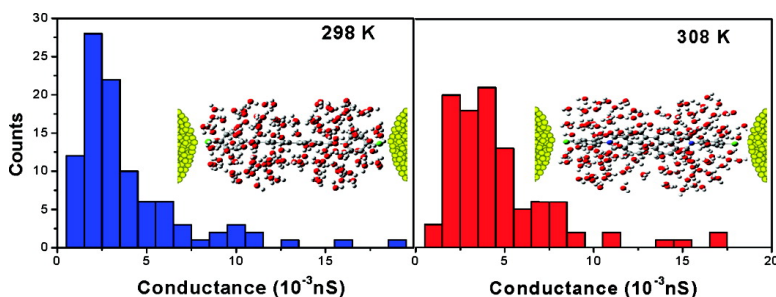


## Temperature-Dependent Statistical Behavior of Single Molecular Conductance in Aqueous Solution

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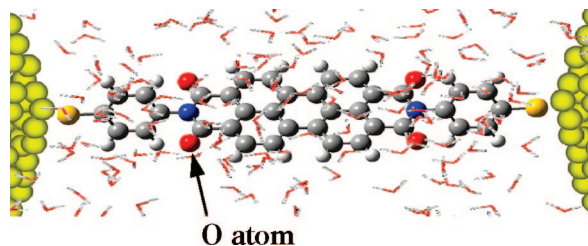
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Breaking junction techniques have been widely used in studying electron transport properties of a single molecule,<sup>1,2</sup> which can however introduce two major uncertainties in measurements, namely, the structure of metal–molecule contact and solvent–molecule interaction.<sup>3,4</sup> The experimentally determined single molecular conductance is often obtained from a statistical analysis of a large number of measurements. In a theoretical study, Hu et al.<sup>5</sup> investigated the statistical characteristics of transport in molecular junctions caused by small changes at the metal–molecule contact region. They have found that the statistically averaged conductance could be in better agreement with the corresponding experiments. The influence of intermolecular interaction on electron transport of the charge transfer molecule has also been examined theoretically.<sup>4</sup> It was found that the formation of hydrogen bonds between the polar groups of the conducting molecule and the surrounding water molecules could drastically reduce the conductance of the wired molecule in the junction. However, all theoretical analyses have ignored the intrinsic contribution from thermal motion of the wired molecule, as well as the surrounding solvent molecules, to the statistical behavior of the conductance. Experimentally, more attention has been paid to understanding the thermal effects on electron transport of single molecules.<sup>6,7</sup> It is particularly important for biosensors at the molecular scale that operate inevitably in solutions at different temperature. Very recently, Li et al.<sup>6</sup> observed that electron transport in perylene tetracarboxylic diimides (PTCDI), covalently bound to two gold electrodes via different linker group, depends on the temperature in the aqueous electrolyte but is independent of temperature in a nonpolar solvent. A two-step thermally activated electron transfer process involving reduction–oxidization of the wired molecule was suggested,<sup>6</sup> but it failed to explain the gate-controlled experiments.<sup>6</sup>

It is noted that the PTCDI molecule possesses four oxygen atoms that are ready to form hydrogen bonds with the surrounding water molecules. The strength and distribution of the hydrogen bond network is known to be temperature-dependent, which could in turn result in the temperature-dependent electron transport. To verify this hypothesis, we have combined electron transport calculations with molecular dynamics simulations for the PTCDI molecular junction in water solution. The schematic drawing of the studied system is given in Figure 1. Molecular dynamics simulations have been carried out for the system consisting of the Au–PTCDI–Au molecular junction<sup>8</sup> and 800 water molecules in a 35.00 Å × 20.00 Å × 32.55 Å cell using the pcff force field<sup>9</sup> in the Cerius<sup>2</sup> package<sup>10</sup> at 298 and 308 K, respectively. The same approach was successfully applied to investigate the solvent effect on the band edge shift of a series of polarized



**Figure 1.** Scheme of the studied molecular junction in water.

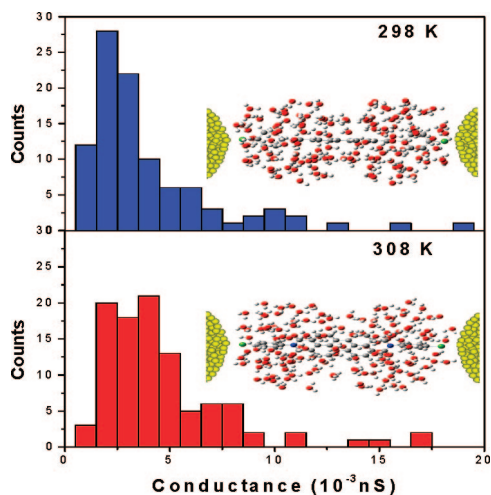
conjugated systems immersed in polarized solvent.<sup>11</sup> We have focused our attention on the influence of thermal motion of water molecules and have assumed that thermal motion of the metal–molecule junction itself is negligible in molecular dynamics simulations. One hundred picosecond dynamics simulations were performed with the former 50 ps as the pre-equilibrium stage and the latter 50 ps for sampling. We have taken 100 snapshots per 0.5 ps over the latter 50 ps simulations at each temperature. Due to the limitation of our computational capacity, smaller systems, consisting of the molecular junction and nearly 60 water molecules, included in the first solvation shell, are selected for computing electron transport properties of the molecular junction using the generalized quantum chemical approach<sup>12</sup> implemented in the QCME program and described in Supporting Information.<sup>8</sup> In the scattering region of the molecular junction, terminal sulfur atoms are placed at the hollow site of three gold atoms in the fcc (111) plane, and the S–Au distance is set to 2.85 Å, which is an optimized distance in the gas phase and was adopted also in our previous work.<sup>13</sup> Electronic structure of each junction–water supermolecular cluster is calculated using density functional theory at the B3LYP level with Lan2DZ basis set as implemented in the Gaussian03 package.<sup>8</sup>

