

# ADDITIONS AND CORRECTIONS

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G. E. Walrafen,\* W.-H. Yang, and Y. C. Chu: Raman Spectra from Saturated Water Vapor to the Supercritical Fluid

Page 1332. The dimer-based interpretation of ref 1 is withdrawn because it gives the *wrong sign* of  $\Delta H$ . The dimer model is replaced by a *rotationally excited monomer* model, in agreement with thermodynamics, and consistent with a measured isosbestic point.<sup>1</sup>

Density-normalized Raman spectra from saturated water vapor indicated an isosbestic point near  $3650\text{ cm}^{-1}$ , Figure 2 of ref 1. This phenomenon presupposes some type of equilibrium, thought previously to be a dimerization<sup>1</sup>. However, recent high-resolution ro-vibrational spectra of water vapor,<sup>2</sup> in which well-known, high ro-vibrational states<sup>3</sup> are readily identifiable, also display the same isosbestic point,  $\approx 3650\text{ cm}^{-12}$ . Hence, the equilibrium is now thought to involve low-to-high ro-excitation mainly of the symmetric stretch of the  $\text{H}_2\text{O}$  monomer.

Luck<sup>4</sup> measured the percentage of free, not hydrogen bonded, OH groups,  $P$ , from infrared absorption spectra of liquid water in equilibrium with its vapor up to 2 degrees ( $372\text{ }^\circ\text{C}$ ) below the critical temperature. He estimated that  $P = 100\%$ , with an uncertainty of less than  $-5\%$ . The heat of vaporization is zero at the critical point; hence it follows that 95% or more of the molecules are monomers in the vapor, in agreement with this erratum. Raman data also indicate that virtually all hydrogen bonds are broken in liquid water at  $400\text{ }^\circ\text{C}$ , despite the fact that the pressure employed, 4000 bar, yielded a density of  $0.9\text{ g/cm}^3$ .<sup>5</sup>

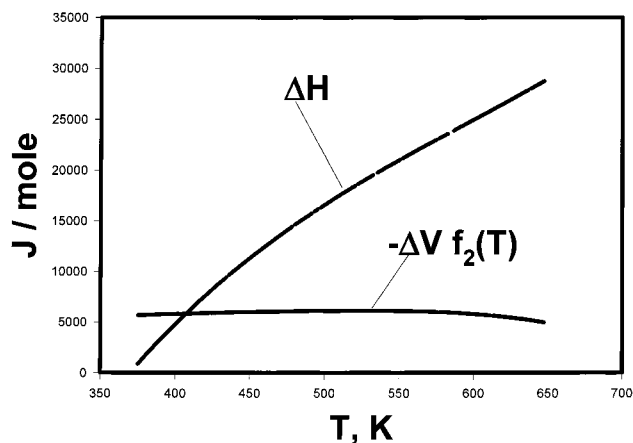
The critical pressure, 221 bar, is negligibly effective in forming hydrogen bonds, when it is recognized that 11 000 bar is associated with the re-formation of all broken hydrogen bonds in liquid water at  $30\text{ }^\circ\text{C}$ ,<sup>6</sup> or  $\approx 27\text{ 000 bar}$  at  $100\text{ }^\circ\text{C}$ .<sup>7</sup>

Water dimers are low-energy states, relative to monomers; energy is required to break hydrogen bonds. The formation of dimers from monomers is exothermic,  $\Delta H$  negative, and thus thermodynamically disfavored with temperature rise, the critical pressure of 221 bar, notwithstanding. These conditions are verified by Figure 1, which depicts the enthalpy and volume change calculated from the equilibrium constant, proportional to  $(A/B)$ , described below. The equilibrium refers to the reaction 1 mol of monomer (zero or low ro-excited) = 1 mol of monomer (high ro-excited); symmetric stretch, which gives high Raman intensity.

The most important feature of Figure 1 is that  $\Delta H$  is positive, whereas the formation of dimers requires a negative  $\Delta H$ .

The symmetric Raman stretch from water vapor occurs at  $3657\text{ cm}^{-1}$  at  $25\text{ }^\circ\text{C}$ .<sup>1</sup> The Raman peak shifts downward to  $\approx 3652\text{ cm}^{-1}$  at  $255\text{ }^\circ\text{C}$ , and then down to  $\approx 3648\text{ cm}^{-1}$  at  $314\text{ }^\circ\text{C}$  (Figure 2, ref 1). A further downward shift to as low as  $3628\text{ cm}^{-1}$  occurs at the critical temperature,  $374\text{ }^\circ\text{C}$  (Figure 1, ref 1).

