Original Contribution

SOME EMPIRICAL CORRELATIONS BETWEEN THE THERMODYNAMIC PROPERTIES OF HYDROGEN CYANIDE, WATER AND ACETYLENE MOLECULES AND THEIR INFRARED SPECTRA

A. T. Atanasov*

Department of Physics and Biophysics, Medical Faculty, Trakia University, Bulgaria

ABSTRACT

A new method for calculating vibrational modes in the infrared region of the spectrum is proposed. 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 can be calculated using $T_G = \Delta G_f^0/S^0$ and $T_H = \Delta H_f^0/S^0$ (in K) as 'apparent' temperatures. After equation of thermal energy kT_G and kT_H (where k is Boltzmann constant) to energy of electromagnetic quanta hf_G and hf_H (where f is frequency in Hz), it can calculate the wavenumbers (in cm^{-1}) of vibrational modes as: kT_G/ch and kT_H/ch (where c is the speed of light and h is the Planck constant).

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

INTRODUCTION

1. Main infrared regions. The molecules can vibrate in many ways, and each way is called a 'vibrational mode'. In terms of wavenumbers of vibrational modes the infrared spectral region spans from 33 to 12820 cm^{-1} [1, 2]. 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 has been used with 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, with the use of wavelength (expressed in nm or μm). On **Figure 1** are given the main selected IR frequencies.
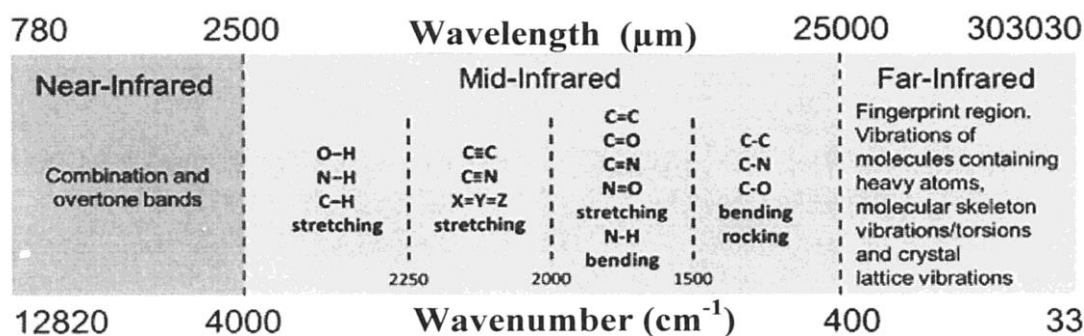
Figure 1. Main Infrared Regions

Correspondence to: *Atanas Todorov Atanasov,*
Department of Physics and Biophysics,
Medical Faculty, Trakia University,
Bulgaria, E-mail: atanastod@abv.bg

2. The classic method of calculating molecular vibrations. The calculation of infrared molecular vibrations [1, 2] is based on the force (spring) constants (k) for the given bond, the 'reduced mass' (μ), and the speed of light (c). The stretching frequency (in cm^{-1}) of given bond on Fig.1 can be calculated by formula:

$$\upsilon= 1/2\pi c\ [k/\mu]^{1/2}=1/2\pi c\ [k(m_1+m_2)/m_1m_2]^{1/2} \tag{1}$$

where the force constants (k) has defined values for single, double and triple bonds:
k= 5×10^5 dyne/cm for 'single bond'
k=10×10^5 dyne/cm for 'double bond'
k=15×10^5 dyne/cm for 'triple bond'

The 'reduced mass' appears a combination between the mass of atoms of the bond:

$$\mu=m_1m_2/m_1+m \tag{2}$$

The mass m_1 and m_2 of the chemical elements are calculated in 'grams' by formula:

$$m=A/N_A,\ grams \tag{3}$$

where A= Atomic mass of given chemical element and N_A= 6.02×10^{23} is Avogadro's number per 1g- mol. The speed of light is taken as: c=3×10^{10} cm/sec.

