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Fano coupling in perturbed solid acid hydroxyls^a

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Abstract. A simple analytical expression for the *Evans* window in the infrared absorption spectrum of hydrogen-bonded basic molecules in protonic zeolites is presented. The expression shows that the essential parameters are the position of the shifted “uncoupled” OH stretching frequency, its width, the position of the in-plane bending overtone and the coupling of this mode with the OH stretching mode. Analysis of the Fermi resonances in the OH stretching band profile provides a method to determine whether adsorbed molecules are hydrogen bonded or protonated.

Introduction

The chemical bond of strongly acidic protons attached to oxygen atoms in the micropores of zeolitic materials is a prototype of non-classical covalent bonding in a solid. In the zeolitic Brønsted acidic site the classically divalent oxygen connects a four-valent (Si) and three-valent (e.g., Al) lattice atom and has also a strong covalent bond with the acidic hydrogen atom. As a consequence the hydrogen–oxygen bond is weakened compared to the bond strength of a free silanol group. This is the basis of the Brønsted acidic nature of protonic zeolites. The non-classical bonding geometry of the bridging hydroxyls in the aluminosilicate Y has recently been analyzed in detail by solid-state NMR spectroscopy¹. Acid zeolites are extensively used as solid acidic catalysts.

The dependence of the proton–oxygen bond strength on structure (nearly 90 different topologies exist²) as well as lattice composition is not well understood, notwithstanding extensive theoretical³ as well as experimental investigations⁴.

An attractive approach to the characterization of the nature of the OH bond is to study its response to weakly interacting basic molecules⁵. The response of the OH bond can be followed by measuring the changes in frequency and intensity of the infrared (IR) absorption of the OH absorption band. Using IR spectroscopy this response has not only been measured for the OH stretching frequencies, but recently also for the in-plane bending modes of deuterated hydroxyl bonds. The deuterated hydroxyl in-plane bending modes⁶ shift to $\sim 880\text{ cm}^{-1}$. Its location in the infrared transparent lattice vibrational window, makes it directly observable by IR transmission spectroscopy.

Interaction of a basic molecule with the zeolitic OH bond weakens this bond. This results in a downward shift of the

OH stretching frequency. Because the motion of the in-plane and out-plane OH bending modes becomes more restricted, these mode frequencies shift upwards⁷.

The acidic OH bond is highly polarizable. Upon interaction of the basic molecule, a considerable dipole develops resulting in a significant increase of the intensity of absorption of the OH stretching mode. Proton-NMR data confirm the increase in positive charge on the proton due to its interaction with the basic molecule⁸. Apart from the downwards shift in IR frequency and increased absorption intensity, there is also a broadening of the shifted OH stretching frequency. This broadening is a characteristic of hydrogen bonding⁹. It results from the coupling of the downwards shifted OH stretching frequency with the low-frequency motion of the adsorbate against the zeolitic proton. Due to the high density of these modes, the IR absorption broadens. Its width is proportional to the shift of the OH stretching frequency.

Interestingly, whereas one expects the appearance of one new band corresponding to the shifted OH frequency, in some cases the shifted stretching frequency appears to give rise to two new peaks. This phenomenon is the subject of the present article. It has been observed for the interaction of the hydroxyl with acetone¹⁰, methanol¹¹, and water¹², as well as acetonitrile¹³. Earlier we suggested an explanation based on Fermi resonance¹³, later supported by extensive experimental evidence⁷. The bands were assigned to be the A,B bands of a strongly perturbed hydrogen bonded system. Here we will provide a short theoretical analysis of the phenomenon and show that this type of Fermi resonance is related to the *Fano* type of resonance¹⁴, characteristic of the coupling of a discrete level with another broad continuous band system. The splitting of the shifted and broadened OH stretching bond frequencies into two sub-bands occurs when the interaction with the absorbing base is so strong that the shifted band system overlaps with overtones of the OH bending modes. The fundamental OH in-plane bending mode¹⁵ is approximately 1100 cm^{-1} . This mode is estimated to shift to 1350 cm^{-1} upon interaction with a strong base⁷. The first overtone of the shifted in-plane OH bond is located at 2700 cm^{-1} . The absorption inten-

^a Dedicated to Prof. Dr. W.M.H. Sachtler on the occasion of his 70th birthday.

