ADDITIONS AND CORRECTIONS

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Anas Al Natsheh,* Alexey B. Nadykto, Kurt V. Mikkelsen, Fangqun Yu, and Juhani Ruuskanen: Sulfuric Acid and Sulfuric Acid Hydrates in the Gas Phase: A DFT Investigation

Page 8914. After reviewing the thermodynamics section of our article and discussing terms included in the cluster internal energy with the technical support staff of ADF software,[1,2] we found that electronic effects were included in the total bonding energy term instead of the internal energy term. This means that the hydration energies given in the original paper have to be recalculated. Recomputed hydration enthalpies, entropies and Gibbs free energy are presented in the modified Table 15 and Figure 10. To examine the sensitivity of our results to the size of the basis set, we have obtained the global minima of sulfuric acid, water, sulfuric acid monohydrates (SW-a), sulfuric acid dihydrates (S2W-a) and sulfuric acid trihydrates (S3W-a) using the PW91 method with the ATZ2P basis set. Compared to the TZP basis set used in the original paper, ATZ2P has one extra diffuse s-STO, diffuse p-STO and polarization functions. A comparison of hydration free energies computed using both TZP and ATZ2P basis sets with the experimental results shows a very good agreement.

Thermodynamics Analysis

Entropies, enthalpies and Gibbs free energies of the cluster formation have been calculated and temperature and pressure dependencies of these properties have been studied. Temperatures and pressures have been selected in such a way as to represent conditions in different layers of the Earth's atmosphere such as troposphere, stratosphere and mesosphere.

The thermochemical analysis has been performed using the ADF software package 2002.03[1,2] and 2005.01b.[1,2]

Table 15 presents the entropies, enthalpies and Gibbs free energies of the different structures of sulfuric hydrates at pressure of 1 atm and temperature of 298.15 K using two possible reaction paths

$$H_2SO_4 + nH_2O \rightarrow H_2SO_4{\cdot}n(H_2O) \qquad n = 1-3 \tag{1}$$

$$H_2SO_4{\cdot}(n-1)(H_2O) + H_2O \rightarrow H_2SO_4{\cdot}n(H_2O) \qquad n = 1-3 \tag{2}$$

Gibbs free energy has been calculated using the following formulas

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

$$\Delta H = \Delta E + \Delta(PV) \tag{4}$$

$$\Delta(PV) \approx \Delta nRT \tag{5}$$

where ΔG is the Gibbs free energy change, ΔH is the change in the enthalpy, T is the temperature, ΔS is the entropy, ΔE is the internal energy change, P is the pressure of the gas, V is the volume of the gas, Δn is the change of moles and R is the universal gas constant.

Comparison of the Gibbs free energies summarized in Table 15 shows that changes in the Gibbs free energy for the first

TABLE 15: Thermodynamic Properties of Sulfuric Hydrates at 298.15 K and 1 atm[a]

str name	ΔS_1	ΔS_2	ΔH_1	ΔH_2	ΔG_1	ΔG_2	ΔG_{2*}	ΔG_{expt}	
SW-a	−32.1		−13.1			−3.5	−2.6	−3.6	±1
SW-b	−32.5		−13.0			−3.3			
SW-c	−32.6		−12.2			−2.5			
S2W-a	−65.4	−33.3	−26.1	−13.0	−6.6	−3.1	−2.6	−2.3	±0.3
S2W-b	−64.0	−31.9	−25.4	−12.3	−6.3	−2.8			
S2W-c	−69.8	−37.7	−25.9	−12.8	−5.0	−1.6			
S2W-d	−62.9	−30.8	−25.2	−12.1	−6.4	−2.9			
S2W-e	−64.9	−32.7	−25.1	−12.0	−5.8	−2.3			
S2W-f	−65.4	−33.3	−23.9	−10.9	−4.4	−0.9			
S2W-g	−68.8	−36.2	−24.3	−12.1	−3.8	−1.3			
S2W-h	−65.3	−33.1	−23.0	−9.9	−3.5	0.0			
S2W-i	−60.2	−28.1	−22.5	−9.4	−4.5	−1.0			
S2W-j	−57.6	−25.4	−22.0	−8.9	−4.9	−1.4			
S2W-k	−59.8	−27.7	−16.8	−3.7	1.1	4.6			
S2W-l	−60.3	−28.2	−16.0	−2.9	2.0	5.5			
S2W-m	−60.9	−28.7	−15.5	−2.4	2.7	6.2			
S3W-a	−102.7	−37.3	−38.1	−12.0	−7.4	−0.9	−1.1		
S3W-b	−103.3	−37.9	−37.0	−10.9	−6.2	0.4			
S3W-c	−103.2	−37.7	−36.5	−10.4	−5.8	0.8			
S3W-d	−95.3	−29.8	−34.8	−8.7	−6.4	0.2			
S3W-e	−94.9	−29.4	−35.3	−9.2	−7.0	−0.4			
S3W-f	−97.9	−32.5	−33.6	−7.5	−4.4	2.1			
S3W-g	−93.9	−28.5	−33.6	−7.5	−5.6	1.0			
S3W-h	−100.7	−35.2	−33.8	−7.7	−3.8	2.8			
S3W-i	−101.3	−35.8	−33.3	−7.2	−3.1	3.5			
S3W-j	−89.5	−24.1	−32.4	−6.3	−5.7	0.9			

