Ion-Induced Reorientation and Distribution of Pentanone in the Air-Water Boundary Layer

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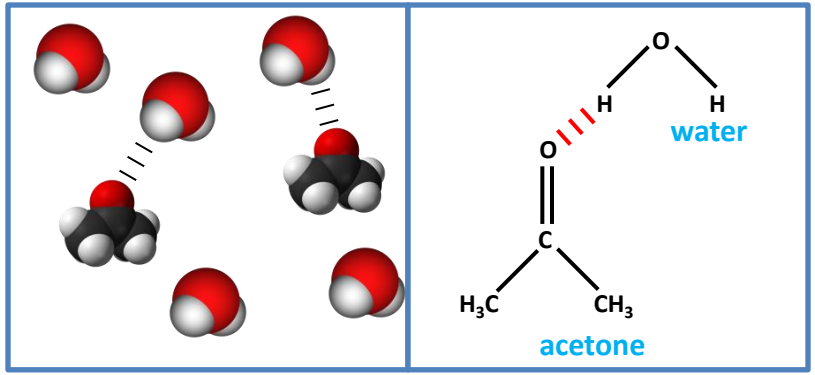
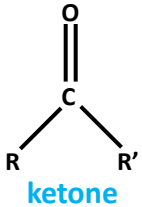
Surface effects in water

- Molecules of acetone in water



- Acetones - the simplest ketone

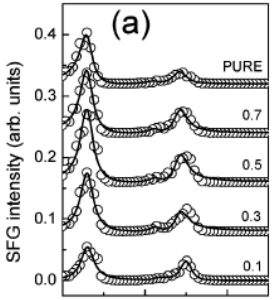


the surface of pure liquids vs the surfaces of mixed liquids

the surface concentration of the alcohol is higher than the bulk concentration (Gibbs surface excess)

the SFG signals from the water–acetone mixtures were larger than those from pure liquids (Chen H, Gan W, Wu BH, Wu D, Guo Y, Wang HF., J Phys Chem B. 2005)

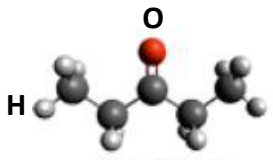
the SF signal from the surface of alcohol–water mixtures in the CH-stretch vibration region was larger at low intermediate concentrations than that from pure alcohol - - enhancement is mainly due to the surface number density of alcohol molecules contributing to SFG (Jaeho Sung , Kyungsu Park , Doseok Kim, J. Phys. Chem. B, 2005)



Overview

- **Atmospheric ketones (adsorption on aerosols). An important problem for humanity drinking water.**

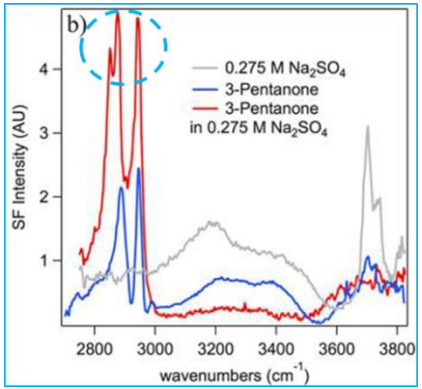
- **Detection of 3-pentanone molecule conformations at the air-water interface with VSFG.**



- **Modification of vibrational modes with solvated ions (a new vibrational mode is seen exclusively for Na_2SO_4).**

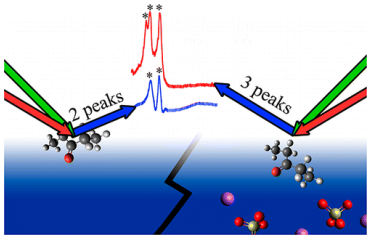
Introduction

- VSF detect changes in the CH, C=O, and OH vibrational stretching responses from 3-pentanone and water as they were affected by the presence of inorganic ions.
- The ions (NaCl, Na_2SO_4, and Na_2CO_3) all contain the sodium cation
- Theoretical calculations to explain the additional vibrational mode for 3-pentanone in Na_2SO_4 solution.