Figure 1. Mode-coupling scheme for interaction of CD_3CN with zeolite proton. δ is the in-plane bending mode. ν_s is the stretching mode. Only ν_s can be excited from the ground state.

sity for overtone excitation is very low. Anharmonic coupling of this sharp mode with the broadened downward shift OH stretching bond leads to intensity stealing. This result in a dip in the broad stretching frequency band system at $\sim 2700 \text{ cm}^{-1}$. Peaks in the absorption spectrum appear around 2500 cm^{-1} and 2800 cm^{-1} due to the absorbing probability left in the origin band system. Because of the strong lattice absorption of zeolites around 1300 cm^{-1} , the upwards shifted OH in-plane bending modes are not directly observable by IR transmission spectroscopy. However, they are observable for deuterated hydroxyls. Table I provides a comparison of the measured shifted in-plane (OD) modes, interacting with CD_3CN and CCl_3CN and the observed Fermi resonance window positions that appear as a dip in the disturbed stretching frequency band system⁷. Similar Fermi window resonances have been observed in the hydrogen bond spectra by Evans¹⁶ in liquids. Ratajzak et al.¹⁷ have proposed such an Evans window for perturbed hydroxyl groups in CsSeO_4 . Here we will present a derivation of an analytical expression for Fano coupling of a single non-optically excitable state (the 2δ overtone), with the optically excitable quasi-continuum provided for by the shifted OH stretching bond.

Resonance theory of the Evans transmission window

The (A,B) IR bond system corresponds to the mode coupling scheme depicted in Figure 1. β' and β are the coupling parameters of the in-plane bending overtone frequency 2δ to the OH stretching frequency ν_s and the low frequency modes ν_{Hj} , corresponding to the vibrations of the hydrogen-bonded adsorbate molecule, respectively. β is a measure of the bandwidth of shifted OH stretching frequency. The transition probability follows from the Golden-rule expression

$$W \approx \sum_i \{ |\langle \phi_0 | \vec{p} | \psi_i \rangle|^2 \cdot \delta(h \cdot \nu - E_i + E_0) \} \quad (1)$$

(Eqn. 1):

ψ_i is the vibrational eigenfunction of the coupled system and ϕ_0 , the vibrational eigenfunction corresponding to the ground state. $\vec{p}$ is the vibrational dipole-moment

operator. ν is the frequency of electromagnetic radiation. Eqn. 1 can be rewritten in terms of the uncoupled modes ϕ_i to give Eqn. 2.

$$W \approx -\frac{1}{\pi} \cdot \text{Im} \cdot \sum_{\alpha, \beta} \{ \langle \phi_0 | \vec{p} | \phi_\alpha \rangle \cdot G_{\alpha\beta} \cdot \langle \phi_\beta | \vec{p} | \phi_0 \rangle \} \quad (2)$$

The Green function matrix element $G_{\alpha\beta}$ is defined as in Eqn. 3,

$$G_{\alpha\beta} = \lim_{\epsilon \rightarrow 0} \langle \phi_\alpha | \frac{1}{(E + i \cdot \epsilon) \hat{I} - \hat{H}} | \phi_\beta \rangle; E = h \cdot \nu + E_0 \quad (3)$$

where $\hat{I}$ is the unit operator and $\hat{H}$ the Hamiltonian of the coupled system. We will solve Eqn. 2 assuming that interaction with IR radiation only excites the uncoupled ν_s modes. This implies Eqn. 4.

$$\langle \phi_0 | \vec{p} | 2 \cdot \delta \rangle = \langle \phi_0 | \vec{p} | \nu_{H,i} \rangle = 0 \quad (4)$$

Using resolvent theory^{1,2}, one deduces the Eqn. 5 for G_{ν_s, ν_s} :

$$G_{\nu_s, \nu_s} = \frac{1}{E + i \cdot \epsilon - \epsilon_{\nu_s} - \beta'^2 \cdot \frac{1}{E - \epsilon_{2\delta}} - \beta^2 \cdot g_{\nu_s, \nu_s}} \quad (5)$$

the Green function of the shifted stretching frequency ν_s ; ϵ_{ν_s} corresponds to the $0 \rightarrow 1$ stretching vibration excitation energy and $\epsilon_{2\delta}$ to the excitation energy of overtone bending mode.

In order to evaluate Eqn. 5 one has to know g_{ν_s, ν_s} . For convenience, we will assume it to be the elliptic function that is the solution of the Cayley tree problem¹⁸

$$\lim_{\epsilon \rightarrow 0} g_{\nu_s, \nu_s} = \frac{E - \epsilon_{\nu_s}}{2 \cdot \beta^2} - \frac{1}{2 \cdot \beta^2} \cdot \sqrt{-4 \cdot \beta^2 + (E - \epsilon_{\nu_s})^2} \quad (6)$$

(Eqn. 6). The use of this approximation provides an analytical expression for Eqn. 2.