[a] $\Delta S_{1,2}$ [cal/(mol K)] is the cluster entropy change, $\Delta H_{1,2}$ (kcal/mol) is the enthalpy change, and $\Delta G_{1,2,2*,expt}$ (kcal/mol) is the change in the Gibbs free energy calculated in 1,2 using the TZP basis set and 2* using the ATZ2P basis set and expt for experimental data by Hanson and Eisele.[5]

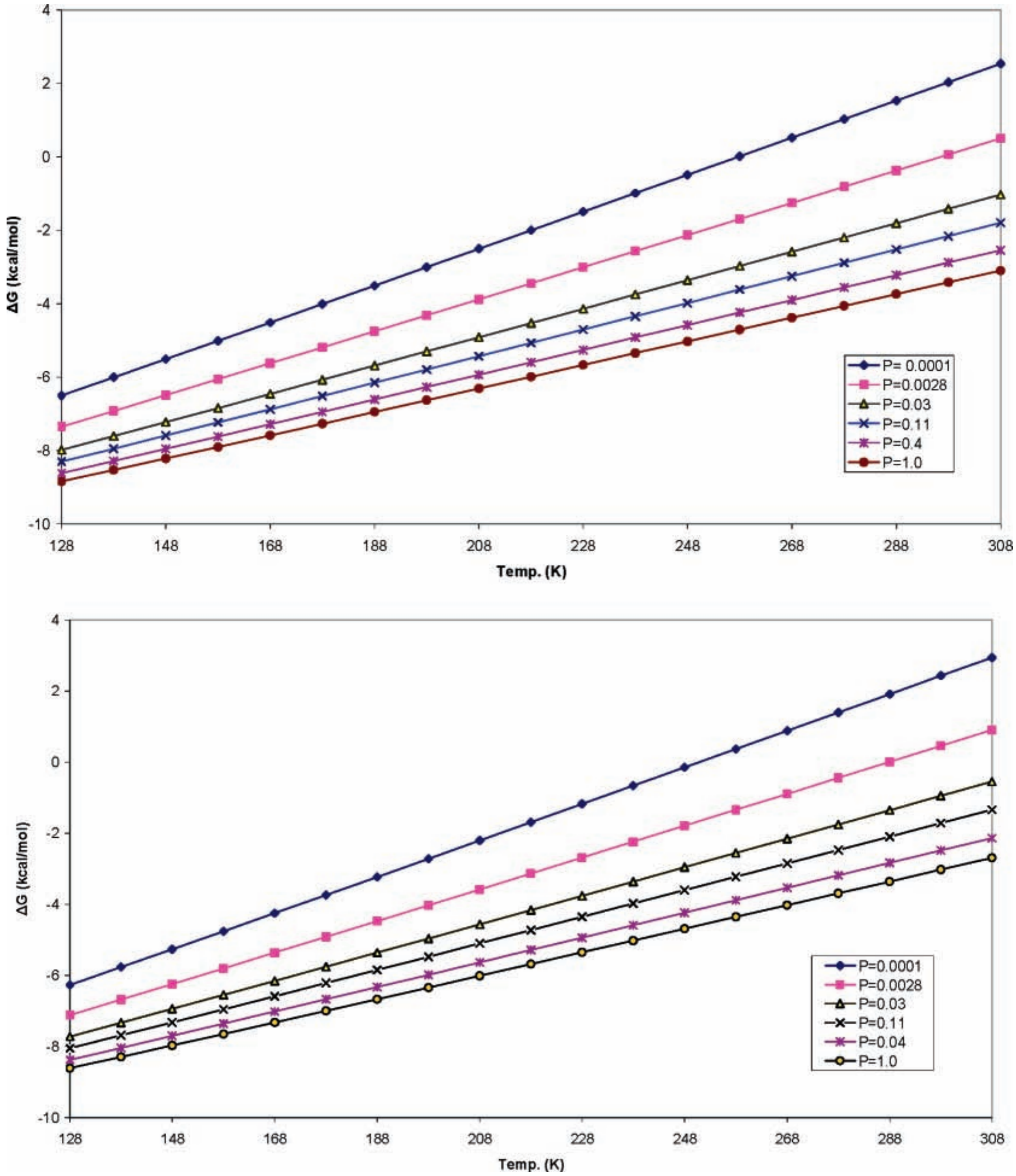

Figure 10. Effect of the pressure and the temperature on the Gibbs free energy of the sulfuric acid monohydrate (SW-a, top) and dihydrate (S2W-a, bottom) molecular conformations.

reaction path are significantly lower than those for the second reaction path. However, in the real atmospheric conditions this reaction path is limited kinetically. The Gibbs free energies for the second reaction path obtained in this study are ~3 and 7 kcal mol^{-1} lower than those given by Re et al.[3] and Bandy and Ianni,[4] respectively. PW91/TZP and PW91/ATZ2P Gibbs free energies are quite close and they are in better agreement with the strong hygroscopic nature of the sulfuric acid and exothermic character of the hydration reaction than those given by Re et al.[3] and Bandy and Ianni.[4] Both PW91/TZP and PW91/ATZ2P results are in very good agreement with experimental values reported by Hanson and Eisele.[5]

