An Isotopic Mass Effect on the Intermolecular Potential

Michael F. Herman,^a Robert P. Currier,^{b,*} and Samuel M. Clegg^b

^aDepartment of Chemistry, Tulane University, New Orleans, LA 70118, USA;
mherman@tulane.edu

^bChemistry Division, Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87545,
USA; currier@lanl.gov; sclegg@Lanl.gov

*Corresponding author

Abstract

The impact of isotopic variation on the electronic energy and intermolecular potentials is often suppressed when calculating isotopologue thermodynamics. Intramolecular potential energy surfaces for distinct isotopologues are in fact equivalent under the Born-Oppenheimer approximation, which is sometimes used to imply that the intermolecular interactions are independent of isotopic mass. In this communication, the intermolecular dipole-dipole interaction between hetero-nuclear diatomic molecules is considered. It is shown that the intermolecular potential contains mass-dependent terms even though each nucleus moves on a Born-Oppenheimer surface. The analysis suggests that mass dependent variations in intermolecular potentials should be included in comprehensive descriptions of isotopologue thermodynamics.

I. Introduction.

Isotopologues are variants of a molecule that differ in the isotopic identity of one or more of the constituent atoms. Classical treatments of molecular species comprised of various stable isotopes assume variations in the isotopologue thermodynamics result directly from mass differences and/or differences in zero point vibrational energy (ZPE).¹⁻⁵ Isotopologue fractionation between phases is then attributed to mass/ZPE differences. Thus, at equilibrium a vapor phase composition is expected to be rich in the lighter isotopologue(s) relative to any condensed phases. Also, chemical bonds involving heavier stable isotopes are assumed to be stronger than lighter one(s) since a stronger bond has a lower ZPE. Kinetic isotope effects then result from differences in activation energy where the reactants, transition state, or both, have different zero point vibrational energies. The net effect is that the activation energy is typically higher, and therefore the reaction is slower, for the carbon bond involving the heavier stable isotope. However, an ever-growing number of documented cases suggest that this classical description fails to fully explain observations. For example, vapor-liquid and vapor-solid equilibrium systems have been found in which inverse fractionation occurs, that is, the vapor phase is the one enriched in heavier stable isotopes.⁵⁻¹⁴ Also, extraction of metals such as cadmium, barium, zinc, and strontium using crown ethers shows a nuclear mass effect where fractionation patterns depend on whether the nuclear mass number is even or odd.¹⁵⁻¹⁹ Chemical reactions do not always follow the classical theory either. For example, during ozone formation the isotopic distribution in the equilibrium product proves to be largely independent of differences in the isotopic mass of the reactants.²⁰⁻²⁴ Such "mass independent" isotope effects have been reported in other chemical reactions.²⁵⁻²⁹ In addition, chemical reactions have been reported in which the heavier species appear to have the faster kinetics.³⁰

In theory, each canonical energetic mode (translational, vibrational, rotational, nuclear, electronic) can make a significant contribution to the thermodynamic behavior. Correlations between these modes (vibrational-rotational coupling, electron-phonon interactions, etc.) can also be important. Proposed explanations of the non-classical observations cited above include adding nuclear field effects³¹⁻³³ and variations in transition state electronic structures.^{24,34} While these improve the classic theory, it is not clear if these extensions alone will constitute a complete thermodynamic description of stable molecular isotopologues. For example, changes in intermolecular potentials as a result of mass-dependent differences in electronic structure are often suppressed or ignored. That is, electronic energy and intermolecular potentials are commonly assumed to be the same for all isotopologues³⁵⁻³⁹ with the Born-Oppenheimer approximation⁴⁰ being invoked to justify this assumption. Under Born-Oppenheimer, the intramolecular potential energy surfaces upon which the nuclei move are independent of isotopic composition. It is often assumed either implicitly or explicitly⁴¹ that, by extension, the intermolecular potentials are then unaffected by changes in isotopic composition. However, the intramolecular and intermolecular potentials are not the same entity. At a fixed temperature, nuclei of different masses can be expected to exhibit different vibrational dynamics on the same intramolecular Born-Oppenheimer surface. As a consequence, the time-averaged sampling of that potential energy surface over a vibrational cycle will differ. Associated with this is a difference in sampling of the electronic configurations underlying that Born-Oppenheimer surface. This in turn could result in differences in the intermolecular potentials as the masses associated with the vibrational motions are changed.

In this communication, the question of whether or not intermolecular potentials are dependent on isotopic composition is probed. Specifically, an analysis of the interaction

between two hetero-nuclear diatomic molecules will demonstrate that, even within the Born-Oppenheimer approximation, the intermolecular potential does depend on the reduced masses. The analysis is very similar to one used to demonstrate the R^{-6} dependence of the London dispersion forces,⁴² although the focus here is on the dependence on isotopic composition. The following demonstration shows that variations in intermolecular potentials associated with isotopic composition can be expected, and therefore contribute to isotopologue thermodynamics.

