

Calculation of Thermodynamic Properties of Solids from Accurate Diffraction Data: Isotope Separation Factor in Systems Containing Crystalline Phase

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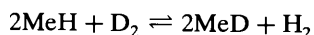
Abstract

A method of calculation of the thermodynamic partition function from accurate X-ray diffraction data has been developed. Dynamical matrix elements (force constants) for LiH were calculated on the basis of X-ray data. From these force constants, the isotope-reduced partition-function ratio (β factor) for the LiH (LiD) crystal and the separation factor $\alpha_{D/H}$ for the isotope exchange in the solid–gas Li(H,D)–(H₂,D₂) system have been calculated. The temperature dependence of the isotope separation factor shows good agreement with the experimental data.

1. Introduction

The final stage of an accurate single-crystal X-ray diffraction data analysis is often the mapping of different forms of the electron density (total, valence, deformation *etc.*) and the construction of an electron-dynamical model for the crystal studied. The qualitative conclusions usually concern the interatomic chemical bonding. Meanwhile, a number of methods have already been developed to calculate some crystal characteristics such as molecular dipole moments, electrostatic field and potential, crystal energy, electric field gradient, diamagnetic susceptibility, optical linear and nonlinear characteristics *etc.* These results can be found in reviews (*e.g.* Spackman, 1992) and books (Tsirelson & Ozerov, 1996; Coppens, 1997). The aim of this work is to develop a method of calculating the thermodynamic properties of a crystal, specifically the isotopic reduced partition-function ratio β , and to apply this function to the calculation of the isotope separation factor α for interacting gas–crystal systems.

For the isotope exchange reaction



the equilibrium isotope separation factor is determined as

$$\alpha_{\text{H/D}} = \left\{ \frac{[\text{H}]}{[\text{D}]} \right\}_{\text{in solid phase}} / \left\{ \frac{[\text{H}]}{[\text{D}]} \right\}_{\text{in gas phase}}$$

(here [H] and [D] mean overall equilibrium concentrations of atoms regardless of their specific chemical

species, *i.e.* $[\text{H}]_{\text{gas}} = [\text{HD}]_{\text{gas}} + 2[\text{H}_2]_{\text{gas}}$ *etc.*). The equilibrium isotope separation factor can be calculated (Andreev & Sicking, 1987) as the ratio

$$\alpha_{\text{H/D}}^0 = \beta_{\text{MeH/MeD}} / \beta_{\text{H}_2/\text{D}_2},$$

where

$$\beta_{\text{XH}_n/\text{XD}_n}^m = \left\{ \frac{Z_{\text{XH}_n}^{\text{quant}}}{Z_{\text{XH}_n}^{\text{class}}} \right\} / \left\{ \frac{Z_{\text{XD}_n}^{\text{quant}}}{Z_{\text{XD}_n}^{\text{class}}} \right\}$$

is the so-called isotope-reduced partition-function ratio or β factor (Bigeleisen & Mayer, 1947; Varshavskii & Vaisberg, 1957). In this equation, Z values are the partition functions of the isotope forms XH_n and XD_n , and m is the number of equivalent atoms in the molecule to be substituted. The superscripts *quant* and *class* refer to the quantum-mechanical and classical partition functions. The β factor is regarded as a fundamental property of a substance in the theory of equilibrium isotope effects. Whereas the separation factor α belongs to the exchange reaction, the β factor belongs to the individual substance and its value indicates the ability of this substance to concentrate the heavy isotope in chemical exchange reactions. If one knows the β factors for a group of substances, one can calculate separation factors for all probable reactions between them; that is why the β factor is a much more general function than the separation factor itself.

