



# Theoretical investigation of the anomalous equilibrium fractionation of multiple sulfur isotopes during adsorption

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## ABSTRACT

Adsorption processes of gaseous molecules are known to be associated with isotopic fractionation, this being supported both experimentally and theoretically. From theoretical considerations [Lasaga, A.C., Otake, T., Watanabe, Y., Ohmoto, H. (2008) Anomalous fractionation of sulfur isotopes during heterogeneous reactions Earth and Planetary Science Letters 268 225–238], this process might also result in a “mass-independent” isotopic fractionation (MIF) of sulfur [i.e.  $\delta^{33}\text{S} \neq 0.515 \times \delta^{34}\text{S}$ ] and could bear on our understanding of the sulfur isotope geological record. The anomalous fractionation could find its origin in the difference in the number of vibrational *bound* states of the adsorption complex (i.e. *unbound* states are neglected) among the four sulfur isotopes. In the present study, the equilibrium isotopic fractionation of sulfur during adsorption is investigated using a similar 1-dimensional (1-D) Morse potential. We demonstrate that no anomalous fractionation is expected when the contribution of all the accessible states (both *bound* and *unbound*) is properly taken into account. These results thus contradict the conclusion of Lasaga et al. [Lasaga, A.C., Otake, T., Watanabe, Y., Ohmoto, H., 2008. Anomalous fractionation of sulfur isotopes during heterogeneous reactions. Earth Planet. Sci. Lett. 268, 225–238.] stating that adsorption reactions would result in anomalous fractionations. Neglecting unbound states in our calculations would actually led to similar anomalous isotope fractionation, showing that the anomalous effect indeed arises from this simplification. Equilibrium adsorption processes are thus not expected to be associated with anomalous fractionation among the four sulfur isotopes.

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## 1. Introduction

The stable isotope fractionation of gaseous molecules which occurs during their adsorption on a surface is a well known process, which has been extensively studied both experimentally and theoretically since the early 40s. In Earth Sciences, adsorption-related isotope fractionation has potential implications, such as the understanding of the stable isotopic compositions of volatile elements in Martian materials (see e.g. Rahn and Eiler, 2001 and Ref. therein). Interestingly experimental data show that several elements/molecules display the *expected* fractionation, the heavier isotope being concentrated in the adsorbed (or condensed) phase rather than in the gas vapor phase. However, this is not always the case, with the noticeable example of  $^{13}\text{C}$  in  $\text{CO}_2$  (see Eiler et al., 2000; Rahn and Eiler, 2001 for discussion).

In nature, the *multiple* stable isotope compositions of a same element, such as O, S, Mg, Fe, and Si are usually tightly correlated (see e.g. Hulston and Thode, 1965; Molini-Velsko et al., 1986; Robert et al.,

1992; Zhu et al., 2001; Farquhar and Wing, 2003; Kehm et al., 2003; Young and Galy, 2004; Ding et al., 2005; Rumble et al., 2007). For sulfur ( $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$ ,  $^{36}\text{S}$ ), the equilibrium fractionation factors between two phases *A* and *B* generally follow the relations