II. Analysis of a model intermolecular potential.

Consider the simple system consisting of two diatomic molecules with all four atoms arranged along a straight line. Assume that the vibration of each molecule can be treated as a harmonic oscillator, and that both molecules have a dipole moment that depends linearly on the bond length of the diatomic. Assume also that the two diatomic molecules contain the same two elements, but their isotopic composition can be different. Examples might include $^{12}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$, or $^{14}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{16}\text{O}$. The Hamiltonian operator for this system of collinear diatomic molecules is given by

$$\begin{aligned} \mathbf{H} &= -\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial x_2^2} + \frac{1}{2} k x_1^2 + \frac{1}{2} k x_2^2 - \frac{(\mu_0 + \mu_1 x_1)(\mu_0 + \mu_1 x_2)}{R^3} \\ &= -\frac{\hbar^2}{2} \frac{\partial^2}{\partial y_1^2} - \frac{\hbar^2}{2} \frac{\partial^2}{\partial y_2^2} + \frac{1}{2} k_1 y_1^2 + \frac{1}{2} k_2 y_2^2 - \frac{(\mu_0 + \mu_1 y_1/\sqrt{m_1})(\mu_0 + \mu_1 y_2/\sqrt{m_2})}{R^3} \\ &= \mathbf{T} + \mathbf{V}(y_1, y_2) \end{aligned} \quad (1)$$

where x_1 and x_2 are the deviation of the bond length from its value at the minimum of the harmonic vibrational potential. The masses m_1 and m_2 are the reduced masses for the vibrations of the molecules, $y_1 = \sqrt{m_1} x_1$ and $y_2 = \sqrt{m_2} x_2$ are mass weighted coordinates, and $k_i = k/m_i$ for $i = 1, 2$. It is assumed that the values of k , μ_0 , and μ_1 are obtained by solving the electronic structure problem within the Born-Oppenheimer approximation, which makes these quantities independent of the isotopic composition of the two diatomic molecules. Note, that the model is

easily generalized to the case where the two diatomics do not contain the same elements by choosing the Born-Oppenheimer quantities k , μ_0 , and μ_1 to be different for the two molecules.

Since the potential energy contains only up to quadratic terms in the coordinates, the model system can be solved analytically. The first and second derivatives of the potential energy are given by

$$\frac{\partial V}{\partial y_1} = k_1 y_1 - a_1 - b y_2 \quad (2)$$

$$\frac{\partial V}{\partial y_2} = k_2 y_2 - a_2 - b y_1 \quad (3)$$

$$\frac{\partial^2 V}{\partial y_1^2} = k_1 \quad (4)$$

$$\frac{\partial^2 V}{\partial y_2^2} = k_2 \quad (5)$$

$$\frac{\partial^2 V}{\partial y_1 \partial y_2} = -b \quad (6)$$

where $a_1 = \mu_0 \mu_1 / (R^3 \sqrt{m_1})$, $a_2 = \mu_0 \mu_1 / (R^3 \sqrt{m_2})$, and $b = \mu_1^2 / (R^3 \sqrt{m_1 m_2})$. Setting $\partial V / \partial y_1 =$

$\partial V / \partial y_2 = 0$, gives the location of the minimum in V as $y_1^{(0)} = (k_2 a_1 + b a_2) / D$ and $y_2^{(0)} = (k_1 a_2 +$

$b a_1) / D$, where $D = k_1 k_2 - b^2$. The values of $x_1 = y_1 / \sqrt{m_1}$ and $x_2 = y_2 / \sqrt{m_2}$ at the minimum in V

are given by $x_1^{(0)} = x_2^{(0)} = \alpha / (k - \beta)$, where $\alpha = \mu_0 \mu_1 / R^3$ and $\beta = \mu_1^2 / R^3$. Defining $z_j = y_j - y_j^{(0)}$ and

$V_0 = V(x_1^{(0)}, x_2^{(0)})$ gives

$$\mathbf{H} = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial z_1^2} - \frac{\hbar^2}{2} \frac{\partial^2}{\partial z_2^2} + V_0 + \frac{1}{2} k_1 z_1^2 + \frac{1}{2} k_2 z_2^2 - b z_1 z_2 \quad (7)$$

The 2x2 matrix of second derivatives of V can be diagonalized to give two uncoupled oscillators

with squared frequencies $\omega_{\pm}^2 = (k_1 + k_2) / 2 \pm \frac{1}{2} [(k_1 - k_2)^2 + 4b^2]^{1/2} = (k / m_1 + k / m_2) / 2 \pm \frac{1}{2} [(k / m_1 -$

$k / m_2)^2 + 4\beta^2 / m_1 m_2]^{1/2}$. The total ground state energy of the system is given by

$$E = \frac{1}{2} \hbar \omega_+ + \frac{1}{2} \hbar \omega_- + V_0 \quad (8)$$

Note that V_0 is independent of the reduced masses m_1 and m_2 since $x_1^{(0)}$ and $x_2^{(0)}$ are independent of the reduced masses.