Figure 2 shows the statistical distributions of conductance of the Au–PTCDI–Au molecular junction in aqueous solution with an external bias of 0.1V and at temperatures of 298 and 308 K, respectively. In comparison with the histogram at 298 K, one can find that, at 308 K, (i) the distribution is broader, (ii) the maximal peak height is lower, and (iii) the maximum peak position shifts to the higher conductance. These results strongly indicate that the thermal motion of water molecules can have a substantial effect on the statistical behavior of conductance of the single molecular PTCDI junction. The envelopes of the histograms are plotted in Figure 3. It can be clearly seen that the peak conductances of molecular junction for 298 and 308 K are found to be 2.24 and 3.75 ( $10^{-3}$  nS), respectively, that is, the conductance at 308 K is about 1.7 times larger than that at 298 K. This finding is in good agreement with the experimental observation.<sup>6</sup> An important message coming out from our calculations is that even within the one-step tunneling model (elastic scattering region), with the inclusion of thermal motion of water molecules, one can also lead

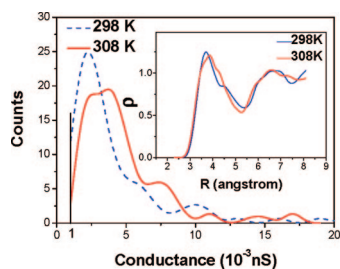
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**Figure 2.** Statistical distribution of conductance for the Au–PTCDI–Au junction in aqueous solution at 298 (top) and 308 K (bottom). Insets are configurations adopted in calculations.



**Figure 3.** Statistical distributions of conductance and radial distribution functions (inset) of water surrounding oxygen atom in PTCDI at 298 and 308 K.

to the conclusion that the conductance of a molecular junction becomes larger with the increase of the temperature.

Test calculations have shown that the conductance has a close relationship with the hydrogen bond distance, that is, the shorter the averaged distance of hydrogen bonds, the smaller conductance it becomes. The inset of Figure 3 shows the radial distribution functions (RDF) of oxygen–oxygen distance between water molecules and the PTCDI molecule at 298 and 308 K, respectively. Apparently, water molecules accounted by this distribution are the ones that have strongest interaction with the PTCDI molecule through hydrogen bonding networks. It is probably not surprising to see that the conductance distributions are closely associated with the RDFs of the first solvation shell. The maximum of the RDF at 298 K is found to be at 3.69 Å, which is about 0.18 Å shorter than that at 308 K. It implies that the water molecules are closely packed around the oxygen atoms of the PTCDI molecule at lower temperature, which results in stronger charge localization on oxygen atoms and reduced conductance of the molecule. At higher temperature, the hydrogen bond network is much looser than that at lower temperature, which explains the observation that the conductance distribution of the molecule at 308 K is broader than that at 298 K. By analysis of RDFs, we can also estimate the number of water molecules within the first solvation shell that can strongly affect the PTCDI molecule. At both temperatures, the width of the first solvation shell is around 5.3 Å, in which 14 water molecules can

be found. It is noted that, for both temperatures, the band gap of junction–water complexes shows different statistical behavior but with almost the same average value,  $\sim 1.2$  eV.<sup>8</sup>

Another important result of the present work is the actual shape of the conductance histogram. In almost all experiments, a Gaussian distribution has been adopted to describe experimental histograms,<sup>6</sup> which is a matter of convenience rather than correctness. Our study presents the first evidence to demonstrate that the use of a Gaussian distribution is absolutely not justified. As clearly shown in Figure 2, there is a threshold for the distribution of the conductance. In the case of the PTCDI molecular junction in water solution, one cannot find any configurations that result in conductance below 1 ( $10^{-3}$  nS). Such a threshold value reflects a simple fact that the distance between the PTCDI and the water molecules cannot be infinitely small, that is, there is also a threshold for the intermolecular distance, which according to the RDFs given in Figure 3 should be around 2.5 Å for the O–O distance between water and PTCDI molecules. It is noted that normally the RDF can also be associated with the profile of interaction energy between the wired molecule and the water molecules. In other words, an experimental conductance histogram could thus be used to extrapolate the interaction energy profile between the molecule and the surroundings. This finding can be further generalized to other types of junctions. For the case where the solvent effect is negligible, the profile of the conductance histogram should provide information about the interaction between the molecule and the electrodes.

In summary, a combination of molecular dynamics simulations and quantum mechanical calculations has allowed us to draw the conclusion that the experimentally observed temperature-dependent conductance of the PTCDI molecular junction in water solution can be attributed to the statistical behavior of elastic electron transport induced by the temperature-dependent thermal motion of water molecules.

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**Supporting Information Available:** Additional experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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