Experimental details

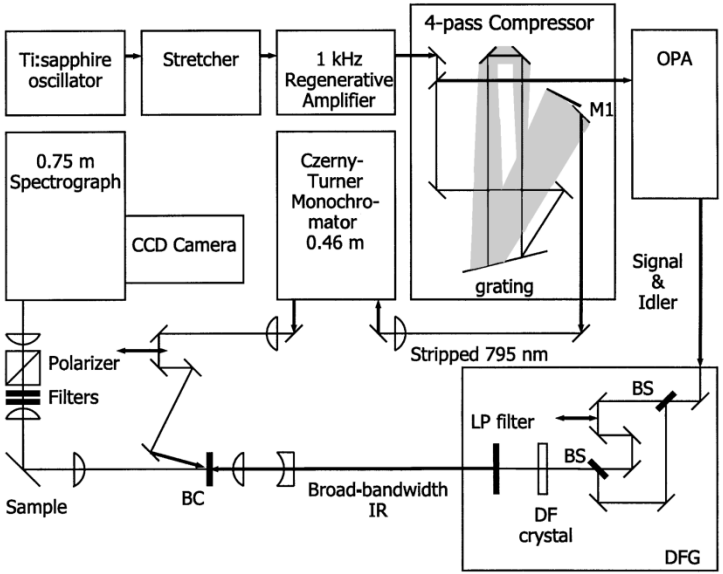
VSFG



The first system for CO region (~1700 cm^{-1})

A second experimental setup for CH (CH_2,CH_3) region (~2900 cm^{-1})

The SSP polarization (SPS polarization was not insufficient signal)



SFG from the water vs 3-pentanone in water

- The energy of O–D vibrational modes is red-shifted from the O–H
- CH vibrational modes are the same as those seen in the VSF spectrum of neat 3-pentanone (Fig.1c)

Free OH

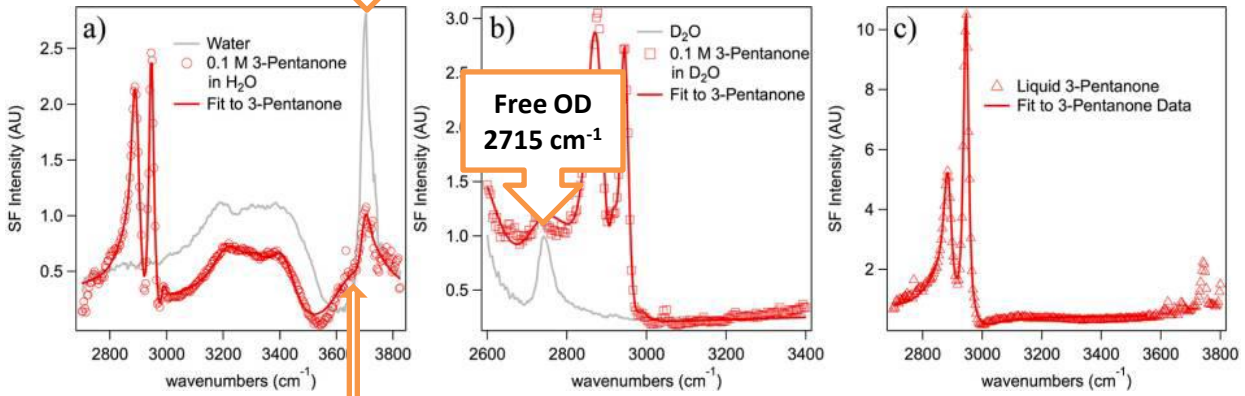


Figure 1. VSF spectra of 3-pentanone (a) in H_2O, (b) in D_2O, and (c) as neat liquid. Spectra were obtained in the SSP polarization scheme. In panel a, the gray trace is the VSF spectrum of neat water for comparison. In panel b, the gray trace is the VSF spectrum of neat D_2O.

Peak from topmost water molecules at 3632 cm^{-1}

Changes in spectrum after adding inorganic salts

The anions of the salts produce electrolyte with strong electric fields that may influence the vibrational modes of 3-pentanone molecules (CO; C=H (CH_2,CH_3))

The peak due ti the asymmetry of a molecule (Fig.2b)