If the two diatomic molecules have the same isotopic composition, then $m_1 = m_2 = m$ and $\omega_{\pm} = \{[k \pm (\mu_1^2/R^3)]/m\}^{1/2} = (k/m)^{1/2}[1 \pm (\mu_1^2/R^3)/k]^{1/2}$. In this case $\frac{1}{2} \hbar \omega_+ + \frac{1}{2} \hbar \omega_- \approx \hbar \omega_0 - \frac{1}{8} \hbar \omega_0 [(\mu_1^2/R^3)/k]^2$, where $\omega_0 = (k/m)^{1/2}$. Note that $-\frac{1}{8} \hbar \omega_0 [(\mu_1^2/R^3)/k]^2$ is an intermolecular (i.e., R dependent) potential that depends on the reduced mass of the diatomics through ω_0 .

Now consider the case where the reduced masses are not equal. In the $R \rightarrow \infty$ limit, the two frequencies approach the independent oscillator limit, $\omega_{+, \infty} = \sqrt{k/m_{<}}$ and $\omega_{-, \infty} = \sqrt{k/m_{>}}$, where $m_{>}$ ($m_{<}$) is the larger (smaller) of the two reduced masses. At large (but not infinite) R , the ground state energy can be written $E = \frac{1}{2} \hbar \omega_{+, \infty} + \frac{1}{2} \hbar \omega_{-, \infty} + V_0 + \Delta V(R, m_1, m_2)$, where the $\Delta V(R, m_1, m_2)$ term can be obtained by expanding $\frac{1}{2} \hbar \omega_+ + \frac{1}{2} \hbar \omega_-$ in terms of the parameter $s = 4(b/|\Delta k|)^2$, where $\Delta k = k_1 - k_2$. The first order term in this expansion is given by

$$\begin{aligned} \Delta V &= \frac{1}{2} \hbar \left[\frac{d\omega_+}{df_+} \frac{df_+}{ds} + \frac{d\omega_-}{df_-} \frac{df_-}{ds} \right] s \\ &= \frac{1}{4} (\hbar/\omega_{+, \infty} - \hbar/\omega_{-, \infty}) (b^2/|\Delta k|) \\ &= \frac{1}{4} \hbar \left(\sqrt{\frac{m_{<}}{k}} - \sqrt{\frac{m_{>}}{k}} \right) \frac{\mu_1^4}{k(m_{>} - m_{<})R^6} \end{aligned} \quad (9)$$

where $f_{\pm} = \omega_{\pm}^2 = (k_1 + k_2)/2 \pm \frac{1}{2} |k_1 - k_2| [1 + 4(b/\Delta k)^2]^{1/2}$. Note that ΔV is an intermolecular potential term that depends on the isotopic composition of the two diatomic molecules. As was shown for the case where reduced masses are equal (i.e. $m_1 = m_2 = m$), the intermolecular potential again shows a mass dependence when the reduced masses are not equal.

III. Discussion.

This analysis of collinear hetero-nuclear diatomic molecules demonstrates that isotopic substitution results in a mass-dependent intermolecular potential. That is, the intermolecular

potential depends on the center-to-center separation distance *and* the isotopic composition through the reduced masses. This is true even when the intramolecular potential energy surface for each diatomic is determined using the Born-Oppenheimer approximation. While the analysis presented here considers only collinear diatomic molecules with permanent dipoles, one can anticipate that the intermolecular potentials between molecules with higher electrostatic moments will also possess a mass dependence, even though the intramolecular potentials are Born-Oppenheimer surfaces. This implies that a complete description of stable isotopologue thermodynamics may likely require including changes in intermolecular potentials as a function of isotopic composition. For example, the complex site-specific fractionation patterns observed during chromatography of the phenolic aldehyde vanillin implies that subtle changes in the intermolecular interactions (in this case vanillin interaction with a silica substrate) can govern isotopologue fractionation.⁴³ In addition, it has been clearly demonstrated that isotopic substitution directly influences structural, thermodynamic, and spectroscopic properties.⁴⁴⁻⁴⁵

The myriad of physical behavior reported in systems containing stable isotopologues suggests that all of the energetic modes, including second order isotope effects, may ultimately prove necessary in developing a comprehensive theory.⁴⁶ It is possible that a case-specific competition between the various energetic modes determines the thermodynamic behavior, and in order to correctly predict which mode(s) dominate, contributions from all the mass-dependent terms must then be considered in any complete description.

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