Formation of cluster systems in condensed matters and IR spectra of liquids

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Abstract

Modern approaches to the interpretation of IR spectra of polyatomic liquids are based on cluster models of the structure of matter. First of all it concerns the far infrared region of the spectrum (20-300 cm$^{-1}$) where rotationally libration motions in the structure of clusters are found. This work is a continuation of research conducted by the authors earlier [G. Melnikov at al. 2015 IOP Conf. Ser.: Mater. Sci. Eng. 81 p 012032]. The authors have adopted a model in which the appearance of spectral bands is explained by libration oscillations vibrations of dimers with different configurations in the structure of clusters.

Introduction

The quantization process in cluster systems is complex and there are numerous experimental and theoretical studies [1-6] devoted to the search of the laws of quantum transitions in the formation and evolution of clusters in liquids. The principles of quantization of oscillation vibration frequencies of dimers were discussed in detail by Kirchhoff and Lida [1] and later were used by Fraser et al. [2]. To describe the structure and rotational spectra of benzene-water dimer Gutowsky H. et al. for transition frequencies used the following ratio [3].

$$\nu = 2(J + 1)(B - D_{Jk}K^2 - D_{Jm}m^2 - D_{JKm}Km - H_{JKm}m^2K^2) - 4(J + 1)^3D_J$$

(1)

where $m = 0, \pm 1, ...$ – quantum number that specifies internal rotation of the dimer; $D, H$ – constant values.

The problem of quantization of symmetric top rotation and rotational spectrum of the dimer SiF4-NH3 is considered in [4, 5]. In [6] the following ratio is proposed to quantize oscillation vibration frequencies in dimers.

$$\nu = 2\bar{B}(J + 1) - 4D_J(J + 1)^3 - 2D_{Jk}(J + 1)K^2$$

(2)

where $\bar{B}, D_J$, and $D_{Jk}$ - constants.

The Equations (1) and (2) demonstrate that if rotational- librational motion of dimers in a cluster is simulated as a diatomic molecule, the energy of this motion can be written as

$$E_{rot} = B_J(J + 1) - D_J\left[J(J + 1)\right]^2 + H_J\left[J(J + 1)\right]^3 + ...$$

(3)
where $B_v, D_v, H_v,...$ are series of powers: $(\nu + 0.5)$.

The frequency spectrum of rotational oscillations vibrations in cluster systems is represented as an expansion in powers of $x$ similar to Dunham series [7], and the constant $D_v$ is called centrifugal tension constant:

$$T(v, J) = \sum_{l, j} Y_l, j \left( v + \frac{1}{2} \right) \left[ j(j + 1) \right]^l$$

Practical use of different expansions in powers $(\nu + 0.5)$ like Dunham series for predicting rotational and vibrational-rotational-librational frequencies of cluster systems is rather difficult, because the expansions contain several empirical constants, the calculation of which requires a great deal of experimental data on the spectra of objects. This paper discusses some alternative ways of predicting frequencies in the IR range.

**The rule of sequential formation of clusters in the structure of liquids**

As a of Density fluctuations in a disordered condensed medium result in the formation of cluster systems that have composition, geometrical dimensions, formation energy and lifetime. In the series of papers [8-11], the authors have shown that under the conditions of dynamic equilibrium a bound state of two particles (a dimer) forms up in the structure of the most probable cluster. These particles make libration oscillations with a frequency $\omega$ determined by the condition:

$$\omega = \sqrt{ \frac{2 \Delta H_{\text{dim}}}{J_{\text{dim}}}} \cdot \sqrt{Z_j}$$

Equation (5) shows that the frequency is determined by the number of particles in the cluster, the number and characteristics of possible dimer configurations that are composed of free molecules.

When the spontaneous collapse of the cluster takes place, the number of particles in its composition changes and becomes equal to $\tilde{Z}_j$, then the frequency of the dimer librational oscillations in the newly formed cluster will be:

$$\omega_j = \sqrt{ \frac{2 \Delta H_{\text{dim}}}{J_{\text{dim}}}} \cdot \sqrt{\tilde{Z}_j}$$

The change in frequency is accompanied by the emission or absorption of the quantum of energy with a frequency:

$$\omega_{\text{q}} = \sqrt{ \frac{2 \Delta H_{\text{dim}}}{J_{\text{dim}}}} \cdot \sqrt{Z_j} \left( 1 - \frac{\tilde{Z}_j}{\tilde{Z}_{j+1}} \right)$$

Assuming that the root in the parenthesis of (7) remains constant, you can set this value as equal to the square root from the "golden section" constant, i.e. set $\frac{\tilde{Z}_j}{\tilde{Z}_{j+1}} = \frac{5}{8} = 0.625$, then the formula (7) can be written as a ratio:

$$\omega_{\text{q}} = 0.2094 \sqrt{ \frac{2 \Delta H_{\text{dim}}}{J_{\text{dim}}}} \cdot \sqrt{F_j}$$

where $F_j = 1, 2, 3, 5, 8, 13, 21, 34, 55,...$ are Fibonacci numbers.
Figure 1 shows a diagram of the spontaneous decay of a cluster with the most probable number of particles \( \hat{Z}_i = 8 \) in accordance with the Fibonacci law.