The density of states of the excited ν_s model, uncoupled from 2δ but coupled to ν_{Hj} then becomes as in Eqn. 7.

$$\rho_{\nu_s}^0 = -\frac{1}{\pi} \cdot \text{Im} \cdot g_{\nu_s, \nu_s} \quad (7a)$$

$$= \frac{1}{2\pi \cdot \beta^2} \cdot \sqrt{4 \cdot \beta^2 - (E - \epsilon_{\nu_s})^2}; (|E - \epsilon_{\nu_s}|^2 < 4 \cdot \beta^2) \quad (7b)$$

Using Eqn. 6, an explicit expression for W can be found, that is valid as long as $|\beta'| \ll |\beta|$. This is the so-called weak coupling limit. A general solution to Eqn. 5 can also be found, as discussed extensively elsewhere¹⁸.

In the weak-coupling limit, use Eqn. 6 leads to Eqn. 8.

$$W(E) \approx |\langle \phi_0 | \vec{p} | \nu_s \rangle|^2 \cdot \left\{ \frac{1}{2} \cdot \sqrt{4 \cdot \beta^2 - (E - \epsilon_{\nu_s})^2} \right\} \times \left\{ \left(\frac{1}{2} \cdot E - \frac{1}{2} \cdot \epsilon_{\nu_s} - \beta'^2 \cdot \frac{1}{E - \epsilon_{2\delta}} \right)^2 + \frac{1}{4} \cdot \left[4 \cdot \beta^2 - (E - \epsilon_{\nu_s})^2 \right] \right\}^{-1} \quad (8)$$

Table I. $\delta(\text{OD})$ band and transmission window minimum^a.

Brønsted		CD_3CN adsorption			CCl_3CN adsorption	
site	$\delta(\text{OD})$	$\delta(\text{OD})$	shift	window	$\delta(\text{OD})$	shift
SiODAL	894	988	94	1977	970	76
SiODFe	865	950	85	1902	930	65

^a Wavenumbers⁷ in cm^{-1} .

Figure 2. Evans window for a few different values of β' and $\epsilon_{v_s} - \epsilon_{2\delta}$ according to Eqn. 8, 4β is the phonon frequency bandwidth, β' the coupling parameter of the in-plane and stretching vibrational modes.

- 1: $\beta' = 0$, the Fermi resonance
 2: $\beta' = 0.2\beta$; $\epsilon_{2\delta} = \epsilon_{v_s} - 0.1\beta$
 3: $\beta' = 0.4\beta$; $\epsilon_{2\delta} = \epsilon_{v_s} - 0.2\beta$

Eqn. 8 can be considered a generalization of the *Fano* expression¹⁴ for auto-ionization, with strong excitation of the continuum wavefunction.

The major extension of the *Fano* result is that now the energy dependence of the density of states of the quasi-continuum is explicitly accounted for. Eqn. 8 is plotted in Figure 2 as a function of β' for a few values of $\epsilon_{v_s} - \epsilon_{2\delta}$.

Discussion and conclusion

The theoretical results illustrate that the two maxima (A,B features) in the experimental hydrogen-bonding spectra are a signature of a disturbed hydrogen stretching bond in resonance with a non-optically active mode. The A,B double peaks belong to the shifted OH stretching mode. The average position of the disturbed OH stretching frequency bond system is related to the weighted average of the frequencies in the A,B region. Disappearance of the two-peak spectrum for strongly interacting bases may indicate formation of protonated ionic intermediates. An example is provided by the spectra of adsorbed NH_3 ¹⁹. Now strong adsorptions are found in the region between 2000–3000 cm^{-1} . There is no indication for a Fermi resonance. The spectrum is to be described as that of disturbed NH_4^+ . In the case of methanol weak A,B bands are observed and an increase of intensities at lower frequencies¹¹. This indicates a highly disturbed low-frequency hydrogen bond that is close to the protonated intermediate, but still has to be described as hydrogen-bonded methanol²⁰.

Sachtler et al.²⁰ have studied the interaction of metal atoms and clusters with zeolitic OH stretching modes. The interaction with zeolitic protons prevents metal particle agglomeration. The IR spectra indicate a decrease in intensity of the shifted IR OH stretching frequencies. Analysis of spectral features in the A,B spectral region would confirm the proposal that the OH bonds are highly disturbed and that the metal atoms can be considered to be in a state that is close to that of the protonated state, but with a strong lattice-hydrogen bond.

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