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STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

Calculations of β-Factors by *ab initio* Quantum-Chemical Methods

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Abstract—The applicability of *ab initio* quantum-chemical methods to calculations of the ratios between the reduced partition functions of isotopic forms (β-factors) and isotope separation factors in chemical isotopic exchange was studied by performing Hartree–Fock calculations with the 6–311++G**(3*df*, 3*p*) basis set of the vibrational frequencies of isotopic forms and β-factors for oxygen, carbon, nitrogen, chlorine, boron, magnesium, lithium, and sulfur isotope substitutions in several molecules. Consideration was primarily given to the results obtained for molecules for which β-factors or the experimental vibrational frequencies of isotopic forms were available. It was shown that quantum-chemical calculations taking into account correlation corrections at the level of the Möller–Plesset second-order perturbation theory gave quite satisfactory results, whose accuracy was comparable with that of the values obtained from experimental frequencies and frequencies calculated from force constants.

Equilibrium (thermodynamic) isotope effects can be used for separating isotopes and in research work in chemistry, biology, and geochemistry. The necessary condition for this is the possibility of the theoretical quantitative estimation of these effects.

The current theory of equilibrium isotope effects makes it possible to calculate isotope effects (isotope separation factors) for equilibrium chemical isotope exchange between two substances if the vibrational spectra of their isotopic forms or force constants that can be used to calculate these frequencies are known. The accuracy of such calculations is comparable with or higher than that of experimental measurements of isotope separation factors.

According to the thermodynamics of chemical isotope exchange [1], if the exchange of element X isotopes occurs in the reaction

$$AX^* + BX = AX + BX^*,$$

the equilibrium isotope separation factor $\alpha_{X^*/X}$ (here, X* is the heavy isotope of element X), which, by definition, is

$$\alpha_{X^*/X} = \frac{\{[X^*]/[X]\}_{\text{in substance A}}}{\{[X^*]/[X]\}_{\text{in substance B}}},$$

can be calculated as

$$\alpha_{X^*/X} = \beta(A)/\beta(B). \qquad (1)$$

Here, [X] and [X*] are the isotope concentrations in the substance and β(A) and β(B) are the so-called reduced ratios between the partition functions of the isotopic forms, or β-factors,[1] which were introduced for the first time in [2]. The β-factor is the ratio between the quantum partition functions of the isotopic forms of the substance divided by the ratio between classical statistical integrals. It follows that, if β-factors are known for several substances, (1) can be used to calculate the separation factors for all chemical isotope exchange reactions between them. This is why β-factors are the most important values in the theory of equilibrium isotope effects.

Equation (1) is a particular case of combining chemical equilibria, because, by its physical meaning, the β-factor of a substance is the equilibrium constant of the isotope exchange reaction between a given substance and a monoatomic gas comprising isotope atoms,

$$AX^* + X = AX + X^*.$$

This factor can, therefore, be calculated by the equation

$$\ln\beta_{AX^*/AX} = \frac{F_{AX} - F_{AX^*}}{kT} - \frac{F_X - F_{X^*}}{kT},$$

where the second term (the difference of the Helmholtz energies of the isotopic forms of the hypothetical monoatomic gas divided by *kT*) is a value that only depends on the masses of the isotopes and remains constant for the given isotope substitution type.

In the harmonic approximation, the β-factor is fully determined by the vibrational frequencies of the isotopic forms of a molecule and is calculated by the formula [2, 3]

$$\ln\beta = \frac{1}{N}\sum_{j=1}^{n}\ln\left\{\frac{\sinh[u_j/2]}{\sinh[u_j^*/2]}\left[\frac{u_j^*}{u_j}\right]\right\}. \qquad (2)$$

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[1] These values are also often denoted by (*s*/*s*')*f*.

Here, N is the number of equivalent atoms in the molecule that are replaced by isotope atoms, n is the number of vibrational frequencies, $u_j = hc\nu_j/kT$ are dimensionless values (so-called reduced frequencies), ν_j are the vibrational frequencies in cm^{-1}, h is the Planck constant, k is the Boltzmann constant, c is the velocity of light, and T is the absolute temperature.