Figure 10 shows ΔG associated with the formation of SW-a (monohydrate of the sulfuric acid) and S2W−a (dihydrate of the sulfuric acid) via the second reaction path as functions of the pressure and temperature. As seen from Figure 10 the temperature dependency of ΔG, which increases with the temperature, is considerable. Comparison of curves in Figure 10 also shows that ΔG increases as pressure decreases. This leads us to conclude that low temperatures and higher pressures are favorable for the gas-phase hydration of the sulfuric acid.

References and Notes

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N. G. Connelly, D. J. H. Emslie, P. Klangsinsirikul, and P. H. Rieger*: Analysis of Electron Paramagnetic Resonance Spectra with Very Large Quadrupole Couplings

Page 12214. The experimental and simulated EPR spectra shown in Figure 2 are incorrect. The correct experimental spectrum is below; the correct simulated spectrum is in Figure 6 (α = 45°) of the original paper.

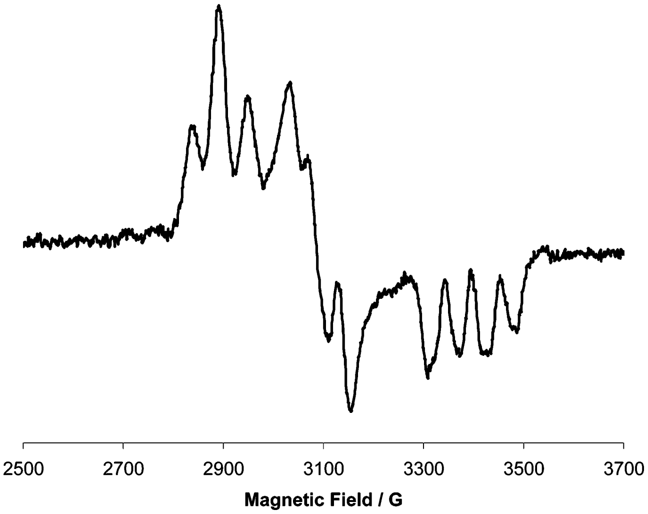

Figure 2. X-Band EPR spectrum of $[(PPh_3)(CO)Rh(RNNNR)_2Ir(CO)(PPh_3)]^+$(**2**) in CH_2Cl_2/thf at 100 K.

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