

Supporting Information

Impact of Specific Interactions Among Reactive Surface Intermediates and Confined Water on Epoxidation Catalysis and Adsorption in Lewis Acid Zeolites

Daniel T. Bregante[‡] and David W. Flaherty^{‡,*}

*[‡]Department of Chemical and Biomolecular Engineering
University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA*

*Corresponding Author

Phone: +1 217-244-2816

Email: dwflhrt@illinois.edu

S1.0 Catalyst Characterization

S1.1 X-Ray Diffraction to Confirm Zeolite Framework

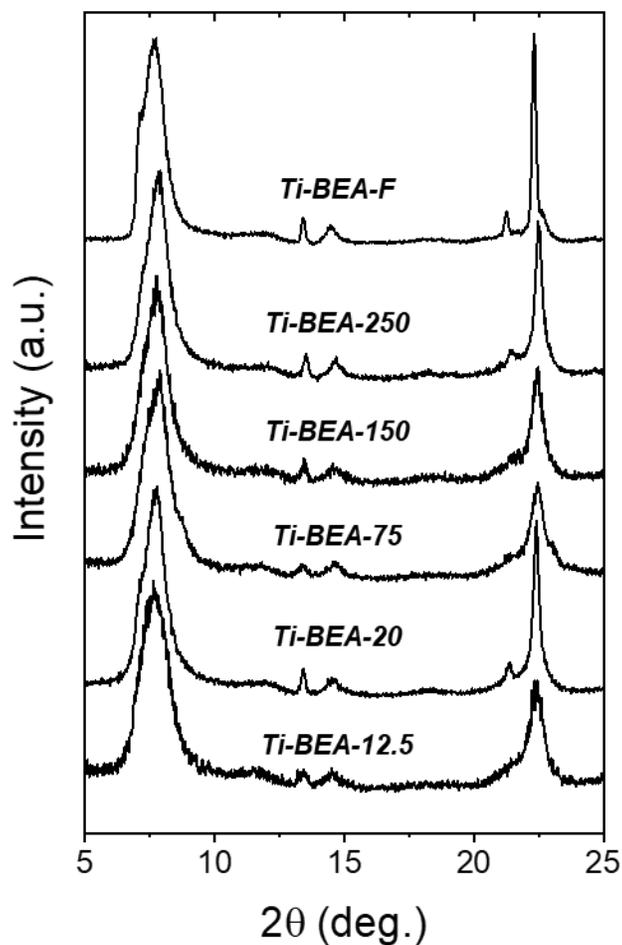


Figure S1. X-ray diffractograms for Ti-BEA used within this study. Diffractograms are vertically offset for clarity.

Figure S1 shows X-ray diffractograms for all Ti-BEA contain diffraction features that are characteristic of the *BEA framework. Notably the sharpness in the features within the diffractogram for Ti-BEA-F is indicative of the high crystallinity of this sample. All other Ti-BEA contain broadening within the diffractogram features that are associated with the presence of internal defects that form upon dealumination with HNO_3 .

