



# Structures and acidity constants of arsenite and thioarsenite species in hydrothermal solutions



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## ABSTRACT

We report a first principles molecular dynamics (FPMD) study of structures and acidity constants of arsenite and thioarsenite species in liquid water from ambient temperature to 573 K. The analyses show that at all temperatures, the OH ligands of arsenite species form H-bonds with solvating water molecules as both donors and acceptors, whereas there are only very weak H-bonds between the SH ligands of thioarsenite species and water. For both arsenites and thioarsenites, the dangling O/S sites form strong H-bonds with hydrogen atoms of water molecules, but the As atoms have almost no interaction with water molecules. The FPMD based vertical energy gap method was applied to calculate the acidity constants. With the evaluated acidity, the species distributions with respect to pH have been derived. The  $pK_{a1}$ s of  $H_3AsO_3$  and  $H_3AsS_3$  demonstrate a decreasing trend with temperature. For arsenites,  $H_3AsO_3$  and  $H_2AsO_3^-$  can coexist, whereas  $HA_2O_3^{2-}$  almost does not exist, due to the notably high  $pK_{a2}$ s of  $H_3AsO_3$ . For thioarsenites,  $H_2AsS_3^-$  and  $HA_2S_3^{2-}$  are always the dominant species in the near neutral pH range from ambient temperature to 573 K.

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## 1. Introduction

Arsenic is a ubiquitous trace element in both low- and high-temperature environments including aquifers, sedimentary rocks, geothermal fluids and hydrothermal ore deposits (Vaughan, 2006). As can enter a variety of mineral phases including sulfides, arsenides and sulfarsenides; therefore As associates with Cu/Au/Ag/Pb/Zn/PGE (platinum group elements) in various metal deposits (Heinrich and Eadington, 1986; Kerr et al., 1999; Hem et al., 2001; Barkov et al., 2004). Due to the variable oxidation states in solutions (i.e., +3 and +5), As can form many aqueous species such as arsenites, arsenates, (oxy)thioarsenites and (oxy)thioarsenates (Perfetti et al., 2008). As is toxic, and an elevated level of As in water has led to massive human health problems in many areas (Charlet and Poly, 2006; Hopenhayn, 2006). Therefore, knowledge of aqueous speciation is crucial for both understanding geochemical behaviors of As and developing techniques for As removal from water (e.g., Jonsson and Sherman, 2008; Watts et al., 2014).

In the last decades, numerous studies of As speciation have been carried out, but many molecular level properties are still poorly documented, especially under high P-T conditions (Zakaznova-Herzog and Seward, 2012). It has been generally accepted that +3 is the common valence of As in geothermal solutions.  $H_3AsO_3$  (arsenous acid) and

$H_3AsS_3$  (thioarsenous acid) containing As(III) are both weak acids; therefore, the acidity constants ( $pK_{as}$ ) are the key thermodynamic quantities for determining the protonation states, significantly influencing the transport and fixation of the moieties in sediments and soils (Watts et al., 2014). The acidity constant of arsenous acid has been well constrained at ambient conditions ( $pK_{a1}$  is within 9.2–9.3) (Zakaznova-Herzog et al., 2006), but the measurements at elevated temperatures are very limited. The SUPCRT92 (Johnson et al., 1992) prediction shows that the  $pK_{as}$  first decrease to 8.2 at 473 K and then increase back to 8.5 at 573 K. In other words, the changes in  $pK_{as}$  are unobvious and limited in only 1.0 pK unit up to 573 K. In contrast, by using an ultraviolet spectrophotometric technique, Zakaznova-Herzog et al. found that the  $pK_{as}$  monotonically decrease to 7.0 as temperature increases to 573 K (Zakaznova-Herzog et al., 2006).

