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Abstract

Full Text

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ON THE PERIODIC REGULARITY OF ISOTOPE EXCHANGE IN DIATOMIC MOLECULES

(Presented by Academician V. N. Kondrat’ ev on 26 VII 1962)

In the statistical calculation of isotope-separation coefficients in isotope-exchange reactions it is convenient to use the ratio of sums over states, from which the symmetry numbers are excluded (^{1}). Ya. M. Varshavsky and S. E. Vaisberg ($^{2-4}$), who called the indicated quantities β-factors,* generalized these quantities to the case of polyatomic molecules and widely applied them in calculations. These authors discovered a very interesting periodic dependence of the β-factors of diatomic hydrides H_i on the atomic number (or, what is the same, on the degree of filling of the outer electron shells) of the element $_i$ bonded to hydrogen (Fig. 1). The purpose of the present article is to explain this regularity and to derive certain quantitative relations.

Fig. 1. Dependence of β-factors (solid line) and force constants k_e (dashed line) of diatomic hydrides on the atomic number N of the element bonded to hydrogen

The β-factor of a diatomic molecule is determined by the vibrational frequencies of the isotopic molecules (see, for example, (^{5}))

$$\beta = \left[\frac{u^*}{u}\, e^{-(u^*-u)/2}\,\frac{1-e^{-u}}{1-e^{u^*}}\right]^{1/n}, \tag{1}$$

* It can be shown (^{5}) that the β-factor is expressed in the following way through the vibrational sums over states:

$$\beta = \left[\left(\frac{Z^*}{Z_{\text{class}}} \right) \Big/ \left(\frac{Z}{Z_{\text{class}}} \right) \right]^{1/n},$$

where Z_{class} and Z are the values of the statistical sum given, respectively, by classical and quantum mechanics.

where $u = hc\omega_e/kT$; ω_e is the vibrational frequency of the isotopic molecule; c is the speed of light; h is Planck’ s constant; k is Boltzmann’ s constant; T is the temperature (°K); n is the number of isotope atoms being substituted in the molecule; the asterisk indicates that the given quantity refers to the heavy isotope. The vibrational frequency, in turn, is determined by the relation

$$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k_e}{\mu}}, \tag{2}$$

where k_e is the force constant, μ is the reduced mass of the molecule, $\mu = mm_0/(m + m_0)$, and m and m_0 are, respectively, the masses of the isotopic atom and the second atom.

Since the reduced mass of the molecule depends monotonically on the mass of the second atom, if the force constant were constant or a monotonic function of atomic number, no periodic dependence of the β-factors could exist. Consequently, the periodic character of the variation of the β-factors must be due to the periodic character of the variation of the force constants ([6]).

To verify this conclusion, Fig. 1 plots the values of the β-factors and the force constants k_e of diatomic hydrides as functions of the atomic number of the element bonded to hydrogen (the values of k_e were calculated from equation (2), on the basis of vibrational frequencies, or taken from Refs. ([7,8])). As is seen from Fig. 1, the quantities β and k_e are approximately proportional. Thus, it may be regarded as established that the periodic dependence of the β-factors is caused by an analogous regularity in the variation of the force constants.

In the case of diatomic molecules, the force constant is the second derivative of the potential energy of the molecule with respect to distance (at the equilibrium point). Since a quantum-mechanical calculation of the potential energy of molecules is still impossible, a theoretical calculation of k_e is likewise impossible (the hydrogen molecule, as is well known, is an exception). It is known only that k_e depends to a considerable degree on the properties of the atoms forming the molecule, on the structure of their electron shell, and on the type of electrons forming the bond ([9]).

For quantitative calculations one may use the empirical Guggenheimer formula ([8])

$$\omega_e = c_1 (z_1 z_2)^{1/4} \mu^{-1/2} r_e^{-c_2}, \tag{3}$$

where z_1 and z_2 are the numbers of electrons in the outer shells of the two atoms forming the molecule; r_e is the equilibrium internuclear distance; $c_1 = (2.065 \div 2.976) \cdot 10^3$ and $c_2 = 0.92 \div 1.23$ are constants found by the author from analysis of experimental data on the vibrational frequencies of more than 150 diatomic molecules.

From equations (2) and (3) we obtain

$$k_e = 4\pi^2 c^2 c_1^2 (z_1 z_2)^{1/2} r_e^{-2c_2}. \tag{4}$$

Hence it is clear that the periodicity in the variation of the force constants of diatomic hydrides, and consequently also of the β-factors, is due to the periodic character of the filling of the electron shells of the second atom z_2 and of the equilibrium internuclear distance of the molecule r_e. The proportionality of the force constant to the geometric mean of the numbers of electrons in the outer shells of the atoms is a remarkable fact. Some qualitative considerations explaining this fact are given in Ref. (^{8}).

Using relations (1) and (2), one can establish a connection between the β-factor and the force constant. In the general case, comparatively cumbersome expressions are obtained; however, they are simplified for $u \ll 2$ or for $u \gg 5$. In the first case (small quantum effects—small

frequencies or high temperatures), according to (1):

$$\beta = \left(1 + \bar{u}\,\Delta u/12\right)^{1/n}, \tag{5}$$

where $\bar{u} = (u + u^*)/2,\ \Delta u = u - u^*$.