S1.2 Diffuse Reflectance UV-Vis to Infer Dispersion of Ti Atoms

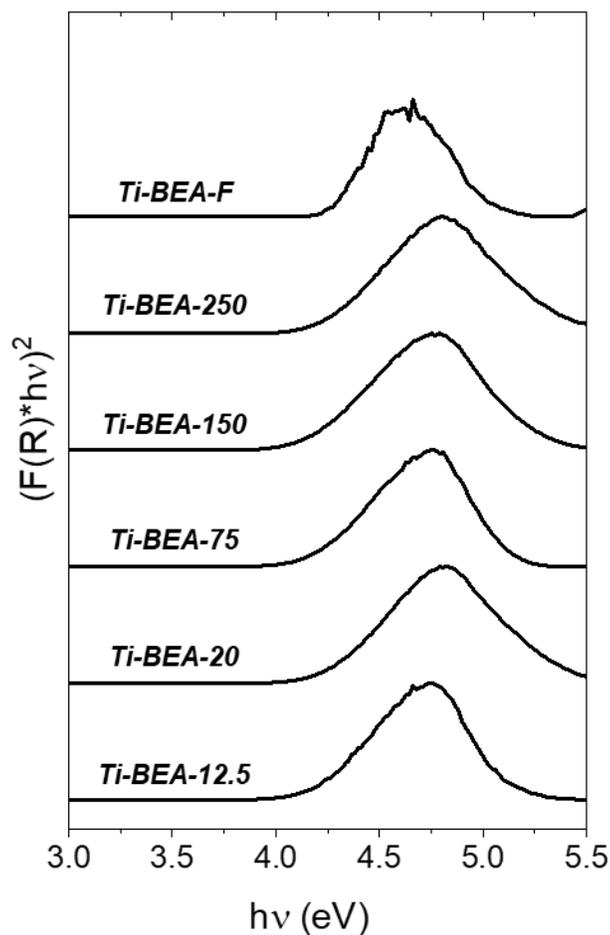


Figure S2. Tauc plots for all Ti-BEA used within this study. Spectra are normalized to the feature at ~ 4.6 eV and are vertically offset for clarity.

Figure S2 shows that all Ti-BEA contain a single UV-vis absorbance feature with a peak near 4.6 eV. The leading edge of this feature was used to determine the bandgap of each Ti-BEA. In all cases, the measured band gaps are similar (4.2 – 4.3 eV) and significantly greater than that of bulk TiO_2 (3.2 eV), which suggests that the Ti atoms in each of these materials is highly disperse and that these materials do not contain spectroscopically-observable bulk or oligomeric TiO_2 .

S1.3 Gas-Phase Infrared Characterization of Ti-BEA-X to Discriminate Differences in $(\text{SiOH})_4$ Density

