

Hydrogen Bonding Interactions between a Representative Pyridinium-Based Ionic Liquid [BuPy][BF₄] and Water/Dimethyl Sulfoxide

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Infrared spectroscopy and density functional theory calculations have been applied to elucidate the hydrogen bonding interactions between water/dimethyl sulfoxide (DMSO) and a representative pyridinium-based ionic liquid, 1-butylpyridinium tetrafluoroborate ([BuPy][BF₄]). It has been found that both solvents can interact with the BuPy⁺cation through the aromatic C-H. The strength of the H-bonds involving the aromatic C-H in water is similar to that in pure [BuPy][BF₄], but is much stronger in DMSO. For DMSO, when it forms H-bonds with the BuPy⁺ cation through its S=O group, its back-side methyl groups act as electron donors, while the butyl group of the cation acts as an electron acceptor. For water, when it forms the strong anion-HOH-anion complex, it can also form H-bonds with the aromatic C-H on the BuPy⁺ cation. This is different from the imidazolium-based ionic liquid, where the strong anion-cation interaction and steric hindrance from the alkyls prevent water molecules from H-bonding with the aromatic C-H other than with the anion.

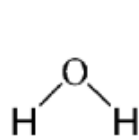
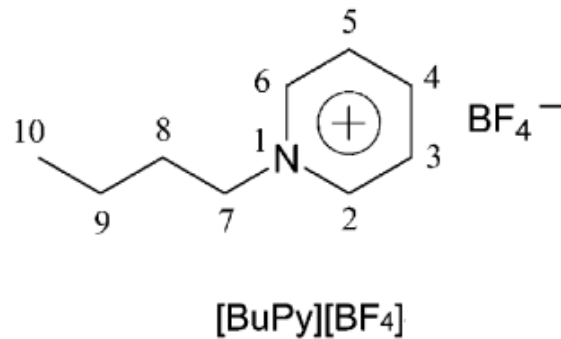
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Important Facts

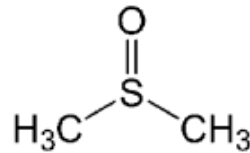
- HB shows significant changes on density, viscosity, surface tension, electrical conductivity, heat capacity, and solubility of IL.
- Addition of water destroy the.....
- - i) 3 D network structure
 - ii) ionic clusters
 - iii) then into ionic pairs surrounded by water
 - iv) ultimately into fully hydrated separated ions
- Complete dissociation in ion pairs in BMIM[BF₄] only at 0.0015
- At higher concentration (0.5, 0.6), ILs form clusters and W molecules interact with the clusters without forming an H-bond network among W

What is excess IR spectroscopy ?

SCHEME 1: Chemical Structures of 1-Butylpyridinium Tetrafluoroborate ([BuPy][BF₄]), H₂O, and DMSO



H₂O



DMSO

Difference between the spectrum of a real solution and that of the respective ideal solution under identical conditions

$$\epsilon^E = \frac{A}{d(C_1 + C_2)} - (x_1\epsilon_1^* + x_2\epsilon_2^*)$$

A - absorbance of the mixture

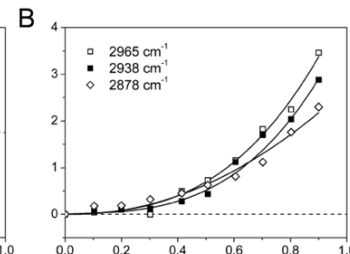
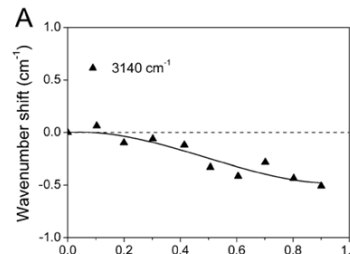
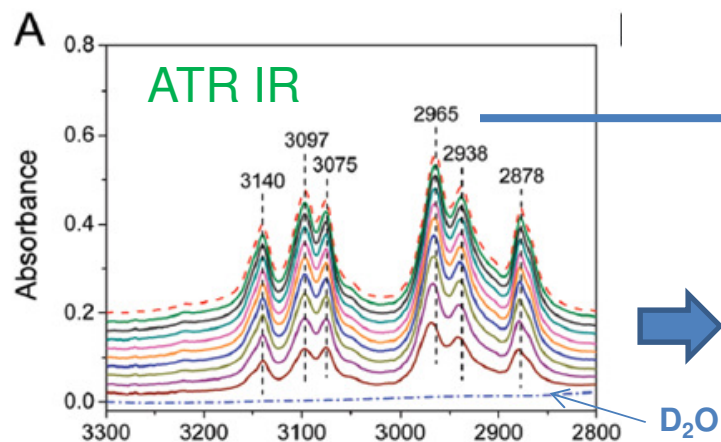
d - light path length

