

Proton Transfer in Polar Solution. Variational Transition State Theory Evaluation of the Rate Constant

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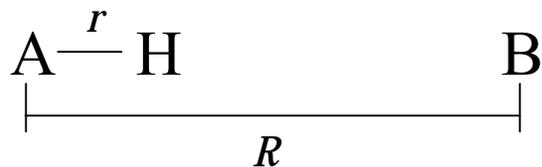
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Support

US DOE, Division of Chemical Sciences (OBES)

Model Proton Transfer System

AH ... B \rightarrow A⁻ ... HB⁺ in methyl chloride



AH - phenol

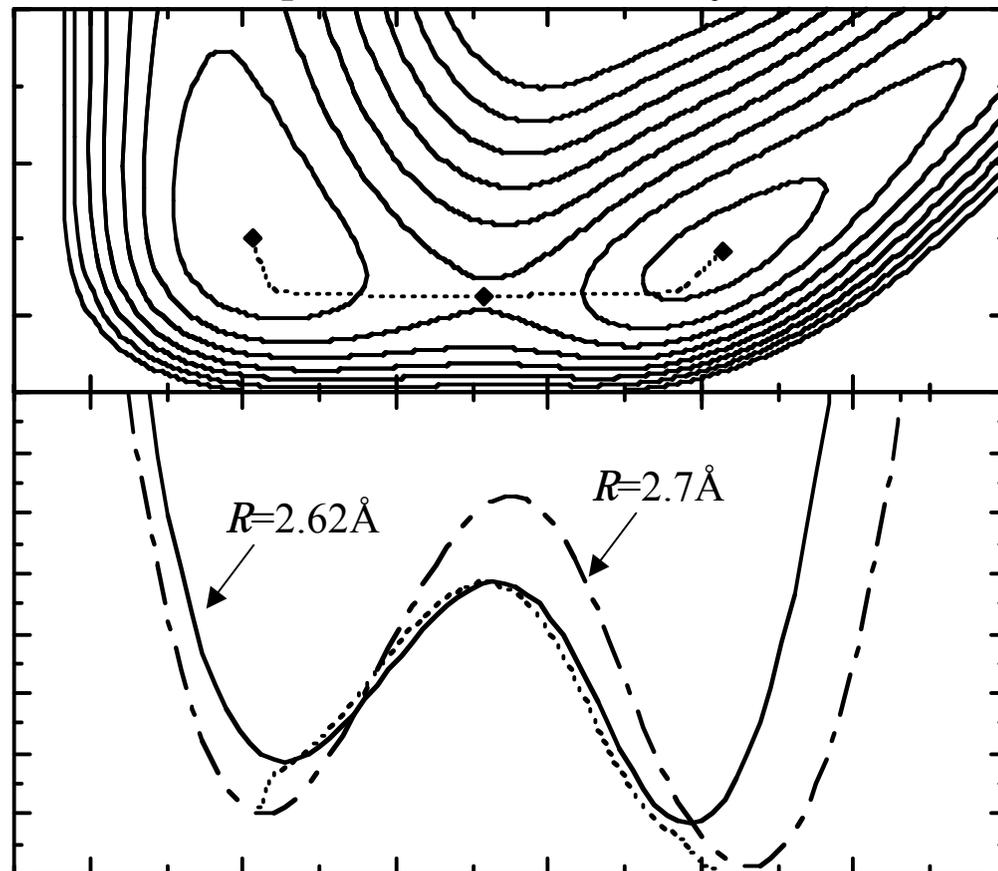
B - trimethylamine

Explicit solute + solvent
model; PMF determined
from solvent averages:

$$\frac{\partial W}{\partial r} = \langle \frac{\partial V_{\text{tot}}}{\partial r} \rangle_{\text{solv}}$$

$$\frac{\partial W}{\partial R} = \langle \frac{\partial V_{\text{tot}}}{\partial R} \rangle_{\text{solv}}$$

PMF for proton transfer in methyl chloride



Comparison of Calculated Proton Transfer Rate Constants (10^{10}s^{-1})

	<u>H</u>	<u>D</u>	<u>H/D KIE</u>
CVT (ES) 0.1	0.01	10	
CVT/SCT (ES)	16	1.0	16
CVT (NES) 0.1	0.01	10	
CVT/SCT (NES)	13	0.8	15
Curve-crossing TST (Azzouz, Borgis, 1993)	0.8	0.02	46
Centroid QTST (Azzouz, Borgis, 1993)	1.0	0.03	40
Surface hop. (Hammes-Schiffer, Tully, 1994)	8	2	4
Quantum Kramers (Antonio, Schwartz, 1999)	1.0	0.01	83

Conclusion: *Large variability in computed rate constants \Rightarrow opportunity for benchmark calculations of dynamical methods*