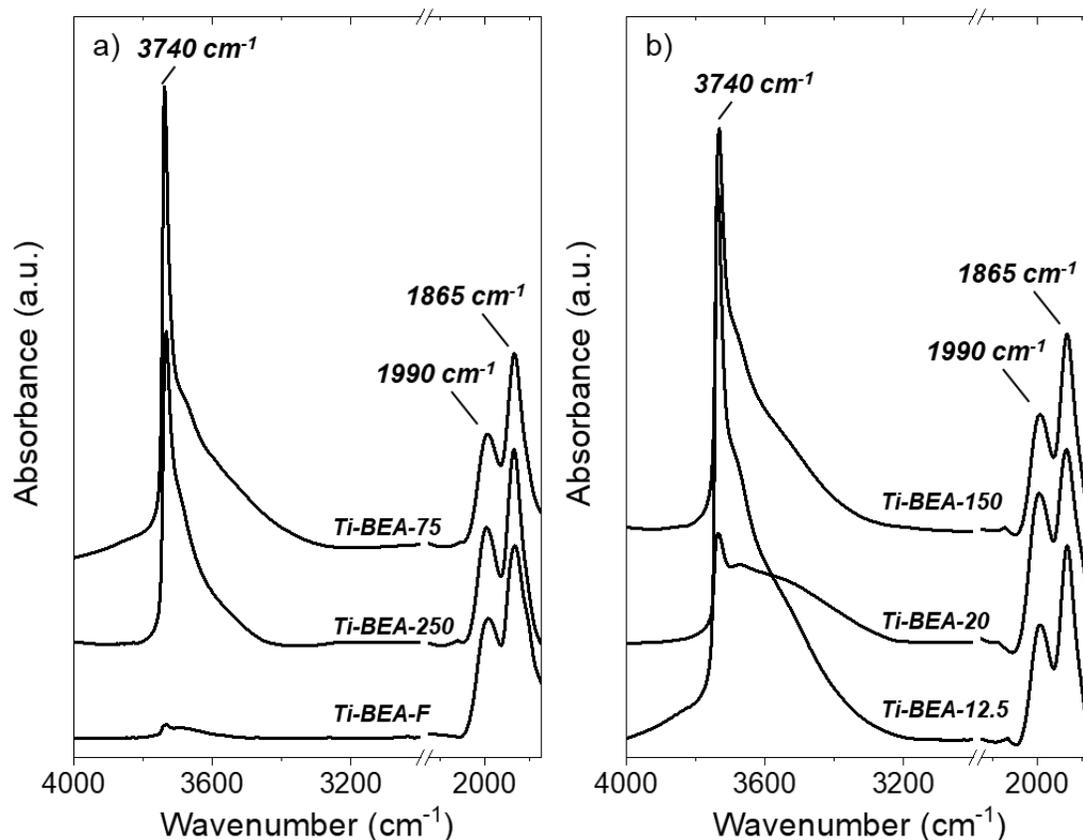


Figure S3. Infrared spectra of dehydrated (a) Ti-BEA-75, Ti-BEA-250, and Ti-BEA-F, and (b) Ti-BEA-12.5, Ti-BEA-20, and Ti-BEA-150. All Ti-BEA were dehydrated *in situ* under flowing He ($50 \text{ cm}^3 \text{ min}^{-1}$) for 3 h at 573 K prior to measurement. Spectra were normalized to the absorbance feature at 1865 cm^{-1} corresponding to $\nu(\text{Si-O-Si})$ overtones (1865 and 1990 cm^{-1}), which is used as an internal standard for comparisons between the density of SiOH groups among Ti-BEA samples. Spectra are vertically offset for clarity.

Figure S3 shows the $\nu(\text{O-H})$ and $\nu(\text{Si-O-Si})$ overtone region of the infrared spectra of dehydrated Ti-BEA. The sharp absorbance feature at $\sim 3740 \text{ cm}^{-1}$ corresponds to isolated SiOH species that are not interacting via H-bonding with nearby H-bond donors or acceptors (i.e., other SiOH). The broadening within the $\nu(\text{O-H})$ region is due to the H-bonding interactions of SiOH with other SiOH (i.e., $(\text{SiOH})_4$) that cause a red shift in these vibrational modes.

Differences in the density of isolated SiOH and $(\text{SiOH})_4$ groups on each material across the series of Ti-BEA are determined by normalizing spectra by the intensity of the $\nu(\text{Si-O-Si})$ modes (i.e., assuming a constant density of framework Si-O-Si bonds) and deconvoluting the peaks for SiOH (3740 cm^{-1}) and $(\text{SiOH})_4$ groups ($3300\text{-}3700 \text{ cm}^{-1}$). The ratios of the integrated areas (Φ_{IR}) for $\nu(\text{O-H})$ of $(\text{SiOH})_4$ ($A_{(\text{SiOH})_4}$) to those for $\nu(\text{Si-O-Si})$ ($A_{(\text{Si-O-Si})}$) provide measures of the relative density of $(\text{SiOH})_4$ for each Ti-BEA.

$$\Phi_{IR} = \frac{A_{(SiOH)_4}}{A_{(Si-O-Si)}} \quad (S1)$$

Table S1 shows that values for Φ_{IR} decrease as the initial ratio of Si:Al increases in the parent BEA zeolites, which is consistent with the trends observed for the total number of Si atoms coordinated to -OH groups (shown by Φ_{NMR}). Φ_{IR} , as defined here, provides semi-quantitative measure for changes in the number of (SiOH)₄ groups that result from differences in synthesis protocols for a given zeolite framework.

Table S1. Relative Densities of Hydrogen-Bonded SiOH (Φ_{IR}) within Ti-BEA

Sample Name	Φ_{IR}
Ti-BEA-12.5	2.30
Ti-BEA-20	1.90
Ti-BEA-75	2.21
Ti-BEA-150	1.64
Ti-BEA-250	1.26
Ti-BEA-F	0.08

S2.0 Isothermal Titration Calorimetry

S2.1 Development of Single-Site Binding Model

Isothermal titration calorimetry has been widely used for studying enzymatic systems, which detail the thermodynamics of the binding configurations.¹⁻² Here, we present a brief mathematical formulation of the single site binding model.

Consider the binding of a n ligands (e.g., $C_8H_{16}O$), L , with an adsorption site (e.g., Ti atoms), M ,



where K is the equilibrium binding constant for the formation of the ML complex (i.e., $n=1$). The equilibrium binding constant is represented by

$$K = \frac{[ML]}{[M][L]} \quad (S3)$$

where the brackets ($[\]$) denote liquid-phase concentrations. These liquid-phase concentrations are related to the total concentrations of each component loaded into the calorimeter cell (denoted with a subscript T) by a mass balance on each component

$$[M]_T = [M] + [ML] \quad (S4)$$

$$[L]_T = [L] + [ML] \quad (S5)$$

Equations S4 and S5 are then substituted into equation S3, so the equilibrium constant is equated to the total concentrations of the titrant and or the adsorption site. Values of K reflect changes in free energy ΔG_{Ads} (and by extension, enthalpies (ΔH_{Ads}) and entropies (ΔS_{Ads})) by

$$\Delta G_{Ads} = -RT \ln(K) = \Delta H_{Ads} - T \Delta S_{Ads} \quad (S6)$$

where R is the ideal gas constant and T is the absolute temperature in Kelvin.