C₁, C₂- molarities of the two components

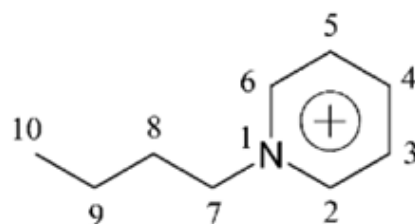
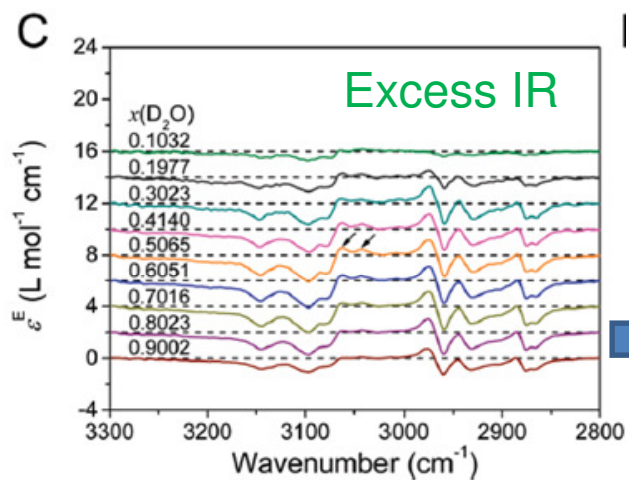
x₁ and x₂- mole fractions of components 1 & 2.

ε₁*ε₂*- molar absorption coefficients of the two components in their pure states.

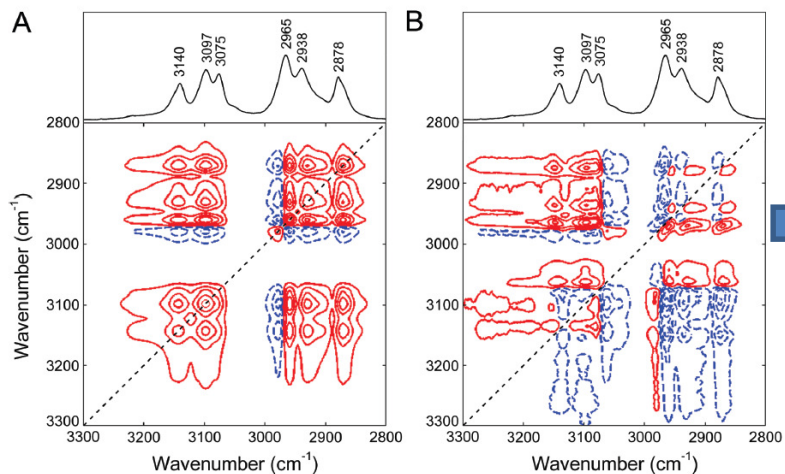
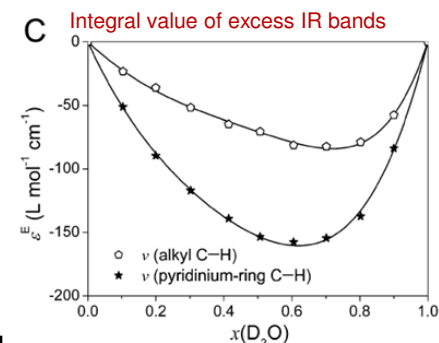
$([\text{BuPy}][\text{BF}_4]) + \text{Water}$



- Ring C-H.....no change
- Increasing water, absorption of all band decreases
- Ring C-H shows similar HB in W as in pure [BuPy]BF₄

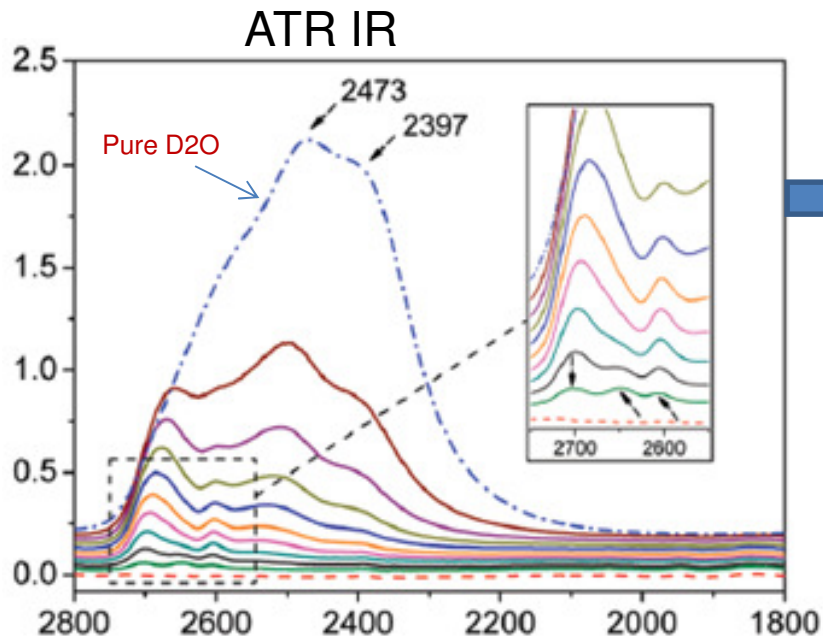


- Negative bands from both ring and alkyl C-H
- Alkyl C-H at 2975 cm⁻¹ shows positive band.....blue shift
- 3062 and 3042 also shows positive band.....not occurs in ATR



