



# A test of the significance of intermolecular vibrational coupling in isotopic fractionation



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## ABSTRACT

Intermolecular coupling of dipole moments is studied for a model system consisting of two diatomic molecules (AB monomers) arranged co-linearly and which can form non-covalently bound dimers. The dipolar coupling is a function of the bond length in each molecule as well as of the distance between the centers-of-mass of the two molecules. The calculations show that intermolecular coupling of the vibrations results in an isotope-dependent modification of the AB-AB intermolecular potential. This in turn alters the energies of the low-lying bound states of the dimers, producing isotope-dependent changes in the AB-AB dimer partition function. Explicit inclusion of intermolecular vibrational coupling then changes the predicted gas-dimer isotopic fractionation. In addition, a mass dependence in the intermolecular potential can also result in changes in the number of bound dimer states in an equilibrium mixture. This in turn leads to a significant dimer population shift in the model monomer-dimer equilibrium system considered here. The results suggest that intermolecular coupling terms should be considered when probing the origins of isotopic fractionation.

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## 1. Introduction

Isotopologues of a molecule differ in the isotope present in one or more of the atoms comprising the molecule. The isotopic composition in a given sample is known to depend on how the constituent molecules were formed and the phase equilibria they underwent. Sample-to-sample variations in isotopic composition are typically a few tenths of 1% and are usually reported as parts per mil (i.e. part per thousand). However, these small deviations can provide important information regarding the processes and conditions that led to the formation of the molecules in a given sample.

Early treatments of isotopologue thermodynamics focused largely on the direct effect of mass differences and differences in zero-point energies [1–5]. Such conventional prescriptions predict, for example, that the vapor phase should always be enriched in the lighter isotopologue when in equilibrium with a condensed phase. In addition, the chemical bonds in a molecule will require more energy to break in a heavier isotopologue due to its lower zero-point vibrational energy. As a result, the activation energy for a

reaction will be higher and the reaction slower for the heavier isotopologue using conventional approaches.

However, there are many experimental cases in which these conventional predictions are incomplete, indicating that other physical aspects can play an important role. For instance, there are examples of vapor-liquid and vapor-solid phase equilibria in which the vapor is enriched in the heavier isotopologue [5–14]. In some chemical processes, such as the extraction of certain metals with crown ethers, fractionation appears to depend significantly on whether the nuclear mass number of the metal atom is even or odd [15–19]. Some chemical reactions also do not obey predictions based solely on zero-point energy considerations, where the heavier species reportedly show faster rather than slower kinetics [20]. Furthermore, the formation of O<sub>3</sub> seems to be largely independent of the isotopic composition of the reactants [21–25], and similar results have also been observed in other reactions [26–30]. Proposed explanations of these observations include changes in the size and spin of the nucleus [31–33] as well as variations in transition state electronic structure [25,34]. Also, in gas chromatography, it has been observed that heavier isotopologues of carbon dioxide can elude from the column before lighter CO<sub>2</sub> isotopologues [35].

It has recently been pointed out that dipole moment variation accompanying changes in the internal coordinates of a molecule

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results in a coupling of the vibrational modes of the different molecules [36]. This leads to a dependence of the intermolecular forces on the isotopic composition of the molecules. In this paper, the significance of this mass dependence arising from the vibrational and Lennard-Jones interactions is investigated quantitatively using a simple 1-D model system consisting of collinear interacting diatomic monomer molecules. The goal is to utilize this model to provide insight into the question of whether inclusion of the intermolecular coupling between different isotopologue vibrations can have a significant effect on the thermodynamic properties of an isotopologue mixture. In our model system, two AB molecules align co-linearly in an AB-AB arrangement, so that the dipole-dipole interaction is attractive, and we also consider the AB-BA and BA-AB configurations in which the dipole-dipole interaction is repulsive. The Lennard-Jones (LJ) interactions employed in this work are strong enough that the attractive interactions support non-covalent bound dimer states in all three configurations. This model is similar in spirit to the one-dimensional model employed by Balan et al. to investigate the isotope dependence of sulfur gas absorption on a surface [37]. In our calculations, isotopic masses and parameters defining the potential energy of the system are taken from the NO molecule, since this is a diatomic molecule with a moderate dipole moment of about 0.16 Debye with a known bond length dependence [38]. The goal of this work is *not* to provide a complete theoretical description of any specific AB-AB dimer, since a complete description would also depend on features not included in this simple model, such as, the rotations of the molecules and the three-dimensional motion of the vector between centers of mass of the two molecules. Furthermore, the isotopic fractionation in a real system would also have to account for any reactions involving covalent bonding. For instance, the real NO molecule has an unpaired electron and can form a covalent bond between the N atoms of the two NO molecules [39]. Since dimers are bound in this model due to the Lennard-Jones interactions, they are an example (within a simplified model) of a van der Waals complex [40–42].

