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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. $\delta^{33}S \neq 0.515 \times \delta^{34}S$] 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.

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}C in 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}S, ^{33}S, ^{34}S, ^{36}S), the equilibrium fractionation factors between two phases *A* and *B* generally follow the relations

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

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

where $^{m}\alpha_{A-B} = (^{m}S/^{32}S)_A / (^{m}S/^{32}S)_B$ and where β and γ 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 $\delta^{m}S = [^{m}S/^{32}S_{\mathrm{sample}} / ^{m}S/^{32}S_{\mathrm{standard}} - 1] \times 1000$, one deduces that $(\delta^{33}S/1000+1) = (\delta^{34}S/1000+1)^{0.515}$ and $(\delta^{36}S/1000+1) = (\delta^{34}S/1000+1)^{1.89}$. Because $\delta^{34}S/1000 < 1$, the latter equations are often simplified and yield the well-known terrestrial fractionation *lines* (TFL):

$$\delta^{33}S = 0.515 \times \delta^{34}S \tag{3}$$

$$\delta^{36}S = 1.89 \times \delta^{33}S \tag{4}$$

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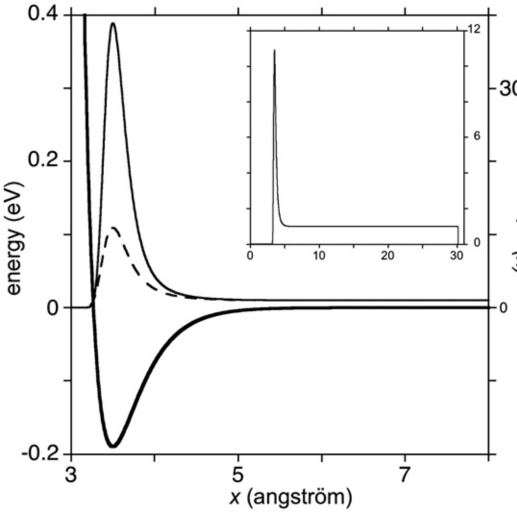


Fig. 1. Morse potential (parameter set (1)) describing the interaction between sulfur atoms and a solid surface (bold line). The function $P^{32}(x)$, proportional to the density of ^{32}S atoms at position x, is represented at 600 and 920 K, by a solid and dashed line, respectively. The decrease in 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 ($\Delta^{33}S > \pm 0.2$‰ where $\Delta^{33}S = \delta^{33}S - 1000 \times [(\delta^{34}S/1000 + 1)^{0.515} - 1]$) 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 $\Delta^{33}S$ up to ±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 (<~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):

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

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^{-1}. These parameters correspond to a force constant of $k_e = 0.548$ mdyn.Å^{-1} and a harmonic frequency of 675 cm^{-1} 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:

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

where m is the mass of the sulfur atom, $\hbar = \frac{h}{2\pi}$, h being the Plank 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:

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

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 θ' values calculated at $T = 400$ K.

Set	D_e (eV)	a (Å^{-1})	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 θ'_{full} and θ'_{trunc} values have been calculated using either all the accessible quantum states or only the bound vibrational states, respectively.

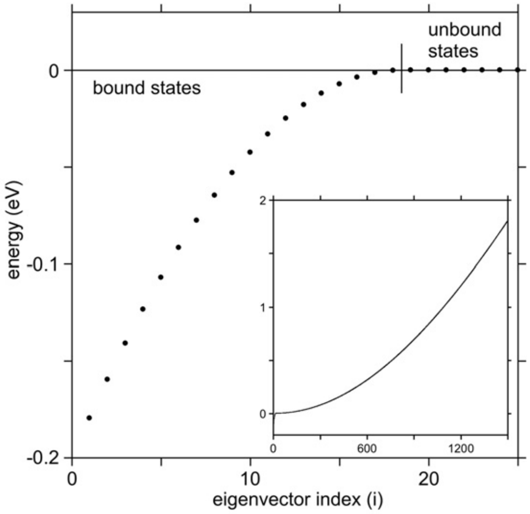


Fig. 2. Enlarged view of the energy levels of the system for the mass 32 as a function of the eigenvector index (parameter set (1)). Eighteen levels have negative energies corresponding to vibrational bound states. Inset: reduced view showing the 1500 energy levels included in the calculation. Note the characteristic quadratic shape and the energy of the highest level (ca. 1.8 eV).