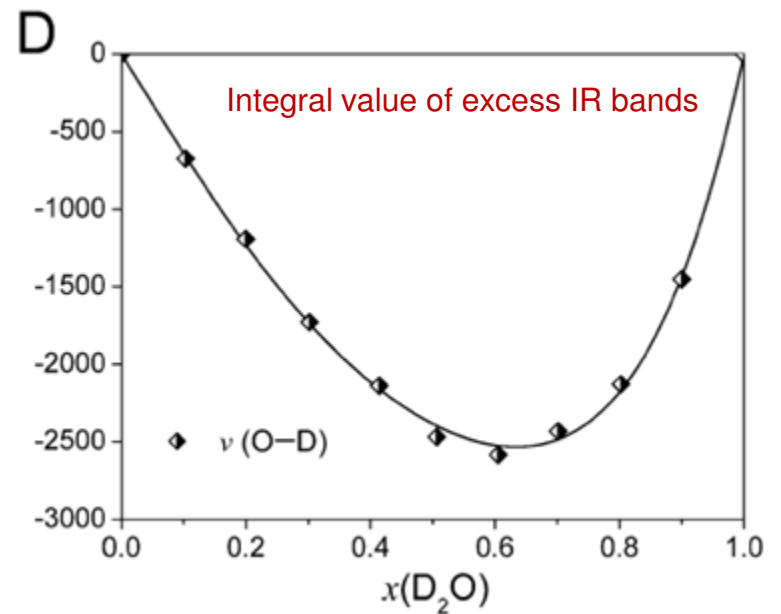
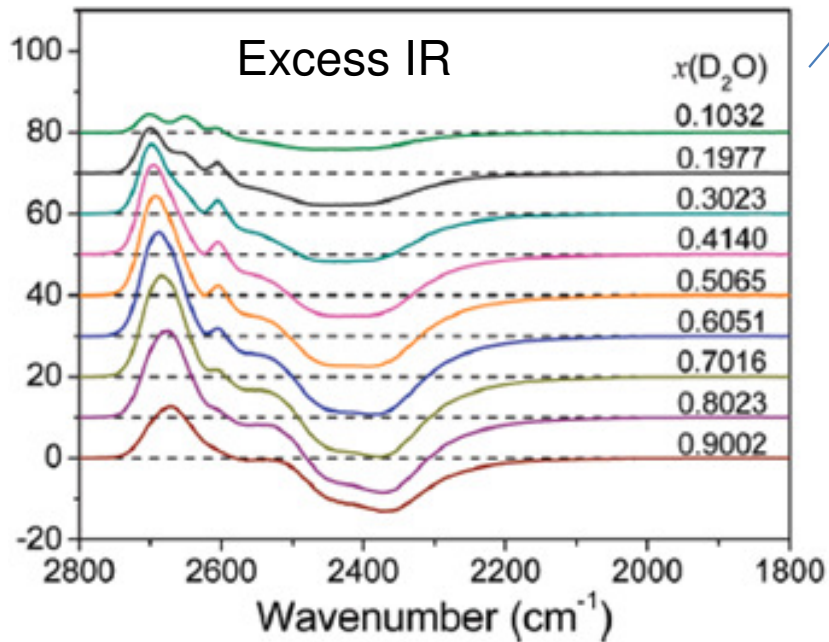
A- Synchronous 2-d correlation spectroscopy
B- Asynchronous 2-d correlation spectroscopy