Within a given ITC experiment, the dependent variable is the total amount of heat released per injection of the titrant ($\frac{dQ}{d[L]_T}$)

$$\frac{dQ}{d[L]_T} = V \sum_i \Delta H_{Ads,i} d[ML_i] \quad (S7)$$

where V is the volume of the sample cell, $\Delta H_{Ads,i}$ is the adsorption enthalpy for the formation of ML , and $d[ML_i]$ is the amount of the ML complex formed during the injection. Equation S7 is then combined with equations S3 – S5 to yield the full form of the single-site binding model that was used to fit the integrated heat data from the ITC experiments.

$$\frac{dQ}{d[L]_T} = \frac{1}{2} V \Delta H_{Ads} \left[1 - \frac{\frac{[L]_T}{[M]_T} + \frac{1}{K[M]_T} - n}{\sqrt{\left(\frac{[L]_T}{[M]_T}\right)^2 + \left(n + \frac{1}{K[M]_T}\right)^2 - 2\frac{[L]_T}{[M]_T} \left(n - \frac{1}{K[M]_T}\right)}}} \right] \quad (S8)$$

S2.2 Sample Dilution Curve to Correct Heats Released Upon Titration

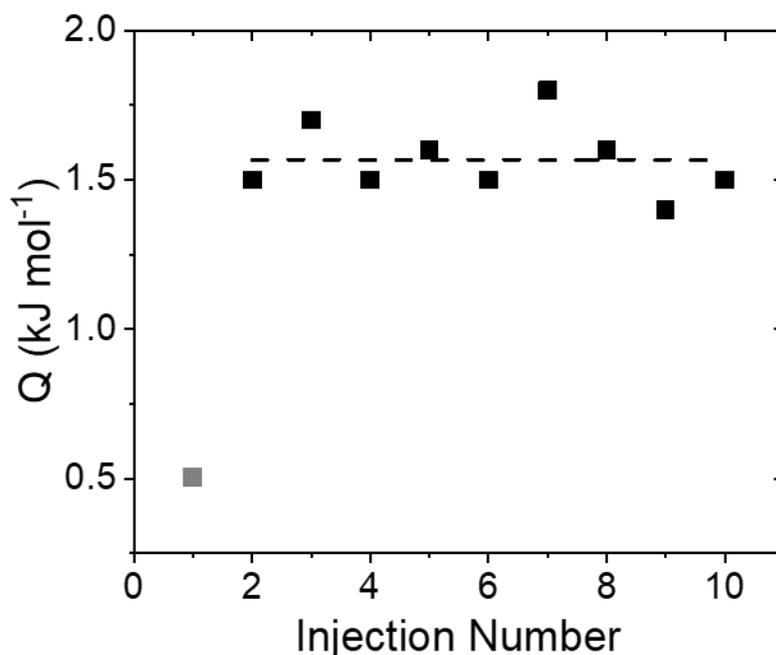
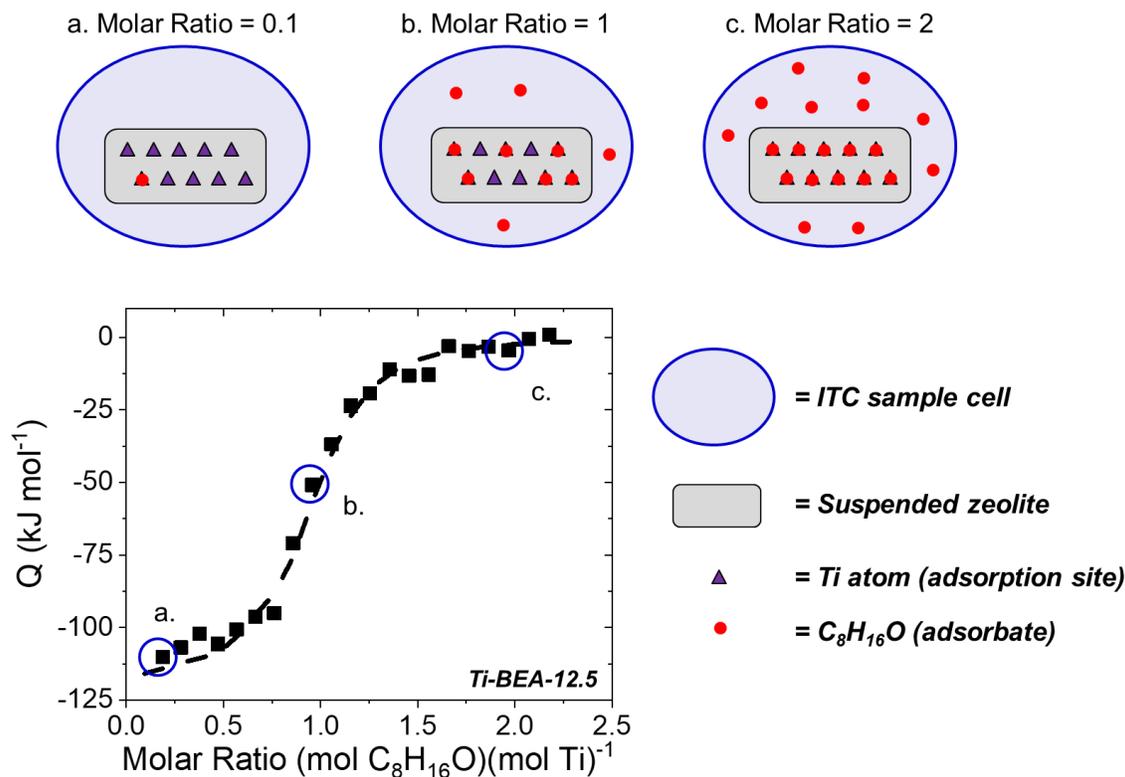