The zero ro-symmetric  $\text{H}_2\text{O}$  stretch, i.e., with the  $J, J'; K_a, K'_a; K_c, K'_c$ , asymmetric top, rotational quantum numbers all zero, occurs at  $3657\text{ cm}^{-12}$ . A high ro-symmetric stretch with  $J, J' = 8, K_a, K'_a = 6$ , and  $K_c, K'_c = 3$ , occurs at  $3628\text{ cm}^{-12}$ . The above-



**Figure 1.**  $\Delta H$  and  $-\Delta V f_2(T)$  calculated from second-degree least-squares fit of  $\ln(A/B)$  vs  $1/T$ , along the saturation curve, where neither pressure nor temperature is constant; see ref 1.

described *downward* shift from  $3657$  to  $3628\text{ cm}^{-1}$  between 298 and  $647\text{ K}$  thus signals high rotational excitation and probably includes hot band effects as well. More importantly, ref 3 indicates a very pronounced clustering,  $\approx 100$  high ro-symmetric stretch levels, in the  $3610\text{--}3650\text{ cm}^{-1}$  range, all below the isosbestic point.

A measure (mainly symmetric stretch) of the ro-vibrational  $\Delta H$  vs temperature is obtained (Figure 1) by using Raman areas above the isosbestic frequency, designated  $B$ , which favors low ro, and below it, designated  $A$ , which favors high ro, levels. (See also the linear  $\ln(A/B)$  vs  $1/T$  approximation, Figure 5 of ref 1.)  $A/B$  is proportional to the equilibrium constant for the  $B = A$  monomer equilibrium, i.e., low-to-high ro monomer excitation.

Figure 1 portrays a detailed fit in which *both*  $\Delta H$  and  $-\Delta V f_2(T)$  were calculated from an exact differential, van't Hoff, Clapeyron approach; see ref 1. (This fit replace Figures 5–8.<sup>1</sup>) The  $\Delta H$  and  $-\Delta V f_2(T)$  values, Figure 1, refer to the reaction 1 mol of monomer (zero or low ro-excited)  $\rightarrow$  1 mol of monomer (high ro-excited), i.e., zero or low ro-symmetric stretch states above the isosbestic point vs a high ro population *distribution* below the isosbestic point. Here, the *full* derivative,  $-d \ln(A/B)/dT^{-1} = -S = (1/R)[\Delta H - \Delta V f_2(T)]$ , where  $f_2(T)$  is the temperature dependence of  $\Delta H_{\text{vap}}/\Delta V_{\text{vap}}$ .<sup>1</sup> The slope,  $S$ , is negative; hence  $\Delta H$  and  $-\Delta V f_2(T)$  ( $\Delta V < 0$ ) both contribute to the rise of  $\ln(A/B)$  with *decreasing*  $1/T$  on the saturation curve; i.e., the ro-vibrational excitation increases isobarically with  $T$  (thermal) and, to a much smaller extent, isothermally with  $P$  (compression).

Figure 1 indicates increasing thermal ro-excitation from  $373\text{ K}$  to the critical point,  $647\text{ K}$ .  $\Delta H$  increases from about  $212\text{ cal/mol}$  at  $373\text{ K}$  to about  $6875\text{ cal/mol}$  at  $647\text{ K}$ . This *sharp* rise in  $\Delta H$  is consistent with an increasing population of high ro states, but not with dimerization, for which the  $\Delta H$  should change very little. Figure 1 also indicates small and roughly constant compressional ro-excitation over the same temperature range.

If dimers were involved the method of Figure 1 would give *negative*  $\Delta H$  values, and their absolute magnitudes should have a very small-temperature dependence, neither of which is observed.

Although significant concentrations of dimers may not exist at the critical point, other strong interactions between monomers are likely to be present. Increasing collisions between monomers up to the critical density should almost certainly give rise to the rapidly increasing rotational quantum numbers. However, the probability of collisions yielding long-lived, linear or nearly linear, O—H $\cdots$ O units is small at high temperatures, especially when a sizable fraction of the molecules have energies above the hydrogen bond energy, about 2.5 kcal/mol.<sup>8</sup> A viable hydrogen bond between linear or nearly linear O—H $\cdots$ O units must execute, e.g., 5–10 O $\cdots$ O stretches, i.e., enough restricted translations between two H<sub>2</sub>O molecules to yield detectable Raman intensity, because the hydrogen bond vibrational period is only about 200 fs. Transient collisions, however linear in O—H $\cdots$ O, but lasting only for times  $\ll$  200 fs cannot be regarded as hydrogen bonds from a Raman point of view.

True, long-lived, dimeric states involving vapor phase water molecules should occur at low temperatures. For example, dimers

probably occur in cold fogs or in supersaturated water vapor such as might be found in a Wilson cloud chamber.<sup>9</sup>

## References and Notes

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