

Comment on “Study on the liquid–vapor interface of water. I. Simulation results of thermodynamic properties and orientational structure”

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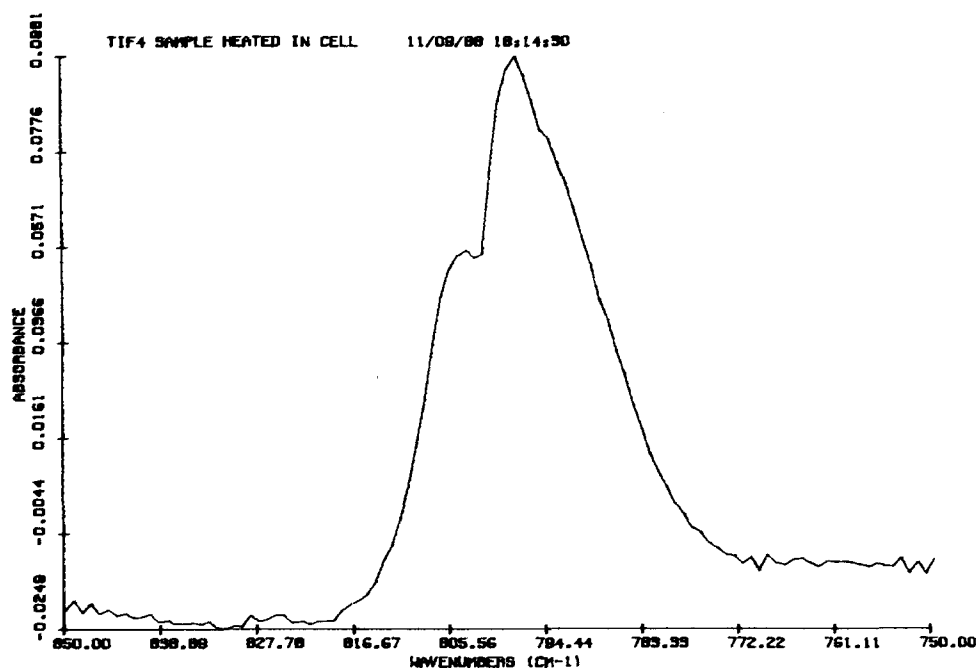


FIG. 1. The infrared spectrum of the ν_3 band of TiCl_4 .

FTIR set at its maximum resolution of 1 cm^{-1} . The band shape is nearly identical to the band shape observed for SiF_4 at this resolution. Since the Q branch is blended with the P branch, the band origin could not be located precisely. However, the Q region maximum of $798 \pm 1\text{ cm}^{-1}$ is in excellent agreement with the frequency of 800 cm^{-1} proposed by Beattie and Jones.⁸ Consequently, our previous assignment for the ν_3 band of TiF_4 is incorrect. This band is the ν_3 band of TiF_4 ; confirming the assignment proposed by Beattie and Jones.⁸

The correct assignment for the 772 cm^{-1} band is currently not known. Although we have recently reproduced the original experiments and now have also produced this product using KF and CaF_2 as the fluorinating agent, no additional bands arising from this molecule have yet been identified. Similar experiments using CCl_4 produced only CCl_3F and CCl_2F_2 in the flow cell. Although the kinetics for the TiCl_4 reaction will differ somewhat, this suggests that

the 772 cm^{-1} band may arise from TiCl_3F or TiCl_2F_2 . Work exploring this possibility is in progress.

The authors would like to thank Professor Ian Beattie for notifying us of his work prior to publication and Professor J. C. Light for allowing us to correct our previous error. We regret any inconvenience that this error may have caused.

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Comment on "Study on the liquid-vapor interface of water. I. Simulation results of thermodynamic properties and orientational structure"

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Theoretical studies of the liquid-vapor interface of water have been presented recently which begin to establish a molecularly detailed description of this surface.¹⁻⁴ These calculations are broadly consistent in the picture suggested

for the molecular structure of the water liquid-vapor interface. However, comparison of the different results obtained for the surface potential indicates that different quantities have been calculated in different works. This comment iden-

tifies the difference and presents a simple formula to evaluate it.