The different multiple mods can be obtained from the basic frequencies as multiple of the vibrational quantum number n+1/2, where n=0, 1, 2, 3 ….and so on.

3. The proposed new thermodynamic method for calculating molecular vibration.
The free energy ΔF, the enthalpy ΔH and the entropy ΔS of each molecule at constant pressure and temperature are connected by Gibbs equation [3]:

$$\Delta G= \Delta H- T\Delta S \tag{4}$$

where T is the absolute temperature of the reaction of molecule formation. The Eq.4 can be transformed as:

$$\Delta G/\Delta S = \Delta H/\Delta S – T \tag{5}$$

The dimension of temperature of molecular formation (T and ratios ΔG/ΔS, ΔH/ΔS) are same – dimension of absolute temperature (K) on Kelvin scale. The same dimensions of T, ΔG/ΔS and ΔH/ΔS ratio 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.:

$$T_G= \Delta G/ \Delta S \tag{6}$$
$$T_H= \Delta H/ \Delta S \tag{7}$$

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= 1.38×10^{-23} J/K is the Boltzmann constant.

These heat energies correspond to electromagnetic quanta (hf), (hf$_G$) and (hf$_H$) with frequencies f (Hz), f_G (Hz) and f_H (Hz) and Planck constant h=6.6262×10^{-34} J·s :

$$hf =kT \tag{8}$$
$$hf_G =kT_G \tag{9}$$
$$hf_H =kT_H \tag{10}$$

The kT_G and kT_H energies are connected to energy of chemical bonds and can be expected their corresponding frequencies match the frequencies of the absorption spectra of their molecules. From Eqns. (8-10) it can calculate the corresponding frequencies f, f_G and f_H :

$$f = kT/h \tag{11}$$
$$f_G = kT_G/h \tag{12}$$
$$f_H = kT_H/h \tag{13}$$

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

$$\lambda= c/f \tag{14}$$

From Eqns. (11-14) it can calculate the frequency expressed in wavenumbers (ν, cm^{-1}) by equation:

$$\nu_G =1/\lambda= kT_G/ch\ (cm^{-1}) \tag{15}$$

where T_G= ΔG/ ΔS (is taken in Kelvin degree), and respectively:

$$\nu_H =1/\lambda= kT_H/ch\ (cm^{-1}) \tag{16}$$

where T_H= ΔH/ ΔS (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 need to use for calculation the 'apparent' temperature and the corresponding frequencies. The indicative survey showed that calculated by this way wavenumbers overlap with real infrared modes of the molecules.

AIM OF THE STUDY
1. To calculate the molecular vibrational modes of hydrogen cyanide (HCN), water (H_2O) and acetylene (C_2H_2) molecules in infrared region by classical method and by proposed new thermodynamic method.

2. To compare results from calculations with experimentally received spectra of the HCN, H$_2$O and C$_2$H$_2$ molecules.

MATERIALS AND METHODS

1. The molecule of HCN, H$_2$O and C$_2$H$_2$ were investigated.
2. The thermodynamic data for Standard molar Gibbs free energy change of molecular formation at 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 HCN, H$_2$O and C$_2$H$_2$ were used **(Table 1)**. The data are given for standard pressure 1 atmosphere and absolute temperature 298.15 K.
3. The experimental spectrum of HCN, H$_2$O, and C$_2$H$_2$ molecules were used for comparison with theoretical calculated molecular vibrations.