The accuracy of (1) and (2) has repeatedly been studied [1, 4]. This accuracy is comparable with that of the harmonic approximation itself and the Born–Oppenheimer approximation, which allows isotope separation factors to be calculated with relative errors not exceeding 2–5%. This is more than satisfactory, because experimental α values involve no less errors.[2] Exceptions are reactions that involve molecular hydrogen, especially at low temperatures, for which errors can reach 15% or more.

When (2) is used to calculate β-factors, the vibrational frequencies of a molecule observed in its optical spectra (ω_j) rather than harmonic frequencies (ν_j) are substituted into (2), which is an effective method for introducing corrections for anharmonicity of vibrations. The influence of such a substitution on calculated $\ln\beta$ values was studied in [1]. It was shown that, for hydrogen isotope substitution (or the isotope substitution of atoms linked with hydrogen), the use of harmonic frequencies exaggerated $\ln\beta$ by 3–5% compared with the true values. This justifies the use of precisely the observed vibrational frequencies. In other isotope exchange reactions, the difference between ω_j and ν_j can be entirely ignored.

The simplicity of calculations of isotope equilibria by (1) and (2) is seeming. The point is that the most serious difficulty in the calculation of β-factors and isotope separation factors in real systems, which are of importance for separating isotopes in practice, and in the use of equilibrium isotope effects in research work is the complexity of the chemical composition of these systems. For instance, when isotope exchange occurs in the aqueous phase, metals are present in the form of variable-composition complexes, and in amalgams, which are often used in chemical isotope exchange reactions, they occur in the form of intermetallic compounds or in the dissolved state.

Even if the composition of molecules and ions that participate in exchange reactions in real systems, for instance, the composition of aquacomplexes, is known, for most of them, complete spectral data on vibrational frequencies are not only difficult but often impossible in principle to obtain, to say nothing of frequency isotope shifts.

In view of this, the potentialities of the quantum-chemical methods for calculating molecular vibrational frequencies and their isotope shifts offer promise for analyzing practically important real systems. These methods can be used to theoretically calculate β-factors for such ions and molecules for which these factors cannot be determined otherwise (as mentioned, precisely such ions and molecules usually participate in exchange in systems of interest for practical applications). However, first we must analyze the errors that calculations of such kind involve. This work is concerned precisely with analyzing the applicability of quantum-chemical methods to calculations of β-factors and isotope separation factors.

Attempts at quantum-chemically calculating force constants, normal vibration frequencies, and thermodynamic functions began virtually immediately after the development of the first quantum-chemical methods for calculating the structure and properties of molecules. As far as calculations of the equilibrium geometry of molecules is concerned, great progress was made fairly soon. The situation with molecular vibrational frequencies was not so simple. Calculations of molecular vibrations by both *ab initio* and semiempirical methods usually gave exaggerated frequency and force constant values.

Nevertheless, the use of *ab initio* methods at this stage (1970s–1980s) in combination with experimental data on vibrational spectra of molecules and traditional calculations of vibrational modes and frequencies allowed the assignments of vibrational frequencies of many molecules to be refined and force constant matrices to be found (because, on the whole, quantum-chemical calculations gave correct structures of force constant matrices).

As concerns calculations of β-factors and isotope separation coefficients, they require higher accuracy of frequency and isotope shift values. In addition, as opposed to other thermodynamic functions, especially heat capacity, the β-factor value is largely determined by high vibrational frequencies. For this reason, the first attempts at calculating β-factors by quantum-chemical methods were unsuccessful. Such an attempt was, for instance, made in [5, 6] with the use of semiempirical methods. The obtained β-factors were, however, exaggerated to an extent that prevented the estimation of isotope separation factors from them. Works [5, 6] showed that semiempirical methods were inapplicable to calculations of isotopic equilibria.