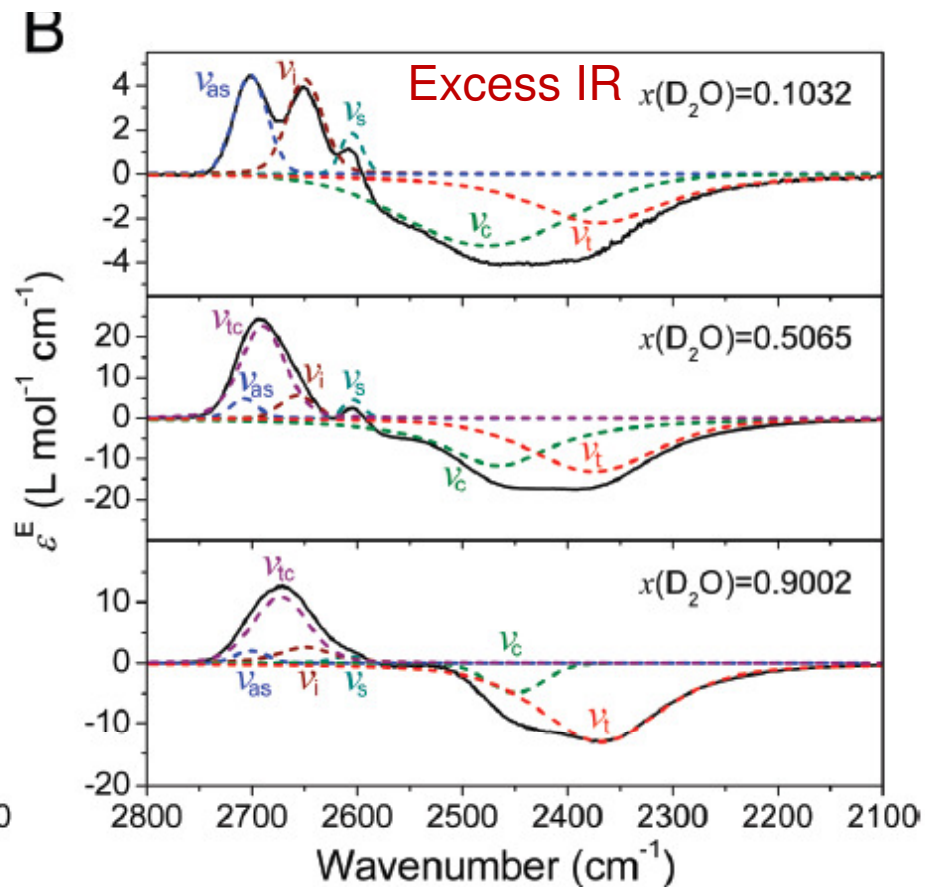
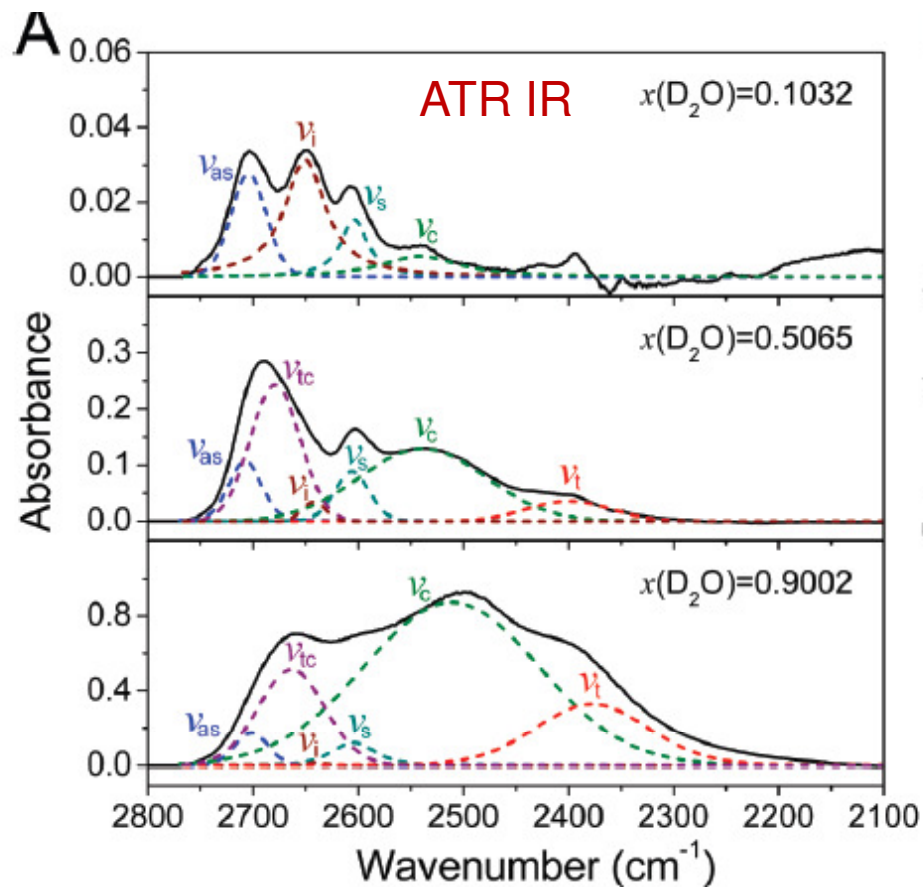
- more correlation bands in the asynchronous spectrum
- positive cross peak at (3098, 2930 cm⁻¹) in synchronous spectrum
- positive peak due to the same changing direction of the absorption coefficients of ring C-H) and alkyl C-H)
- asynchronous shown the cross peak (3096, 2936 cm⁻¹) also positive



- In the presence of IL...2 or 3 new band originates
- Decrease in lower wavenumber absorption....decrease number of H-bonded D2O
- Higher wavenumber new peak....single or more weakly interacting D2O embedded in IL environment

Number of positive and negative bands occurs shows the appearance and disappearance of W structure in IL