Table 1. *Thermodynamic characteristics of HCN, H$_2$O and C$_2$H$_2$ molecules [4].*

Molecule		Structure	ΔG_f^0, kJ/mol	ΔH_f^0, kJ/mol	S^0, J/mol·K
Hydrogen cyanide (HCN)		H-C≡N	407.5	437.6	202.6
Water	(H$_2$O)	H-O-H	-237.14	-285.83	69.95
Acetylene	(C$_2$H$_2$)	H-C=C-H	210.7	226.88	201

RESULTS

1. A. Hydrogen Cyanide molecule (theoretical data)

The HCN molecule is linear with fundamental frequencies: v_2 = 712 cm^{-1}, v_3 = 3289 cm^{-1} and v_1 = 2100 cm^{-1} [5]. The latter frequency (band 1) has not been observed directly since the band associated with it is of extremely low intensity- **Figure 2**. It can be seen that the frequency about 1400 cm^{-1}, which is located between 712 cm^{-1} and 3289 cm^{-1} is absent from the theoretical data.
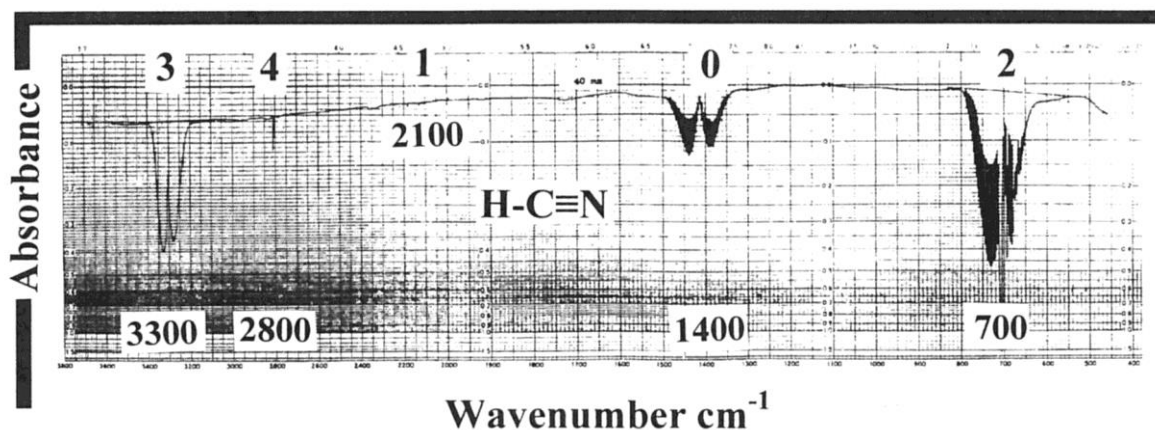

Figure 2. An original IR spectrum of Hydrogen Cyanide HCN [5].

B. Calculation of molecular vibrations of HCN by classical method. The calculation of vibrational modes of the C-H and C≡N bond gives the frequencies 3023cm^{-1} and 1983 cm^{-1} respectively. It can be seen that these theoretical calculated frequencies do not fully coincide with the experimental frequencies from the absorption spectrum of HCN. For example, the calculated frequency of 1983 cm^{-1} is nearest to v_1 = 2100 cm^{-1} and the calculated frequency of 3023 cm^{-1} is near to v_3 = 3289 cm^{-1}. However, the theoretical calculation can't predict the frequency at 712 cm^{-1}, 1400cm^{-1} and 2800 cm^{-1}which are present in the spectrum of the HCN molecule.

In these calculations it was used: force constants k= 5×10^5 dyne/cm for 'single bond' (C-H bond) and force constant k=15×10^5 dyne/cm for 'triple bond' (C≡N bond). The mass of m$_H$, m$_C$ and m$_N$ were calculated in 'grams' by relations: m$_H$ =1/6.02×10^{23} = 0.166×10^{-23}g, m$_C$ =12/6.02×10^{23} = 1.99×10^{-23}g and m$_N$ =14/6.02×10^{23} = 2.33×10^{-23}g.

