A CORRELATION BETWEEN THE THERMODYNAMIC PARAMETERS OF 1-BUTANOL, 2-BUTANOL, l-PROPANOL MOLECULES AND THEIR INFRARED SPECTRA

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ABSTRACT:

The method is based on the thermodynamic parameters of the molecules- standard molar Gibbs free energy change of molecular formation ΔG_f^0 (kJ/mol), standard molar enthalpy change of molecular formation ΔH_f^0 (kJ/mol) and standard molar entropy of molecule S^0 (J/mol·K). From these thermodynamics parameters the vibrational modes in infrared diapason can be calculated using $T_G=\Delta G_f^0/S^0$ and $T_H=\Delta H_f^0/S^0$ ratios, considered as 'apparent' temperatures. After conversion of the thermal energy kT_G or kT_H (k is Boltzmann constant) to energy of electromagnetic quanta $E=h\nu$ (h is Planck constant), an frequencies in infrared spectral range are derived $1/\lambda=kT_G/ch$ (cm^{-1}), where $\lambda= c/\nu$ (c is speed of light). The calculated frequencies coincide with the vibrational mode on infrared spectrum of given corresponding molecule. The difference between the theoretically calculated frequencies and the experimentally measured ones in the infrared spectra of the studied molecules is within 50 cm^{-1}.

Key words: *IR spectrum, Gibbs free energy, enthalpy, entropy*

INTRODUCTION

Main infrared regions. The molecules can vibrate in many ways, and each way is called a 'vibrational mode'. In terms of wavenumbers of the transition frequencies the infrared spectral region (IR) spans from 33 to 12820 cm^{-1} [1]. The entire infrared range is divided into 3 areas: near-infrared (12820-4000 cm^{-1}), mid-infrared (4000-400 cm^{-1}), far-infrared (400-33 cm^{-1}). The near-infrared region is poor in specific absorptions. Consist of overtones and combination bands resulting from vibrations in the mid-infrared region of the spectrum. The mid-infrared region provides structural information for most organic molecules. The far-infrared region has been less investigated than the other two regions. It contains spectra mainly of inorganic molecules. The low energies of infrared quanta is not sufficient, to cause electronic transitions, but they are large enough to cause changes in the frequency and amplitude of molecular vibrations. Infrared spectra have been represented as percent of transmittance versus either the wavenumber of the wavelength. The use of wavenumbers (expressed in cm^{-1}) is standard. In Figure 1 the main selected IR regions are given.

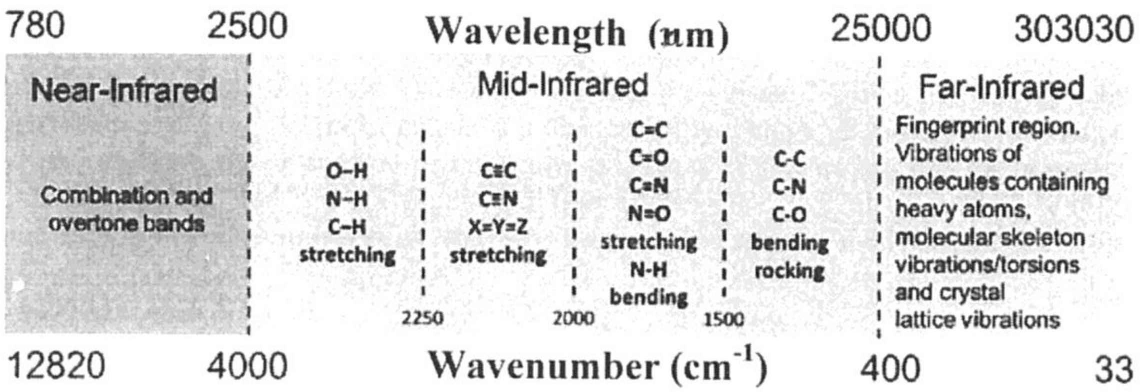

Fig.1. Main infrared regions

The proposed new thermodynamic method for calculating molecular vibration in IR diapason. The method firstly was developed by Atanasov [2]. The theoretical basis of the method is given below.