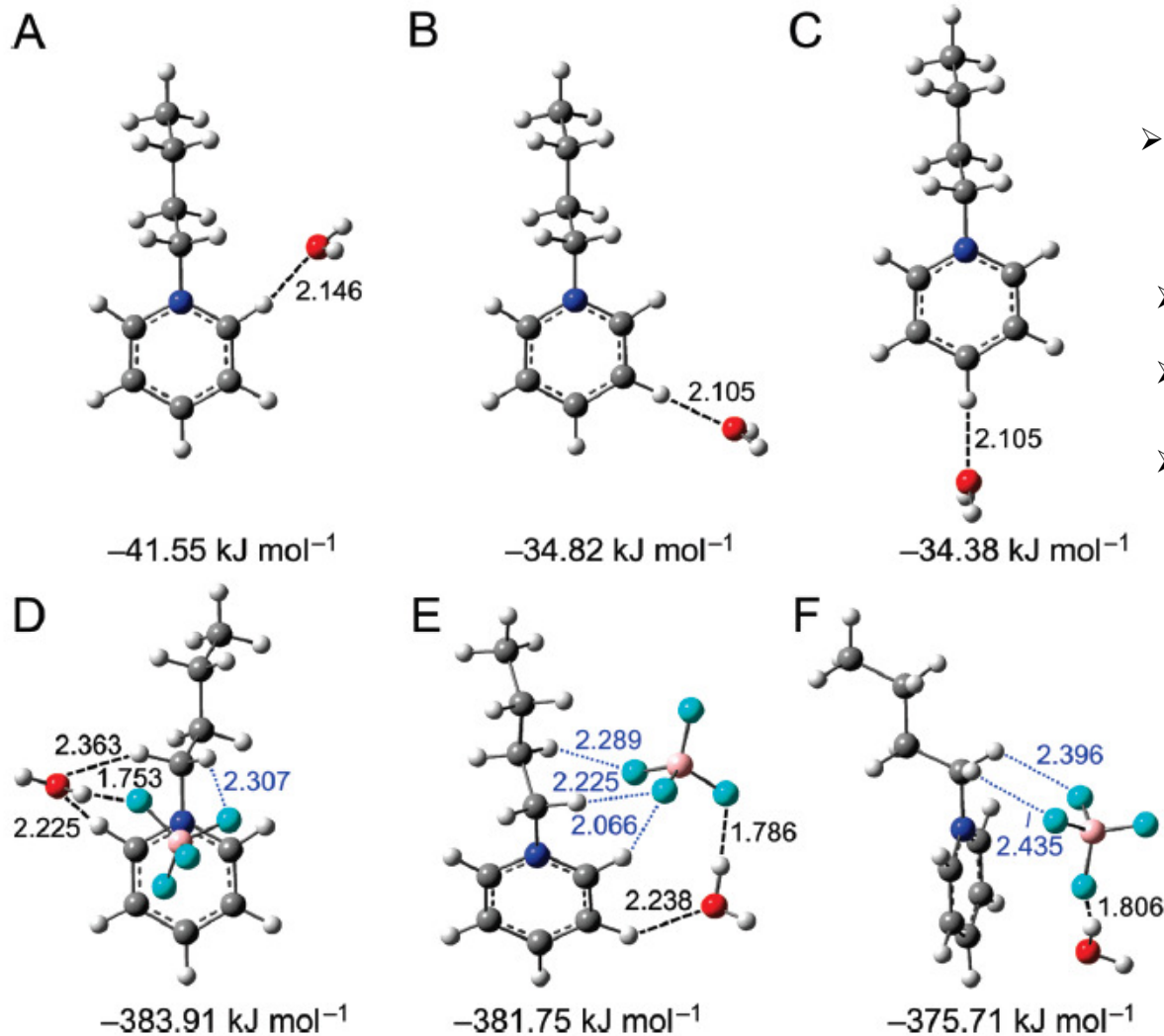


1. First, at low concentrations, single water molecules are isolated from each other and embedded in the IL environment
2. Then, as the water content increases, the water clusters form. When the size of the clusters is big enough ($x(\text{D}_2\text{O}) > 0.4$), some tetrahedral H-bonded D_2O molecules appear.
3. Finally, the self-associated D_2O clusters but not tetrahedral H-bonded D_2O become dominant at highest water concentrate

TABLE 1: Assignments of the Absorption Bands in the O–D Stretching Vibrational Region Based on Published Studies^{13,24,27} and Our DFT Calculations

wavenumber (cm^{-1})	assignment	abbreviation
~ 2704	ν_{as} of D_2O doubly H-bonded to BF_4^-	ν_{as}
2680–2660	terminal OD of self-associated D_2O clusters, H-bonded to BF_4^-	ν_{tc}
~ 2650	HDO formed by H/D isotope exchange	ν_{i}
~ 2604	ν_{s} of D_2O doubly H-bonded to BF_4^-	ν_{s}
2540–2440	self-associated D_2O clusters	ν_{c}
2400–2370	tetrahedrally H-bonded D_2O	ν_{t}

Theoretical possible geometry



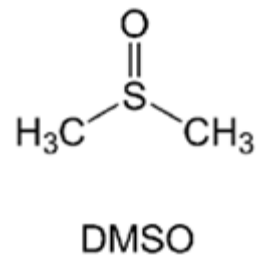
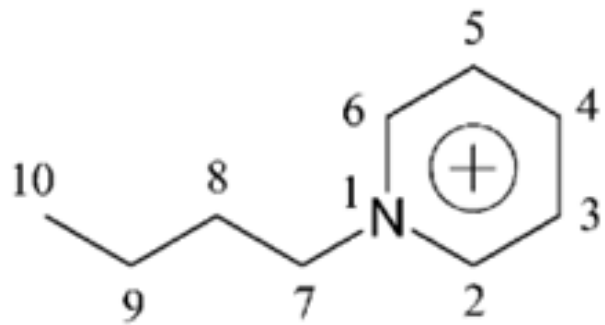
- H-bonds can exist between C2,6-H, C3,5-H, or C4-H on the pyridinium ring and the O atom of H₂O
- first conformer is the most stable
- Energy difference 7 KJ/mol
- all the C-H on ring can form H-bonds with W