C. Calculation of molecular vibrations of HCN by new thermodynamic method. The calculation of T$_G$=ΔG/ΔS 'apparent' temperature was based on Gibbs free energy ΔG_f^0 = 407.5 kJ/mol and entropy of HCN molecule S^0=202.6 J/mol·K [3]. The calculated 'apparent' temperature, corresponding to Gibbs free energy is: T$_G$=ΔG_f^0/S^0=407.5×10^3/202.6=2.011×10^{3}K. The corresponding frequency calculated by formula (15) is:v^0_{TD}=1/λ=kT$_G$/ch(cm^{-1})=1396.3 cm^{-1}. The abbreviation 'v^0_{TD}' is used to indicate that the frequency is calculated by the thermodynamic method. The calculated frequency v^0_{TD} =1396.3 cm^{-1} correspond to

3

1400 cm^{-1} band on IR spectrum of HCN. From ν^0_{TD} frequency it can receive the frequencies of the other modes in IR spectra of HCN on **Figure 2** (**Table 2).**

Table 2. Calculation of vibrational modes of HCN in cm^{-1}

1396.3cm^{-1} → 1400 cm^{-1} (0 band)
1396.3cm^{-1} × 1.5 = 2094.5cm^{-1}→2100 cm^{-1} (1 band)
1396.3cm^{-1} : 2.0 = 698.15cm^{-1} → 712 cm^{-1} (2 band)
1396.3cm^{-1} × 2.0 = 2792.6 cm^{-1}→ 2800 cm^{-1} (4 band
1396.3cm^{-1} × 2.5 = 3490 cm^{-1}→ 3200-3400 cm^{-1} (3 band)

From **Table 2** is seen that the derivative modes can be obtained from the main mode ν^0_{TD} =1396.3 cm^{-1} as multiple of 1.5, 2.0, 2.5, 3.0…, and so on.
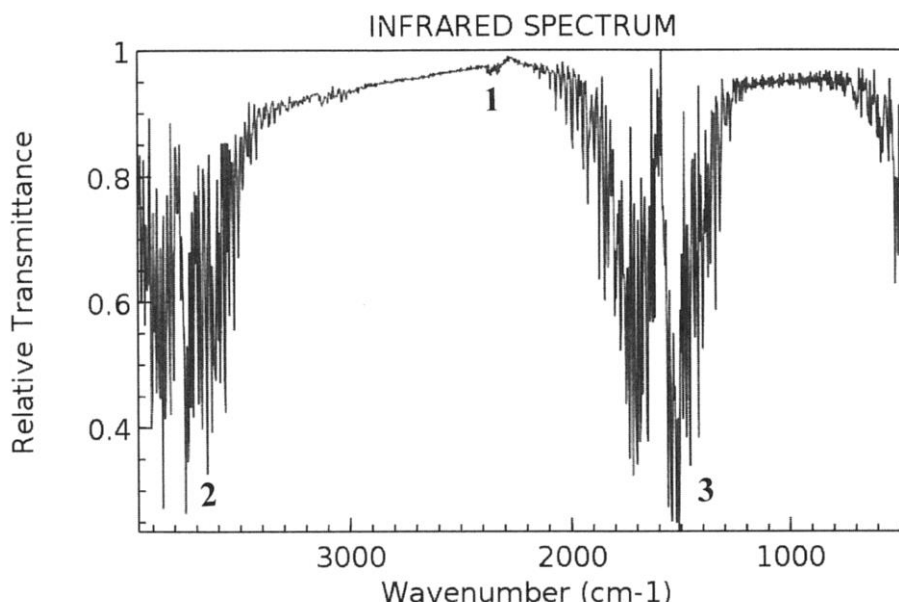
2. Water molecule.
A. Calculation of molecular vibrations of water by classical method.
An original water infrared spectrum is shown on **Figure 3**.

The calculation of mode of the O-H bond gives the frequency of 2994.16 cm^{-1}. From **Figure 3** it can be seen that these theoretical calculated frequency do not coincide with the experimental frequencies on the IR spectrum of H_2O.

