Some specific features of spectral bands location in the infrared spectra of crystals and liquids

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Abstract. A cluster model of condensed matter has been used to demonstrate that the observed peaks in the IR spectra of crystals and liquids correspond to the most stable cluster structures with the number of particles forming series of Fibonacci numbers. The relationship between the frequencies obeys the golden section rule.

1. Introduction

Recently the efforts to interpret the patterns forming in the location of spectral lines in different spectrum areas by applying the mathematical golden section rule have become more intense [1-6]. Moorman C. M. and Goff J. E. in their paper (2007) [1] studied a mechanical model of the oscillations of two physical bodies connected by weightless elastic springs in horizontal direction and obtained the resulting quadratic equation of motion of a system in the classical case.

\[
\left(\omega^2 - 3\omega_0^2 \right) \omega^2 + \left( \omega_0^2 \right)^2 = 0
\]

(1)

The solution of equation (1) yields two positive roots for oscillation frequencies

\[
\omega_s = \frac{\omega_0}{2} \left( \sqrt{5} \pm 1 \right)
\]

(2)

that are related with the well-known rule of golden section: \( \varphi = \left( \sqrt{5} + 1 \right)/2 = 1.61803... \), \( \varphi^{-1} = \varphi - 1 = 0.61803... \) and can be presented in a compact form

\[
\omega_2 = \varphi \omega_0
\]

(3)

i.e. natural frequencies of the considered mechanical system are related with the golden proportion in a simple manner.

In their paper Hopkins A. B., Stillinger F H and Torquato S. (2010) [2] investigated the densest local packaging (DLP) of not intersecting single diameter spheres in Euclidean space. It was shown that in any measurement region the radius of the spherical area on the surface which accommodates the centers of fifteen non-intersecting spheres and the radius of this sphere as such are in golden proportion relationship. In [3] Heyrovská R. (2013) based on experimental data on the wavelengths for hydrogen atom spectral lines demonstrated that the position of these lines in the spectrum can be represented by simple functions of the golden proportion. The review of studies where golden proportion is applied to interpret spectral properties of condensed matters can be found in [4-6].
2. Cluster model and IR spectra of liquids

Studies of condensed matter spectra in the IR region show that spectral bands appear due to rotations and librations of dimers in the structure of clusters. The more particles a cluster contains, the higher frequency of dimer’s libration motions corresponds to this cluster in the IR spectrum. In the context of dynamic equilibrium of a cluster formation in classical approximation the equality will be

\[ \frac{J_{\text{dim}} \omega^2}{2} = \frac{\hat{Z}}{2} \varepsilon_{\text{eff}} \]  \hspace{1cm} (4)

where \( J_{\text{dim}} \) is the moment of inertia relative to the principal axes for different configurations of the dimer, \( \omega \) - is cyclic frequency librations, \( \hat{Z} \) - is a most probable number of particles in the cluster, \( \varepsilon_{\text{eff}} \) - the effective depth of the potential well of the interaction potential.

Following the model developed earlier in [7-9, 19], we shall write the density of clusters distribution according to the number of particles contained in their composition in the form of gamma function with the integer value of the parameter \( m = 4 \)

\[ f(Z) = \frac{e^{\frac{4}{6}Z^3}}{6} \cdot e^{-\lambda Z} \] \hspace{1cm} (5)

The most probable number of particles in cluster \( \hat{Z} \) corresponds to the maximum value of the function \( f(Z) \) and is defined by [7-9, 19]

\[ \hat{Z} = m - \frac{1}{\lambda} = (m - 1)\theta = \frac{3\pi^2}{4} \eta \exp(\eta) \] \hspace{1cm} (6)

where \( \eta \) - is the cluster structure packing factor which is determined in context of the model of hard spheres by formula \( \eta = \eta_c \rho^* \), \( \rho^* \) - is the reduced density of the liquid, \( \eta_c \) - the coefficient of atomic packing in a critical point.

The depth of the potential well of the effective interaction potential is determined by the depth of the potential well of the pair interaction potential \( \varepsilon_0 \) and the most probable number of particles \( \hat{Z} \) in a cluster [10, 19]

\[ \varepsilon_{\text{eff}} = \varepsilon_0 + \Delta \varepsilon = \varepsilon_0 + \left( \frac{\hat{Z} - 1}{\hat{Z} + 1} \right)^2 kT \] \hspace{1cm} (7)

In their paper Piech M, at al. (2002) [11] successfully used a similar effective potential to account for the nearest-neighbor interaction in the system of interacting particles; Wang Dingdi, at al. (2013) in [12] simulated rotational-vibration motion of a dimer in closest neighboring environment based on the example of a dimer of iodine atoms in a rigid nano-channel and demonstrated that the set of frequencies lies in the far infrared region of the spectrum.

