

determined as 4.7, 4.7, and 1.6 kcal/mol for I, II, and III, respectively.<sup>3</sup> The measured increases in  $\Phi_F$  by factors of 35 for I and 6 and 4 for II and III show that while the efficiencies of H bonding are similar for I and II the enhancement of fluorescence yield by H bonding is far greater for I than either II or III. At  $-196^\circ$  both I and II show a sharp increase in fluorescence and decrease in P and T-T absorption intensities at low propanol concentrations, but the magnitude of this effect is much greater for I than II. Thus an additional factor besides H bonding must contribute to give the effects we observe.

Lim and Yu<sup>8</sup> have shown that upper ( $n, \pi^*$ ) states either triplet or singlet perturb the phosphorescence emission. Since H bonding raises the ( $n, \pi^*$ ) levels much more than singlets, the relative interactions should be changed. Thus the H-bond strength and the strength of the ( $n, \pi^*$ ) interaction should couple to perturb singlet and triplet state properties in hydroxylic solvents. Lim and Yu showed that either of two mechanisms could be operative. (1) The emitting  $^1(\pi, \pi^*)$  state is coupled with the  $^1(n, \pi^*)$  by vibrational coupling. In turn, the  $^1(n, \pi^*)$  state is spin-orbit coupled to the lowest  $^3(\pi, \pi^*)$  state. (2) The  $^1(\pi, \pi^*)$  level is spin-orbit coupled to a  $^3(n, \pi^*)$  level which is coupled to the  $^3(\pi, \pi^*)$  emitting level. The positions of  $^3(n, \pi^*)$  states intermediate in energy between the fluorescent  $^1(\pi, \pi^*)$  level and the phosphorescent  $^3(\pi, \pi^*)$  level are not known. The energy of the lowest  $^1(n, \pi^*)$  level has been determined indirectly by Coppens, *et al.*<sup>4</sup> The lowest  $^1(n, \pi^*)$  band in these compounds has been estimated to be 327 nm for I and II and 314 nm for III. Theoretically these authors calculate the energies to be 327 nm for I; 319 nm for II; and 314 nm for III.

Mechanism (1) of Lim and Yu seems to best fit our results. This follows from the fact that P and T-T absorption intensities decrease at very small propanol concentrations. If the  $^1(n, \pi^*)$  state is responsible for the main interaction, then H bonding decreases the interaction energy decreasing the amount of triplet formation. However, if the main transfer process occurs *via* the  $^3(n, \pi^*)$  we expect the intensity of P and T-T absorption to be increased at low propanol concentrations. (This is observed in our previous work for 1,2:7,8-dibenzacridine<sup>2</sup>.) Thus, unless the  $^3(n, \pi^*)$  level is fortuitously just lower in energy than the emitting  $^1(\pi, \pi^*)$  level our data favor an interaction involving the  $^1(n, \pi^*)$  level.

The interactions we observe can be understood in terms of both H bonding and the position of the  $^1(n, \pi^*)$  level. For III there is a low H-bonding probability and the energy gap between the fluorescent level at 350 nm and the  $^1(n, \pi^*)$  level at 314 nm is  $3200 \text{ cm}^{-1}$  while for I and II it is  $2000 \text{ cm}^{-1}$  and either  $2000$  or  $2600 \text{ cm}^{-1}$ . All of our data point to the fact that interaction is greater for I than for II.

Lim and Yu<sup>8</sup> also found that the degree of polarization of phosphorescence of I changed to a much larger degree than did that of II, indicating a much larger degree of vibronic spin-orbit interaction in I. These data all tend to show better agreement with the theoretical value of  $^1(n, \pi^*)$  for II found by Coppens, *et al.*,<sup>3</sup> rather than the experimental value.

Significant changes occur in F and in T-T absorption at propanol concentrations above 1% at  $-196^\circ$ . These seem to be due to a change in the structure of the glassy matrix. We have suggested this elsewhere<sup>2</sup> and it seems to be a general occurrence in most heterocyclics we have studied. The shifts in the T-T absorption spectrum of III can be attributed to the same effect. The shift in the T-T absorption of II occurs at too low a propanol concentration to be attributable to a change in glass composition. Also, the shift in phosphorescence is  $100 \text{ cm}^{-1}$  to lower energies compared with a  $400\text{-cm}^{-1}$  shift in T-T absorption. The conclusion seems to be that the upper absorbing triplet level is itself shifted by the H bonding and it may be influenced by an ( $n-\pi^*$ ) level.