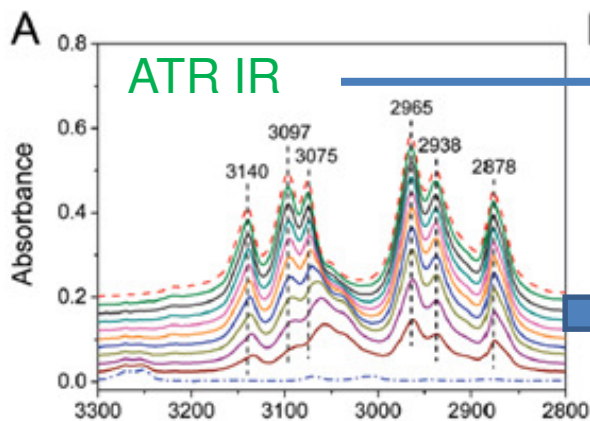
Result is distinct from the interactions between imidazolium ring and water

water can form H-bonds with the anion and the cation of [BuPy][BF₄] simultaneously

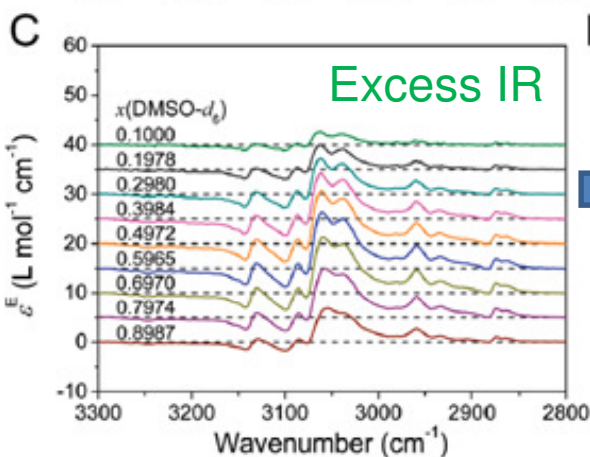
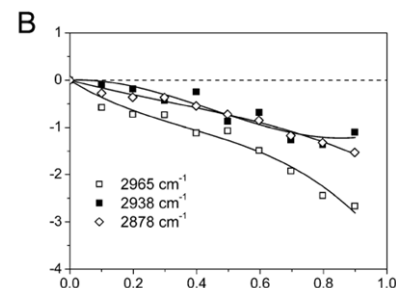
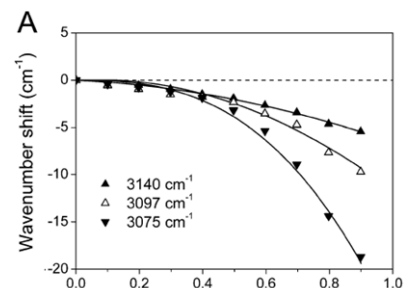
Thermal energy = KT
 2.48 kJ/mol
 0.60 kcal/mol

$([\text{BuPy}][\text{BF}_4]) + \text{DMSO}$

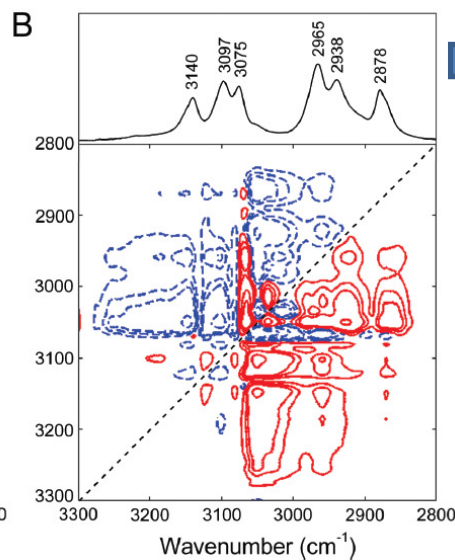
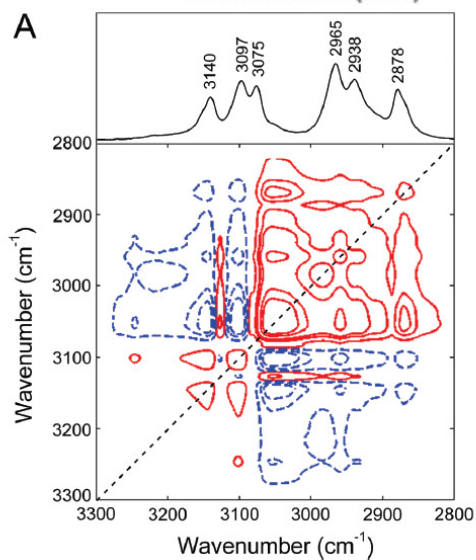