In these calculations it was used: force constants k= $5×10^5$ dyne/cm for 'single bond' (O-H bond). These mass of m_H and m_O were calculated in 'grams' by relations: m_H =$1/6.02×10^{23}$ = $0.166×10^{-23}$g and m_O =$16/6.02×10^{23}$ = $2.6578×10^{-23}$g.

Figure 3. Infrared liquid H_2O spectrum [6].

**B. Calculation of molecular vibration of water by thermodynamic method.**
The calculation of T_G=$\Delta G/\Delta S$ 'apparent' temperature was based on Gibbs free energy ΔG^0_f = -237.14 kJ/mol and entropy of H_2O molecule S^0=69.95 J/mol·K [3].

Because the negative values of ΔG^0_f, the 'apparent' temperature corresponding to Gibbs free energy must be represented as the absolute value of the ratio: T_G=$|\Delta G^0_f/S^0|$ =237.14×10^3/69.95=3.39×10^{3}K. The corresponding stretching frequency calculated by formula (15) is:ν^0_{TD}=1/λ=kT_G /ch(cm^{-1})=2353.3 cm^{-1}.

The calculated basic frequency of ν^1_{TD} =2353.3 cm^{-1} correspond to small middle band (band 1) on IR spectrum of H_2O (Fig.3). From ν^1_{TD} frequency it can receive the frequency of other modes i.e: ν^1_{TD} ×1.5 = 3529.95 cm^{-1} (band 2) and ν^1_{TD} :1.5 = 1568 cm^{-1} (band 3). The calculation of T_H= $|\Delta H^0_f/S^0|$ based on enthalpy ΔH^0_f= -285.83 kJ/mol and entropy S^0=69.95 J/mol·K of H_2O molecule [3] gives frequency of 2836.39 cm^{-1}. This frequency does not correspond to any band on IR spectrum of water.

3. Acetylene.
A. Calculation of molecular vibration of acetylene by classical method. An original spectrum of acetylene is shown on **Figure 4.**
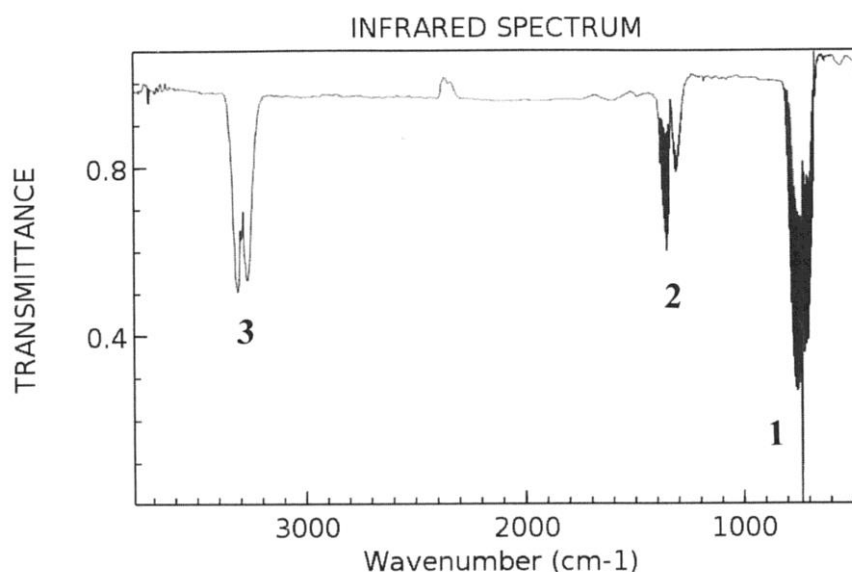
Figure 4. Acetylene Infrared gas Spectrum [6].

The calculation of modes of the C-H and C≡C bonds gives the frequency of 3023cm^{-1} and 5251.6 cm^{-1} respectively. It can be seen that these theoretical calculated frequencies do not coincide with the experimental frequencies on the IR spectrum of C_2H_2.