### The Equilibrium Rate of Exchange of Water Molecules at the Air-Water Interface Using Nuclear Magnetic Resonance Spectroscopy

by Dinesh O. Shah

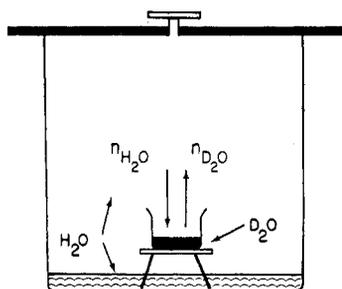
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When water and its vapor are in equilibrium, the number of molecules leaving the water surface is the same as the number entering the water surface from the vapor. As a result, there is no net change in the number of molecules either in the vapor or in the liquid phase. In this study the equilibrium rate of exchange of water molecules at the air-water interface has been determined using nuclear magnetic resonance (nmr) spectroscopy. In nmr spectra,  $\text{H}_2\text{O}$  shows a resonance signal at  $\tau$  4.8 (ppm) with respect to external TMS, whereas  $\text{D}_2\text{O}$  does not.<sup>1</sup> Moreover, the area under a resonance peak is proportional to the number of protons present in the sample. Therefore, one can determine quantitatively the amount of  $\text{H}_2\text{O}$  present in  $\text{D}_2\text{O}$ .

Figure 1 schematically shows the experimental arrangement used to measure the rate of exchange of water molecules at the interface. A large glass tank (12-in. diameter; 12-in. height), containing water and an

(1) H. Inoue and T. Nakagawa, *J. Phys. Chem.*, **70**, 1108 (1966).



EQUILIBRIUM RATE OF EXCHANGE  
OF WATER MOLECULES AT THE  
AIR-WATER INTERFACE

Figure 1. A schematic diagram showing the experimental arrangement to measure the equilibrium rate of exchange of water molecules at the interface.

empty 50-ml capacity beaker placed on a stand, was kept covered for a period of 2–3 days to achieve equilibrium conditions between the water and its vapor at  $25 \pm 0.5^\circ$ .  $D_2O$  (2 ml) (purity  $\approx 99.8\%$ ) was delivered by a pipet through a hole in the cover to the beaker. In the actual experiment seven empty beakers were placed in the glass tank. The content of each beaker was taken out after a specific time interval (0, 5, 10, 15, 20, 40, or 60 min) and transferred to an nmr sample tube. The area under the water resonance peak in the nmr spectra increased with time, indicating the increase in water content of  $D_2O$  (Figure 2). The results were reproducible within  $\pm 5\%$ , which essentially depended upon the reproducibility of the integrator of the nmr spectrometer. The inset in Figure 2 is a calibration plot of the area under the water peak and the volume per cent of  $H_2O$  in  $D_2O$ . The slope of the calibration plot indicates an increase of 11 units of area for each volume per cent of  $H_2O$  added in  $D_2O$ . The slope of the area under water peak vs. time plot gives an increase of 19.2 units of area per hour, which corresponds to 1.745 vol %  $H_2O$  in  $D_2O$ . Since the original amount of  $D_2O$  was 2 ml, its 1.745 vol % corresponds to 34.9 mg of  $H_2O$ . Hence, this suggests that the net amount of  $H_2O$  that entered the  $D_2O$  from vapor phase in 1 hr was 34.9 mg. Since the cross-sectional area of the beaker was  $11.339 \text{ cm}^2$ , the net amount of  $H_2O$  exchanged per  $\text{cm}^2$  per hour at equilibrium was 3.07 mg.