Division of Z^{quant} by Z^{class} simplifies calculations, eliminates the necessity to take into account symmetry numbers and is a well established procedure in the theory of equilibrium isotope effect. It is easy to calculate the β factor for gaseous and/or liquid substances. In this case, a reasonably accurate value for the β factor can be calculated using vibrational frequencies of isotopic forms of the given substance. However, if the substance is a crystal, serious problems arise in calculations because of the continuous nature of vibrational spectra of crystals. Unlike molecules with a few vibrational frequencies, a crystal has many fundamental frequencies (of the order of magnitude of Avogadro's number) and crystal vibrational properties are described in terms of the vibrational frequency

distribution function $g(\nu)$. This function determines the number of vibrational frequencies in the unit interval [$g(\nu)\Delta\nu$ is the number of frequencies in the interval $\Delta\nu$]. To calculate the β factor for a crystal, one has to know this function both for the initial and for the isotope-substituted crystal. In all cases, some assumptions concerning the interatomic force constants of the crystal must be introduced. This explains why there are only a few publications on the calculations of β factors for crystalline solids. For the sake of comparison, it bears mentioning that the number of publications describing β -factor calculations for gases and liquids reaches the hundreds (see Knyazev *et al.*, 1992, and references therein). Moreover, many calculations of the β factor for crystals are based on the simple Einstein oscillator model. This approach is rather crude because of the strong frequency dispersion. In general, direct integration over the first Brillouin zone is possible provided the force constants (the dynamical matrix) of a crystal are known. Because the β factor is a thermodynamic function of a crystal, the method of moments (Maradudin *et al.*, 1977) or other methods based on the summation of fast-converging series can be used.

The β -factor calculations in the case of ionic crystals is developed in the present work. The calculation of the isotope effects between the solid and gas phases in the Li(H, D)–(H₂, D₂) system on the basis of accurate X-ray diffraction data has been performed. The choice of this system for theoretical studies was determined by the following factors. LiH contains the lightest atoms. This facilitates the analysis of the results. There is also a strong dispersion of optical modes in this crystal and, as a result, the Einstein approximation is not valid. Finally, for the assessment of our method, accurate X-ray diffraction data (Calder *et al.*, 1962, and especially Vidal-Valat *et al.*, 1992), experimental data on phonon spectra, hydrogen-isotope separation factors and calculation of the separation factor in the LiH–H₂(D₂) system by alternative methods are all available in the literature (Benedek *et al.*, 1969).

In order to estimate the atomic electron-dynamical parameters, an analysis of the accurate X-ray diffraction data for the LiH (LiD) single crystals has been performed. These parameters, once determined, were then used to evaluate the interatomic potentials, the force constants (elements of the dynamical matrix), moments of the vibration frequency distribution function and thermodynamic functions including the β factors and finally the α values for the system studied.

2. Multipole refinement for LiH (LiD)

The accurate X-ray diffraction data presented by Calder *et al.* (1962) and Vidal-Valat *et al.* (1992) were included in the calculation procedure in the framework of the Hansen–Coppens multipole model (Hansen &

Coppens, 1978). In the general expression

$$\rho_{\text{atomic}}(\mathbf{r}) = P_c \rho_{\text{core}} + P_v \kappa'^3 \rho_{\text{valence}}(\kappa' r) + \sum_{l=0}^4 \kappa''^3 R_l(\kappa'' r) \sum_{m=-l}^l P_{lm} Y_{lm}(\mathbf{r}/r), \quad (1)$$

only the two first spherically symmetric terms were considered. All deformation terms were omitted because of large parameter correlation or symmetry restrictions. The set of structure amplitudes from the paper of Vidal-Valat *et al.* (1992) measured at room temperature and treated by the authors for all necessary corrections (putting aside the stated violation of the Born–Oppenheimer approximation in LiH) was finally chosen because it provided both the best fit of observed and calculated values and the optimum conditions to proceed with the calculation of the isotope separation factor and the comparison with experiment. Multipole parameters were derived from least-squares refinement using the *MOLLY* program (Hansen & Coppens, 1978). The occupancies of valence orbitals (P_v), the radial expansion–contraction values κ' and temperature coefficients B for both atoms are listed in Table 1. Two core electrons for Li were taken into account in ρ_{core} calculations. The discrepancy factors are presented as well.