The computer experiments considered here treat a lamellar system with periodic boundary conditions. All densities are unchanged by translation in a plane parallel to the interface which we label as the xy plane. The z axis is perpendicular to the interface. Consider a plane at elevation z_l located within the liquid film symmetrically midway between the interfaces with the vapor phase and a second plane similarly disposed within the vapor film at elevation $z_v < z_l$. The average net electrical charge between the two planes is zero. The difference in the electrostatic potential at elevations z_v and z_l is then given by the formula^{2,5}

$$\phi(z_l) - \phi(z_v) = 4\pi \int_{z_v}^{z_l} dz' \rho_q(z') z', \quad (1)$$

where $\rho_q(z)$ is the mean charge density at height z . This integral is the total dipole moment of the charge density in the interfacial region.

The difference in question can be traced to the evaluation of the total dipole moment of the charge density in the interfacial region. In some works,^{1,4} the total dipole moment of the charge in the interfacial region has been equated with the sum of the molecular dipole moments of those molecules with centers between the two planes. Alternatively,² a distribution of partial charges has been assumed for each molecule and the total dipole moment of the charge in the interfacial region is evaluated by including all partial charges located in the region between z_v and z_l .

These two calculations give different answers for the same computer simulation data. If the data of Ref. 2 are analyzed by computing the average sum of the z component of the molecular dipole moments associated with the TIP4P model of water, then the electrostatic potential change in going from the vapor to the liquid phase is estimated to be (0.79 ± 0.04) V. If the same data are analyzed using the partial charges of the same force model, the result is the value reported in Ref. 2 (-0.13 ± 0.04) V. The difference between the two results is large compared both to the quantities under consideration and to the estimated statistical uncertainties.

A simple formula which indicates the source of this difference can be derived as follows⁶: Since the molecules are neutral and because the system is inhomogeneous only along the z direction, the charge density can be represented by

$$\rho_q(z) = -\frac{d}{dz} \left[P_z(z) - \frac{d}{dz} Q_{zz}(z) + \cdots \right]. \quad (2)$$

Here $P_z(z)$ is the z component of the density of molecular dipoles and $Q_{zz}(z)$ is the zz component of the density of molecular quadrupoles:

$$P_\alpha(\mathbf{r}) = \left\langle \sum_{m=\text{molecules}} \delta(\mathbf{r} - \mathbf{r}_m) \left[\sum_j q_{jm} [\mathbf{r}_{jm}]_\alpha \right] \right\rangle, \quad (3a)$$

$$Q_{\alpha\gamma}(\mathbf{r}) = \left\langle \sum_{m=\text{molecules}} \delta(\mathbf{r} - \mathbf{r}_m) \times \left(\frac{1}{2} \right) \left[\sum_j q_{jm} [\mathbf{r}_{jm}]_\alpha [\mathbf{r}_{jm}]_\gamma \right] \right\rangle. \quad (3b)$$

Here \mathbf{r}_m is an arbitrarily chosen center within the m th mole-

cule. The quantity $[\mathbf{r}_{jm}]_\alpha$ is the α th Cartesian component of the position of the j th partial charge, q_{jm} , of the molecule m with respect to the center \mathbf{r}_m . If the Eq. (2) for the charge density is inserted into Eq. (1) we obtain precisely

$$\phi(z_l) - \phi(z_v) = 4\pi \int_{z_v}^{z_l} dz' P_z(z') - 4\pi [Q_{zz}(z_l) - Q_{zz}(z_v)]. \quad (4)$$

