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Hydrogen bond and surface stress relaxation by aldehydic and formic acidic molecular solvation

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ABSTRACT

Solvation of aldehydes and formic acids has an important impact to health care because these additives can damage DNA and denature proteins causing cancers with the mechanism behind remaining great challenge. From the perspective of solvent hydrogen bond (O:H—O or HB with ":" being the electron lone pair of oxygen) transition from the mode of the ordinary water to the hydrating states, we examined the solvation bonding dynamics and the solute capabilities of O:H—O bond and surface stress transition using differential Raman spectroscopy and contact angle detection. Results suggest that besides the short-range O:H van der Waals (vdW) bond, the H ↔ H and O: ⟺ :O repulsive intermolecular interactions, and the molecular dipolar polarization play important roles in disrupting the solution network and surface stress. Observations may infer the manner of DNA fragmentation by aldehyde and formic acid disruption.

1. Introduction

Aldehydes are the most common indoor pollutants that are harmful to our health. Characterized by a wide range of sources, high level, toxicity, and long duration, aldehydes have been recognized as key factors of cancer development. As an indoor pollutant, aldehyde contamination causes damage of the DNA-protein cross-linking and binding to form adducts [1,2]. Formaldehyde and acetaldehyde adsorption damages the DNA of human peripheral blood lymphocytes [3,4]. Likewise, formic acids play an important role in biomedical and cosmetic applications [5]. Oral administration of concentrated acetic acid can corrode the mouth and cause oral mucosa, esophageal and gastric mucosal damage, and even lead to gastric perforation [6]. Once the acetic acid is absorbed by human body, hemolysis, acute renal failure, acute liver failure, disseminated intravascular coagulation and circulatory shock may occur [7,8]. There are numerous applications of propionic acid in the food and chemical industries, such as a food preservative and as a component in plasticizers, perfumes and pharmaceuticals [9,10]. Current research is mainly focused on the possible mechanism of DNA breakage and binding. Molecular scale understanding of DNA-aldehyde and aldehyde-aldehyde interactions and the functionalities of formic acids remains a challenge.

From the perspective of solvent hydrogen bond transition from the mode of the ordinary water to the hydrating states and the solution surface stress, we examined the solvation dynamics and the solute capabilities of aldehydes and formic acids using differential Raman spectroscopy and contact angle detection. Results suggest that beside the short-range O:H vdW bond, H ↔ H and O: ⟺ :O repulsive interactions, molecular dipolar interaction plays an important role in disrupting the solution network and surface stress.

2. Principles

2.1. Hydrogen bond (O:H—O) cooperativity

Solvation of organic crystal dissolves the crystal into individual molecular dipoles surrounded with protons H^+ or electron lone pairs ":" pertained to O anions. The molecular H^+ and ":" interact with their alike or unlike of the solvent H_2O to form the O:H vdW bond, H ↔ H anti-HB or O: ⟺ :O super-HB repulsive interactions, as they do in solutions of acid, base, and salt [11–13]. An addition of excessive H^+ or electron lone pair ":" will form the inter-proton and inter-lone-pair interaction, which called the H ↔ H anti-HB or O: ⟺ :O super-HB, accordingly. The O:H—O bonds in the hydration shells, or solute –solvent interface, relax cooperatively, which govern the performance of the solution such as the surface stress, solution temperature, and the critical pressures and temperatures for phase transition [13].

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Table 1
O:H—O segmental cooperative relaxation in length, vibration frequency, and surface stress with respect to $d_{L0} = 1.6946$ Å, $d_{H0} = 1.0004$ Å, $\omega_{H0} = 3200\ cm^{-1}$, $\omega_{L0} = 200\ cm^{-1}$, $\gamma_s = 72.5$ mN/m at 277 K upon excitation by heating, compression, molecular undercoordination (skin, cluster, droplet, nanobubble) and acid, base, salt, alcohol solvation [15,16].[a]

		Δd_H	$\Delta\omega_H$	Δd_L	$\Delta\omega_L$	$\Delta\gamma_s$	Remark	Ref
Liquid water	Heating	<0	>0	>0	<0	<0	d_L elongation; d_H contraction; fluctuation	[17]
	Under-coordination					>0	d_H contraction; d_L elongation; polarization; supersolidity	[18]
	Compression	>0	<0	<0	>0	–	d_L compression; d_H elongation	[13]
Aqueous solution	YX salt	<0	>0	>0	<0	>0	Y^+ and X^- polarization	[19–21]
	HX acidic					<0	H ↔ H fragilization; X^- polarization	[11]
	YOH basic	>0	>0	>0	>0	>0	O: ⟺ :O compression; Y^+ polarization; solute H—O contraction	[12]
		<0	<0	<0	<0			
	Alcohol	>0	<0	>0	<0	–	Intermolecular interaction; solute dipolar induction	[22]

[a] X = F, Cl, Br, I; Y = Li, Na, K, Rb, Cs.