Scattering factors for neutral atoms and ions were used. The latter gave the charge value close to the quantum-chemical ionic charge 0.8e.†

The multipole model enables us to represent the electron density (ED) in the analytical form. The total and deformation ED maps did not show any unusual features. They showed the generally accepted representation of the ionic bonds with a small admixture of covalent interaction, which manifests itself as a small positive region along the Li–H bond.

3. Estimation of dynamic matrix elements

Harmonic approximation and two-particle interactions only were taken into account. This model is valid for crystals with localized valence electrons. ‘Localization’ means that electrons are spatially located close to the atomic sites, which minimizes the overlap of multipoles centered at different nuclei. This requirement is better satisfied by ionic crystals than it is with metals and covalent crystals.

According to Lazarev *et al.* (1985), the distance-dependent potential energy of two interacting pseudo-atoms μ and ν in a crystal is

$$\Phi = \Phi_c + \Phi_{nc} \quad (2)$$

$$\Phi_c = \Phi_{nn} + \Phi_{en} + \Phi_{ee}, \quad (3)$$

† The result 0.2e presented by Ozerov *et al.* (1996) corresponds to the difference between the charges of ions in the initial approximation (1e) and the resulting charges.

Table 1. Results of the multipole refinement of the structure parameters of the LiH crystal

Scale factor	0.9800 (21)
Temperature parameters (\AA^2)	
B_{Li}	1.1713 (54)
B_{H}	2.3456 (1323)
Parameters of the multipole modes	
Li κ'	2.1816 (2522)
H κ'	0.8225 (176)
Li P_ν	0.1504 (521)
H P_ν	1.849 (52)
$R(F)$	0.0103
$R_w(F)$	0.0025
$R(F^2)$	0.0186
$R_w(F^2)$	0.0050
GOF	3.05

where Φ_c and Φ_{nc} are Coulomb and non-Coulomb potentials, respectively. Each term in these sums can be presented in the form

$$\Phi_{nn} = z_\mu z_\nu / |\mathbf{R}| \quad (4)$$

$$\Phi_{en} = -z_\mu \int d\mathbf{r} \rho_{\text{at}\nu}(\mathbf{r}) / |\mathbf{r} - \mathbf{R}| - z_\nu \int d\mathbf{r} \rho_{\text{at}\mu}(\mathbf{r}) / |\mathbf{r} - \mathbf{R}| \quad (5)$$

$$\Phi_{ee} = \iint d\mathbf{r} d\mathbf{r}' \rho_{\text{at}\mu}(\mathbf{r}) \rho_{\text{at}\nu}(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|. \quad (6)$$

Here z_μ and z_ν are the nuclear charges, $|\mathbf{R}|$ is the internuclear distance, and nn , en and ee denote the nuclear–nuclear, nuclear–electron, and electron–electron interactions. The electron-density functions $\rho_{\text{at},\mu}(\mathbf{r})$ and $\rho_{\text{at},\nu}(\mathbf{r})$ for atoms μ and ν can be presented as a multipole series. This allows the calculation of the integral (6) analytically according to the procedure described by Su & Coppens (1992). The Hartree–Fock core and valence radial wavefunctions were replaced by the optimized Slater exponents. The parameters for these exponents were taken from the tables of Clementi & Raimondi (1963). Such a substitution had no influence on the results of our calculations.