Figure S4. Heats released upon titration of $C_8H_{16}O$ (20 mM, 39 mM H_2O , in CH_3CN) into aqueous CH_3CN (39 mM H_2O) as a function of titration number at 313 K (250 rpm stirring). Each titration was 1 μL in volume. The transparent point was omitted from calculations of the heat of mixing due to common errors associated with early injections. The dashed line represents the heat of mixing that is associated with the dilution of $C_8H_{16}O$ into solutions of CH_3CN .

Figure S4 shows the heats released upon mixing of $C_8H_{16}O$ into CH_3CN (0.1 – 1.1 mM $C_8H_{16}O$). The constant value with successive titrations suggests that this value corresponds to the heat of infinite dilution, which is further supported by similar values obtained for more-dilute titration solutions of $C_8H_{16}O$. This heat of mixing was used to correct the isotherms for the titration of $C_8H_{16}O$ into Ti-BEA materials by adding this value to all heat values to correct for changes due to non-adsorption processes.

S2.3 Schematic Depicting Sequential C₈H₁₆O Titration of Ti Atoms within Ti-BEA-X



Scheme S1. Depiction of C₈H₁₆O titration of Ti atoms within Ti-BEA-X at C₈H₁₆O:Ti molar ratios of a) 0.1, b) 1, and c) 2. These approximate molar ratios are indicated on a representative adsorption isotherm for the titration of Ti-BEA-12.5 with C₈H₁₆O in CH₃CN (anhydrous) at 313 K. The dashed curve represents the fitting of a single-site binding model (Section S2.1). A legend is provided within the scheme to guide the reader in interpreting how C₈H₁₆O binds to active sites.

Scheme S1 shows a visual representation for the titration of Ti atoms with C₈H₁₆O with increasing amount of epoxide added to the system. At low molar ratios of C₈H₁₆O to Ti (e.g., 0.1; Scheme S1a), all C₈H₁₆O molecules that are introduced into the sample cell bind to Ti atoms, which is inferred from the large enthalpies of adsorption at low coverage (i.e., $\Delta H_{\text{Ads}} \sim -100$ kJ mol⁻¹; Table 2). The inflection point in the adsorption isotherm indicates the stoichiometry in binding between the adsorbate and the adsorption site. In the limit of equimolar C₈H₁₆O and Ti atoms (Scheme S1b), the partition between C₈H₁₆O in the fluid phase and bound to Ti atoms is dictated by the free energy of adsorption. As the ratio of C₈H₁₆O to Ti increases further (e.g., beyond a molar ratio of 2 for this system; Scheme S1c), each Ti atom present in BEA binds one C₈H₁₆O and the additional amounts of C₈H₁₆O added to the cell remain in solution. This is shown by integrated heats released (per injection) that approach that of the heat of dilution.

