

## Comments on electronic energy levels for photoinjection into polar fluids

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The nature of electronic energy levels involved in photoinjection into polar fluids is discussed. We assert that electrons are not injected into quasifree states as is generally presumed. Rather a solvent trap level which is a precursor to the solvated electron is dominant. Arguments based on known solvent properties are used to support our contention.

Photoemission into fluids is being used to probe electrode surfaces.<sup>1,2</sup> Recent reviews by Gerschler *et al.*<sup>3</sup> and by Pleskov and Rotenberg<sup>4</sup> promote the use of photoemission in studies of the surface structure and in studies of the solution double layer and electrode kinetics, respectively. Unfortunately, all of the above discussions are hampered by misconceptions of the electronic energy levels in polar fluids.

In an investigation of the photoemission process itself, Dogonadze *et al.*<sup>5</sup> show that the injection level in H<sub>2</sub>O is 0.2 eV above the hydrated electron energy. Photoinjection into NH<sub>3</sub> has been observed in our laboratory,<sup>6</sup> and the injection level recently measured by Itaya *et al.*<sup>7</sup> to be 0.22 eV above the ammoniated energy. These measurements are consistent with other observations of photoemission more than 1 eV below vacuum.<sup>1,3,6</sup> Except for our own work, all authors mentioned above assume injection into a quasi-free-electron level which is then followed by rearrangement of the solvent to form a solvated electron. In this paper we discuss the nature of the quasi-free state, explain why injection into this level is inconsistent with other solvent properties, and suggest an alternative injection level.

The quasi-free-electron level has been examined in polar solvents by Kestner and co-workers.<sup>8,9</sup> The term "quasi-free" is derived from the delocalized nature of the electronic wave function. Because the wave function extends over a large volume, the electron sees a large array of random dipole moments. Thus it is unaffected by the polar character of the solvent. The lowest energy for the quasi-free electron,  $V_0$ , corresponds to the bottom of the conduction band. This band is, of course, empty in the pure fluid.  $V_0$  is determined by the long-range electronic polarizability of the fluid and by short-range repulsions. Calculations of  $V_0$  for *nonpolar* fluids agree well with measurements from photoemission experiments.<sup>10</sup> Values range from +1.05 eV for He to -0.63 eV for Xe.  $V_0$  has not been determined for polar liquids. Estimates by Gaathon and Jortner<sup>11</sup> place  $V_0$  in H<sub>2</sub>O

at +0.19 eV with respect to the vacuum state and at -0.22 eV for NH<sub>3</sub>.

The solvated electron levels  $e_s$  are established to be below -1.35 eV in NH<sub>3</sub>,<sup>7</sup> and approximately -1.7 eV in H<sub>2</sub>O.<sup>9</sup> A  $V_0$  only 0.2 eV above the solvated electron is far too negative and is inconsistent with the theory. Further evidence of this inconsistency can be found in optical and transport work.

An energy-level diagram for the solvated electron in H<sub>2</sub>O and NH<sub>3</sub> is given in Fig. 1. There is a well-known optical transition from the 1s to the 2p level of 1.7 eV in H<sub>2</sub>O and 0.8 eV in NH<sub>3</sub>.<sup>9</sup> The existence of a bound-to-bound (or bound-to-free) transition within the model rules out  $V_0$  lying closer to  $e_s$  than 1.7 or 0.8 eV. Certainly,  $V_0$  cannot lie as close to the  $e_s$  as 0.2 eV without drastically distorting the optical-absorption curve.<sup>12</sup>

The mobility of the solvated electron lies in the range  $10^{-2}$ – $10^{-1}$  cm<sup>2</sup>V<sup>-1</sup>sec<sup>-1</sup>.<sup>10</sup> Such mobilities are

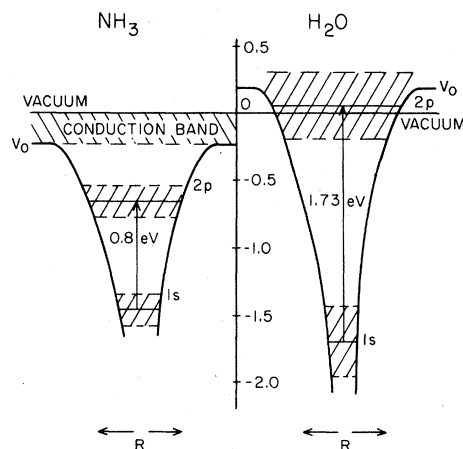


FIG. 1. Model of a potential well for a solvated electron in NH<sub>3</sub> and H<sub>2</sub>O. Electronic energy relative to vacuum (eV) is shown versus the radius  $R$  of the solvent cavity. The optical transition (0.8 and 1.73 eV) from the ground 1s state to the 2p state is indicated. These energies are broadened by disorder. Also shown is the bottom of the conduction band  $V_0$ .

associated with localized carriers.<sup>13</sup> However, the mobility is much higher than that of any other positive or negative ion in solution. In the limit of infinite dilution the mobility of  $e_s$  varies inversely with the viscosity (Walden's rule)<sup>14</sup> as for any other ion. Furthermore, the thermopower<sup>15</sup> indicates a large negative heat of transport. All of the above results eliminate transport by quasi-free electrons as well as the existence of  $V_0$  at energies close to  $e_s$ . Of course, in concentrated *metal*-ammonia solutions there is a nonmetal-metal transition<sup>12</sup> at which transport involves delocalized states.

