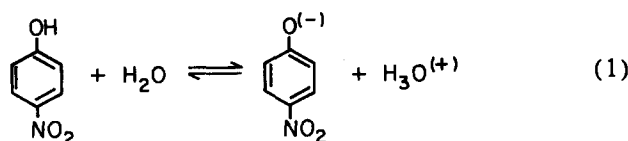


# Study of chemical reactions by surface second harmonic generation: *p*-Nitrophenol at the air-water interface

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In recent years, optical second harmonic generation (SHG) has been shown to provide valuable new information on a number of interfacial properties.<sup>1</sup> Since SHG is electric dipole forbidden in the bulk, this technique can be used to probe selectively the interfacial layer between two centrosymmetric media. Thus a wide variety of surfaces have been studied by this technique; a substantial amount of knowledge has been gathered about concentration, orientation, and spectroscopy of the species at the interfaces.<sup>2-13</sup> In our earlier work, we focused our attention on the relative<sup>12</sup> and absolute<sup>13</sup> orientation of molecules at the surface of liquid solutions. We now address the question of how the asymmetry in the forces experienced by the molecules in the interfacial region affects simple chemical equilibria. Specifically, using this technique we have investigated the acid-base equilibrium between *p*-nitrophenol (HA) and its anion (A<sup>-</sup>).



As we will show, not only do the concentrations of the various species in the interfacial region differ from their bulk values, but also the relative concentrations do not correspond to the bulk equilibrium constant. The "equilibrium constant" in the surface region is vastly different from that in the bulk. The key factor is most likely the reduced polarity at the surface due to the low density of molecules on the vapor side of the surface. The effect of this is to decrease the stability of charged species, e.g., A<sup>-</sup>, to such an extent that the equilibrium in the interfacial region overwhelmingly favors the neutral undissociated HA molecules. It is to be noted that although the concentrations are dependent on their position, varying in a continuous, though very sharp way, from the bulk vapor to the bulk liquid, we can still define an average concentration for each of the species in this inhomogeneous region. We then seek to compare the relative average concentrations of the species in the interfacial region, e.g., A<sup>-</sup>/HA, with the relative concentrations given by the bulk equilibrium constant. In order to treat the position-dependent concentrations (activities) in the interfacial region, we would use the chemical potential, since its value for a given species is the same at all positions in the system, i.e., bulk liquid, vapor, and the inhomogeneous interfacial region. Discussions of this approach will be postponed to a later publication.

The experimental setup consisting of a cavity-dumped, synchronously pumped dye laser, and single photon counting electronics is described elsewhere.<sup>13</sup> The component of the surface second order nonlinear susceptibility  $\vec{\chi}_s^{(2)}$  per-

pendicular to the plane of incidence was measured by setting the analyzer to collect only the *s*-polarized SH light. Such an arrangement is selected because it contains the contribution from the surface region alone and not the bulk region.<sup>2</sup>

The observed *s*-polarized SH field amplitude ( $E_s^{2\omega}$ ) as a function of bulk pH of the solution is shown in Fig. 1. We found in earlier work<sup>13</sup> that up to a monolayer the nonlinear susceptibility  $\vec{\chi}_s^{(2)}$  can be written as

$$\vec{\chi}_s^{(2)} = N_s \langle \vec{\alpha}^{(2)} \rangle, \quad (2)$$

where  $N_s$  is the number of molecules per unit area of the surface and  $\vec{\alpha}^{(2)}$  the molecular polarizability. From this relation it follows that the second harmonic field  $E_s^{2\omega}$  is linear in  $N_s$ . As the bulk pH is varied, the relative amount of HA and A<sup>-</sup>, as given by the bulk equilibrium constant for reaction (1) changes. This results in a change in  $N_s$ , as the latter depends on bulk concentrations. At low pH, the bulk concentration of HA has its largest value and this leads to a high surface coverage of neutral HA molecules. In accordance with this an intense signal (about 80 times that of water) was observed. In extremely alkaline media (pH > 10), the bulk HA molecules are almost totally converted into the anion and we found that the SH signal decreased to the value obtained from pure water. If there was a significant anion concentration at the surface we would readily observe it since its SH signal should be more than 10 times that of water. The possibility of undissociated sodium phenolate formed by neutralization with NaOH being present at the surface is