The Φ_{ee} potential cannot be calculated analytically. Therefore, the asymptotic method was used for the calculation of the Coulomb part of Φ_{ee}

$$\lim_{R \rightarrow \infty} \Phi_{ee} = P_\mu P_\nu / |\mathbf{R}|, \quad (7)$$

where P_μ and P_ν are the electron core occupancies for the μ and ν atoms. All corrections to Φ_{ee} due to the spatial dispersion of the electron density were included in the term Φ_{nc} . Because of the rapid decrease of the repulsive forces with distance, this term was written as $A/|\mathbf{R}|^n$, where A and n are constants. The value of n depends on the principal quantum numbers for the filled electron shells of the interacting atoms (Ashcroft & Mermin, 1976; Shanker *et al.*, 1978). In accordance with Urusov (1987), the number $n = 5$ was chosen for the evaluation of force constants for lithium hydride. In order to find the value of A , the crystal energy minimum principle was used. The energy of a crystal in

a state of equilibrium is the sum

$$E(R) = E_c(R) + C_5 A / R^5, \quad (8)$$

where E_c is the Coulomb energy calculated from formulae (5), (6) and (8); C_5 is the corresponding lattice sum (Ashcroft & Mermin, 1976). Therefore, the potential energy for a pair of interacting atoms is determined as

$$\Phi = (z_\mu z_\nu + P_\mu P_\nu) / R - z_\mu V_{\nu\nu_c}(R) - z_\nu V_{\nu\nu_c}(R) + A / R^n, \quad (9)$$

where $V_{\nu\nu_c}(R)$ is the electrostatic potential created by the electrons of the ν th atom at the μ th atom nucleus:

$$V_{\nu\nu_c}(R) = V_c(R) + V_\nu(R) + V_d(R). \quad (10)$$

According to Hansen & Coppens (1978), c , ν and d subscripts denote core, valence and deformation contributions, respectively. Each term in (10) has the form

$$V_i(R) = P_i A_{n_i,l}^*(R, 2\kappa_i \xi_i) Y_l, \quad (11)$$

where P_i , κ_i and ξ_i are values related to multipole expansion, ξ being the optimized Slater exponent index ($\xi_{\text{H},1s} = 1.0$, $\xi_{\text{Li},1s} = 2.69$, $\xi_{\text{Li},2s} = 0.64$). Expressions for functions $A_{n,l}^*$ depend on the n and l quantum numbers of the wavefunction corresponding to a given multipole (Su & Coppens, 1992). The following functions were used:

$$A_{1,0}^* = \{2 - \exp(-2\kappa\xi R)[2\kappa\xi R + 2]\} / 2R \quad (12)$$

$$A_{2,0}^* = \{24 - \exp(-2\kappa\xi R)[(2\kappa\xi R)^3 + 6(2\kappa\xi R)^2 + 18(2\kappa\xi R) + 24]\} / 24R, \quad (13)$$

as well as their first and second derivatives with respect to R . All these functions approach the Coulomb limits as $R \rightarrow \infty$. Therefore, one can treat the second term in these formulas as the value related to the effective shielding of charges.

4. Calculation of reduced-isotope partition-function ratio

The value of the β factor for a crystal can be calculated as

$$\ln \beta = \iiint_V \sum_{i=1}^{3r} \ln \left\{ \frac{\text{sh}[u_i^*(\mathbf{k})/2]}{\text{sh}[u_i(\mathbf{k})/2]} \left[\frac{u_i(\mathbf{k})}{u_i^*(\mathbf{k})} \right] \right\} dV. \quad (14)$$

Here V is the first Brillouin zone, $u_i(\mathbf{k}) = hcv_i(\mathbf{k})/kT$ are the so-called 'reduced' frequencies, $v_i(\mathbf{k})$ are vibrational frequencies in cm^{-1} corresponding to wavevector \mathbf{k} and r is the number of atoms in the unit cell. Squares of vibrational frequencies are the eigenvalues of the dynamical matrix $\mathbf{D}(\mathbf{k})$ with elements

(Landau & Lifshits, 1976)

$$D_{\alpha\beta}^{\mu\nu}(\mathbf{k}) = (M_{\mu}M_{\nu})^{-1/2} \sum_{\mathbf{R}} \Lambda_{\alpha\beta}^{\mu\nu}(\mathbf{R}) \exp(i\mathbf{k}\mathbf{R}). \quad (15)$$