homogeneous gas phase distant from the surface ($x>d$), and a finite domain close to the surface ($x<d$):

$$ {}^{m}\alpha_{ads-gas} = \frac{C^{m}_{ads}\,C^{32}_{gas}}{C^{m}_{gas}\,C^{32}_{ads}} \tag{8} $$

The concentration of adsorbed atoms, C^{m}_{ads}, is proportional to the integral of $P^m(x)$ between 0 and d; whereas $P^m(x)$ is normalized by $P^m(x)=1$ at any temperature in the homogeneous region ($x>d$). The normalization condition ensures that the gas pressure is the same for the various isotopes. The constant $A(T,m)$ is then proportional to the inverse of the partition function of the 1-D ideal gas. The isotopic fractionation factor is thus directly obtained from the function $P^m(x)$:

$$ {}^{m}\alpha_{ads-gas} = \frac{\int_0^d P^m(x)dx}{\int_0^d P^{32}(x)dx} \tag{9} $$

In the low temperature limit ($kT<<D_e$), $P^m(x)$ is dominated by the lower bound states whereas the highest vibrational levels are not populated. In that case, the sum in Eq. (7) can be safely restricted to the bound states, and Eq. (9) becomes:

$$ {}^{m}\alpha_{ads-gas} \approx \sqrt{\frac{m_{32}}{m}}\,\frac{\sum_{i'=0}^{i'max} exp\left(-\frac{E^m_{i'}}{kT}\right)}{\sum_{i=0}^{imax} exp\left(-\frac{E^{32}_{i}}{kT}\right)} \tag{10} $$

where the sums run over all the bound vibrational states. This equation corresponds to Eq. (17) of Lasaga et al. (2008), but is only valid at low temperatures. On the contrary, Eqs. (7) and (9) are more general and also valid at high temperatures.

In practice, the Schrödinger Equation (Eq. (6)) is numerically solved using a finite difference method. The box is divided into 5000 points and the second derivative of the wavefunction at the position $x(n)$, where n is the position index, is expressed as a function of the value of the wavefunction at the positions $x(n-1)$, $x(n)$ and $x(n+1)$. The resolution of Eq. (6) is thus obtained by diagonalizing a 5000×5000 tridiagonal matrix. The eigenvalues and eigenvectors of this matrix correspond to the energy levels and to the related wavefunctions of the system. The summation in Eq. (7) is performed on a range of energy levels large enough to ensure the calculation convergence at the highest temperature considered, i.e. until the results are independent of the truncation limit. This condition is fulfilled when the occupation of higher energy levels is small enough to be neglected even at the highest temperature. In the present study, the summation is performed over the first 1500 eigenstates, corresponding to a maximum energy of 1.8 eV. The highest energy levels thus require temperatures of ca. 20,000 K to be significantly populated, well above the maximum temperature considered (1000 K). The same fractionation factors (within 0.001‰) were obtained using 3000 or 5000 meshing, indicating that the calculation is well converged over the whole temperature range.