At the same time, the combined use of experimental vibrational frequencies and calculations even with fairly limited basis sets gives good results for β-factors. For instance, the $\beta_{^{11}\mathrm{B}/^{10}\mathrm{B}}$ factors for boric acid and polyboric acids were calculated in [7] with the 6-31G(*d*)

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[2] These are not errors of mass spectrometric measurements, whose accuracy is very high, but errors caused by ambiguities involved in the determination of molecular forms to which the observed effect should be assigned when (1) is used (see below). When isotope methods are applied to study natural objects, in particular, isotopic geochemistry objects, errors related to the incomplete establishment of equilibria (kinetic factor) are added.

basis set. The experimental vibrational frequencies were, however, known for one of the isotopic forms of these molecules, which allowed the calculated vibrational frequencies of isotopomers to be corrected by multiplying them by a factor of about 0.95, which was determined by comparing the calculated and experimental frequencies. Unfortunately, as mentioned above, such scaling can not always be performed for many practically important molecules and ions participating in isotope separation reactions because experimental vibrational frequencies are not known for these species.

We showed in [8] that, generally, it is sufficient to use the 6-311G*(3*d*) basis set to calculate the β-factors of lithium aquacomplexes, which are ion–dipole complexes. The introduction of additional polarization and diffuse functions virtually did not change the calculated β-factor values (the difference of the lnβ values for $\mathrm{Li(H_2O)}_n^+$-type complexes calculated using the 6-311G*(3*d*) and 6-311++G**(3*df*, 3*p*) basis sets did not exceed 1%). We can, however, hardly expect equally good results for aquacomplexes of doubly charged ions, not to mention transition metal complexes, which are characterized by substantial contributions of covalent bonds to oxygen–metal interactions.

To estimate the feasibility of quantum-chemically calculating β-factors, we calculated the vibrational frequencies of isotopic forms and β-factors for several molecules participating in the exchange of chlorine (^{37}Cl/^{35}Cl), nitrogen (^{15}N/^{14}N), carbon (^{13}C/^{12}C), oxygen (^{18}O/^{16}O), manganese (^{26}Mg/^{24}Mg), and some other element (boron, sulfur, and lithium) isotopes. The selection of molecules for calculations was determined by the availability of independent data on their β-factors (reference data) with which comparisons could be made. In the first place, molecules for which experimental vibrational frequencies of both isotopic forms and molecules whose calculated β-factors were discussed in the literature from the point of view of their accuracy were selected. The experimental spectra of the isotopic forms of NO_2, HNO_2, FNO_2, and D_2O were taken from [9]; those of HCOOH, from [10]; of N_2O, CO_2, HNO_3, and NO, from [11, 12]; of DCO_2^-, from [13]; and of CH_2F_2, from [14]. The calculated frequencies of NO were reported in [15], and of $(CH_3)_2NH$, in [16]. The calculated β-factors of CH_4 and C_3H_8 were taken from [17]; of NH_3, NO_2, NO_2^-, NO_3^-, NH_4^+, CH_3NH_2, and N_2, from [18]; and of H_2O and H_2S, from [19]. The frequencies of H_2CO, CH_3CH_3, HCCH, and CO_2 were calculated with the use of the same force constants and geometric parameters as in [4]. The experimental data on the spectra of diatomic molecules were taken from handbook [20]; these data were used to calculate force constants, isotopic form frequencies, and β-factors for these molecules. The β-factors of ClO_4^-, ClO_3^-, ClO_2, CN^-, HCN, and D_2O were taken from classic work [21]; those of FNO_2, HCO_3^-, CO_3^{2-}, and CH_3OH, from [22]; and the β-factor of H_3BO_3, from [7].

The β-factors of molecules were calculated with the use of the PC GAMESS program [23, 24] by the restricted Hartree–Fock method. Unrestricted Hartree–Fock calculations were performed for NO, NO_2, ClO_2, MgH, and MgF. The 6-311++G**(3*df*, 3*p*) basis set and effective core potentials [25] were used for all molecules, because our preliminary calculations of β-factors showed that the use of these potentials did not introduce significant errors and virtually had no effect on β-factor values. The calculations were performed with and without taking into account correlation corrections at the level of the Möller–Plesset second-order perturbation theory (MP2).

