

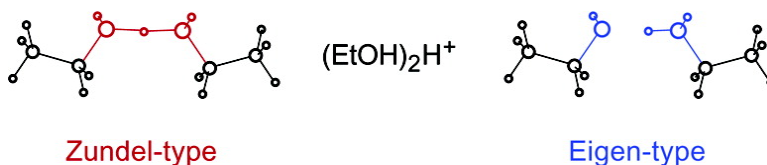
Communication

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IR Spectrum and Structure of Protonated Ethanol Dimer: Implications for the Mobility of Excess Protons in Solution

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The solvation and mobility of excess protons in hydrogen-bonded liquids are among the most fundamental chemical and biological processes (e.g., aqueous acid–base chemistry, conducting proton wires, biological proton pumps).¹ A molecular level description of these proton-transfer phenomena requires the characterization of short-lived H-bonded network structures. Spectroscopic studies of isolated size-selected clusters yield direct structural and energetic information on such fundamental networks and provide the basis for interpreting condensed-phase spectra, which often suffer from (in)homogeneous broadening.² The present work reports the first spectroscopic observation of the isolated protonated ethanol dimer and its N₂-microsolvated clusters, (EtOH)₂H⁺–(N₂)_n with *n* = 0–2. It complements previous mass spectrometric experiments, which mainly focused on the (EtOH)₂H⁺ reactivity, without providing direct structural information.³ The presented IR and theoretical data of (EtOH)₂H⁺–(N₂)_n address directly the central question of the degree of proton delocalization in this basic building block of an alcohol proton wire and its dependence on (a)symmetric solvation. The excess proton may either be more or less equally shared between both EtOH units, EtHO–H⁺–OHet (Zundel-type structure),¹¹ or largely localized on one EtOH molecule, EtOH₂⁺–OHet (Eigen-type structure).^{1k}

IR photodissociation (IRPD), a sensitive technique of cluster ion spectroscopy,⁴ was recently applied to pure and mixed protonated water/methanol clusters.^{1g,1h,2a,4a,5} The (H₂O)₂H⁺ spectra are consistent with the C₂-symmetric Zundel structure predicted by sophisticated calculations.⁶ Corresponding (CH₃OH)₂H⁺ spectra are still lacking. IRPD spectra of larger (H₂O)_n(CH₃OH)_mH⁺ clusters (*n* + *m* > 2) show that the excess proton is either strongly localized on one or (nearly) equally shared between two solvent molecules, emphasizing the importance of solvated Eigen- and Zundel-type ions as fundamental structural motifs occurring in H-bonded networks.⁵ The preference for one or the other ion core depends on the number, position, and type of solvent molecules.

Early calculations for (EtOH)₂H⁺ yield an Eigen-type EtOH₂⁺–OHet structure^{3g} with a binding energy for EtOH loss comparable to a recent measurement (*D*₀ ≈ 150 kJ/mol).^{3a} In contrast, our calculations⁷ predict two Zundel-type EtHO–H⁺–OHet conformers, **1a/b**, which differ merely by the orientation of the Et groups (Figure 1).⁸ Significantly, both dimers have similar O–H bond distances and stretch wavenumbers (Table 1). The low isomerization barrier (*V* = 3.2 kJ/mol) between the more stable **1a** and the less stable **1b** (ΔE = 0.6 kJ/mol) implies that, on average, EtHO–H⁺–OHet can be considered as a C₂-symmetric ion. Less stable non-proton-bound EtOH₂⁺–EtOH isomers also exist on the (EtOH)₂H⁺ potential such as the precursor for C₂H₅⁺ transfer leading to dehydration of (EtOH)₂H⁺.⁹ The IRPD spectra of (EtOH)₂H⁺–(N₂)_n will answer the key question whether EtOH₂⁺-centered or EtHO–H⁺–OHet-centered structures are more stable.

IRPD spectra of (EtOH)₂H⁺–(N₂)_n are obtained in a tandem quadrupole mass spectrometer (QMS1/2) coupled to an ion source