The only assumption involved here is that, at equilibrium, the rate of exchange of molecules at the water vapor–water interface is the same as that at the water vapor– $D_2O$  interface. This seems valid in view of the fact that both  $H_2O$  and  $D_2O$  have approximately the same surface tension, *i.e.*, 72.75 dyn/cm for  $H_2O$  and 72.80 dyn/cm for  $D_2O$ .<sup>2</sup> This suggests that molecules at the surface experience the same cohesive force in both liquids. It should be pointed out that the present experiment measures only the net number of  $H_2O$  molecules that enter and remain into  $D_2O$  liquid from the vapor phase as a result of exchange of molecules at the

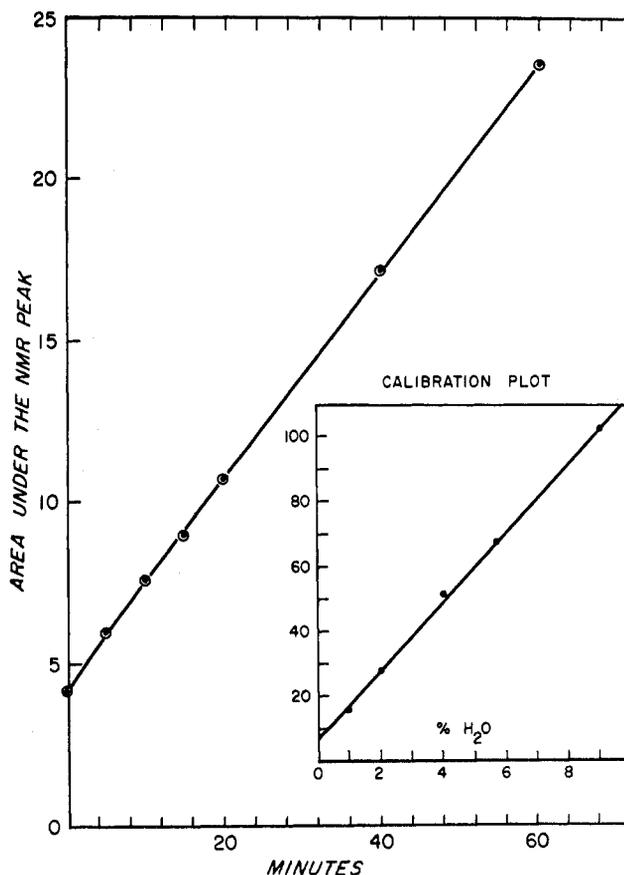


Figure 2. The plot of area under the water peak in the nmr spectra of  $D_2O$  from the beaker vs. time: inset, a calibration plot for the area under the water peak vs. volume per cent of  $H_2O$  added to  $D_2O$ .

air–water interface when water vapor is at its equilibrium concentration, and does not measure the total number of molecules striking the interface from vapor phase or the number of molecules leaving the liquid phase. The rate of exchange of water molecules at the air–water interface at equilibrium ( $3.07 \text{ mg/cm}^2 \text{ hr}$ ) determined in this work is much smaller than the rate of evaporation of water ( $30\text{--}72 \text{ mg/cm}^2 \text{ hr}$  depending upon the distance between the desiccant and the interface) observed in our own laboratory as well as by other investigators.<sup>3</sup> In the evaporation measurements a desiccant is suspended close to the water surface, which causes a gradient of partial pressures, and hence a faster rate of transport occurs. In equilibrium conditions, there is no such gradient involved. It is evident that the diffusion resistance of the boundary layer will decrease in the presence of a desiccant near the interface as compared with that in the equilibrium conditions. Therefore, the conditions at the interface would be strikingly different during evaporation as compared with those at equilibrium.

(2) W. J. Moore, "Physical Chemistry," 3rd ed, Prentice-Hall, Englewood Cliffs, N. J., 1962, pp 453 and 229.

(3) R. J. Archer and V. K. La Mer, *Ann. N. Y. Acad. Sci.*, **58**, 807 (1954).