- Ring C-H.....red shifted
- In water it was...blue shifted
- DMSO and water show different influence on cation



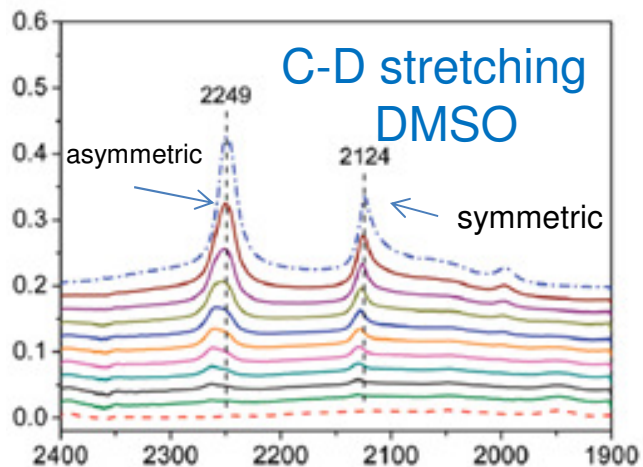
- negative excess bands at higher wavenumbers are due to the red shift of the IR bands
- ring C-H is the direct interaction for dms



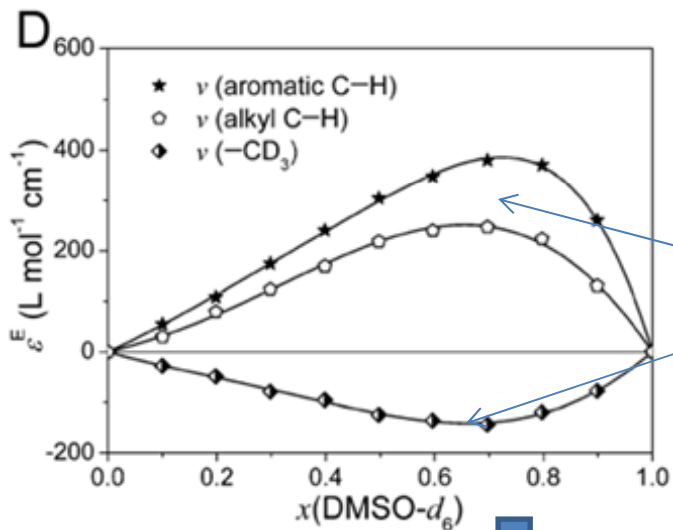
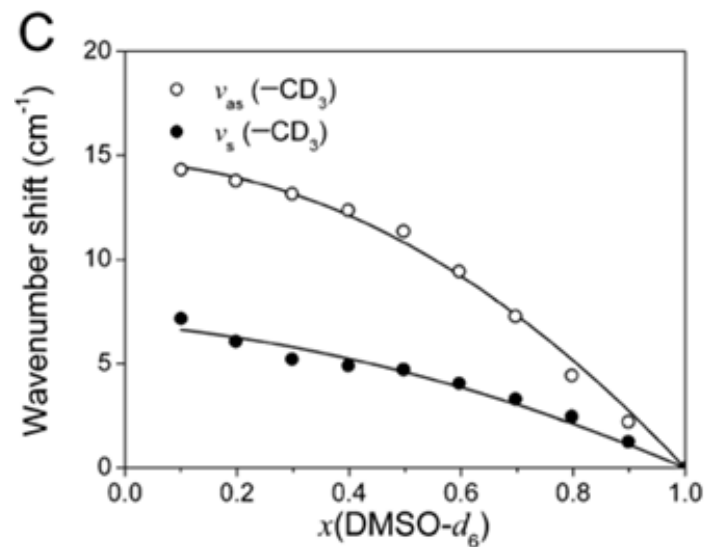
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- B- Asynchronous 2-d correlation spectroscopy

- 3140 and 2965 cm⁻¹ two representative bands...ring and alkyl

According to Noda's rule, negative cross peak in both spectra suggest that the absorption coefficient of ring C-H varies prior to that of alkyl C-H with increasing DMSO-*d*₆ content



Blue shifted by 14.3 and 7.2 cm^{-1}



- The directions of their band shifts are also opposite
- roles played by these alkyl groups are different

- ring C-H, the significant increase in molar absorptivity Agreement to red shift
- no spectroscopic evidence shows the alkyl C-H acts as preferential interaction sites