The free energy ΔF, the enthalpy ΔH and the entropy ΔS of given chemical reaction at constant pressure and temperature are connected by Gibbs equation [3]:

$\Delta G= \Delta H - T\Delta S$ (1)

where T is the absolute temperature of the reaction. The Eq.1 can be transformed as:

$\Delta G/\Delta S = \Delta H/\Delta S – T$ (2)

The dimensions of temperature T (in K) and ratios ΔG/ΔS (in K), and ΔH/ΔS (in K) are same- in Kelvin absolute scale. The same dimensions of T, ΔG/ΔS and ΔH/ΔS ratios gives reason regard the ratio between the Gibbs free energy change ΔG and the entropy change ΔS, as well as the ratio between the enthalpy change ΔH and the entropy change ΔS as 'apparent' temperatures i.e.:

$T_G= \Delta G/ \Delta S$ (3)

$T_H= \Delta H/ \Delta S$ (4)

Because of the absolute temperature by Kelvin scale is always positive we have to use the absolute (positive) values of T_G and T_H in all calculations.

The temperature of reaction (T) and the 'apparent' temperature T_G and T_H corresponds to heat energies: kT, kT_G and kT_H , where $k= 1.38\times10^{-23}$ J/K is the Boltzmann constant.

These heat energies correspond to electromagnetic quanta (hν), ($h\nu_G$) and ($h\nu_H$) with frequencies ν, ν_G and ν_H :

$h\nu =kT$ (5)

$h\nu_G =kT_G$ (6)

$h\nu_H =kT_H$ (7)

Because of the kT_G and kT_H energies are connected to energy of given chemical bounds and it can expect that their corresponding frequencies are correlated with the frequencies of absorption spectra of their molecules. From Eqns.(5-7) it can calculate the corresponding frequencies ν, ν_G and ν_H:

$\nu = kT/h$ (8)

$\nu_G = kT_G/h$ (9)

$\nu_H = kT_H/h$ (10)

The frequency ν (Hz) of the electromagnetic waves is connected to wavelength λ (m) and speed of light c (m/s) through:

$\lambda= c/\nu$ (11)

From Eqns. (8-10) it can calculate the wavenumbers of electromagnetic waves in cm^{-1}:

$\nu_G =1/\lambda= kT_G/ch\ (cm^{-1})$ (12)

where $T_G= \Delta G/ \Delta S$ (is taken in Kelvin degree), and respectively:

$\nu_H =1/\lambda= kT_H/ch\ (cm^{-1})$ (13)

where $T_H= \Delta H/ \Delta S$ (is taken in Kelvin degree).

Analogically, in the case of simple molecules, the data for standard Gibbs free energy change of molecular formation ΔG_f^0 (kJ/mol), standard molar enthalpy change of molecular formation ΔH_f^0 (kJ/mol) and standard molar entropy of molecule S^0 (J/mol·K) is needed to use for calculation the 'apparent' temperature and the corresponding frequencies. The indicative surveys showed that calculated by this way wavenumbers overlap with real infrared spectral modes of the molecules.

AIM OF THE STUDY

1. To calculate the molecular vibrational modes of 1-butanol: $CH_3CH_2CH_2CH_2OH$, 2-butanol: $CH_3CHOHCH_2CH_3$ and l-propanol: $CH_3CH_2CH_2OH$ molecules in infrared region by classical method and by proposed new thermodynamic method.
2. To compare the results received from the two calculations with experimentally received spectra of the 1-butanol, 2-butanol and l-propanol molecules.

MATERIALS AND METHODS

1. The molecule of 1-butanol $CH_3CH_2CH_2CH_2OH$, 2-butanol $CH_3CHOHCH_2CH_3$ and l-propanol $CH_3CH_2CH_2OH$ were investigated.
2. The thermodynamic data for Standard molar Gibbs free energy change of molecular formation (ΔG_f^0, kJ/mol), Standard molar enthalpy change of molecular formation (ΔH_f^0, kJ/mol) and Standard molar entropy of molecule (S^0, J/mol·K) of 1-butanol, 2-butanol and l-propanol were used (Table 1) . The data are given for standard pressure 1 atmosphere and absolute temperature 298K.
3. The experimental spectrum of 1-butanol, 2-butanol and l-propanol molecules were used for comparison with theoretical calculated molecular vibrations.