No significant changes with NaCl

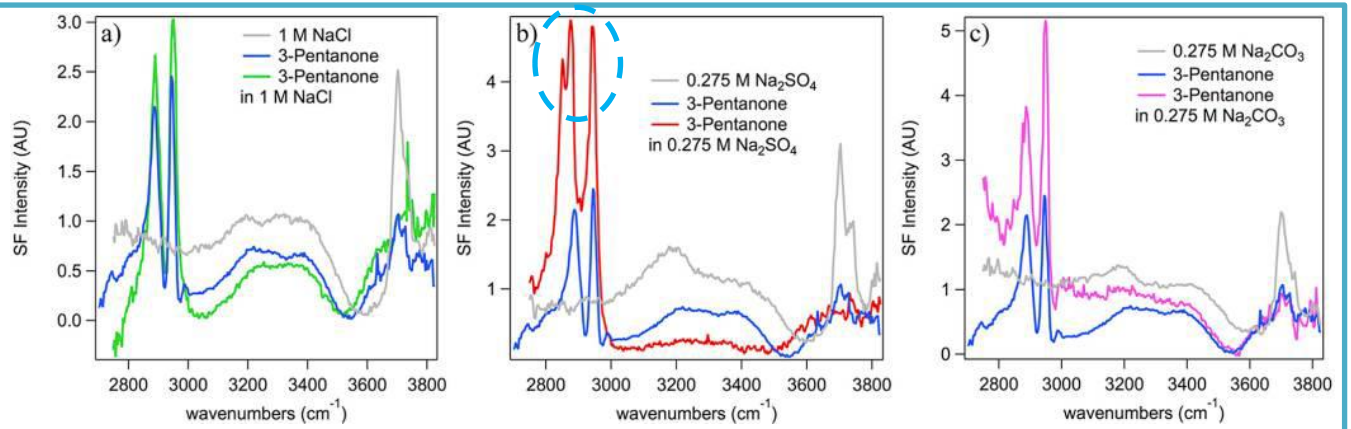


Figure 2. VSF spectra of 3-pentanone in (a) 1 M NaCl solution, (b) 0.275 M Na_2SO_4 solution, and (c) 0.275 M Na_2CO_3 solution. In each panel, the gray trace is the neat-water spectrum; the blue trace is the VSF spectrum of 0.1 M 3-pentanone in water, for reference. All data were recorded in the SSP polarization scheme.

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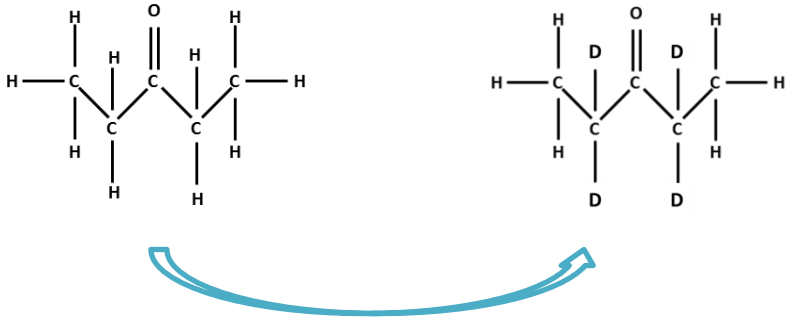
3-pentanone vs 3-pentanone-d_4 in D_2O



3-pentanone

3-pentanone-d_4
[$CH_3CD_2C(=O)CD_2CH_3$]

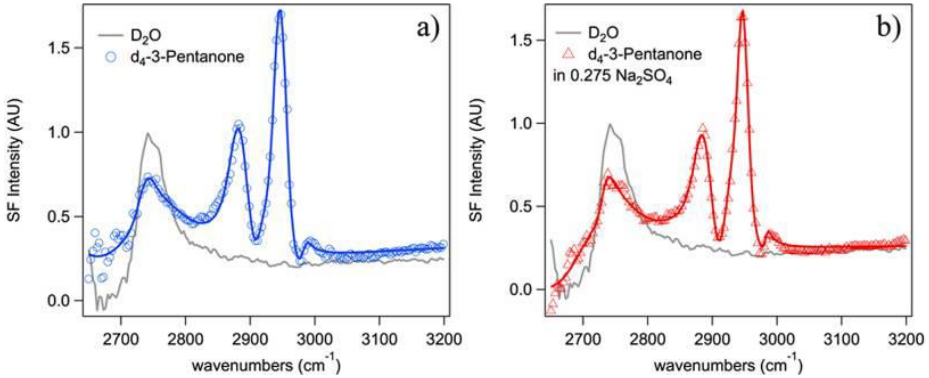


Figure 3. VSF spectra of 0.1 M 3-pentanone-d_4 in (a) D_2O and (b) 0.275 M Na_2SO_4 solution in D_2O. The data are represented by symbols, and the solid lines are the results of spectral fitting. In each panel, the gray trace is the neat-D_2O spectrum for comparison.