Substituting the values of u from equation (2), we obtain

$$\beta^n\big|_{u<2} = 1 + \frac{1}{96\pi^2}\left(\frac{h}{kT}\right)^2 \left(\frac{1}{\mu} - \frac{1}{\mu^*}\right) k_e, \tag{6}$$

i.e., the quantity $(\beta^n - 1)$ is proportional to the force constant. In the second case (sufficiently low temperatures or large frequencies, when the vibrations are not yet excited and the correction $\left(\frac{1 - e^{-u}}{1 - e^{-u^*}}\right)$ in equation (1) may be neglected), we find

$$\beta^n\big|_{u>5} = \sqrt{\mu/\mu^*}\, e^{b\sqrt{k_e}} \tag{7}$$

where*

$$b = \frac{1}{4\pi}\frac{h}{kT}\left(\sqrt{\frac{1}{\mu}} - \sqrt{\frac{1}{\mu^*}}\right).$$

Fig. 2. Dependence of β-factors on the force constants k_e: 1 —diatomic hydrides of the first and second periods of the periodic table of elements; 2 —lithium halides $Li^{6-7}F$, $Li^{6-7}Cl$, $Li^{6-7}Br$, $Li^{6-7}J$.

Figure 2: Fig. 2. Dependence of β-factors on the force constants k_e: 1 —diatomic hydrides of the first and second periods of the periodic table of elements; 2 —lithium halides $Li^{6-7}F$, $Li^{6-7}Cl$, $Li^{6-7}Br$, $Li^{6-7}J$.

In both cases the β-factor increases monotonically with increasing k_e (the data for hydrides shown in Fig. 1 refer to the second case, when $u \geq 5$). The concerted change of β^n and k_e is seen from Figs. 1 and 2. Figure 2 shows the dependence of β^n ($n = 1$, except for the hydrogen molecule, where $n = 2$) on k_e for hydrides of the first and second periods of the periodic table. The same figure also gives data for the lithium halides $Li^{6-7}F$, $Li^{6-7}Cl$, $Li^{6-7}Br$, $Li^{6-7}J$ (the β-factors were calculated by the authors). In this case as well, when $2 < u < 5$, β^n and k_e are correlated.

Fig. 2. Dependence of β-factors on the force constants k_e: 1 —diatomic hydrides of the first and second periods of the periodic table of elements; 2 —lithium halides $Li^{6-7}F$, $Li^{6-7}Cl$, $Li^{6-7}Br$, $Li^{6-7}J$.

Using relations (6) and (4), we obtain

$$\beta^n\Big|_{u<2} = 1 + \frac{1}{24}\left(\frac{hc}{kT}\right)^2 c_1^2 (z_1 z_2)^{1/2} r_e^{-2c_2} \frac{m^* - m}{m^* m}. \tag{8}$$

From (7) and (4) it follows that

$$\beta^n\Big|_{u>5} = \sqrt{\frac{\mu}{\mu^*}}\, \exp\left[\frac{c_1}{2}\frac{hc}{kT}\left(\sqrt{\frac{1}{\mu}} - \sqrt{\frac{1}{\mu^*}}\right)(z_1 z_2)^{1/4} r_e^{-c_2}\right]. \tag{9}$$

Equations (8) and (9) constitute a quantitative formulation of the periodic regularity in the variation of β-factors: (8) for the region of small quantum effects, when $u \leq 2$, and (9) for the region of large quantum effects, when $u \geq 5$ (the case of hydrides). They relate the β-factor to the filling of electron shells and, moreover, show that the β-factors depend not only on the filling of the electron shells but also on the internuclear distance.

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* For small $\Delta m/m$, we find

$$b \approx \frac{h}{8\pi kT}\frac{\Delta m}{m^2}\sqrt{\mu},$$

respectively, for $m \gg m_0$,

$$b \approx \frac{h}{8\pi kT} \times \frac{\Delta m}{m^2}\sqrt{m_0},$$

and for $m \ll m_0$,

$$b \approx \frac{h}{8\pi kT}\frac{\Delta m}{m^{3/2}}.$$

As is known, the internuclear distance of diatomic hydrides also changes periodically (see Fig. 3, constructed from data [6,7]); within a period (with increasing z_2), r_e decreases, while at constant z_2, r_e increases (dashed curves in Fig. 2). An increase in the internuclear distance with increasing N leads to a decrease in the β-factors (at $z_2 =$ const) as the atomic number of the element bonded to hydrogen increases (Fig. 1). The decrease of r_e within a period leads to a strengthening of the periodic dependence of the β-factor on the atomic number of the second (nonisotopic) atom.

Fig. 3 Fig. 4

Fig. 3. Dependence of the equilibrium internuclear distances r_e of diatomic hydrides on the atomic number N of the element bonded to hydrogen

Fig. 4. Dependence of the β-factors of diatomic lithium compounds (Li^{6-7}) on the atomic number N of the element bonded to lithium. The lines connecting the points of maxima and minima are drawn, conventionally, as straight lines

Since the derived relations (8) and (9) are general in character, the regularities considered in the variation of the β-factors are valid not only for hydrogen, but also for any monovalent element. There are insufficient spectral data to construct the curve of the periodic regularity in the variation of β-factors for other elements. However, the available information on vibrational frequencies makes it possible to find extrema on the indicated curve for some monovalent elements, for example Li^{6-7}, as is shown in Fig. 4 (the β-factors of the corresponding diatomic lithium compounds were calculated by the authors).

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Note: Figure translations are in progress. See original paper for figures.