Carbon β-factors for hydrocarbons: Modified method of isotopic bond numbers

V.B. POLYAKOV[1]* AND J. HORITA[2]

[1]Institute of experimental mineralogy RAS, 142432, Ac. Osypyana ul., 4, Chernogolovka, Moscow region, Russia (*correspondence: polyakov@iem.ac.ru)

[2]Department of Geosciencies, Texas Tech University, Lubbock, Texas 79409-1053, USA (juske.horita@ttu.edu)

We calculated carbon β-factors for 258 hydrocarbon (HC) molecules and their fragments by Bigeleisen-Mayer equation using the rigid rotator – harmonic oscillator model. Normal frequencies of molecular vibrations of major (^{12}C) isotopologues were taken from a database elaborated by Prof. Gribov *et al*. (1989, 2008). The normal frequencies for minor isotopologues were calculated substituting appropriate mass of ^{12}C isotope by that of ^{13}C. Force constants, molecular geometry, interatomic distance and interchemical bond angules were supposed to be the same for major and minor isotopes. Temperature dependence of the β-factors were fitted by the 5-order sign alternating polynomial:

$$\ln\beta=\Sigma(-1)^{i-1}A_i x^i;\ \ x_i=10^6/T^2;\ i=1,2,\ldots5. \qquad (1)$$

Galimov (1973, 2006) expressed the carbon β-factor as sum of increments of chemical bonds of carbon atom undergoing the $^{13}C/^{12}C$ isotope substitution.

$$\beta = 1+ \Sigma L_i, \quad (2)$$

where L is the increment of the i-th chemical bond or the isotope bond number (IBN), depending on a kind of the chemical bond.

We have referred the IBN to the logarithmic form:

$$\ln\beta = \Sigma L_i, \quad (3)$$

providing better accuracy. We have postulated that the IBN for a given chemical bond depends on not only a kind of this chemical bond but also is affected by chemicals bonds which are its neighbors. Based on this postulate, we find that there are 72 types of chemical bonds in HC with different IBN.

Based on Eq. (3) and used calculated 258 β-factors, we have constructed redundant linear system of 258 equations containing 72 unknowns based on Eq. (3). Solving this system by the least squares method, we have computed the IBN for 72 types of chemical bonds in the temperature range from 200 to 800 K. The temperature depenedence for every computed IBN has been fitted by the polynomial (1). One can calculate the carbon β-factors for any HC using the 72 IBN found here. Uncertainty of such calculations does not exceed 0.0030 (3.0 ‰) 298.15 K and 0.0018 (1.8 ‰) at 400 K.