asymmetric vibrational mode in the molecule in the methylene part

C=O Vibrational Stretching Mode

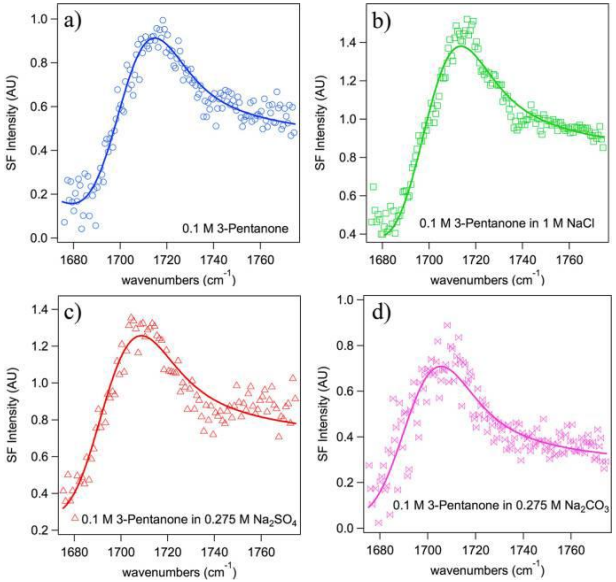


Figure 4. VSF spectra of the carbonyl vibrational stretching mode of 0.1 M 3-pentanone in (a) H_2O, (b) 1 M NaCl solution, (c) 0.275 M Na2SO4 solution, and (d) 0.275 M Na_2CO_3 solution. The data are presented as symbols, and the solid lines represent the spectral fits. All data were recorded in the SSP polarization scheme.

The C=O stretching peak relatively unchanged

Types of conformers

Classical molecular dynamics (MD) calculations is the method of analyses of molecule distribution or density of molecules, forces between molecules.

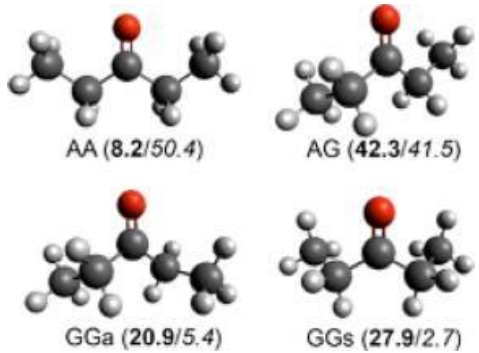


Figure 5. Representations of the conformers of 3-pentanone found by DFT calculations. The 1st numbers in the brackets below each structure is the percentage of structures with this conformation in the MD simulations of 3-pentanone in water. The 2nd numbers in the brackets – is in the gas-phase.

several unique types of conformers

Calculated Structures and Spectra of 3-Pentanone

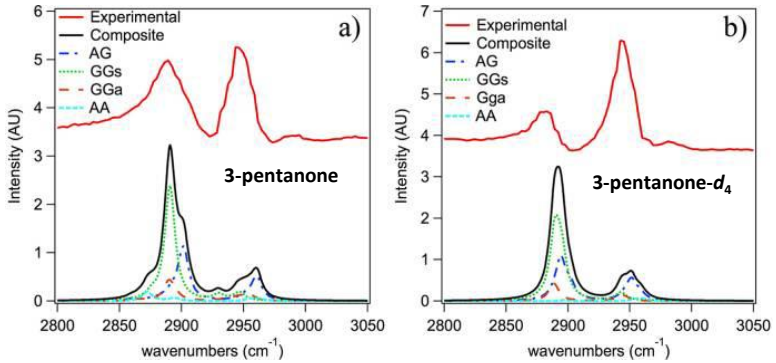


Figure 6. Comparison of the modeled spectrum (lower black trace) with the observed VSF spectrum (red top trace) for (a) 3-pentanone and (b) 3-pentanone-d_4. The black solid trace represents the composite spectrum of all observed conformers and their relative populations. The spectra resulting from the individual conformers are presented underneath the black trace.