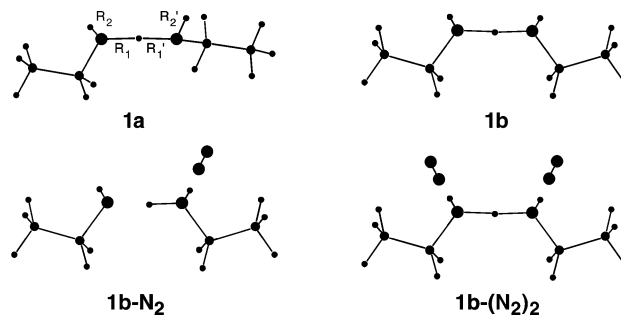


Figure 1. Structures of selected (EtOH)₂H⁺–(N₂)_n clusters (*n* = 0–2).⁷

Table 1. Selected O–H Bond Properties of (EtOH)₂H⁺–(N₂)_n^a

cluster	<i>R</i> ₁ [Å]	<i>R</i> ₂ [Å]	ν_{OH} [cm ⁻¹]	<i>I</i> _{OH} [km/mol]	<i>D</i> _e [kJ/mol]
1a	1.209	0.966	3637 (ν_s)	98	
	1.191	0.966	3629 (ν_a)	117	
1b	1.200	0.966	3635 (ν_s)	63	
	1.200	0.966	3633 (ν_a)	159	
1a-N₂	1.332	0.965	3457 (ν_b)	690	18.8
	1.097	0.977	3645 (ν_f)	90	
1b-N₂	1.328	0.965	3446 (ν_b)	720	19.0
	1.101	0.976	3652 (ν_f)	89	
1a-(N₂)₂	1.214	0.972	3517 (ν_s)	402	15.5
	1.186	0.972	3511 (ν_a)	727	15.8
1b-(N₂)₂	1.200	0.972	3515 (ν_s)	360	15.8
	1.200	0.972	3508 (ν_a)	798	15.8

^a Bond lengths, scaled ($\times 0.9613$) stretch wavenumbers, and IR intensities. N₂ binding energies are also listed.

and an octopole ion trap.¹⁰ (EtOH)₂H⁺–(N₂)_n are generated by electron ionization of a pulsed molecular beam composed of EtOH and N₂,^{3h} mass selected by QMS1, and irradiated by a tunable IR laser pulse (ν_{IR}) in the octopole. Resonant vibrational excitation induces evaporation of EtOH or N₂ ligands. The generated fragment ions are selected by QMS2 and monitored as a function of ν_{IR} to obtain the IRPD spectra of (EtOH)₂H⁺–(N₂)_n shown in Figure 2.

Table 2 lists the positions, widths, and assignments of the transitions observed. The broad band at 3625 cm⁻¹ (A) in the (EtOH)₂H⁺ spectrum is assigned to the unresolved symmetric and antisymmetric free O–H stretch modes ($\nu_{s/as}$) of internally excited EtHO–H⁺–OHet ions, in good agreement with $\nu_{s/as}$ calculated for **1** (e.g., ν_s = 3637 and ν_{as} = 3629 cm⁻¹ for **1a**). As the photon energy, $E(\nu_{\text{IR}})$ ≈ 43 kJ/mol, is well below the binding energy of (EtOH)₂H⁺ (*D*₀ ≈ 150 kJ/mol),^{3a} only sequence transitions of hot ions **1** with internal energy E_{int} > 107 kJ/mol are detected in single-photon absorption.¹¹ The resulting large width of A (94 cm⁻¹) implies that minor contributions of EtOH₂⁺-centered structures cannot be excluded, because A also covers ν_{OH} of neutral EtOH (Figure 2).

In contrast to (EtOH)₂H⁺, the (EtOH)₂H⁺–(N₂)_n spectra display narrow bands (≤ 24 cm⁻¹), because IR excitation of vibrationally cold clusters is sufficient to evaporate the weakly bound N₂ ligands

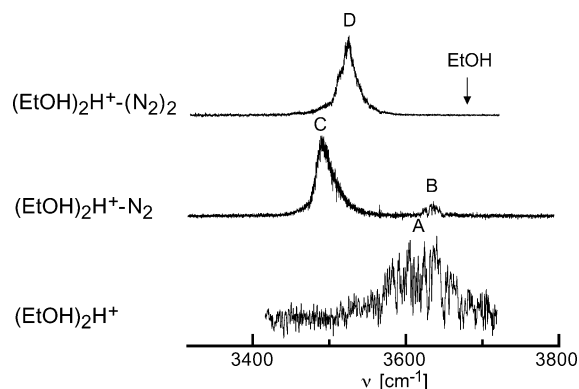


Figure 2. IRPD spectra of $(\text{EtOH})_2\text{H}^+(\text{N}_2)_n$ recorded in the EtOH_2^+ ($n = 0$) and $(\text{EtOH})_2\text{H}^+$ ($n = 1, 2$) fragment channels. The arrow indicates the position of ν_{OH} of the most stable EtOH isomer.¹²

Table 2. Band Maxima, Widths (fwhm in Parentheses), and Assignments of the Transitions Observed for $(\text{EtOH})_2\text{H}^+(\text{N}_2)_n$

n	band	position [cm^{-1}]	mode	ion
0	A	3625 (94)	$\nu_{\text{s/as}}$	1
1	B	3633 (20)	ν_{f}	1-N₂
1	C	3490 (24)	ν_{b}	1-N₂
2	D	3524 (20)	$\nu_{\text{s/as}}$	1-(N₂)₂