Here \mathbf{k} is the wavevector, $\Lambda_{\alpha\beta}^{\mu\nu}$ are force constants, μ and ν are basis atom indices (from 1 to r), α and β are direction indexes (x , y or z), M is the atomic mass, $\mathbf{R} = l\mathbf{a} + m\mathbf{b} + n\mathbf{c}$, \mathbf{a} , \mathbf{b} and \mathbf{c} being the basis vectors of the direct lattice and l , m and n representing integers. Instead of direct integration over the first Brillouin zone according to (14), various other methods can be used, the most convenient for crystals being the 'method of moments'. The n th moment μ_n of the spectral density of phonons is equal to $(1/3rN) \sum_{i=1}^{3rN} \nu_i^n$, where $3rN$ is the overall number of frequencies. Calculation of moments can be reduced to the matrix products and the summation of matrix elements. Algebraic solutions obtained this way can be useful for theoretical interpretation of isotope effects.

On the basis of moments, the value of the β factor can be calculated as (Bigeleisen, 1958)

$$\begin{aligned} \ln \beta = & (1/24)(hc/kT)^2 \delta(\mu_2) - (1/2880)(hc/kT)^4 \delta(\mu_4) \\ & + (1/181\,440)(hc/kT)^6 \delta(\mu_6) \\ & - (1/9\,676\,800)(hc/kT)^8 \delta(\mu_8) \\ & + (5/23\,950\,080\,000)(hc/kT)^{10} \delta(\mu_{10}) - \dots, \quad (16) \end{aligned}$$

where $\delta(\mu_{2n}) = \mu_{2n} - \mu_{2n}^*$.

5. Application to the LiH–H₂(D₂) system

The first-, second- and third-nearest neighbors in the crystal lattice of LiH were taken into account in the summation procedure over 27 uniformly distributed points in the irreducible part of the first Brillouin zone. As calculation showed, this number of points was sufficient. While for isotope substitution of elements heavier than hydrogen no more than the first three even moments are needed in formula (16), in our case (H/D substitution) as many as the first 11 even moments

appeared to be necessary in order to achieve the needed accuracy (about 2%). The moments of the phonon spectrum for LiH and LiD were calculated on the basis of force constants determined according to the scheme presented above and were used in the calculation of β and the separation factor. It should be noted that the dispersion of the optical mode of the phonon spectrum for these hydrides is significant. This is an additional argument against using the simple Einstein three-dimensional-oscillator model for calculating the thermodynamic properties of ionic hydrides.

The temperature dependence of the calculated hydrogen isotope separation factor α is presented in Fig. 1 together with the experimental results by Ryskin & Stepanov (1969). One can see that the results of our calculations agree reasonably well with the experiment.

6. Conclusions

Reasonable agreement between experimental and theoretical separation factors suggests that the method developed can be used for estimating the β factors for ionic crystals, including the substitution of hydrogen for deuterium and tritium. It should be emphasized that X-ray diffraction data were successfully used for calculating the physico-chemical characteristics of the gas–solid system. This is particularly important because many ionic crystal solids are of geochemical interest and their β factors are important for geochemical research studies. The phonon-frequency-distribution data for these crystals are limited and the approach presented here may be useful.

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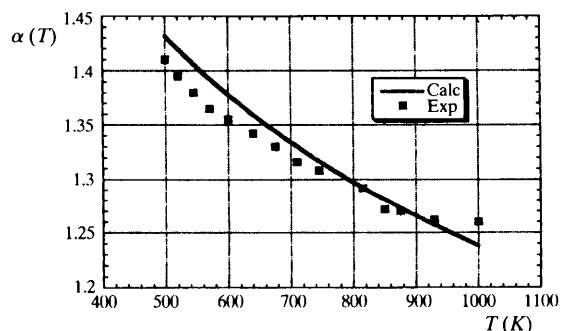


Fig. 1. Temperature dependence of the separation factor $\alpha_{D/H}$ in the system LiH(D)(solid)–H₂(D₂)

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