Table 1. Thermodynamic characteristics of 1-butanol $CH_3CH_2CH_2CH_2OH$ (liquid), 2-butanol $CH_3CH(OH)CH_2CH_3$ (liquid) and l-propanol $CH_3CH_2CH_2OH$ (liquid) molecule [4]

Molecule	**Structure**	**ΔG_f^0, kJ/mol**	**ΔH_f^0, kJ/mol**	**S^0, J/mol·K**
1-butanol	$CH_3\,CH_2\,CH_2\,CH_2\,OH$	-162.5	-327.3	225.8
2-butanol	$CH_3CHOHCH_2CH_3$	-177	-342.6	214.9
l-propanol	$CH_3CH_2CH_2OH$	-170.7	-304.6	193

RESULTS

1. Calculation of molecular vibrations of 1-butanol (liquid) molecule by thermodynamic method. The calculation of $T_G=\Delta G/\Delta S$ 'apparent' temperature was based on Gibbs free energy ΔG_f^0 = -162.5 kJ/mol and entropy of 1-butanol molecule S^0=225.8 J/mol·K [4]. Because the negative values of ΔG_f^0, the 'apparent' temperature corresponding to Gibbs free energy must be represented as the absolute value of the ratio: $T_G = |\Delta G_f^0/S^0| = 162.5\times10^3/225.8 = 0.71966\times10^3$K. The corresponding frequency calculated by formula (12) is: $\nu^0_{TD} = 1/\lambda = kT_G/ch$ (cm^{-1}) = 499.6 cm^{-1} for Boltzmann constant $k=1.38\times10^{-23}$ J·K, speed of light $c=3.10^8$m/s and Planck constant $h=1.662\times10^{-34}$ J·s. The calculated frequency ν^0_{TD} = 499.6 cm^{-1} correspond to 500 cm^{-1} band on IR spectrum of 1-butanol. This frequency fall in Mid-infrared diapason (400-4000 cm^{-1}) and provides structural information for 1-butanol molecule. From ν^0_{TD} frequency it can receive the frequencies of the other modes in IR spectra of 1-butanol on Fig.2 (see Table 2).

Table 2. Calculation of vibrational modes of 1-butanol

499.6 cm^{-1} → 500 cm^{-1} (0 band)
499.6 cm^{-1} × 1.5 = 749.4 cm^{-1}→ 750 cm^{-1} (1 band)
499.6 cm^{-1} × 2.0 = 999.2 cm^{-1} → 1000 cm^{-1} (2 band)
499.6 cm^{-1} × 2.5 = 1249 cm^{-1}→ 1250 cm^{-1} (3 band
499.6 cm^{-1} × 3 = 1498.8 cm^{-1}→ 1500 cm^{-1} (4 band)
499.6 cm^{-1} × 4 = 1998.4 cm^{-1}→ 2000 cm^{-1} (5 band)

499.6 cm^{-1} × 6 = 2997.6 $cm^{-1} \rightarrow$ 3000 cm^{-1} (6 band)
499.6 cm^{-1} × 6.5 = 3247.4 $cm^{-1} \rightarrow$ 3250 cm^{-1} (7 band)

From Table 2 is seen that the derivative modes can be obtained by multiplying of the main mode ν^0_{TD} = 499.6 cm^{-1} to 1.5; 2; 2.5; 3 …. , and so on.