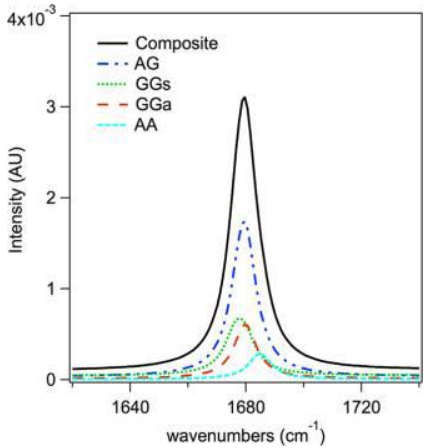
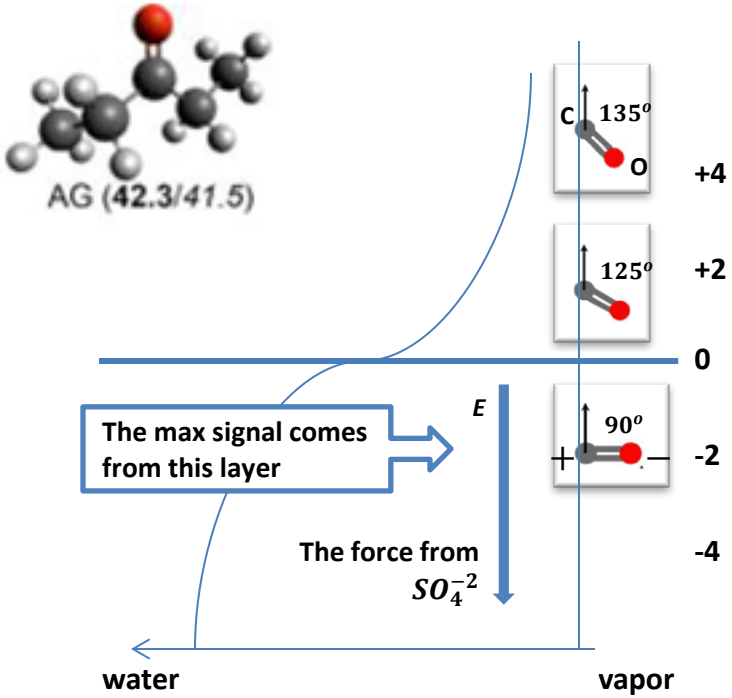


Figure 7. Calculated VSF spectrum in the carbonyl vibrational stretching region for 0.1 M 3-pentanone in water. The black trace represents the composite of the various conformers and their relative populations. The contributions from the individual conformers are also presented.

Computational Analysis of 3-Pentanone in Water and Na_2SO_4 Solution



To investigate how the spectrum is expected to change in both the CH and CO stretching regions with the proposed reorientation, the *YYZ* $\chi_{NL}^{(2)}$ tensor element was calculated as a function of orientational angle. This was done for the carbonyl stretching mode and the methylene symmetric stretching mode of the AG conformer.

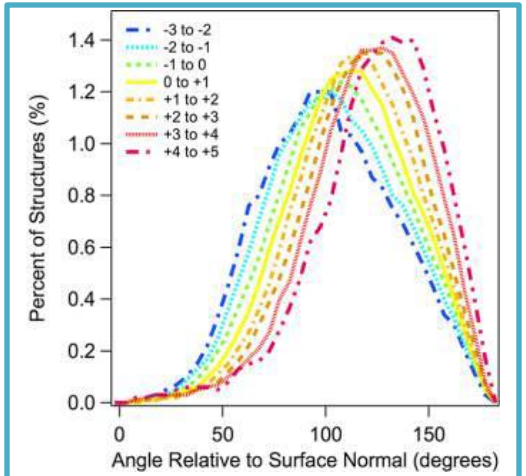
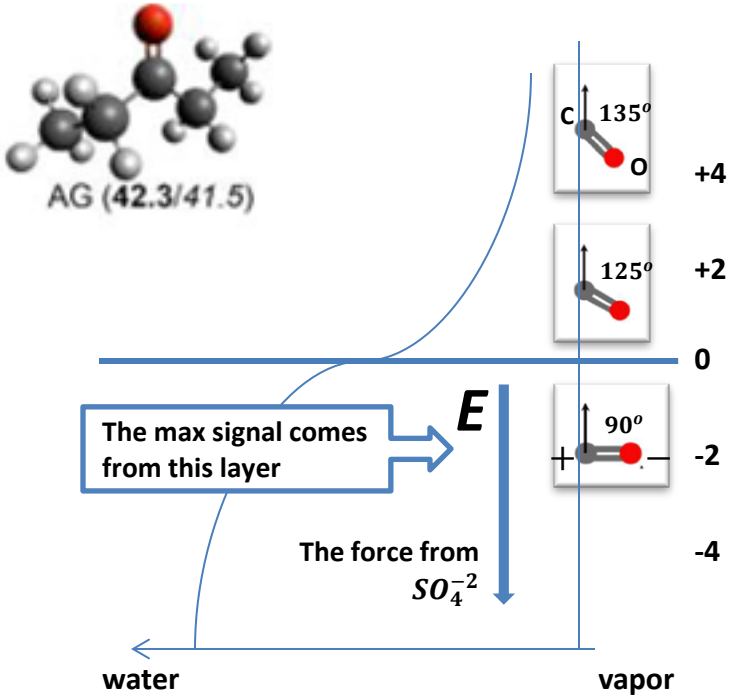


Figure 8. Calculated distribution of the carbonyl angle relative to the surface normal at various depths. An angle of 90° relative to the surface normal corresponds to the C=O in plane with the water surface.