In these calculations it was used: force constants k= 5×10^5 dyne/cm for 'single bond' (C-H) and force constant k=15×10^5 dyne/cm for 'triple bond' (C≡C). The mass m_H and m_C were calculated in 'grams' by relations: m_H =$1/6.02\times10^{23}$ = 0.166×10^{-23}g and m_C =$12/6.02\times10^{23}$ = 1.99×10^{-23}g.

B. Calculation of molecular vibration of acetylene by thermodynamic method.
The calculation of T_G=$\Delta G/\Delta S$ 'apparent' temperature was based on Gibbs free energy ΔG_f^0 = 210.7 kJ/mol and entropy of C_2H_2 molecule S^0=201J/mol·K [4].

The 'apparent' temperature was estimated to be: T_G=$\Delta G_f^0/S^0$=$210.7\times10^3/201$ =1.048×10^3K. The corresponding frequency calculated by formula (15) is: ν^1_{TD} =$1/\lambda$= kT_G /ch (cm^{-1})=720 cm^{-1}. The calculated frequency ν^1_{TD} =720 cm^{-1} correspond to biggest band (band 1) on IR spectrum of acetylene (Fig.4). From ν^1_{TD} frequency it can receive frequencies of the others modes i.e: ν^1_{TD} ×20 = 1440 cm^{-1} (band 2) and ν^1_{TD} ×4.5 = 3240 cm^{-1} (band 3). The calculation of T_H= $\Delta H_f^0/S^0$ based on enthalpy ΔH_f^0=226.88 kJ/mol and entropy S^0=201 J/mol·K of acetylene molecule [3] gives frequency of 784.33 cm^{-1}.This frequency is

near to 720 cm^{-1} and correspond too with band 1 on IR spectrum of acetylene. This result due to the approximate values of ΔG_f^0 = 210.7 kJ/mol and of ΔH_f^0=226.88 kJ/mol.

DISCUSSION
The study on IR spectra of over 50 molecules (unpublished data) showed the calculating 'apparent' temperatures and corresponding frequency are more relevant to experimental IR spectra, when are calculated on the base of $\Delta G_f^0/S^0$ than $\Delta H_f^0/S^0$ ratio. For example: in the case of Hydrogen cyanide the calculation of T_H=$\Delta H/\Delta S$, based on enthalpy ΔH_f^0=437.6 kJ/mol and entropy S^0=202.6 J/mol·K of HCN molecule gives frequency of 1499.34 cm^{-1}. This frequency closer to 1500 cm^{-1} than to 1400 cm^{-1} and falls outside the peak 2 on Fig.2. In the case of H_2O molecule the calculated by classical method frequency 2994.16 cm^{-1} do not correspond to any band on IR water spectrum. The same is situation with acetylene molecule. This shows that the infrared spectra related more to Gibbs free energy, rather than enthalpy of the molecular formation. In many cases the calculated basic frequencies (ν_{TD}) fall in far-infrared region (below 400 cm^{-1}), but its multiple mods (who overlap with the actual absorption frequencies) are located in mid-infrared spectral region. The different multiple mods can be obtained from the basic frequencies ν_{TD}. For this purpose the basic frequency must be represented as multiple of 1.5, 2.0, 2.5, 3.0…, and so on.

From the presented results, it can be seen that the calculated by thermodynamic method frequencies coincide with the experimental absorption frequencies on the infrared spectrum of the studied molecules. The proposed method gives possibility for theoretical prediction of potential absorption frequencies (mods) in the infrared spectrum of the unknown molecules. A similar relationship between the vibrational assignment and the thermodynamic properties of some simple molecules were sought by other authors too. A similar relationship between the vibrational assignment and the thermodynamic properties of some simple molecules were sought previously by other authors too [7, 8]. The proposed new method may be a good complement to recently existing methods for spectral analyses.

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