The quadrupolar terms appearing in this equation represent the difference in the electrostatic potential obtained by the two approaches described above and this is the result which was sought. Because z_l and z_v are in isotropic phases

$$Q_{zz}(z_l) = \left(\frac{1}{3} \right) \text{Tr} [Q_{\alpha\gamma}(z_l)] = \left(\frac{1}{6} \right) \left\langle \rho_l \left[\sum_j q_{jm} r_{jm}^2 \right] \right\rangle, \quad (5)$$

for example, where ρ_l is the molecular density of the liquid phase. This quantity is generally nonzero and is a property of the bulk liquid. Eq. (4) is independent of the choice of the molecular center in evaluating molecular multipole moments. It should be noted particularly that the integral of the molecular dipole density $P_z(z)$ (and, thus, the electrostatic potential obtained by the first method discussed above) generally does depend on the choice of center at which the molecular dipole is located, even for the neutral molecule systems considered here.

For the TIP4P model under the conditions studied in Ref. 2, the quadrupole terms of Eq. (4) are found to be 0.91 V. This is to be compared with the empirical difference of $[(0.79 \pm 0.04) - (-0.13 \pm 0.04)]$ V = (0.92 ± 0.06) V. Reference 4 reported only the value of the integral on the right-hand side of Eq. (4). Those values ranged between 0.10 V and 0.17 V for temperatures between 400 and 250 K. Under the conditions of that work, the quadrupolar contributions shown in Eq. (4) range from 0.7 to 0.8 V. Therefore, if the partial charges of the CC model of water⁷ used in Ref. 4 are taken literally, the surface potential estimates obtained from the data of Ref. 4 should be approximately -0.6 V.

The spatial variation of the electrostatic potential through the interfacial region also is significantly affected by nondipolar features of the charge distributions of the water molecules. Reference 2 explicitly presented the electric fields, $E_z(z)$, compared them with $-4\pi P_z(z)$, and noted that these two quantities behave differently with progress through the interfacial region. For investigation of the interfacial electric fields, truncation of Eq. (2) is approximate and unnecessary. The interfacial electric fields can be obtained simply from the relations utilized in Ref. 2 which imply Eq. (1) for the electrostatic potential.

These results and Eq. (4) can provide an interpretation for the small value of the surface potential indicated⁸ for liquid water, since in that case the quadrupolar and dipolar terms can contribute oppositely. For liquids less polar than water, the contribution from the molecular quadrupole density of the bulk phases could dominate the surface potential.

Equation (4) indicates yet again² that slight adjustment of the molecular charge distributions could bring the computed surface potentials into agreement with recent experi-

mental estimates of the surface potential.⁸ However, ambiguities still exist regarding interpretation of the available experimental data⁹ and adjustments are not pursued here.

Note added in proof. The comments above are also relevant to the more recent contribution of M. Matsumoto and Y. Kataoka, *J. Chem. Phys.* **90**, 2390 (1989) on the liquid-vapor interface of methanol.

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ERRATA

Erratum: Solvent dynamical effects in electron transfer: Numerical predictions of molecularity effects using the mean spherical approximation [*J. Chem. Phys.* **90**, 1720 (1989)]

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The first line of text on p. 1721 was inadvertently omitted during transfer from the galley proofs to the final journal format, so that parts of the two sentences at the bottom of p. 1720 and the top of p. 1721 are missing. The text should read: "The consequent nonexponential relaxation kinetics arise physically from the differing environments of solvent mole-

cules close to and distant from the solute. Wolynes^{3(c)} recently outlined a linearized microscopic treatment of nonequilibrium solvation which can account for such spatially dependent dynamical effects, and applied it within the so-called 'mean spherical approximation' (MSA) which treats the solvent as hard spheres with imbedded dipoles.²³"

Erratum: The benzene ground state potential surface. II. Harmonic force field for the planar vibrations [*J. Chem. Phys.* **87**, 2564 (1987)]

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The final six entries in Table X of Ref. 1 should be reversed in sign and these valence force constants are given in Table I. These signs are consistent with the symmetry force constants in Table XI of Ref. 1 and with the transformation using coordinates defined in Table II of Ref. 1.