$$^{33}\alpha_{A-B} = \left( ^{34}\alpha_{A-B} \right)^\beta \quad (1)$$

$$^{36}\alpha_{A-B} = \left( ^{34}\alpha_{A-B} \right)^\gamma \quad (2)$$

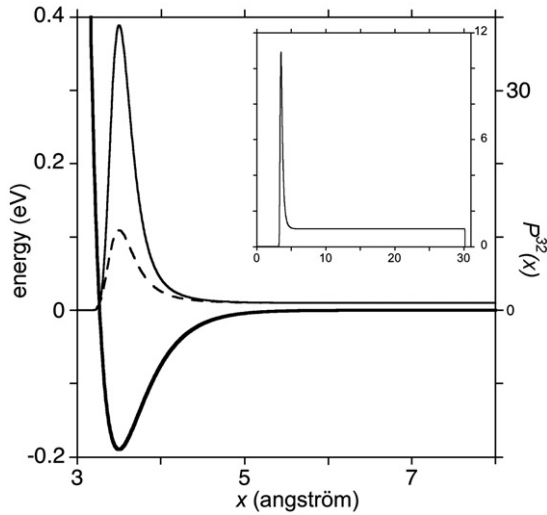
where  $^m\alpha_{A-B} = (^m\text{S}/^{32}\text{S})_A / (^m\text{S}/^{32}\text{S})_B$  and where  $\beta$  and  $\gamma$  are inferred from the mass of the considered isotopes (Bigeleisen and Mayer, 1947; Young et al., 2002), here  $\beta \sim (1/32 - 1/33) / (1/32 - 1/34) = 0.515$  and  $\gamma \sim (1/32 - 1/36) / (1/32 - 1/34) = 1.89$ . Using the conventional delta notation, where  $\delta^m\text{S} = [^m\text{S}/^{32}\text{S}_{\text{sample}} / ^m\text{S}/^{32}\text{S}_{\text{standard}} - 1] \times 1000$ , one deduces that  $(\delta^{33}\text{S}/1000 + 1) = (\delta^{34}\text{S}/1000 + 1)^{0.515}$  and  $(\delta^{36}\text{S}/1000 + 1) = (\delta^{34}\text{S}/1000 + 1)^{1.89}$ . Because  $\delta^{34}\text{S}/1000 < 1$ , the latter equations are often simplified and yield the well-known terrestrial fractionation *lines* (TFL):

$$\delta^{33}\text{S} = 0.515 \times \delta^{34}\text{S} \quad (3)$$

$$\delta^{36}\text{S} = 1.89 \times \delta^{34}\text{S} \quad (4)$$

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**Fig. 1.** Morse potential (parameter set (1)) describing the interaction between sulfur atoms and a solid surface (bold line). The function  $P^{32}(x)$ , proportional to the density of  $^{32}\text{S}$  atoms at position  $x$ , is represented at 600 and 920 K, by a solid and dashed line, respectively. The decrease in the maximum density at 3.5 Å reflects the thermally induced desorption of sulfur atoms. Inset: full range representation of  $P^{32}(x)$  at 920 K. Note the flat domain corresponding to the homogeneous gas phase.

Significant deviations from the terrestrial fractionation line ( $\Delta^{33}\text{S} > \pm 0.2\%$  where  $\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \times [(\delta^{34}\text{S}/1000 + 1)^{0.515} - 1]$ ) are usually referred to as *mass-independent fractionation* (MIF) or *anomalous isotope fractionation* and have been extensively reported for sulfur and oxygen isotopes (for review see Thiemens, 2006). For sulfur, the MIF mostly occurs within Archean rocks (e.g. Farquhar et al., 2000, 2007 and Ref. therein) with  $\Delta^{33}\text{S}$  up to  $\pm 12\%$ .

Anomalous isotopic composition ratios are usually related to gas-phase photolytic reactions (e.g. Thiemens and Heidenreich, 1983; Farquhar et al., 2001; Gao and Marcus, 2001; Lyons, 2007, in press) but it has been recently suggested, based on theoretical considerations (Lasaga et al., 2008), that equilibrium solid–gas adsorption might also cause anomalous sulfur isotopic fractionation, provided that adsorption energies are weak enough ( $< \sim 30$  kJ/mol). However, the high temperature increase of some fractionation factors and related departure from the TFL, cast some doubts on the validity of the theoretical approach used in this study. This oversimplified theoretical approach is based on two assumptions: (i) the adsorbing species move in a one-dimensional Morse potential and the fractionation is calculated from the vibrational free energy of this system (natural adsorption processes likely involve a much larger range of bond types and interactions between inter- and intra-molecular vibrations which are not taken into account); (ii) the free-energy of the adsorbed species is calculated considering *only* the bound vibrational states, i.e. without including the contribution of the unbound states. Assumption (i) is based on the hypothesis that the surface–sulfur bond can be considered decoupled from other vibrational modes and its direct verification would be quite cumbersome. Assumption (ii) is not *a priori* justified for high temperatures. For example, the modeling of the high temperature thermodynamic properties of diatomic molecules requires the incorporation in the partition function of continuum and quasi-bound rotational states located above the dissociation limit (Mies and Julienne, 1982; Taubmann, 1995; Angelova and Frank, 2005; Babou et al., 2009). Here, we will show by using numerical simulation that the anomalous fractionation reported by Lasaga et al. (2008) is a direct consequence of assumption (ii) and that no anomalous fractionation is predicted in a one-dimensional system when the contribution of all the accessible states (both bound and unbound) is properly taken into account.