Computational Analysis of 3-Pentanone in Water and Na_2SO_4 Solution



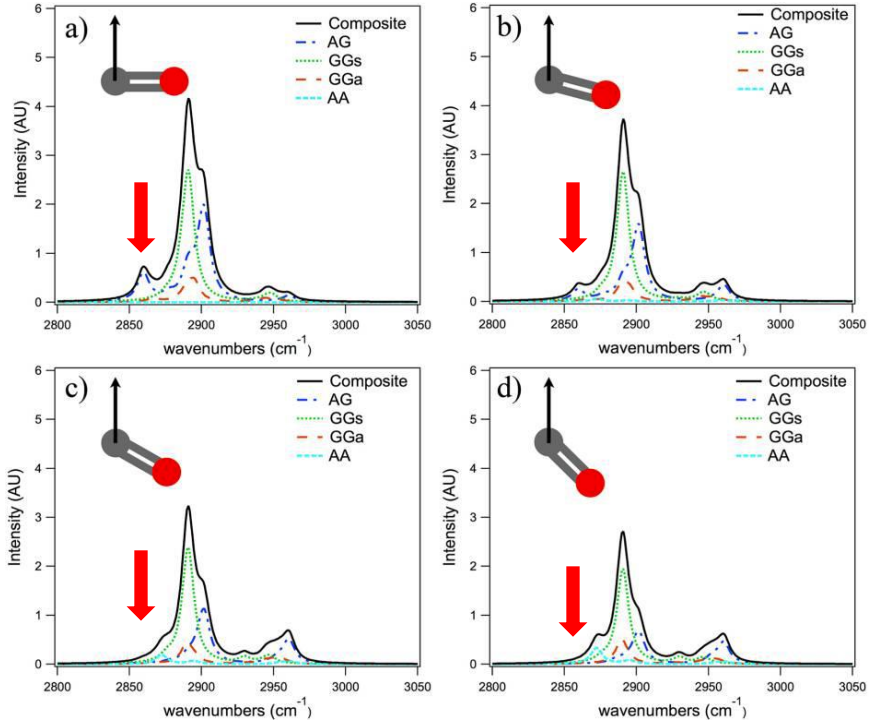
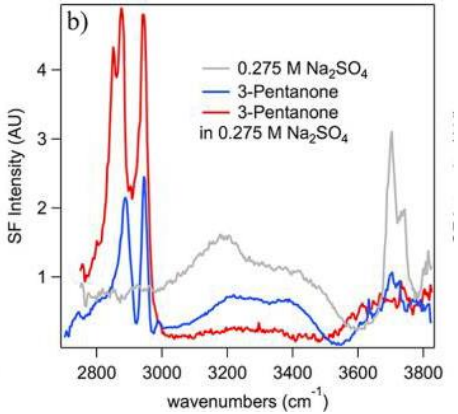
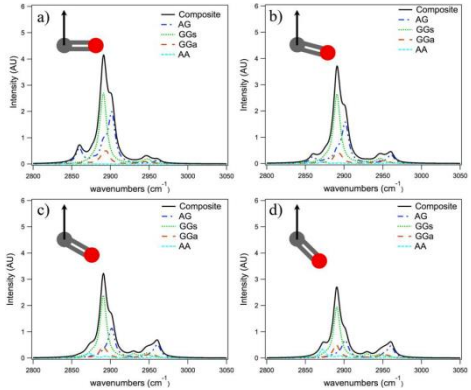


Figure 9. Calculated spectra of 3-pentanone in the CH vibrational mode region at various angles of the carbonyl group: (a) 90° (carbonyl in plane with the surface), (b) 105°, (c) 120°, and (d) 135°. The black trace is a composite of the individual conformers, and the contributions from each conformer are also presented.

Conclusions





In atmospheric waters, the presence of sulfate is common and likely to cause a similar effect, thus causing polar organic molecules to reside deeper in the interface. Although we are able to observe this behavior for 3-pentanone only because of its unique properties, we expect this to be a general phenomenon.