Tables 1–4 contain the results of β-factor calculations for various molecules (at 300 K) by quantum-chemical and traditional methods and the relative errors that these values involve. Taken as reference values are experimental β-factors or, in their absence, β-factors that are determined from vibrational frequencies calculated from force constants (NCA (normal coordinate analysis) values in the tables). If a molecule contains identical nonequivalent atoms, the atoms involved in isotope exchange are labeled by asterisks. The values obtained based on the experimental frequencies of isotopic forms, in some instances (for H_2O, H_2S, and NH_3, whose β-factors were taken from [26]) taking into account anharmonic and other corrections, are treated as experimental.

The tables show that calculations with the 6-311++G**(3*df*, 3*p*) basis set without correlation corrections give virtually exact lnβ values for molecules with ionic bonds. If the atom involved in isotope exchange is linked with its neighbors by strong covalent bonds, such calculations, as expected, systematically exaggerate the lnβ values.

Calculations with correlation corrections at the MP2 level give quite satisfactory results. The error in the lnβ values obtained in such calculations generally does not exceed the errors introduced by approximations involved in the definition of the β-factor itself and the errors involved in experimental measurements of isotope separation factors in real systems.

Several discrepancies between the calculated and reference values should be discussed separately. First, consider the HNO_3 molecule. It is possible that the spectra of the isotopic forms of this molecule in the gas phase were determined not very accurately, or the spectra were distorted by the association of molecules and other effects. It is likely that the frequencies were also incorrectly assigned for oxygen isotope substitution in

Table 1. Experimental results and β-factor values calculated for boron ($^{11}B/^{10}B$ substitution), sulfur ($^{34}S/^{32}S$), magnesium ($^{26}Mg/^{24}Mg$), lithium ($^{7}Li/^{6}Li$), and chlorine ($^{37}Cl/^{35}Cl$) compounds

Substance	I	II	III	IV	Substance	I	II	III	IV
H_3BO_3	0.2208	–	0.2307 (4)	0.2119 (–4)	HCl	0.0044	0.0046 (5)	0.0050 (14)	0.0048 (9)
H_2S	0.0110	0.0106	0.0124 (13)	0.0117 (6)	Cl_2	0.0072	0.0074 (3)	0.0087 (21)	0.0078 (8)
MgO	–	0.0147	0.0163 (11)	0.0111 (–24)	ClO_4^-	–	0.0813	0.0893 (10)	0.0779 (–4)
MgH	–	0.0038	0.0041 (8)	–	ClO_3^-	–	0.0467	0.0618 (32)	0.0535 (15)
MgF	–	0.0140	0.0147 (5)	–	LiCl	0.0029–0.0033	–	0.0030	0.0030
LiF	–	0.0711	0.0733 (3)	0.0663 (–7)	ClO_2	–	0.0308	0.0414 (34)	–
LiH	–	0.0236	0.0249 (6)	0.0247 (5)	NaCl	0.0026	–	0.0024 (–8)	0.0023 (–12)

Note: I, experiment; II, NCA; III, 6-311++G**; and IV, MP26-311++G**; errors, %, are given in parentheses.

Table 2. β-Factor values for carbon compounds, $^{13}C/^{12}C$ substitution

Substance	I	II	III	IV	Substance	I	II	III	IV
CO	–	0.0920	0.1074 (17)	0.0911 (0)	HC≡CH	–	0.1114	0.1277 (15)	–
CO_2	0.1674	0.1729 (3)	0.2022 (21)	0.1775 (6)	CH_3CH_3	–	0.1261	0.1377 (9)	0.1302 (3)
CO_3^{2-}	–	0.1759	0.1989 (17)	0.1631 (–7)	HCOOH	0.1481	–	0.1942 (31)	0.1702 (15)
HCO_3^-	–	0.1773	0.2046 (15)	0.1738 (–2)	$DCOO^-$	0.1743	–	0.1918 (10)	0.1669 (–4)
$H_2C{=}O$	–	0.1421	0.1608 (13)	0.1412 (–0)	CH_2F_2	0.1507	–	0.1767 (17)	0.1586 (5)
CH_4	–	0.1076	0.1188 (10)	0.1133 (5)	$CH_3C^*H_2CH_3$	–	0.1392	0.1554 (12)	0.1455 (5)
CN^-	–	0.0839	0.0958 (14)	0.0788 (–6)	$C^*H_3CH_2C^*H_3$	–	0.1250	0.1386 (11)	0.1312 (5)
HCN	–	0.1139	0.1434 (26)	0.1168 (3)	CH_3OH	–	0.1247	0.1447 (16)	0.1335 (7)

Note: See Table 1.