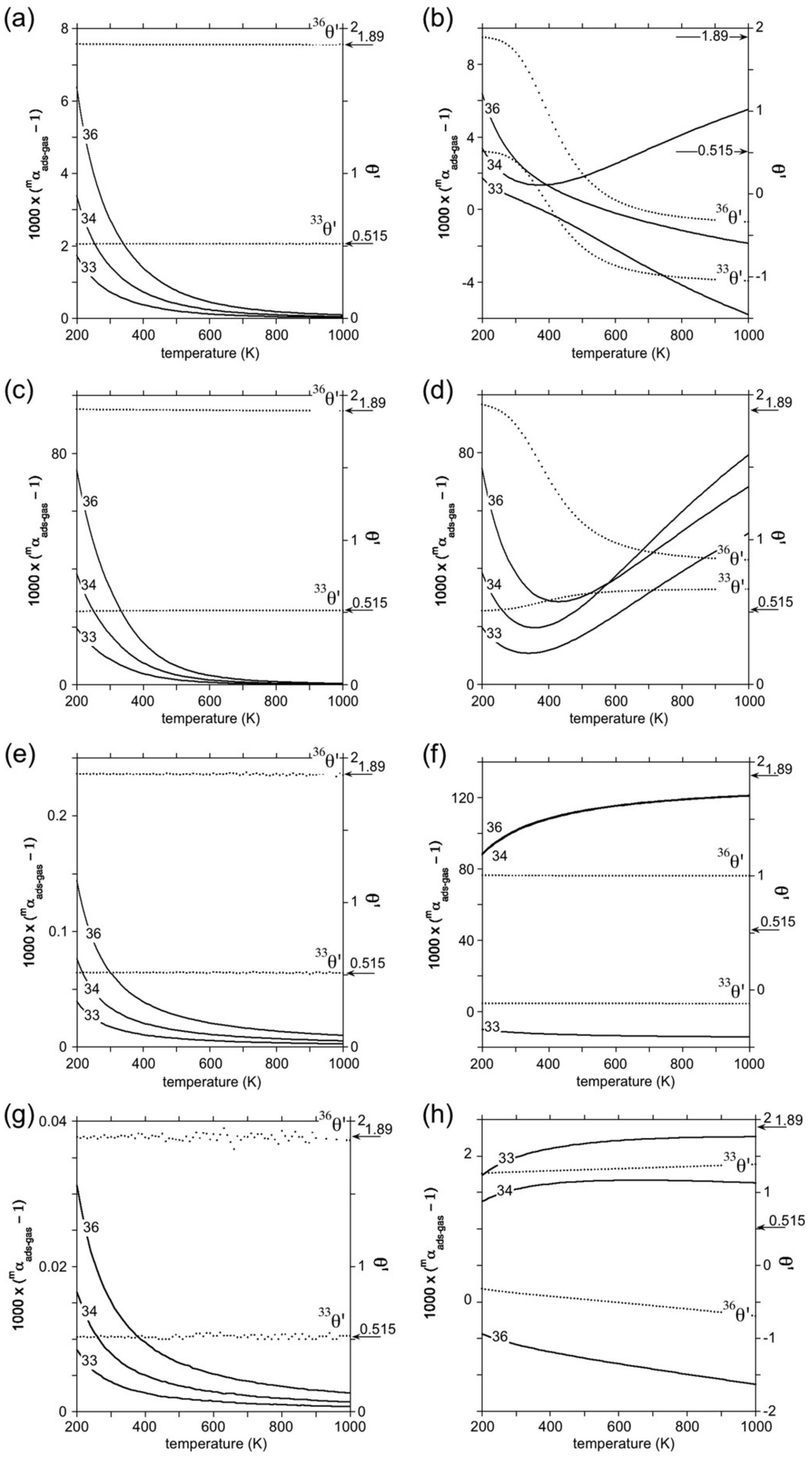
3. Results

Setting the reference zero energy at the dissociation limit of the Morse potential (Eq. (5)), the vibrational bound states are defined by their negative energies (Fig. 2). The numerical resolution of the Schrödinger equation leads to 19 vibrational bound states for ^{34}S and ^{36}S, and 18 for ^{32}S and ^{33}S (parameter set (1), Table 1). In contrast, positive energies display the characteristic quadratic behavior as a function of the eigenvector index observed for a particle in a square well. In the present study, these states are referred to as “unbound” states because the associated particle can freely travel in the box.

The probability to find an atom at a distance d from the surface, is then calculated using Eq. (7) for temperatures ranging between 200 and 1000 K. The function $P^m(x)$ presents a maximum at 3.5 Å and is almost constant for distances larger than 6 Å (Fig. 1). The maximum of $P^m(x)$ coincides with the minimum of the potential well, defined by the equilibrium distance parameter ($x_e=3.5$ Å). Its intensity is inversely correlated to the temperature, reflecting the thermally induced desorption of atoms from the surface.