Thioarsenites have been experimentally studied for many years including their solubility measurements (Mironova and Zotov, 1980; Webster, 1990; Eary, 1992; Clarke and Helz, 2000) and spectroscopic techniques (Helz et al., 1995; Wood et al., 2002; Wilkin et al., 2003; Bostick et al., 2005; Beak et al., 2008). However, the experimental reports on  $pK_{as}$  of thioarsenites are still scarce. Recently, Zakaznova-Herzog and Seward measured the  $pK_{a2}$  and  $pK_{a3}$  (6.53 and 9.29, respectively) of  $H_3AsS_3$  at ambient conditions and obtained the  $pK_{a1}$  (3.77) by linear extrapolation of  $pK_{a2}$  and  $pK_{a3}$  (Zakaznova-Herzog and Seward, 2012). However, to our knowledge, the acidity constants and solution structures at elevated T-P have not been reported until now.

Quantum chemical methods have been applied to investigate arsenic species (Tossell, 1997, 2003; Zakaznova-Herzog et al., 2006;

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Helz and Tossell, 2008; Tossell and Zimmermann, 2008; Zimmermann and Tossell, 2009). In those studies, the molecular structures and  $pK_a$ s of oxy/thio acids of As(III) and As(IV) were calculated by using the geometry optimization approach with continuum solvent models. The molecular structures have been successfully reproduced, but due to the oversimplification of solvent effects, the calculated  $pK_a$  results can be far from the experimental results. For example, 11.5 and 5.0 are obtained for the  $pK_{a1}$ s of  $H_3AsO_3$  and  $H_3AsS_3$  (Zimmermann and Tossell, 2009), which are close to the experimental results of 9.2 and 3.77, respectively (Zakaznova-Herzog et al., 2006; Zakaznova-Herzog and Seward, 2012). However, the calculated  $pK_{a2}$  and  $pK_{a3}$  of  $H_3AsS_3$  are 13.8 and 18.5, respectively, which are 7 pK units higher than the experimental results (Zakaznova-Herzog and Seward, 2012). In addition, it is very hard to investigate the high T-P conditions of geologic interest with traditional quantum chemical approaches.

By integrating electronic structure calculations and molecular dynamics sampling, first principles molecular dynamics (FPMD) treats solutes and solvents at the same quantum mechanical level and is therefore able to provide reliable thermodynamics quantities and detailed microscopic information of aqueous systems (Marx and Hutter, 2009). FPMD has been successfully applied to investigate metal complexes under the conditions of geologic and geochemical interest, e.g.,  $Cu^{2+}$ ,  $Cu^+$ ,  $Ag^+$ ,  $Au^+$ ,  $Zn^{2+}$  and  $Y^{3+}$  complexes (Sherman, 2007, 2010; Liu et al., 2010a,b, 2011; Mei et al., 2013, 2014; Pokrovski et al., 2013).

FPMD based  $pK_a$  calculation techniques have been developed in the last few years. The vertical energy gap method developed by the Sprik group has been validated on many organic and inorganic systems (Cheng and Sprik, 2010; Cheng et al., 2009; Costanzo et al., 2011; Liu et al., 2013d; Sulpizi et al., 2012; Sulpizi and Sprik, 2008). Extensive tests on molecular acids spanning over 20 pK units demonstrate that an accuracy of 2 pK units can be achieved (Sulpizi and Sprik, 2008, 2010; Cheng et al., 2009; Costanzo et al., 2011). This method has also been applied on mineral interfaces, including oxides (Cheng and Sprik, 2010; Sulpizi et al., 2012; Liu et al., 2014a), hydroxides (Liu et al., 2013b) and clay minerals (Tazi et al., 2012; Liu et al., 2013c, 2014b). Furthermore, by using this technique, we have reproduced the  $pK_{as}$  of molybdic acid up to 573 K within 2 pK units, indicating that this method is able to capture the effect of temperature (Liu et al., 2013a).

In this study, FPMD simulations are carried out to investigate the solution structures and acidity constants of  $H_3AsO_3$  and  $H_3AsS_3$  from ambient temperature to 573 K. The solution structures of the molecular and anion species are characterized in detail. The  $pK_{as}$  are computed using the FPMD-based vertical energy gap method. Comparison with available experimental data indicates an accuracy of approximately 1 pK unit. With the acidity constants, the species distributions versus pH have been derived for the two acids.

