlation of the carbonyl stretch region of acetic acid –  $\text{CCl}_4$  mixtures, (c) dephasing constants  $T_2$  and center frequencies of the slowly dephasing CO stretch vibrations extracted from CARS measurements.

The assignment of the modes can be clarified by concentration dependent measurements. The Raman spectrum of AA in the unpolar  $\text{CCl}_4$  shows a systematic change with decaying AA content towards a spectrum with a single remaining, rather narrow band located at approx.  $1668 \text{ cm}^{-1}$  (see spectrum 10 vol% AA in  $\text{CCl}_4$  in Fig. 2a). In unpolar organic solvents AA forms at low concentrations cyclic dimers. They exhibit two equally strong HBs and for symmetry reasons a single Raman active mode in the relevant part of the spectrum to which the band at  $1668 \text{ cm}^{-1}$  is assigned. In CARS measurements of diluted AA also only one strong contribution can be observed located at the same frequency and with a dephasing time of 0.6 ps (Fig. 2b). Figure 2c shows the concentration dependent frequencies and dephasing constants found by CARS for different concentrations. Since the center frequencies do not vary and the dephasing time shows a linear behavior with respect to the concentration the mode has to be assigned to the same vibration in all discussed samples, i.e. to the cyclic dimer. This in turn means that in neat AA the cyclic dimer can be clearly separated from other contributions by ultrafast CARS with time delayed probe pulses.

### 4. Conclusion and prospects

We performed CARS measurements with ultrafast excitation and picosecond probe pulses on AA. The technique allows separating a distinct feature, which is caused in this case by the cyclic dimer, from other, overlapping vibrational contributions. The discrimination between signals from different structural motives is based on exploiting the difference in dephasing constants. This observation opens the possibility to detect a certain structural configuration in a mixture of existing structures with high time resolution. Especially, it should also be possible to watch the reformation of a HB network after a strong perturbation.

### References

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