S3.0 Example Time- and Phase-Domain ATR-IR Spectra

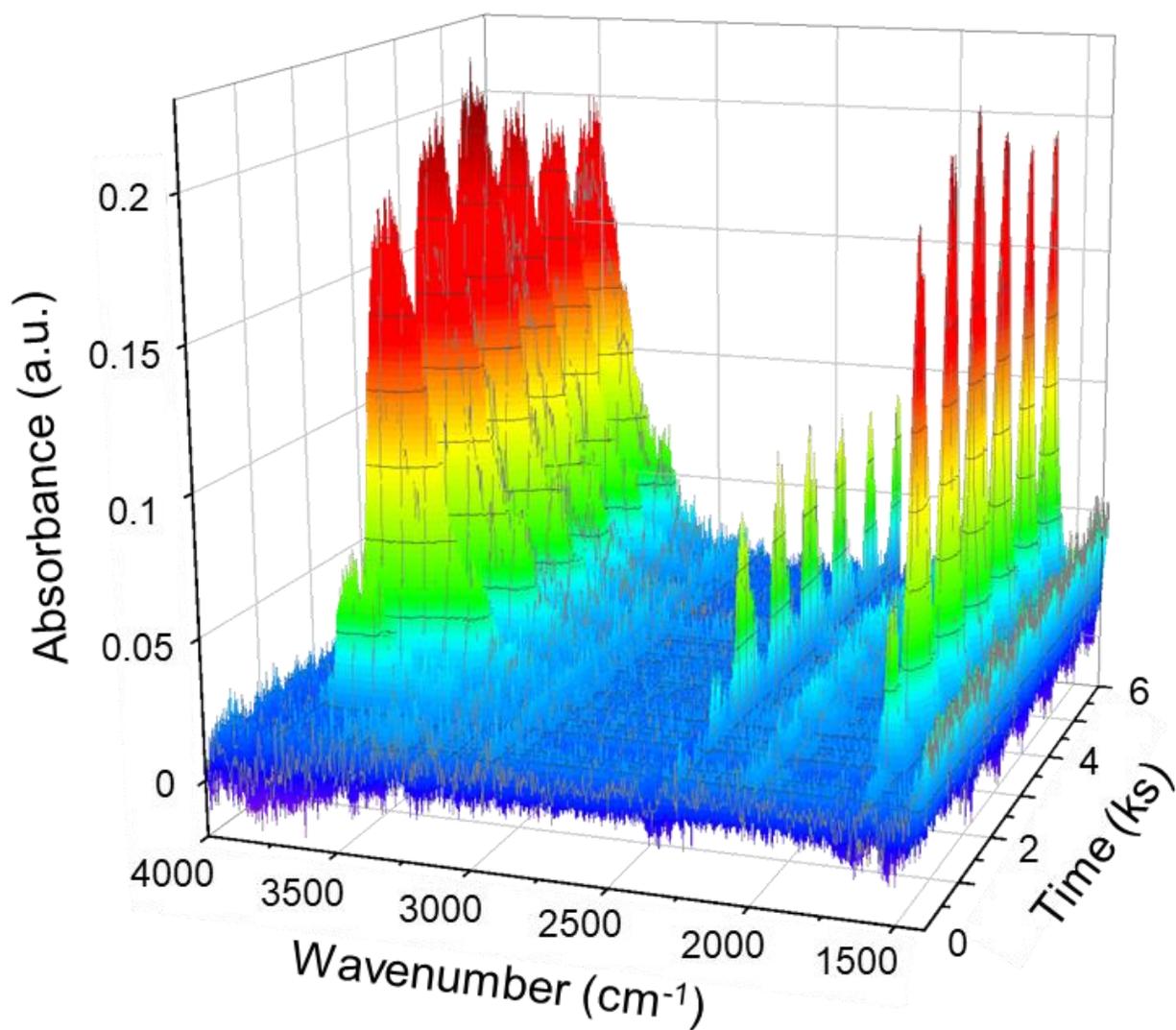


Figure S5. Representative time-resolved infrared spectra obtained *in situ* during the modulation of H₂O within CH₃CN over Ti-BEA-F (450 s period length, 313 K).