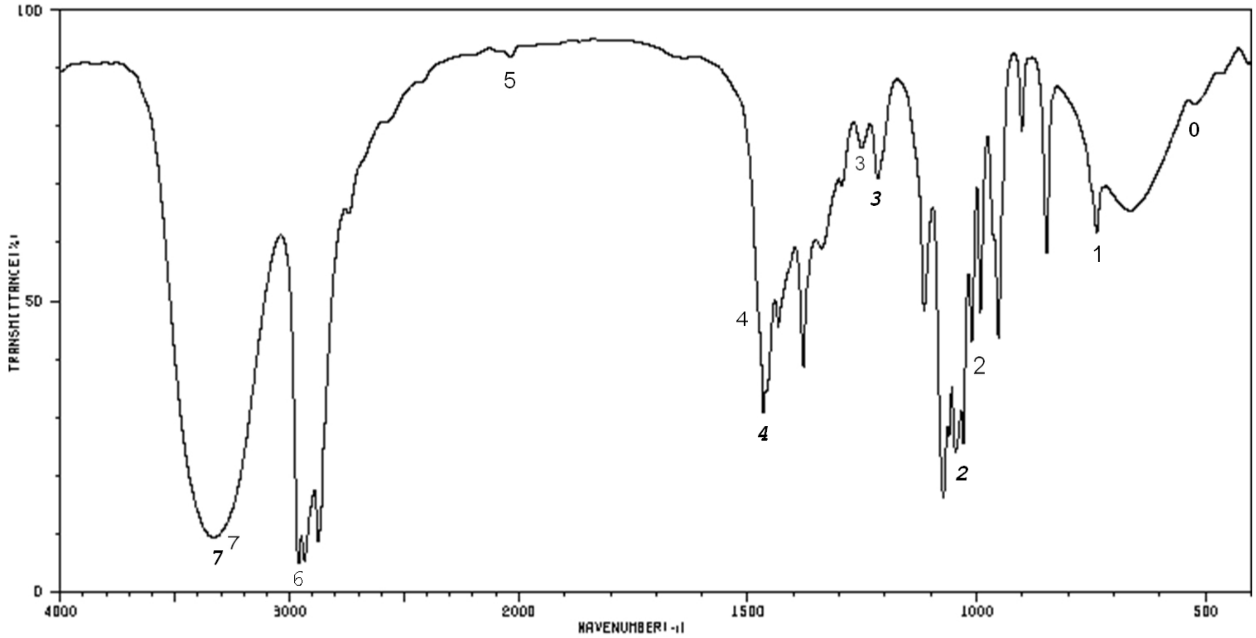

Fig.2. An original IR spectrum of 1-butanol ($CH_3CH_2CH_2CH_2OH$) molecule [5]

On Fig.2 it can be seen that band 2 is placed no more than 50cm^{-1} from band 2'. The same is situation for the bands: 3 and ***3***, 4 and ***4*** and 7 and ***7***. So, the theoretically calculated values for bands 3, 4 and 7 a placed no more than 50 cm^{-1} for the real maximum values for the bands ***3***, ***4*** and ***7***.

Interesting is the fact that the very small bands (0 and 5) overlaps to theoretically calculated values.

2. Calculation of molecular vibration of 2-butanol (liquid) by thermodynamic method.

The calculation of $T_G=\Delta G/\Delta S$ 'apparent' temperature was based on Gibbs free energy ΔG_f^0 = -177.0 kJ/mol and the entropy of 2-butanol molecule S^0 = 214.9 J/mol·K [4].

Because the negative values of ΔG_f^0, the 'apparent' temperature corresponding to Gibbs free energy must be represented as the absolute value of the ratio: $T_G = |\Delta G_f^0/S^0| = 177.0\times10^3/214.9 = 0.8236\times10^3$ K. The corresponding frequency calculated by formula (12) is: $\nu^0_{TD} = 1/\lambda = kT_G /ch$ (cm^{-1}) =571.78 cm^{-1} (for Boltzmann constant $k = 1.38\times10^{-23}$ J·K, speed of light $c = 3\times10^8$ m/s and Planck constant $h = 1.662\times10^{-34}$ J·s).

The calculated basic frequency of ν^0_{TD} = 571.78 cm^{-1} correspond to band -0 on IR spectrum of 2-butanol. This frequency fall in Mid-infrared diapason (400-4000 cm^{-1}) and provides structural information for 2-butanol molecule. From ν^0_{TD} frequency it can receive the frequencies of the other modes i.e: ν^0_{TD} × 1.5 = 857.67 cm^{-1} (band 1); ν^0_{TD} × 2 = 1143.56 cm^{-1} (band 2); ν^0_{TD} ×2.5 = 1429.45 cm^{-1} (band 3); ν^0_{TD} × 5 = 2858.9 cm^{-1} (band 4); ν^0_{TD} × 6 = 3430.68 cm^{-1} (band 5).

The calculation of $T_H = \Delta H_f^0/S^0$ based on enthalpy $\Delta H_f^0 = -342.6$ kJ/mol and entropy $S^0 = 214.9$ J/mol·K of 2-butanol molecule [4] gives frequency of 1106.6 cm^{-1}.This frequency is near to 1150 cm^{-1} and correspond to band 2 on IR spectrum of 2-butanol. This result due to the approximate values of $\Delta G_f^0 = 210.7$ kJ/mol and $\Delta H_f^0 = 226.88$ kJ/mol.