The fractionation factors are calculated by considering the equilibrium between a domain defined from 0 to $d=10$ Å, containing the adsorbed atoms, and the rest of the box, which corresponds to the homogeneous gas (Fig. 3a). The fractionation factors depend on the integration domain and display a regular variation for a value of d ranging between 5 and 30 Å (Fig. 4). For the selected domain (0–10 Å), fractionation factors vary from 6‰ for the mass 36 at 200 K to less than 0.1‰ for the three isotopes at high temperature, which corresponds to the classical limit. They follow a quadratic law as a function of the reciprocal temperature ($\propto 1/T^2$). Heavier isotopes present larger fractionation factors, indicating that heavier atoms are preferentially adsorbed. These observations are consistent with previous models and observations of isotopic equilibrium between gas and condensed phases (Höpfner, 1969 and Ref. therein). Over the whole temperature range (200–1000 K), the isotopic fractionation factors closely follow the terrestrial fractionation relations, with

Fig. 3. Left: Isotopic fractionation factors (solid lines) between adsorbed S, occurring in a volume extending between $x=0$ and $x=10$ Å from the surface, and a homogeneous gas, (a), (c), (e), and (g) correspond to the parameter sets (1), (2), (3) and (4), respectively. The fractionation factors display a quadratic decrease as a function of temperature. Heavier isotopes are preferentially adsorbed onto the surface. The corresponding theoretical $^{33}\theta'$ and $^{36}\theta'$ values (horizontal dotted curves) are independent of temperature and equal to 0.515 and 1.89, respectively, evidencing the absence of anomalous isotopic fractionation. Right: Isotopic fractionation factors (solid lines) obtained for the same volume but restricting the calculation to the bound vibrational states only, (b), (d), (f) and (h) correspond to the parameter sets (1), (2), (3) and (4), respectively. Note the unphysical behavior of the isotopic fractionation factors observed at high temperature, which should tend to one in the classical limit. This leads to a strong anomalous isotopic fractionation, with significant departure of $^{33}\theta'$ and $^{36}\theta'$ (dotted curves) from the TFL values (0.515 and 1.89, respectively).


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
1000 x (mα ads-gas − 1)
θ'
temperature (K)
36θ'
33θ'
1.89
0.515
36
34
33
200
400
600
800
1000

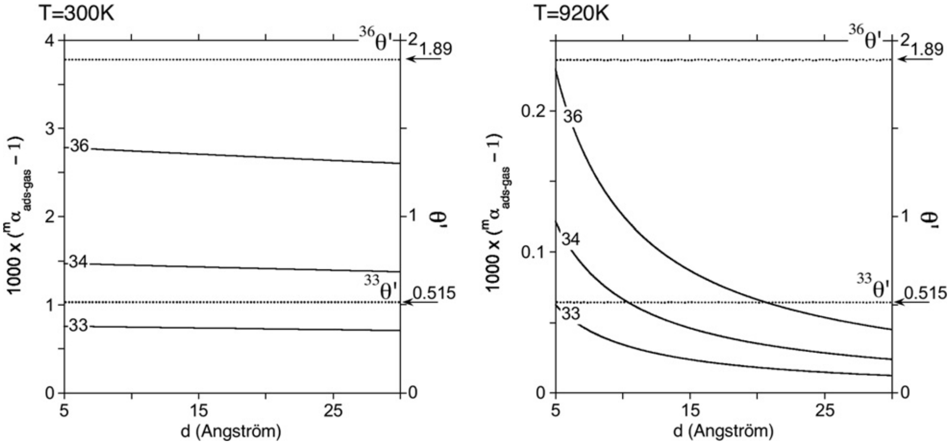


Fig. 4. Dependence of the isotopic fractionation factors (solid lines) on the integration range *d* calculated at $T = 300$ K and $T = 920$ K for the parameter set (1). The constant $^{33}\theta'$ and $^{36}\theta'$ values (horizontal dotted curves) evidence that the standard mass-dependent behavior does not depend on the integration range. Note that the fractionation factors are much lower at 920 K than at 300 K.