Based on the formulas (4) and (7) the set of frequencies in the IR spectrum is defined by [10]

\[ \omega_i = \sqrt{\frac{2 \Delta H_{\text{dim}}}{J_{\text{dim}}}} \frac{\sqrt{Z_i}}{\sqrt{1 + \left( \frac{\hat{Z} - 1}{\hat{Z} + 1} \right)^2 \frac{kT}{\varepsilon_0}}} \] \hspace{1cm} (8)

Equation (8) implies the existence a of minimum frequency in the IR spectrum, and this frequency is determined by
\[ \omega_{\text{min}} = \sqrt[2]{\frac{2 \Delta H_{\text{dim}}}{J_{\text{dim}}}} \]  

where \( \Delta H_{\text{dim}} \) is the enthalpy of dimer configuration formation.

In the first approximation, Eq (8) considering (9) yields a simpler expression for predicting the set of frequencies in the IR spectrum of a liquid:

\[ \omega_i = \omega_{\text{min}} \sqrt{Z_i} \]  

where \( Z_i \) is a set of "magic" numbers that specify the number of particles in the most stable clusters.

Reduced frequency \( \omega_* = \omega / \omega_{\text{min}} \) is a universal function of the square root of the number of particles in a cluster. In light of (10) the function of clusters distribution in accordance with the number of particles (5) contained in their composition permits us to find the distribution function of frequencies in the IR spectrum of a liquid:

\[ f(\omega_*) = \frac{A^4}{3} \omega_*^7 \cdot e^{-A \omega_*^2} \]  

The most probable reduced frequency \( \hat{\omega}_* \) corresponds to the maximum function \( f(\omega_*) \) and is equal to

\[ \hat{\omega}_* = \sqrt{\frac{7}{2}} \theta = \sqrt{\frac{7}{6}} \sqrt{Z} \]

Figure 1 shows a) curves of frequency allocations (11) for liquid argon at various temperatures on the saturation line, which indicates natural displacement of frequency maximum \( \Theta_* \) depending on the number of particles in the cluster and b) a similar function taken for liquid CCl\(_4\) to illustrate the golden rule in the IR spectrum.

**Figure 1.** a) The distribution of frequencies in the IR spectrum of liquid argon (5), and b) a similar function for CCl\(_4\) obtained by means of pair interaction potential [Moore et. al. 1995 J. Chem. Phys. 103, 9. 3327].

The study of patterns of the relative allocation of the most probable frequencies in the IR spectra of liquids revealed that there is a clear functional relationship between the frequencies \( \hat{\omega}_* \), \( \omega'' \), and \( \omega' \), which is defined by mathematical golden rule.
\[ \frac{\omega'' - \omega'}{\omega'' - \omega'''} = \frac{\omega'' - \omega'}{\omega'' - \omega'''} = \varphi = \frac{1 + \sqrt{5}}{2} = 1.6180339... \]  

Equation (14) implies the existence of the most stable cluster formations in liquids with the most probable number of particles represented by Fibonacci series: 0; 1; 2; 3; 5; 8; 13; 21; 34; 55; 89; 144; ..., wherein the monatomic inert gases and organic liquids are characterized by small clusters with the most probable number of particles: 1; 2; 3; 5; 8; 13. According to formula (10) such set of "magic" numbers corresponds to a set of frequencies in the IR spectrum:

\[ \omega'' = (1 + \varphi) \omega_n - \varphi \omega' \]  

For small water clusters with \( \omega_{\min} = 85.8 \text{ cm}^{-1} \), we shall obtain the following a set of frequencies: 121, [120] \text{ cm}^{-1}, 149 [145] \text{ cm}^{-1}, 192 [190] \text{ cm}^{-1}, 242 [240] \text{ cm}^{-1}, 310 \text{ cm}^{-1}. Experimental frequency values [13-15] are given in square brackets. They prove the validity of applying the golden section to the analysis of the IR spectra of liquids.

The results of comparison between frequency values obtained by formula (10), Raman and IR spectroscopy experimental data available for crystals and liquids with different structures, different nature and intensity of the intermolecular interaction (such as 1-nitro-4- (trifluoromethoxy) benzene, water, ice, 4-tert butyl benzyl selenocyanate) are given in table 1. These data show good agreement between the calculations according to the rules of golden section and spectroscopy experimental data in the far region of IR spectra of a liquid.

Within the width of spectrum \( \Delta \omega \) at the level \( \frac{1}{2} f_{\max}(\omega_n) \) it is possible to estimate the lifetime of the most probable cluster with some selected conditions of a liquid state (see. figure 1).