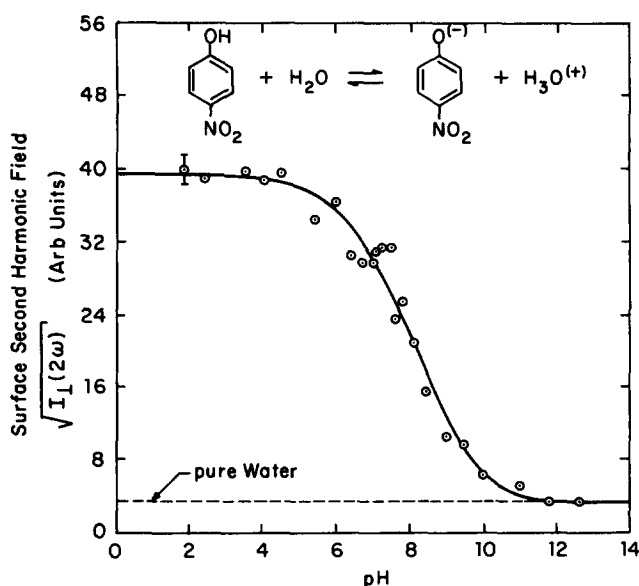


FIG. 1. *s*-polarized surface second harmonic field,  $E_s^{2\omega}[\sqrt{I_s(2\omega)}]$  of an aqueous solution of *p*-nitrophenol as a function of pH at 22 °C.

also unlikely since its presence would have produced a second harmonic signal much above that of water. We therefore conclude that the anion once formed does not stay at the surface and thus in alkaline media the interfacial region is made up of water molecules alone. From our second harmonic measurements we estimate that the ratio of  $A^-$  to HA is at least 50–100 times smaller in the interfacial region than in the bulk solution. The equilibrium in the interfacial region is thus clearly shifted towards the neutral molecules and differs markedly from its bulk value.

Although Fig. 1 is similar to a neutralization curve the  $pH(7.9 \pm 0.2)$  at which the SH signal amplitude reduces to half its maximum value is different from the  $pH(7.15)$  at which the concentration of undissociated HA in the bulk decreases to half. This is not surprising since the bulk  $pH$  controls the concentration of HA in the bulk, while the surface concentration  $N_s$  is not a simple linear function of the latter. This point will be pursued in our future work. It is furthermore of interest to note the sensitivity of surface second harmonic generation as demonstrated by these results. Under the conditions described in this work, when the SH signal changes by a factor of 80, we found that the surface tension changed by less than 10%.

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## State-resolved differential cross sections for the reaction $D + H_2 \rightarrow HD + H^a$

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The  $H + H_2$  exchange reaction has long been recognized as an important and fundamental meeting ground between theory and experiment in the field of chemical dynamics.<sup>1</sup> An accurate theoretical description of this reaction is relatively tractable because it occurs on a single potential energy surface which is accurately known<sup>2</sup> and because the number of coupled channels required for convergence of quantal dynamical calculations is relatively small.<sup>3</sup> Experimentally, however, it is difficult to obtain microscopic dynamical information on this reaction, because of its high potential energy barrier, small cross sections, and the lack of convenient state-selective detectors for  $H_2$ .

Despite these difficulties, spectroscopic methods have been used recently with great success by Gerrity and Valentini,<sup>4</sup> Marinero, Rettner, and Zare,<sup>5</sup> Tsukiyama, Katz, and Bersohn,<sup>6(a)</sup> and Gerlach-Mayer *et al.* to obtain integral product rotational and vibrational state distributions for the reaction  $H + D_2 \rightarrow HD + D$ , and the kinetic energy dependence of the integral reaction cross section. The experimental results have been compared with coupled-states calculations by Schatz<sup>7</sup> and with quasiclassical trajectory calculations by Blais and Truhlar.<sup>8</sup> The agreement between theory and ex-

periment is generally quite good, but perhaps more remarkable is the fact that the quantal coupled-states results and the quasiclassical trajectory results are so similar to each other. Apparently the integral cross sections are not very sensitive to quantal effects such as resonances or tunneling, in the kinetic energy ranges of these experiments. It is, therefore, important also to measure state-resolved differential cross sections, which one generally expects to be more sensitive than the integral cross sections to subtle features of the reaction dynamics.

Although the earliest attempt was reported in 1963,<sup>9</sup> there have been very few successful molecular beam experiments on the  $H + H_2$  exchange reaction. The earlier studies yielded only the product angular distributions.<sup>10,11</sup> The first crossed beam experiments on this reaction to incorporate measurements of the product speed distribution were reported recently by Götting, Mayne, and Toennies.<sup>12</sup> However, the resolution in those experiments was limited by the very broad speed distribution of reactant atoms formed in an arc discharge source.

In this Communication, we describe crossed beam experiments on the reaction  $D + H_2 \rightarrow HD + H$ , in which a