$^{33}\theta' = \ln(^{33}\alpha_{\text{ads-gas}}) / \ln(^{34}\alpha_{\text{ads-gas}}) \approx (^{33}\alpha_{\text{ads-gas}} - 1) / (^{34}\alpha_{\text{ads-gas}} - 1) = 0.515 \pm 0.001$ and $^{36}\theta' = \ln(^{36}\alpha_{\text{ads-gas}}) / \ln(^{34}\alpha_{\text{ads-gas}}) \approx (^{36}\alpha_{\text{ads-gas}} - 1) / (^{34}\alpha_{\text{ads-gas}} - 1) = 1.89 \pm 0.005$. Remarkably, the values of $^{33}\theta'$ and $^{36}\theta'$ do not depend on the integration range, which defines the adsorbed state (Fig. 4). The three other parameter sets defining the Morse potential also lead to a decrease of fractionation factors as a function of temperature and to usual mass-dependent relations (Fig. 3c,e,g).

4. Discussion

The results obtained using our simple 1-D adsorption model significantly differ from those reported by Lasaga et al. (2008) using a similar model. The absence of anomalous isotopic fractionation is directly linked to the incorporation of "unbound" accessible states in our calculations, whereas Lasaga et al. (2008) restrict their thermodynamic modeling of the adsorbed molecule to the bound vibrational states. Applying such restriction to our model by limiting the sum in Eq. (7) to bound states also leads to anomalous isotopic fractionation (Fig. 3b). This observation holds for all the parameter sets (Fig. 3b,d,f,h), corresponding to intermediate (0.19 eV) and very small adsorption energies (0.0171 eV), with a number of bound states ranging from 4 to 19 (Table 1). As anticipated, the departure from TFL increases with temperature, when the population of upper vibrational states becomes significant. For the same reason, the anomalous effect