The relationship to estimate the lifetime of a cluster in a fluid with the most probable number of particles in its structure will have the form of [19]

\[ \Delta \tau = \frac{\tau_0}{\sqrt{(Z - 1)}} \]  

If the value \( \hat{Z} = 2 \) the formula will correspond to the dimer’s lifetime in a liquid \( \Delta \tau_{\text{dim}} = \tau_0 \), which can be determined by independent spectroscopic methods. For a free stable particle \( \hat{Z} = 1 \), formula (16) corresponds to the passage to the limit and presumes an infinite lifetime.

For liquid argon near its melting point at \( T = 85 K \) the lifetime of a cluster with the most probable number of particles \( \hat{Z} \approx 7 \) estimated by the formula (16) will yield the value \( \Delta \tau = 2.5 \times 10^{-12} \text{ c} \).

Time of life of cluster systems in liquids cannot be defined by experimental methods, this value can be estimated only indirectly in the context of specific assumptions or theories, that is why the relation (16) obtained through the cluster model is very important for understanding formation and disintegration processes running with cluster systems in liquids. For instance, the lifetime of hydrogen bonds in water is of the same order as the time of dipole relaxation and agrees with the estimations of a cluster’s lifetime (\( \Delta \tau = 3.7 \times 10^{-12} \text{ c} \)) in accordance with the formula (16).
Table 1. IR spectra of ice crystals modifications and some liquids with Fibonacci series.