Table 3. Calculation of vibrational modes of 2-butanol

571.78 cm^{-1} → (0 band)
571.78 cm^{-1} × 1.5 = 857.67 cm^{-1}→ (1 band)
571.78 cm^{-1} × 2.0 = 1143.56 cm^{-1} → (2 band)
571.78 cm^{-1} × 2.5 = 1429.45 cm^{-1}→ (3 band)
571.78 cm^{-1} × 5 = 2858.9 cm^{-1}→ (4 band)
571.78 cm^{-1} × 6 = 3430.68 cm^{-1}→ (5 band)

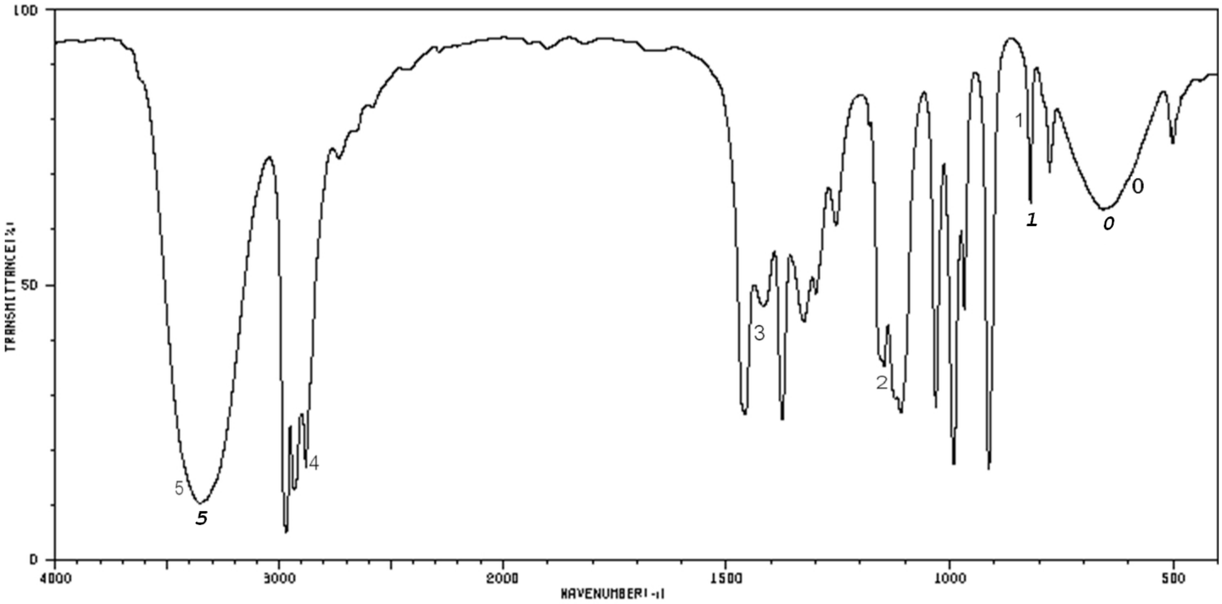

Fig.3. An original infrared spectrum of 2-butanol ($CH_3CHOHCH_2CH_3$) molecule [5]

From Fig.3 is observed that the theoretically calculated values for bands 1 and 5 a placed no more than 50 cm^{-1} from the real maximum bands ***1*** and respectively ***5***. The bands 2, 3 and 4 exactly calculated. The basic theoretically calculated band 0 is placed about 50 cm^{-1} from the maximum band ***0***.

3. Calculation of molecular vibration of l-propanol ($CH_3CH_2CH_2OH$) by thermodynamic method.

The calculation of $T_G = \Delta G/\Delta S$ 'apparent' temperature was based on Gibbs free energy $\Delta G_f^0 = -170.7$ kJ/mol and entropy of $CH_3CH_2CH_2OH$ molecule $S^0 = 193$J/mol·K [4].

The 'apparent' temperature was estimated to be equals to: $T_G = |\Delta G_f^0/S^0| = 170.7\times10^3/193 = 0.884455\times10^3$K. The corresponding stretching frequency calculated by formula (12) is: $\nu^0_{TD} = 1/\lambda = kT_G/ch$ (cm^{-1})=616.44 cm^{-1} (for Boltzmann constant $k = 1.38\times10^{-23}$ J·K, speed of light $c = 3.10^8$m/s and Planck constant $h = 1.662\times10^{-34}$ J·s).

The calculated frequency $\nu^0_{TD} = 616.44$ cm^{-1} correspond to wide band (band 0) on IR spectrum of l-propanol (Fig.4). From ν^0_{TD} frequency it can receive the frequency of the other modes i.e: $\nu^0_{TD} \times 2 = 1232$ cm^{-1} (band 1) and $\nu^0_{TD} \times 5.5 = 3390.42$ cm^{-1} (band 2).