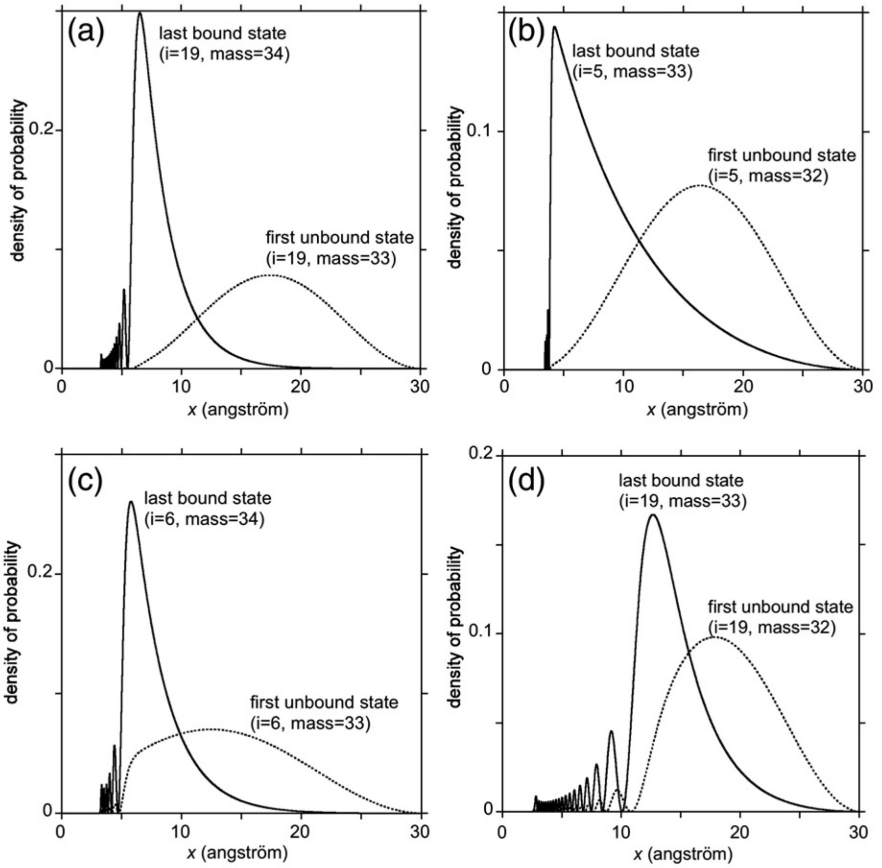


Fig. 5. Density of probability $|\Psi_i^m(x)|^2$ of the state *i*, corresponding to the last bound state of mass *m* and first unbound state of mass m − 1. (a),(b),(c), and (d) correspond to parameter sets (1), (2), (3), and (4), respectively. Note the delocalization of the last bound state of mass m and the overlap with the first unbound state of mass m − 1.

related to the restriction to bound states appears at a lower temperature in the case of smaller adsorption energy (parameter sets (3) and (4)). One should also note that a too low truncation limit in Eq. (7) can lead to a spurious increase of isotopic fractionation factors and MIF at high temperature, even when unbound states are included in the calculation.

According to Lasaga et al. (2008), the restriction to bound states is supported by the observation that unbound states are delocalized over the whole box, whereas bound states are well localized in a region close to the surface. However, a closer examination of the density of probability associated with the last bound state of mass 34 in parameter sets (1) and (3) reveals that the particle is already significantly delocalized and that its wavefunction significantly overlaps with that of the first unbound state of mass 33 (Fig. 5). The same observation is also valid for the two other parameter sets, with the last bound state of mass 33 overlapping with the first unbound state of mass 32. Therefore, there is no *a priori* reason to exclude the unbound states to describe the isotopic equilibrium of adsorbed molecules.

At this point, it could be argued that by definition an adsorbed molecule is bonded to the surface, thus only displaying bound states. In fact, such definition leads to a thermodynamic system which spatial extension is ill-defined because of the significant overlap between the bound and unbound states of the various isotopes. Adsorbed species correspond to a spatially well-defined thermodynamic system only when the potential well is deep enough and the temperature low enough to ensure a bijective relation between adsorption and location in a finite volume. In that case, unbound states can be safely neglected because their population is almost zero at relevant temperatures. As pointed out by Lasaga et al. (2008), this kind of adsorption reaction, corresponding to strong chemisorption, is not expected to produce MIF. It corresponds to the low-T limit of our model.

Finally, we note that the fractionation of sulfur isotopes is most often related to the dramatic changes in the chemical properties of sulfur associated with oxidation or reduction reactions. When these reactions occur at the surface of a mineral, they can be decomposed into at least three steps including adsorption of reactants onto the solid surface, electronic exchange between the adsorbed molecules and the surface or other adsorbed molecules, and desorption of the reaction products (Brown et al., 1999). These processes involve various energetic barriers determining the reaction rates. Here again, there is no *a priori* reason to exclude unbound states because a particle meeting the surface with enough kinetic energy to reach the transition states will interact more efficiently with the surface.

From these observations, it is unlikely that simple adsorption equilibrium can lead to anomalous fractionation of sulfur isotopes. Our results do not exclude kinetic mechanisms, such as those involved in the electron exchange between adsorbed molecules and minerals or in the dissociation rate of excited transition states; these however remain to be investigated (see e.g. Chakraborty and Bhattacharya, 2003). Thus, in our present state of understanding, atmospheric processes involving photolytic dissociation of SO_2 and self-shielding mechanisms still appear to be the most viable mechanisms to explain the strong anomalies of the sulfur isotopic composition measured in Archean samples (Farquhar et al., 2000, 2007; Thiemens, 2006; Lyons, 2007, in press).

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Erratum

Erratum to "Theoretical investigation of the anomalous equilibrium fractionation of multiple sulfur isotopes during adsorption" [Earth Planet. Sci. Lett. 284 (2009) 88–93]

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The harmonic frequency corresponding to a force constant of $k_e = 0.548$ mdyn Å^{-1} and a mass 32 has been erroneously reported at 675 cm^{-1}. The correct value is 170.5 cm^{-1}. This error does not affect any other result or conclusion of the article.

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