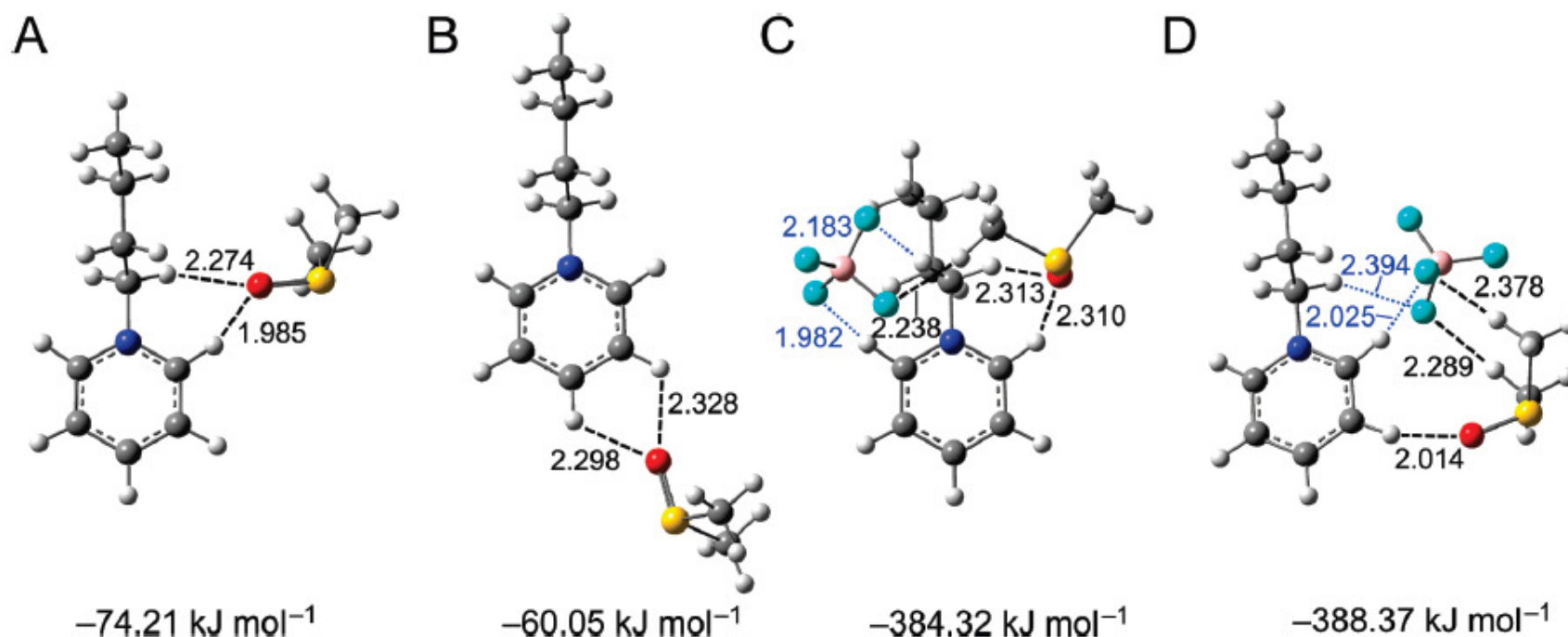
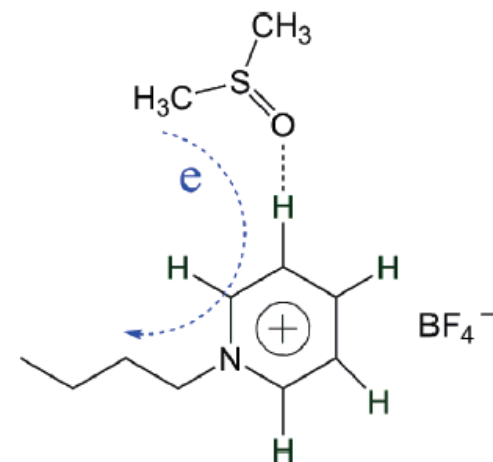


Figure 10. Possible positions and corresponding interaction energies for a DMSO molecule interacting with BuPy⁺ cation (A and B) and [BuPy][BF₄] (C and D). H-bonds involving DMSO molecules are denoted by dashed lines, those between the anions and cations are denoted by dotted lines, and the corresponding H···O and H···F distances are labeled in angstroms.

TABLE 2: Natural Population Analysis Charges (q , in e) of the Methyl and Butyl Groups in the Monomers and Their Changes (Δq) upon Formation of BuPy⁺–DMSO (Figure 10A,B) and [BuPy][BF₄]–DMSO (Figure 10C,D) Complexes

	$q(\text{monomer})$	Δq			
		Figure 10A	Figure 10B	Figure 10C	Figure 10D
2CH ₃ (DMSO)	-0.238	0.091	0.071	0.068	0.072
C ₄ H ₉ (BuPy ⁺)	0.354	-0.008	-0.013		
C ₄ H ₉ ([BuPy] [BF ₄])	0.346			-0.011	-0.006

SCHEME 2: Charge Transfer Model of the Alkyl Groups upon H-Bonding between DMSO and BuPy⁺ Cation^a



Conclusions

- (1) Water molecules preferentially interact with the BF_4^- anion, while DMSO can also interact with the anion through weak H-bonds of its methyl groups. Both water and DMSO can interact with the BuPy⁺ cation, and the favorable sites are the aromatic C-H with slight differences based on their specific positions on the ring.
- (2) A charge transfer model of the alkyl groups upon H-bonding between DMSO and BuPy⁺ cation has been proposed. The alkyl groups linked to the H-bond acceptor are electron-donating, while those connected to the H-bond donor are electron-withdrawing, both making positive contributions to the stability of the H-bond.
- (3) The strong anion-HOH-anion interaction can be accompanied by the H-bond between the O atom of water molecule and the aromatic C-H of the cation in [BuPy][BF₄].