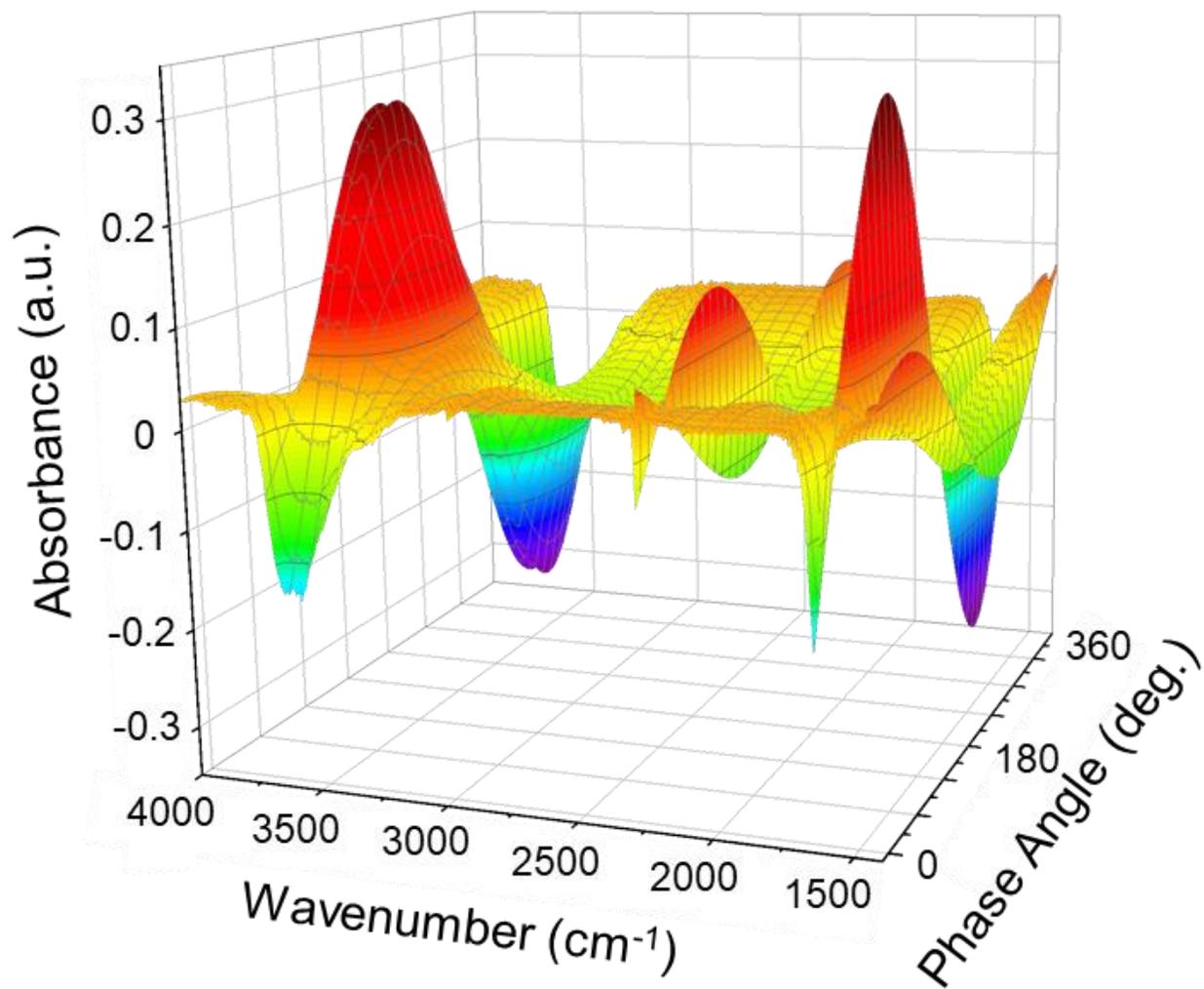


Figure S6. Phase-resolved infrared spectra that result from phase-sensitive detection of the time-resolved spectra in Figure S2.

