

Second-order correction to the Bigeleisen–Mayer equation due to the nuclear field shift

(reduced partition-function ratios/Born–Oppenheimer approximation)

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ABSTRACT The nuclear field shift affects the electronic, rotational, and vibrational energies of polyatomic molecules. The theory of the shifts in molecular spectra has been studied by Schlembach and Tiemann [Schlembach, J. & Tiemann, E. (1982) *Chem. Phys.* 68, 21]; measurements of the electronic and rotational shifts of the diatomic halides of Pb and Tl have been made by Tiemann *et al.* [Tiemann, E., Knöckel, H. & Schlembach, J. (1982) *Ber. Bunsenges. Phys. Chem.* 86, 821]. These authors have estimated the relative shifts in the harmonic frequencies of these compounds due to the nuclear field shift to be of the order of 10^{-6} . I have used this estimate of the relative shift in vibrational frequency to calculate the correction to the harmonic oscillator approximation to the isotopic reduced partition-function ratio $^{208}\text{Pb}^{32}\text{S}/^{207}\text{Pb}^{32}\text{S}$. The correction is 0.3% of the harmonic oscillator value at 300 K. In the absence of compelling evidence to the contrary, it suffices to calculate the nuclear field effect on the total isotopic partition-function ratio from its shift of the electronic zero point energy and the unperturbed molecular vibration.

Recent experiments have shown that chemical equilibrium isotope-exchange separation factors are not necessarily a linear function of the atomic mass differences of the isotopomers (1–8). The most extensive experiments are those of Fujii *et al.* (5–8), which involve the exchanges of the isotopes ^{232}U , ^{233}U , ^{234}U , ^{236}U , and ^{238}U between an aqueous phase and an anion-exchange resin. The aqueous phase is principally U(IV); the resin phase is principally U(VI), hydrated or complexed uranyl ion. In each of these exchange reactions the heavy isotope concentrates in the aqueous phase, that is U(IV). The nonlinearity and the fact that the heavy isotope concentrates in the U(IV) species arise from the shift in the minimum of the electronic potential energy due to the different nuclear sizes and shapes of the isotopomers. This is known as the nuclear field shift. A quantitative calculation of this effect (9) is in excellent agreement with experiment.

The calculation is based on the addition of a term due to the nuclear field shift to the Bigeleisen–Mayer equation for the logarithm of the isotopic separation factor and the reduced partition-function ratio. Analogous to the Bigeleisen–Mayer function, $\ell n(s/s')f_0$, we define $\ell n(s/s')f_{\text{ns}}$ as the nuclear field correction and $\ell n(s/s')f_{\text{T}}$ as the total reduced partition-function ratio corrected for the nuclear field shift.

$$\ell n(s/s')f_{\text{T}} = \ell n(s/s')f_{\text{ns}} + \ell n(s/s')f_0 \quad [1]$$

The nuclear field shift correction is simply,

$$\ell n(s/s')f_{\text{ns}} = (E_{\text{H}}^{\circ} - E_{\text{L}}^{\circ})/kT \quad [2]$$

where $(E_{\text{H}}^{\circ} - E_{\text{L}}^{\circ})$ is the difference in the ground state electronic energy.

Table 1. Correction to the isotopic vibrational partition-function ratio of $^{208}\text{Pb}^{32}\text{S}/^{207}\text{Pb}^{32}\text{S}$ due to the nuclear field shift

$^{208}\text{Pb}^{32}\text{S}$
$\nu_{\text{e}} = 428.14 \text{ cm}^{-1}$ $G(u_{\text{e}}) = 0.15996$
$\delta\nu_{\text{e}}(^{207}\text{Pb} - ^{208}\text{Pb}) = 0.1379 \text{ cm}^{-1}$
$\Delta\nu_{\text{p}} = 4.28 \times 10^{-4} \text{ cm}^{-1}$ (est.)
$\ell n(s/s')f_0(300 \text{ K}) = 0.15996 \times (6.61 \times 10^{-4})$
$\ell n(s/s')f_{\text{boc}} - \ell n(s/s')f_0 = 0.15996 \times (2.05 \times 10^{-6})$.

The Bigeleisen–Mayer equation is based on the Born–Oppenheimer approximation and uses an isotope-independent potential energy; it also assumes simple harmonic vibrations. Because the vibrational force constants are the second derivatives of the electronic energy with respect to the mutual distances between atoms, a correction needs to be applied to $\ell n(s'/s')f_0$ for the nuclear field shift. The formal theory of the nuclear field shift on the equilibrium force constant of a diatomic molecule has been given by Schlembach and Tiemann (10). From the theory and their data on the electronic and rotational spectra of diatomic Pb chalcogenides and Tl halides, Tiemann *et al.* (11) estimated the relative vibrational frequency shifts in these compounds resulting from the nuclear field shifts to be of the order of 10^{-6} . I now show that a relative frequency shift of this order of magnitude is a negligible, second-order correction to $\ell n(s/s')f_0$.

In my study of the nonlinearity of the isotope separation factor, I found it convenient to use the first finite polynomial approximation to $\ell n(s/s')f_0$ because this utilizes the isotopomer masses directly.

$$\ell n(s/s')f_0 = (1/24) (\hbar/kT)^2 \frac{\Delta m_{\text{L}}}{m_{\text{L}}^2} (\langle \nabla^2 U_{\text{L}} \rangle). \quad [3]$$

For the present purpose it is more convenient to use the Bigeleisen–Mayer free energy function, $G(u_{\text{e}})$, for the calculation of the correction to $\ell n(s/s')f_0$. We write

$$\ell n(s/s')f_{\text{boc}} = \sum_{\text{L}} G(u_{\text{e}})(u'_{\text{Lboc}} - u_{\text{Lboc}}), \quad [4]$$

where $u_{\text{Lboc}} = h\nu_{\text{Lboc}}/kT$ and ν_{Lboc} is the vibrational frequency corrected for the nuclear field shift and $G(u) = 1/2 - 1/u + (e^u - 1)^{-1}$. To calculate $(\nu'_{\text{Lboc}} - \nu_{\text{Lboc}})$ we set the nuclear field shift correction in the heavy isotope equal to zero. Then,

$$\nu'_{\text{Lboc}} = \nu'_{\text{LBO}} + \Delta\nu'_{\text{p}} \quad [5]$$

where ν'_{LBO} is the Born–Oppenheimer frequency and $\Delta\nu'_{\text{p}}$ is the perturbation due to the nuclear field shift. In Table 1 I summarize the results of the calculation of $\ell n(s/s')f_{\text{boc}}$ for $(^{207}\text{Pb}^{32}\text{S}/^{208}\text{Pb}^{32}\text{S})$. The correction to $\ell n(s/s')f_0$ due to the nuclear field shift is estimated to be 0.3% of the value of $\ell n(s/s')f_0$. It is a second-order correction. This estimate of the

effect of the nuclear field shift on the vibrational frequency suggests that the correction to the Bigeleisen–Mayer equation due to the nuclear field shift can be limited to the ground-state energy correction alone, Eq. 1.

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