## 2. Methodology

### 2.1. Systems

Table 1 lists the systems and T-P conditions. The temperatures are 330 K, 473 K and 573 K, and the pressures at 473 K and 573 K are the

**Table 1**  
Simulated T-P conditions and numbers of water molecules.

T-P conditions	Acid	Number of water molecules
Ambient	$H_3AsS_3$	60
	$H_3AsO_3$	62
473 K–1.55 MPa	$H_3AsS_3$	51
	$H_3AsO_3$	53
573 K–8.59 MPa	$H_3AsS_3$	41
	$H_3AsO_3$	43

saturated vapor pressures. The slightly elevated temperature of ambient conditions is meant to avoid the glassy behavior of liquid water found at lower temperatures (VandeVondele et al., 2005b). The simulation cells are 3D periodically repeated cubic boxes with a side length of 12.43 Å. In the initial configuration, the acid molecule is placed in the center of the box, and the water molecules are inserted around the acid. The number of water molecules approximately reproduces the density of liquid water at the corresponding T-P condition based on the equation of state of water (Wagner et al., 2000).

### 2.2. First principles MD

All simulations were performed by using the CP2K/QUICKSTEP package (VandeVondele et al., 2005a). In QUICKSTEP, density functional theory is implemented with the hybrid Gaussian plane wave (GPW) approach (Lippert et al., 1997). BLYP functional was applied for the exchange–correlation (Becke, 1988; Lee et al., 1988). GTH-type pseudopotentials (Goedecker et al., 1996) were used for core configurations. Valence configurations for H, O, S and As are  $1s^1$ ,  $2s^22p^4$ ,  $3s^23p^4$ , and  $4s^24p^3$ , respectively (Krack, 2005). The cut off for the electronic density was set to 280 Ry.

Born–Oppenheimer molecular dynamics (BOMD) simulations were carried out with a wave function optimization tolerance of  $1.0E-6$  that allowed a time step of 0.5 fs. The temperature was controlled with the Nosé–Hoover chain thermostat. For each system, the production run was performed for 5.0 ps–10.0 ps following a prior equilibration simulation for at least 2.0 ps.

### 2.3. $pK_a$ calculation

The  $pK_a$ s of the acids were calculated using the FPMD-based vertical energy gap method. With this method, the proton of the acid (denoted as AH) is gradually transformed into a dummy atom (i.e., a classical particle with no charge), and the free energy of this transformation (denoted as  $\Delta_{dp}A_{AH}$ ) is calculated with the thermodynamic integration approach:

$$\Delta_{dp}A_{AH} = \int_0^1 d\eta \langle \Delta_{dp}E_{AH} \rangle_{\eta} \quad (1)$$

where  $\eta$  is the coupling parameter that is increased from 0 (reactant) to 1 (product).  $\Delta_{dp}E$  stands for the vertical energy gap, defined as the difference of potential energies between the reactant state and the product state. The averages of the vertical energy gaps are derived from MD trajectories, which are generated by sampling the restrained mapping potential:

$$H_{\eta} = (1-\eta)H_R + \eta H_P + V_r \quad (2)$$

where  $H_R$  and  $H_P$  stand for the reactant and product states, respectively.

**Table 2**

The parameters used in the harmonic potentials (Eq. (3)) restraining the dummy particles. Equilibrium bond lengths ( $d_0$ ) are in Bohr, and equilibrium angles ( $\alpha_0$ ) are in radians. All of the coupling constants are in a.u.

Acids	$n_d$	$d_0$	$k_d$	$n_{\alpha}$	$\alpha_0$	$k_{\alpha}$
$H_3AsO_3$	1	1.89	0.1	1	1.92	0.1
$H_3AsS_3$	1	2.56	0.1	1	1.61	0.1
$H_2AsS_3^-$	1	2.56	0.1	1	1.61	0.1
$HAsS_3^-$	1	2.55	0.1	1	1.61	0.1

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