## 2. Theoretical model

We consider the isotopic equilibrium between sulfur atoms in a homogeneous gas phase and sulfur atoms adsorbed on a reactive surface. The adsorption of atoms makes it possible to properly treat both the gas and adsorbed phases using a simple “particle-in-a-box” model. In particular, the present model avoids uncontrolled assumptions on the reduced mass accounting for the vibrational properties of the adsorbed molecular species and on the decoupling of surface–sulfur vibration from other molecular vibrational modes, as those done by Lasaga et al. (2008). Following Lasaga et al. (2008), the interaction between the S atoms and the surface is described by a one-dimensional Morse potential (Fig. 1):

$$V(x) = D_e [1 - \exp(-a(x - x_e))]^2 - D_e \quad (5)$$

with  $x_e = 3.5$  Å. The surface is located at  $x = 0$  and we consider a finite box with a width of 30 Å. Four sets of parameters ( $D_e$ ,  $a$ ) have been considered (Table 1) covering the range of adsorption energies and multiplicity of vibrational bound states investigated by Lasaga et al. (2008). Since all the parameter sets lead to the same qualitative results, the results will be discussed in detail only for the parameter set (1):  $D_e = 0.19$  eV and  $a = 3.0$  Å<sup>-1</sup>. These parameters correspond to a force constant of  $k_e = 0.548$  mdyn.Å<sup>-1</sup> and a harmonic frequency of 675 cm<sup>-1</sup> for the mass 32.

In such a finite size system, the energy is quantified, i.e. only discrete energy values are accessible, and the position of a sulfur atom is defined by a wavefunction  $\Psi_i^m(x)$ , which is a solution of the Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi_i^m(x)}{\partial x^2} + V(x) \Psi_i^m(x) = E_i^m \Psi_i^m(x) \quad (6)$$

where  $m$  is the mass of the sulfur atom,  $\hbar = \frac{h}{2\pi}$ ,  $h$  being the Planck constant, and  $E_i^m$  is the energy related to the wavefunction  $\Psi_i^m(x)$ . Assuming that the population of energy levels follows a Boltzmann statistic, the probability to find a sulfur atom at a certain position  $x$  is then:

$$P^m(x) = A(T, m) \sum_{i=0}^{\infty} |\Psi_i^m(x)|^2 \exp\left(-\frac{E_i^m}{kT}\right) \quad (7)$$

where the sum runs over all the accessible states and where  $A(T, m)$  is a normalization constant which depends on the temperature  $T$  and the atomic mass  $m$ . The probability distribution  $P^m(x)$  has a maximum near the surface and a finite constant value for  $x > d$ , for values of  $d$  sufficiently large (typically 7 Å, Fig. 1).

The equilibrium isotopic fractionation factor  ${}^m\alpha_{\text{ads-gas}}$  related to adsorption can be obtained by calculating the ratio of the isotopic concentration ratios ( $C^m/C^{32}$ , with  $m = 33, 34, 36$ ) between the

**Table 1**

Sets of parameters describing the Morse potential, number of bound states, and  $\theta'$  values calculated at  $T = 400$  K.

Set	$D_e$ (eV)	$a$ (Å <sup>-1</sup> )	$n_{32}$	$n_{33}$	$n_{34}$	$n_{36}$	${}^{33}\theta'_{\text{trunc}}$	${}^{36}\theta'_{\text{trunc}}$	${}^{33}\theta'_{\text{full}}$	${}^{36}\theta'_{\text{full}}$
1	0.19	3.	18	18	19	19	-0.144	0.952	0.515	1.890
2	0.19	12.2	4	5	5	5	0.580	1.423	0.513	1.900
3	0.0171	3.	5	5	6	6	-0.117	1.004	0.515	1.890
4	0.0171	0.88	18	19	19	19	1.298	-0.422	0.511	1.889

The  $\theta'_{\text{full}}$  and  $\theta'_{\text{trunc}}$  values have been calculated using either all the accessible quantum states or only the bound vibrational states, respectively.

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