S4.0 Additional ATR-IR Data for H₂O within Ti-BEA-250

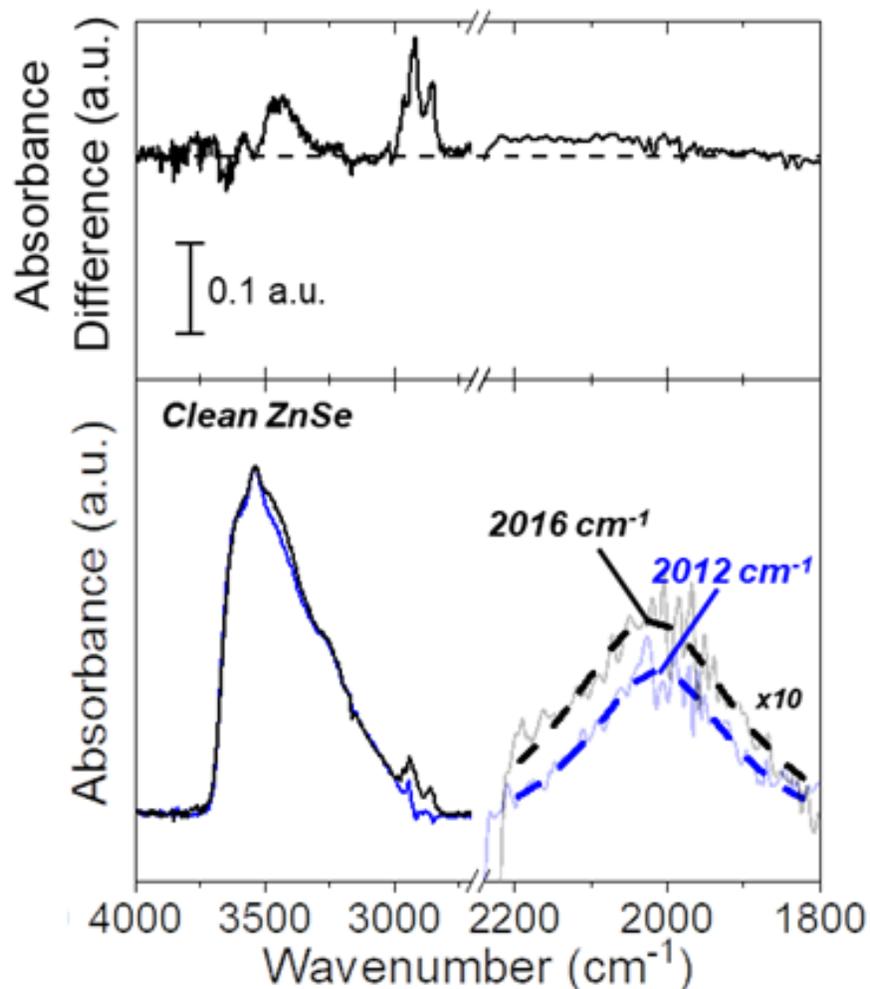


Figure S7. Infrared spectra obtained through multivariate analysis of modulation excitation experiments (Section 2.4) of H₂O in CH₃CN (0 – 5.5 M H₂O; blue) and in a solution of C₈H₁₆O in CH₃CN (0.1 M C₈H₁₆O, 0 – 5.5 M H₂O; black) over a clean ZnSe internal reflection element. All spectra are normalized to the most-intense ν(O-H) feature (~3540 cm⁻¹) and have a resolution of 5 cm⁻¹. The region between 1800 – 2250 cm⁻¹ have been scaled by the multiplier indicated. The dashed curves represent Lorentzian fits, which were used to quantify the peak center of the combination band. The top spectra is the difference spectra that represents that changes in the vibrational features for H₂O that result from the presence of C₈H₁₆O.

References:

1. Baker, B. M.; Murphy, K. P., Evaluation of Linked Protonation Effects in Protein Binding Reactions Using Isothermal Titration Calorimetry. *Biophys. J.* **1996**, *71*, 2049-2055.
2. Dam, T. K.; Roy, R.; Pagé, D.; Brewer, C. F., Thermodynamic Binding Parameters of Individual Epitopes of Multivalent Carbohydrates to Concanavalin A As Determined by "Reverse" Isothermal Titration Microcalorimetry. *Biochemistry* **2002**, *41*, 1359-1363.