($D_0 \approx 12$ kJ/mol). In the most stable $(\text{EtOH})_2\text{H}^+-\text{N}_2$ cluster, N_2 forms a nearly linear H-bond to one of the free OH groups of $(\text{EtOH})_2\text{H}^+$ (Figure 1).^{4b,13} Bands B and C at 3633 and 3490 cm^{-1} (intensity ratio $I \approx 7.5$) are assigned to the free and N_2 -bound O–H stretch modes of **1-N₂** (ν_{f} and ν_{b}), consistent with the predicted values (e.g., 3645 and 3457 cm^{-1} , $I \approx 7.7$ for **1a-N₂**). The H-bond with N_2 slightly destabilizes the O–H donor bond,^{4b,13} resulting in a red shift of ≈ 135 cm^{-1} and an IR enhancement. As the potential along the proton-transfer coordinate in proton-bound dimers is usually flat,^{4,6} a switch from a $\text{EtOH}-\text{H}^+-\text{OHEt}$ to a $\text{EtOH}_2^+-\text{OHEt}$ core is observed upon asymmetric solvation with a single N_2 ligand. The calculated **1a/b-N₂** structures closely resemble a EtOH_2^+ ion solvated by EtOH and N_2 . Hence, $\nu_{\text{f}} = 3633$ cm^{-1} is close to ν_{OH} of neutral EtOH (3678 cm^{-1}),¹² consistent with a relatively small perturbation by the nearby EtOH_2^+ ion.

A symmetric microsolvation environment is again restored upon addition of a second N_2 ligand (Figure 1). The $(\text{EtOH})_2\text{H}^+(\text{N}_2)_2$ spectrum displays a single peak at 3524 cm^{-1} (D), which corresponds to the unresolved $\nu_{\text{s/as}}$ modes of $\text{EtOH}-\text{H}^+-\text{OHEt}$ -centered structures, **1-(N₂)₂**. The detection of a single peak indicates weak coupling between the two (nearly equivalent) N_2 -solvated O–H oscillators, and the predicted $\nu_{\text{s/as}}$ values of **1-(N₂)₂** (3517 and 3511 cm^{-1} for **1a-(N₂)₂**) nearly match the experiment. As the N_2 complexation energies in the $n = 2$ complex are smaller than for $n = 1$ ($D_e \approx 16$ vs 19 kJ/mol), the red shifts in the O–H donor stretch modes are reduced to ≈ 101 cm^{-1} . The lack of IR signals above 3580 cm^{-1} demonstrates that EtOH_2^+ -centered isomers are not detected. As the ion source predominantly produces the most stable isomer of a given cluster ion,^{13,14} $\text{EtOH}-\text{H}^+-\text{OHEt}$ -type geometries are concluded to be the most stable structural motif of $(\text{EtOH})_2\text{H}^+$ for symmetric solvation. As the N_2 binding energies are small, the same conclusion can also be drawn for isolated $(\text{EtOH})_2\text{H}^+$. The major effects of the weakly bound N_2 ligands are cooling of the $(\text{EtOH})_2\text{H}^+$ unit and a reduction of the lowest dissociation threshold (messenger technique).^{4,14}

In conclusion, IRPD spectra and calculations of $(\text{EtOH})_2\text{H}^+(\text{N}_2)_n$ demonstrate that the excess proton in $(\text{EtOH})_2\text{H}^+$ is shared equally between both EtOH molecules under symmetric (micro)-solvation conditions ($n = 0/2$). Apparently, substitution of two H atoms in $(\text{H}_2\text{O})_2\text{H}^+$ by Et groups does not affect the topology of the proton-transfer potential. In addition, calculated properties of the free O–H bonds in $(\text{H}_2\text{O})_2\text{H}^+$ and $(\text{EtOH})_2\text{H}^+$ are very similar,¹⁵ indicating that Et groups have only a minor stabilizing effect on the free O–H bonds. Future efforts will be aimed at the investigation of larger $(\text{EtOH})_q\text{H}^+-\text{L}_n$ clusters to further elucidate the development of H-bonded networks (proton wires) in liquid alcohols.

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- (15) Calculations for $(\text{H}_2\text{O})_2\text{H}^+$ (C_2 symmetry) yield 3680 and ≈ 3600 cm^{-1} for the antisymmetric and symmetric O–H stretch vibrations, respectively, which agree with available experimental data to within 15 cm^{-1} .^{5a} Calculated O–H bond lengths of $(\text{H}_2\text{O})_2\text{H}^+$ and **1b** differ by merely $|\Delta R_2| \leq 0.002$ Å and $|\Delta R_1| \leq 0.001$ Å.

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