Therefore, one needs to understand the O:H—O bonds transition from the vibration mode of ordinary water to the hydrating states in terms of their stiffness (frequency shift) and number fraction (phonon abundance). The O:H—O bond consists the weaker O:H intermolecular (in terms of bond energy and vibration frequency: ~0.1 eV; ~200 cm^{-1}) and the stronger H—O intramolecular (~4.0 eV; 3200 cm^{-1}) short-range interactions. The Coulomb repulsion between electron pairs on adjacent oxygen ions couples the O:H—O bond and ensures its cooperative relaxation in segmental length and vibration frequency [14] as summarized in Table 1. As a consequence of O:H—O bond relaxation and electron polarization or depolarization, the solution surface stress varies with solute concentration and external excitation compared with the standard situation of water at 277 K [15,16].

As a strongly correlated and fluctuating system, water prefers the statistic mean of the tetrahedrally-coordinated, two-phase structure in a bulk-skin or a core-shell manner of the same geometry but different O:H—O bond lengths. The O:H vdW bond and the H—O bond segmental disparity and the O—O coupling allow the segmented O:H—O bond to relax oppositely – an external stimulus dislocates both O ions in the same direction but by different amounts. The softer O:H vdW bond always relaxes more than the stiffer H—O bond with respect to the H^+ coordination origin. The ∠O:H—O containing angle θ relaxation contributes only to the geometry and mass density. The O:H—O bond bending has its specific vibration mode that does not interfere the H—O and the O:H stretching vibrations [20].

2.2. Differential phonon spectrometrics (DPS)

The Raman spectroscopy provides a powerful tool monitoring the O:H—O bonding dynamics with high precision. A Raman spectral peak features the Fourier transformation of all bonds vibrating in the same frequency from the real space, irrespective of their locations or orientations in the liquid, solid, or vapor phase of the same substance. One can only probe the statistic mean of the vibrations and its fluctuation excited by external stimuli. The spectral peak frequencies correspond to the respective bond stiffness and the peak area to the abundance that is proportional to the number of bonds contributed [15]. The frequency shift $\Delta\omega_x$ represents, in the first order approximation, the stiffness of the O:H vdW bond stretching vibration and H—O cooperative relaxation as a function of the segmental length d_x and energy E_x [23],

$$\Delta\omega_x \propto \sqrt{E_x/\mu_x}/d_x \propto \sqrt{(k_x + k_c)/\mu_x} \tag{1}$$

The subscript $x = L$ denotes the O:H vdW characterized by the stretching vibration frequency at ~200 cm^{-1} and $x = H$ denotes the H—O bond with characteristic phonon frequency of ~3200 cm^{-1} in the bulk water. The k_x and k_C are the force constants or the second differentials of the intra/inter molecular interaction and O—O Coulomb coupling potentials. The k_C is the coupling by O—O repulsion. The $\Delta\omega_x$ also varies with the reduced mass μ_x of the specific x oscillator. However, from the O:H—O bond Raman spectra, one could hardly be able to gain quantitative information on the transition of the stiffness, fraction, and fluctuation order of bonds by solvation.

Compared with the convention of Gaussian decomposition, the differential phonon spectrometrology (DPS) [24,25] merely purifies the transition of the phonon stiffness (frequency shift), abundance (peak area), and fluctuation order (linewidth) by differencing the spectra collected from water before and after solvation upon all spectra peak areas being normalized. To gain quantitative information on the number fraction of O:H—O bonds transiting from water to the hydration shells, one can integrate phonon abundance gain or the DPS peak area, called the fraction coefficient for the specific x peak as a function of solute concentration C,

$$f_x(C) = \int_{\omega_m}^{\omega_M} \left[\frac{I_{solution}(C,\omega)}{\int_{\omega_m}^{\omega_M} I_{solution}(C,\omega)d\omega} - \frac{I_{H_2O}(0,\omega)}{\int_{\omega_m}^{\omega_M} I_{H_2O}(0,\omega)d\omega} \right] d\omega. \tag{2}$$

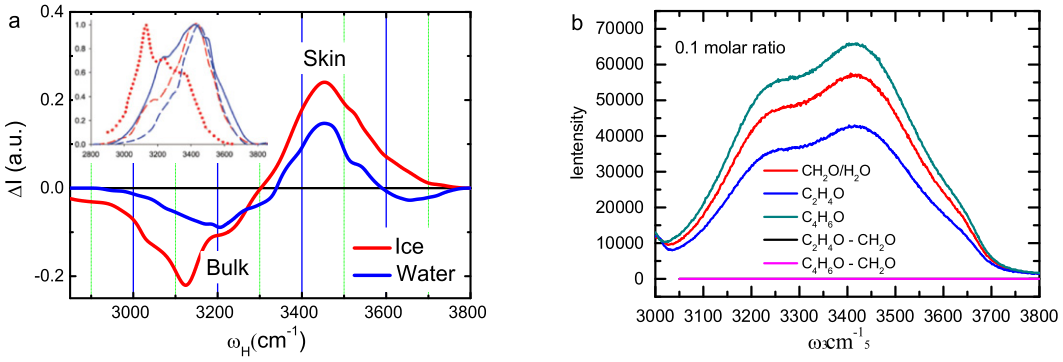

Fig. 1. Illustration of the (a) DPS process [29] for the raw spectra (inset) measured from water and ice skin [28]. (b) The minimization of the "'artefacts' of detection" by spectral peak area normalization. The DPS peak area integration features the fraction and the frequency shift features the bond stiffness transition from the ordinary H—O bond vibration mode (valley) to the mode of hydration shell (peak). The raw spectra for aldehydes solvation resolve the significant reflectivity but the DPS minimizes this effect.