Ionic motion of the electron in which it drags along part of its solvation shell undoubtedly contributes to charge transport. However, ionic processes do not account for the mobility being so high nor for the thermoelectric results. An alternative mechanism<sup>16</sup> portrayed in Fig. 2 is used to interpret the transport data. The electron can tunnel or hop from its cavity into an adjacent site where thermal fluctuations form a shallow potential well,  $e_t$ . Once in this shallow trap, the electron further organizes the solvent to form a stable solvated electron.

The shallow trap  $e_t$  also appears in descriptions of the trapping of high-energy electrons (pulse radiolysis). These electrons are injected at energies well above  $V_0$ . The localization process has been closely followed in alcohols,<sup>17</sup> where the presence of  $e_t$  can be observed spectroscopically. Localization in  $H_2O$  and  $NH_3$  develops in the order of picoseconds and  $e_t$  has not yet been resolved.<sup>18,19</sup>

An energy-level diagram<sup>20</sup> for the states we have discussed is shown in Fig. 3. There is the conduction band for energies above  $V_0$ . The pair of

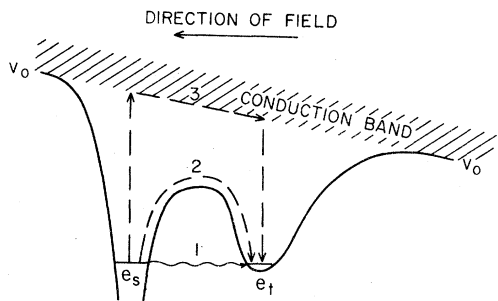


FIG. 2. Illustration of electron transport. The electron in the solvated state  $e_s$  moves into an adjacent solvent trap  $e_t$  formed by thermal fluctuations;  $e_t$  is lowered by the potential gradient. The electron can move by (1) tunneling, (2) activated hopping, or (3) activation to the conduction band. Process (3) is unlikely in  $NH_3$  and  $H_2O$ . Not shown is pure ionic motion of the solvated electron in which the solvation shell is dragged along. Adapted from Ref. 16.

states represented by  $e_s$  and its precursor  $e_t$  are, of course, broadened by disorder. The difference in energy of two such states is generally called a Stokes shift. The pair  $e_t$  and  $e_s$  can be visualized as a redox pair<sup>3</sup> except that the concentration of the oxidate ( $e_t$ ) is not well defined as it is for chemical species. However, as these derive from thermal fluctuations, they are abundant. Other intrinsic levels associated with  $H^+$ ,  $OH^-$ ,  $NH_2^-$ , etc., also exist.<sup>20</sup>

The initial solvent trap  $e_t$  was introduced in descriptions of transport and radiolysis work. There are compelling reasons to indicate that this level is important for electron injection from an electrode as well. The states in the liquid and in the electrode must be juxtaposed for charge transfer to occur. The question then is into what levels in the fluid will the electron move. The trap states  $e_t$  are more accessible as they lie lower than the conduction band and are the only ones available around 1 eV below the vacuum level. Furthermore, these states are numerous as only small thermal fluctuations in position and orientation of the solvent molecules are needed to trap an electron. Since traps exist without the electron, injection can occur without further changes in the molecular configuration and the Franck-Condon principle is not violated. Therefore, we assert that the level observed in all photoemission experiments to date is  $e_t$ .

As the photon energy is increased above the threshold, higher portions of the  $e_t$  distribution

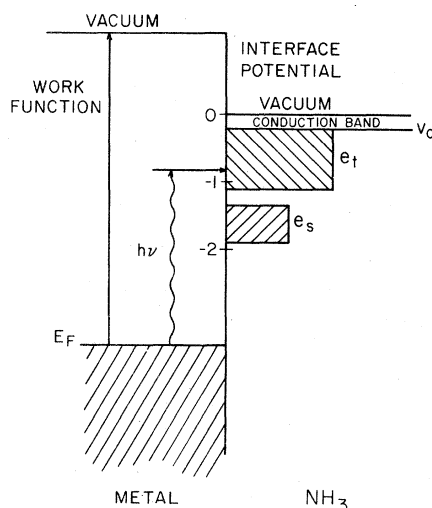


FIG. 3. Energy levels at the metal-electrolyte interface in eV. The electron excited by a photon  $h\nu$  is injected into the solvent trap level  $e_t$ . Then the solvent rearranges to form a solvated electron of energy  $e_s$ . These levels are broad because of disorder. Only with high-energy photons will the electrons enter the solution conduction band of energies  $V_0$  and above.

are populated. With further increases of photon energy,  $V_0$  will eventually be reached, resulting in a further increase in photocurrent. Such an increase was observed in  $\text{NH}_3$  by Itaya *et al.*<sup>7</sup>

It must be recognized that the dipole layer at the surface or adsorbed ions may participate in forming  $e_t$ . Thus the energy distribution of traps at the surface will differ from that in the bulk fluid. Prior treatments of the interface as merely a potential barrier may well be too simplistic. Trasatti<sup>21</sup> has shown the water orientation on the surface to be important in electron injection.

Clearly the states in the liquid must be well understood if photoemission is to be used to probe

surface states on an electrode in that liquid. It therefore seems that at the moment nonpolar liquids are much better suited for such purposes.<sup>22</sup>

We have shown that studies of the solid-electrolyte interface cannot ignore the details of electronic states in the electrolyte. In particular, the role of the initial solvent trap in the injection process must be recognized as dominant at low injection energies.

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