The calculation of $T_H=|\Delta H_f^0/S^0|$ based on enthalpy $\Delta H_f^0=-304.6$ kJ/mol and entropy $S^0=193$ J/mol·K of l-propanol molecule [3] gives frequency of 1095.65 cm^{-1} (band 3). This is real peak on the infrared spectrum of l-propanol. From this basic bend the derivate modes can be received (1643.48 cm^{-1} and 3286.95 cm^{-1})-peak 4 and 5 respectively.

Table 4. Calculation of vibrational modes of l-propanol

616.44 cm^{-1} → (0 band) (calculated by T_G)
616.44 cm^{-1} × 2.0 = 1232 cm^{-1} → (1 band)
616.44 cm^{-1} × 5.5 = 3390.42 cm^{-1}→ (2 band
1095.65 cm^{-1} → (3 band) (calculated by T_H)
1095.65 cm^{-1} × 1,5 = 1643.48 cm^{-1}→ (4 band)
1095.65 cm^{-1} × 3 = 3286.95 cm^{-1}→(5 band)

On Fig.4 it can be seen that the band 5 is placed near to band 2.

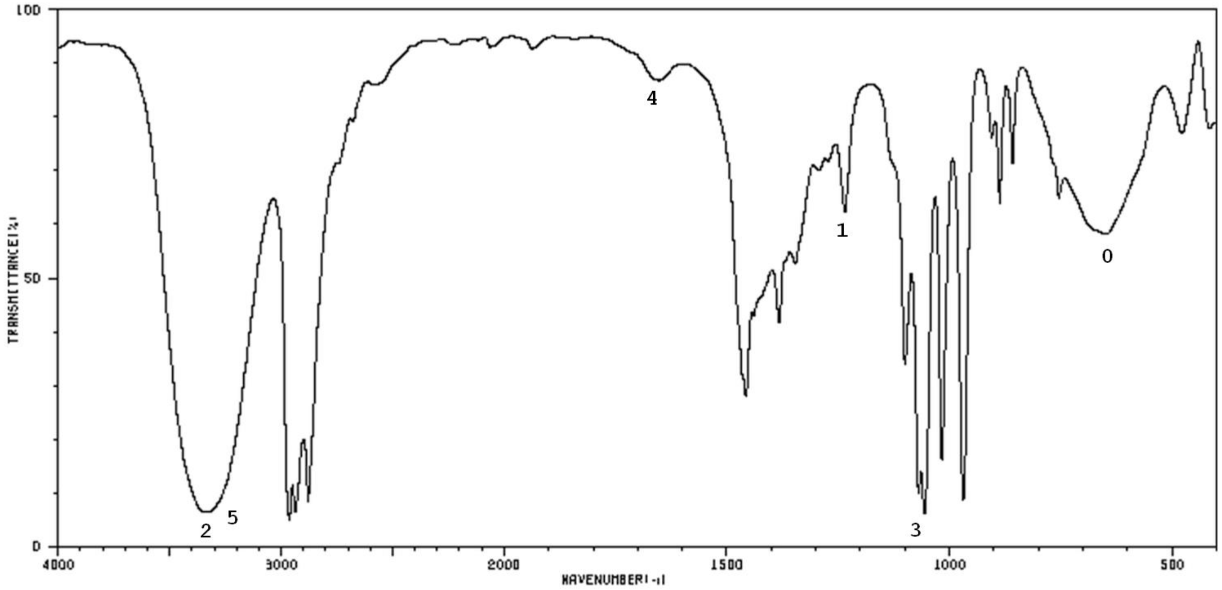

Fig.4. An original infrared spectrum of l-propanol ($CH_3CH_2CH_2OH$) molecule [5]

For l-propanol the theoretically calculated bands overlaps with the real ones. The bands 2 and 5 a placed very near and correspond to one and same band.

DISCUSSION

By the proposed method can only calculate 2 basic frequencies. The first frequency corresponds to free energy and entropy of molecules, and the second frequency corresponds to the enthalpy and entropy of the molecules. The different multiple mods can be obtained from the basic frequencies ν^0. For this purpose the basic frequency must be represented as multiple of 1.5, 2.0, 2.5, 3.0…, and so on [6].

In the most general case, the calculated frequencies do not differ from the actual frequencies by more than 50 cm^{-1}. The proposed method gives possibility for theoretical prediction of potential absorption frequencies in the infrared spectra of unknown molecules.

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