Table 3. β-Factor values for oxygen compounds, $^{18}O/^{16}O$ substitution

Substance	I	II	III	IV	Substance	I	II	III	IV
D_2O	0.0932	0.0836 (–10)	0.0906 (–3)	0.0825 (–12)	HO*NO	0.0937	–	0.1269 (35)	0.1006 (7)
CO	–	0.0997	0.1164 (17)	0.0987 (–1)	HONO*	0.1012	–	0.1018 (1)	0.0727 (–28)
CO_2	–	0.1108	0.1291 (17)	0.1101 (–1)	HCOO*H	0.1100	–	0.1167 (6)	0.1013 (–8)
CO_3^{2-}	–	0.0862	0.0937 (9)	0.0780 (–10)	HCO*OH	0.0990	–	0.1187 (20)	0.1028 (4)
$H_2C{=}O$	–	0.0904	0.1080 (19)	0.0917 (1)	NO	0.1168	–	0.1139 (–73)	–
					H_2O	0.0610	0.0587 (–4)	0.0703 (15)	0.0642 (5)

Note: See Table 1.

nitrous acid. Indeed, the authors of the original work did not take into account the existence of this substance in three rather that two molecular forms. The experimental frequencies of D_2O are obviously exaggerated. Estimates based on the most accurate data taking into account anharmonic and other corrections [26] give the $\ln\beta_{D_2{}^{18}O/D_2{}^{16}O} = 0.0671$ value. The calculated β-factor values reported in [21] for CN^- are obviously exaggerated, and the β-factor values for CO_3^{2-} [21] are also so. This is not surprising, because [21] is a fairly old work. The conclusion can be drawn that, in many instances, quantum-chemical calculations give more accurate estimates of β-factors than those obtained based on experimental frequencies, because such calculations exclude errors caused by incorrect assignments of the frequencies of the isotopic forms of molecules.

Table 4. β-Factor values for nitrogen compounds, $^{15}N/^{14}N$ substitution

Substance	I	II	III	IV	Substance	I	II	III	IV
N_2	–	0.0767	0.0928 (21)	0.0711 (–7)	NO	0.0617	0.0633 (3)	0.0774 (25)	–
$(CH_3)_2NH$	–	0.0914	0.1072 (17)	0.0974 (7)	NO_2	0.0977	0.1025 (5)	0.1208 (24)	–
HNO_3	0.1116	–	0.1781 (60)	0.1477 (32)	*trans*-HNO_2	0.0875	–	0.1109 (27)	0.0819 (–6)
NO_3^-	–	0.1427	0.1739 (22)	0.1515 (6)	NO_2^-	–	0.0934	0.1091 (17)	0.0916 (–2)
NH_3	0.0619	0.0670 (8)	0.0718 (16)	0.0667 (8)	FNO_2	0.1368	0.1396 (2)	0.1735 (27)	0.1396 (2)
FNO	–	0.0849	0.1038 (22)	0.0842 (–1)	NH_4^+	–	0.0905	0.1057 (17)	0.0983 (9)
HCN	–	0.0634	0.0825 (30)	0.0660 (4)	CH_3NH_2	–	0.0819	0.0892 (9)	0.0816 (0)
N*N*O	0.1001	–	0.1261 (26)	0.0968 (–3)	CN^-	–	0.0621	0.0706 (14)	0.0581 (–6)
ClNO	–	0.0720	0.0852 (18)	0.0764 (6)					

Note: See Table 1.

To summarize, the approach based on calculations of the β-factors of molecules and ions by *ab initio* quantum-chemical methods should be considered well grounded.

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