For the exchange of molecules across the interface, one could conceptually consider that in half of the surface area the molecules go from the vapor to the liquid and in the other half from the liquid to the vapor phase. Therefore, it can be considered that in a 1-cm<sup>2</sup> area at the interface, 3.07 mg of H<sub>2</sub>O molecules go into D<sub>2</sub>O through a 0.5-cm<sup>2</sup> area, and from the other 0.5 cm<sup>2</sup> the same number of D<sub>2</sub>O molecules goes to the vapor phase. In order to calculate the number of water molecules coming out of the interface from an area equal to that of a water molecule, we have to first determine the number of water molecules that can be accommodated in 0.5 cm<sup>2</sup> of area at the interface. Dividing the number of molecules that comes out of 0.5 cm<sup>2</sup> of the interface per second by the number that can be accommodated in 0.5 cm<sup>2</sup> gives the number of molecules that will come out of the area equal to that of a water molecule per second. Let us consider the number of H<sub>2</sub>O molecules that can be accommodated in a 1-cm<sup>2</sup> area of the interface. Using the density of water at 25° (0.997 g/ml) and the Avogadro number, the number of H<sub>2</sub>O molecules in 1 ml is found to be  $0.337 \times 10^{23}$ . The average thickness of the first layer of water molecules at the interface can be assumed to be 2.88 Å calculated<sup>2</sup> from van der Waals constant *b* or from measuring dimensions of sealed space-filling Fisher-Taylor-Hirschfelder molecular models in various orientations. The number of H<sub>2</sub>O molecules present in a layer of 1 cm<sup>2</sup> area and 2.88 Å thickness was found to be  $0.96 \times 10^{15}$ . Therefore, the number of molecules in 0.5 cm<sup>2</sup> of the interface is  $0.48 \times 10^{15}$ . The average number of molecules that will come out of an area equal to that of a water molecule per second will be  $2.8544 \times 10^{16}$  (*i.e.*, the number of molecules leaving 0.5 cm<sup>2</sup> of area at the interface per second) divided by  $0.48 \times 10^{15}$ . This number is found to be 59.46. *This suggests that about 60 molecules per second escape from the interface from an area equal to that of a water molecule and hence the average residence time of a water molecule at the interface will be 1/60th of a second.* Thus, the escape of water molecules from the liquid to the vapor phase seems to be a slow process as compared with other molecular processes. This may be related to the high surface tension of water ( $\approx 72$  dyn/cm). In organic liquids having low surface tension, this process may be considerably more rapid. Theoretical calculations on the number of H<sub>2</sub>O molecules striking the interface from the vapor phase and those entering into the liquid have been reported elsewhere.<sup>4</sup>

In summary, the present paper reports, using nmr spectroscopy, that the molecular exchange at equilibrium is a relatively slow process and that 3.07 mg of water is exchanged at the interface in equilibrium per cm<sup>2</sup> per hr at 25°, which corresponds to 60 water molecules leaving (or entering) the interface per second from an area equal to that of a water molecule.

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(4) D. O. Shah, Proceedings of 70th AIChE National Meeting, 1971, p 24.

### Formation of Diamond. V. The Substitution of Nitrogen-15 for Nitrogen-14 in Diamond

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Comparison of defects and impurities in natural and synthetic diamond has attracted attention,<sup>2</sup> not only for the insights such study might afford on the origin of natural material but also for its value in understanding the mechanical properties of the crystals.

The theoretical work and studies of the peculiarities of spectra of particular natural crystals have proceeded further than the search for experimental generality. A difficulty occurs in the search for charged centers other than nitrogen, because the nitrogen display in spin resonance spectra includes a central line at  $g = 2.002$  which would obscure the spectrum of trapped electrons if they were present. Experiments which might avoid this difficulty include: (1) compensation of the spin-active nitrogen with for example boron or aluminum; (2) study of the synthetic diamond formed in the absence of a catalyst in the hope that the concentration of nitrogen would be different; and (3) supposing the nitrogen to be chemically necessary to the nucleation of the diamond, study of diamonds synthesized in the presence of <sup>15</sup>N, which has a different nuclear spin and hence a different spin resonance spectrum (two esr lines symmetrically about  $g = 2$ ).

Experiments of the first type have been done but have given no useful information, perhaps because the conditions needed for boron and aluminum diffusion also permit the out-diffusion of trapped electrons. The experimental challenge remaining is twofold: first,

(1) General Electric Co., West Lynn, Mass. 01905.

(2) See for example (a) W. V. Smith, P. P. Sorokin, P. L. Gelles, and G. T. Lasher, *Phys. Rev.*, **115**, 1546 (1959); (b) R. M. Deming, *Amer. Mineral.*, **46**, 740 (1961); (c) C. M. Huggins and P. Cannon, *Nature*, **194**, 829 (1962); (d) R. J. Cook and D. H. Whiffen, *Proc. Roy. Soc., Ser. A*, **295**, 99 (1966); (e) R. P. Messmer and G. D. Watkins, *Phys. Rev. Lett.*, **25**, 656 (1970).