Conventional Monte Carlo and molecular dynamics simulations are often performed using force fields to model the interactions between the different atoms, or groups of atoms, in each of the molecules. Such simulations generally do not account for the bond length dependence of the coupling of the vibrations of different molecules. Thus, the question of the thermodynamic significance of the mass-dependent intermolecular coupling is an important one. Hou et al. have recently reported calculations which demonstrate that inclusion of the dependence of the H<sub>2</sub>O-Ar potential energy surface on the *intramolecular* coupling of the vibrational modes of H<sub>2</sub>O is necessary to obtain a high level of accuracy [43]. This work, on the other hand, focuses on *intermolecular* vibrational couplings. It should also be noted that several computational studies on the quantum nature of hydrogen isotopes in water and in hydrogen shift reactions have been performed using quantum path integral techniques [44–48]. The less computationally demanding method presented here would not, in its current form, account for the light nuclei quantum effects considered in those studies. The quantum path integral calculations would also account for the isotope mass dependence for the interactions between the molecules that is considered in this work, as would higher-level quantum chemistry methods. However, force fields are still useful for large systems, and it is important to note that obtaining the correct isotope fractionation requires that these bond length dependent intermolecular interactions be included.

The organization of this paper is as follows. The one dimensional, co-linear two AB model is described in Section 2.1. The semiclassical method used for evaluating the two AB bound state energies is presented in Section 2.2. Results are presented in Section 2.3, which show that mass dependent intermolecular

vibrational couplings can have an important effect on isotopic fractionation in the non-covalent monomer-dimer reaction, and the mass dependent interaction also results in changes in the fraction of AB present in dimer form. These results and their potential importance in more complicated molecular systems are discussed in Section 3.

## 2. Calculations

### 2.1. AB dimer model

The model employed in this work consists of two AB molecules (denoted as 1 and 2) with all four atoms aligned co-linearly, as shown in Fig. 1 for an AB<sub>1</sub>-AB<sub>2</sub> alignment. The separation between the centers-of-mass (COM) of the two molecules is denoted as R and the bond lengths for the two molecules are r<sub>1</sub> and r<sub>2</sub>. The model potential energy for this alignment then has the following form:

$$V(R, r_1, r_2) = V_M(r_1) + V_M(r_2) + V_{AA}(R + a_1 r_1 - a_2 r_2) + V_{BB}(R - b_1 r_1 + b_2 r_2) + V_{AB}(R + a_1 r_1 + b_2 r_2) + V_{AB}(R - b_1 r_1 - a_2 r_2) + V_\mu(R, r_1, r_2) \quad (1)$$

where a<sub>j</sub>r<sub>j</sub> and b<sub>j</sub>r<sub>j</sub> are the distances of the A and B atoms, respectively, from the COM of molecule j (j = 1 or 2),

$$V_M(r) = D(1 - \exp[-\alpha(r - r_e)])^2 \quad (2)$$

is the Morse potential employed to model the bond length dependence of the energy of a AB molecule,

$$V_{IJ}(r) = 4\epsilon_{IJ}[(\sigma_{IJ}/r)^{12} - (\sigma_{IJ}/r)^6] \quad (3)$$

(with IJ = AA, BB, or AB) is the Lennard-Jones (LJ) interaction between atoms I and J separated by the distance r, and

$$V_\mu(R, r_1, r_2) = -2\mu(r_1)\mu(r_2)/R^3 \quad (4)$$

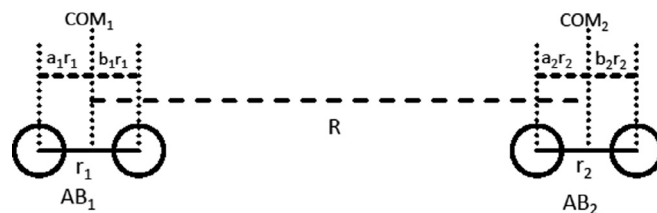
is the dipole-dipole interaction between the two molecules. The dipoles are taken to have a bond length dependence of the form

$$\mu(r) = \mu_0 + \mu_1(r - r_e) + \mu_2(r - r_e)^2. \quad (5)$$

The potential energy for the AB-BA and BA-AB case are obtained by changing the sign in Eq. (4) and the appropriate modification of the signs before a<sub>1</sub>, a<sub>2</sub>, b<sub>1</sub>, and b<sub>2</sub> in the LJ terms in Eq. (1).

The LJ parameters  $\epsilon_{AA}$ ,  $\epsilon_{BB}$ ,  $\sigma_{AA}$ , and  $\sigma_{BB}$  employed here are literature values for N and O obtained from fits to experimental data [49,50]. The LJ parameters for the interaction between an A atom and a B atom are obtained using the combining rules

	AB <sub>1</sub>	AB <sub>2</sub>
Isotopologue Case 1:	<sup>14</sup> A <sup>16</sup> B	<sup>14</sup> A <sup>16</sup> B
Isotopologue Case 2:	<sup>14</sup> A <sup>16</sup> B	<sup>15</sup> A <sup>16</sup> B
Isotopologue Case 3:	<sup>15</sup> A <sup>16</sup> B	<sup>15</sup> A <sup>16</sup> B



**Fig. 1.** Co-linear AB-AB system. The left circle for each molecule is the A atom and the right circle is the B atom. R is the distance between the center of mass of AB<sub>1</sub> and the center of mass of AB<sub>2</sub>. The bond lengths for the two molecules are r<sub>1</sub> and r<sub>2</sub>. The a<sub>j</sub>r<sub>j</sub> is the distance of the A atom from the center of mass of molecule j (j = 1, 2), and b<sub>j</sub>r<sub>j</sub> is the distance of the B atom from the center of mass of the molecule.

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