|                | Far –infrared spectrum of ice II at 1 bar and 100 K | Far –infrared spectrum of ice IX at 1 bar and 100 K | Far –infrared spectrum of ice V at 1 bar and 100 K | Far –infrared spectrum of 1-nitro-4-(trifluoromethoxy) benzene | Far –infrared spectrum of 4-tert butyl benzyl selenocyanate |
|----------------|-----------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
|                | $F_i = \hat{Z}$                                      | $F_i = \hat{Z}$                                      | $F_i = \hat{Z}$                                      |                                                               |                                                               |
|                | $\omega_{\text{min}} = 75 \text{ cm}^{-1}$          | $\omega_{\text{min}} = 106.8 \text{ cm}^{-1}$       | $\omega_{\text{min}} = 139 \text{ cm}^{-1}$         |                                                               |                                                               |
|                | Calc. [16]                                         | Calc. [16]                                         | Calc. [16]                                         |                                                              |                                                              |
| 2              | 106                                                | 106.5                                              | 151                                                | 151.4                                                        | 185                                            |
| 3              | 130                                                | 136.1                                              | 185                                                | 186.4                                                        | 241                                            |
| 5              | 168                                                | 239                                                | 237                                                | 311                                                          | 325                                            |
| 8              | 212                                                | 302                                                | 294.8                                              | 393                                                          | 293                                            |
| 13             | 270                                                | 385                                                | -                                                  | -                                                            | 373                                            |
| 21             | 344                                                | 435                                                | 489                                                | -                                                            | -                                              |
|                | $D_2O, \quad \omega_{\text{min}} = 106.8 \text{ cm}^{-1}$ | $D_2O, \quad \omega_{\text{min}} = 97 \text{ cm}^{-1}$ | $D_2O, \quad \omega_{\text{min}} = 176.8 \text{ cm}^{-1}$ |                                                              |                                                              |
|                | Calc. [16]                                         | Calc. [16]                                         | Calc. [16]                                         |                                                              |                                                              |
| 2              | 106                                                | 106.5                                              | 151                                                | 151.4                                                        | 185                                            |
| 3              | 130                                                | 136.1                                              | 185                                                | 186.4                                                        | 241                                            |
| 5              | 168                                                | 239                                                | 237                                                | 311                                                          | 325                                            |
| 8              | 212                                                | 302                                                | 294.8                                              | 393                                                          | 293                                            |
| 13             | 270                                                | 385                                                | -                                                  | -                                                            | 373                                            |
| 21             | 344                                                | 435                                                | 489                                                | -                                                            | -                                              |
|                | $\omega_H_2O/\omega_{D_2O}$                         | $\omega_H_2O/\omega_{D_2O}$                         | $\omega_H_2O/\omega_{D_2O}$                         |                                                              |                                                              |
| 2              | 1.031                                              | 1.031                                              | 1.031                                              |                                                              |                                                              |
| 3              | 1.030                                              | 1.030                                              | 1.030                                              |                                                              |                                                              |
| 5              | 1.030                                              | 1.030                                              | 1.030                                              |                                                              |                                                              |
| 8              | 1.031                                              | 1.031                                              | 1.031                                              |                                                              |                                                              |
| 13             | 1.032                                              | 1.032                                              | 1.032                                              |                                                              |                                                              |
| 21             | -                                                  | -                                                  | -                                                  |                                                              |                                                              |
|                | Far –infrared spectrum of ice V at 1 bar and 100 K  | Far –infrared spectrum of 1-nitro-4-(trifluoromethoxy) benzene | Far –infrared spectrum of 4-tert butyl benzyl selenocyanate |                                                             |                                                             |
|                | $F_i = \hat{Z}$                                      | $\omega_{\text{min}} = 67.2 \text{ cm}^{-1}$       | $\omega_{\text{min}} = 89.1 \text{ cm}^{-1}$       | $\omega_{\text{min}} = 99 \text{ cm}^{-1}$                  | $\omega_{\text{min}} = 181.8 \text{ cm}^{-1}$ |
|                | Calc. [17]                                         | Calc. [17]                                         | Calc. [17]                                         | Calc. [17]                                                   | Calc. [17]                                                   |
| 2              | 95                                                 | 95                                                 | 126                                                | 126                                                          | 135                                            |
| 3              | 116                                                | 154                                                | 152                                                | 165                                                          | 165                                            |
| 5              | 150                                                | 199                                                | 200                                                | 214                                                          | 200                                            |
| 8              | 190                                                | 252                                                | -                                                  | 270                                                          | 260                                            |
| 13             | 242                                                | 321                                                | -                                                  | 344                                                          | 340                                            |
| 21             | 308                                                | -                                                  | -                                                  | -                                                            | -                                              |
|                | $\omega_H_2O/\omega_{D_2O}$                         | $\omega_H_2O/\omega_{D_2O}$                         | $\omega_H_2O/\omega_{D_2O}$                         |                                                              |                                                              |
| 2              | 1.016                                              | 1.016                                              | 1.016                                              |                                                              |                                                              |
| 3              | 1.013                                              | 1.013                                              | 1.013                                              |                                                              |                                                              |
| 5              | 1.015                                              | 1.015                                              | 1.015                                              |                                                              |                                                              |
| 8              | 1.016                                              | 1.016                                              | 1.016                                              |                                                              |                                                              |
| 13             | 1.016                                              | 1.016                                              | 1.016                                              |                                                              |                                                              |
| 21             | -                                                  | -                                                  | -                                                  |                                                              |                                                              |
|                | Far –infrared spectrum of 4-tert butyl benzyl selenocyanate | Far –infrared spectrum of 4-tert butyl benzyl selenocyanate | Far –infrared spectrum of 4-tert butyl benzyl selenocyanate |                                                             |                                                             |
|                | $F_i = \hat{Z}$                                      | $\omega_{\text{min}} = 24 \text{ cm}^{-1}$         | $\omega_{\text{min}} = 87.7 \text{ cm}^{-1}$       | $\omega_{\text{min}} = 99 \text{ cm}^{-1}$                  | $\omega_{\text{min}} = 181.8 \text{ cm}^{-1}$ |
|                | Calc. [18]                                         | Calc. [18]                                         | Calc. [18]                                         | Calc. [18]                                                   | Calc. [18]                                                   |
| 2              | 34                                                 | -                                                  | 124                                                | 124                                                          | 140                                            |
| 3              | 42                                                 | -                                                  | 152                                                | 171                                                          | -                                              |
| 5              | 54                                                 | 58                                                 | 196                                                | 198                                                          | 221                                            |
| 8              | 88                                                 | 68                                                 | 248                                                | 240                                                          | 280                                            |
| 13             | 102                                                | 92                                                 | 216                                                | 234                                                          | 280                                            |
| 21             | 142                                                | 117                                                | 302                                                | 320                                                          | 331                                            |
|                | $\omega_H_2O/\omega_{D_2O}$                         | $\omega_H_2O/\omega_{D_2O}$                         | $\omega_H_2O/\omega_{D_2O}$                         |                                                              |                                                              |
| 2              | -                                                  | -                                                  | -                                                  |                                                              |                                                              |
| 3              | -                                                  | -                                                  | -                                                  |                                                              |                                                              |
| 5              | -                                                  | -                                                  | -                                                  |                                                              |                                                              |
| 8              | -                                                  | -                                                  | -                                                  |                                                              |                                                              |
| 13             | -                                                  | -                                                  | -                                                  |                                                              |                                                              |
| 21             | -                                                  | -                                                  | -                                                  |                                                              |                                                              |
| 34             | -                                                  | -                                                  | -                                                  |                                                              |                                                              |
3. Conclusion
In disordered condensed media (dense gases, liquids and polymers) clusters are distributed according to the number of particles in their composition, which can be described by two-parameter gamma function. Notable is that the parameter that specifies the order of distribution is equal to $m = 4$, the shape parameter is the function particle packing ratio in the structure of a cluster $\theta = f(\eta)$.

In their composition the most stable clusters contain such number of particles that forms Fibonacci series. These clusters determine the position of the maxima in the IR spectra of liquids. It has been proved that reduced frequencies, that correspond to the maxima of the IR spectra, are proportional to the square root of the average number of particles in the most stable clusters. Theoretical suppositions have been verified by experimental data obtained for liquids with different molecular structures.

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