![Diagram of the spontaneous decay of a cluster](image)

**Figure 1.** A diagram of the spontaneous decay of a cluster \(( \hat{Z}_i = 8 )\) according to the Fibonacci law

Polyatomic molecules with complex geometric shapes can form a number of possible configurations of a dimer, that will have different moments of inertia relative to the main axes and energies of configuration formation. In the formula (8) to designate the value before the multiplier \( \sqrt{F_i} \) we’ll introduce the notation

\[
\omega_{\text{min},i} = 0.2094 \sqrt{\frac{2 \Delta H_{\text{dim},j}}{J_{\text{dim},j}}} \quad (9)
\]

where \( \omega_{\text{min},i} \) - is minimal frequency for the selected \( i \)-th configuration of the dimer.

The set of frequencies in IR spectra of a liquid is determined according to formulas (8) and (9) by simple relationship

\[
\omega_i = \omega_{\text{min},i} \sqrt{F_i} \quad (10)
\]

The existence of spectral bands in IR spectra suggests certain rules of quantization of librational oscillations of dimers in the structure of clusters.

In order not to use the cumbersome and time-consuming calculations by Dunham scheme, we’ll use an alternative representation of Fibonacci series. It is possible to apply de Moivre-Binet formula, which is written as [12-13]:

\[
F_n = \frac{1}{\sqrt{5}} \left( \frac{1 + \sqrt{5}}{2} \right)^n - \left( \frac{1 - \sqrt{5}}{2} \right)^n \quad (11)
\]

with \( n \geq 0, n = 0,1,2,\ldots \) it is possible to demonstrate that there is asymptotic behavior, which allow us to represent Fibonacci series as a power function of the golden section base \( \phi = 1.618039\ldots \) [12-13].
\[ F_n = \frac{1}{\sqrt{5}} \phi^n \]  

(12)

With various integer values of \( n \) we’ll obtain integral values of the Fibonacci sequence, despite the fact that \( \sqrt{5} \) and \( \phi \) are irrationals number, then according to formulas (10) and (12) the rules of frequencies quantization in IR spectra of liquids can be written

\[ \omega_{mn} = \omega_{\min} \cdot 5^{-\frac{1}{4}} (\phi)^{\frac{1}{2}J_L} \]  

(13)

where \( J_L = 0,1,2,... \) - librational quantum number.

Fibonacci numbers can also be expressed in terms of Chebyshev polynomials according to recurrence relations or in terms of trigonometric functions [14-15]. Considering the formula (9) the ratio (13) can be written in final form as

\[ \omega_j = 0.1423 \sqrt{\frac{2\Delta H_{\dim,j}}{J_{\dim,i}}} (\phi)^{\frac{1}{2}J_L}, \]  

(14)

**Calculation results and their comparison with experimental data**

Let’s check the validity of the obtained relations (10) and (14) by applying them to liquid benzene as the most studied object. It has been established that benzene molecules can form three types of dimer configurations [16-19]: Sandwich (S), T-shaped and parallel-displaced (PD) configurations that differ in the value of the equilibrium distances between the centers of molecule masses \( R_{\dim} \), the energy of configuration formation (dimer’s binding energy) \( \Delta H_{\dim} \) and the moment of inertia \( J_{\dim} \) in relation to the axis going through the center of masses in the configuration.

It is hardly possible to calculate the exact moment of inertia of the dimeric configuration and its formation energy for liquids with complex multi-nuclear molecules. So the value \( \omega_{\min,i} \) in the formula (14) shall be considered as an empirical constant.

Table 1 shows the frequencies of libration oscillations of benzene dimers in the structure of the clusters calculated by formula (10). They have been calculated dimers containing in their structure different numbers of particles with different values of \( \omega_{\min,i} \). By applying the Fibonacci series and the formula (10) we could predict the position of spectral bands in benzene IR spectrum within a wide frequency range (\( 20 \text{cm}^{-1} - 6000 \text{cm}^{-1} \)), moreover it was found that benzene can have clusters with the number of particles varying from 2 to 6700, however, the most probable number of particles is determined by Erlang distribution and ranges from 3 to 21 depending on the parameters of the state of a liquid [8].

The accepted model of IR spectra formation in organic liquids allows to predict the position of spectral bands with an accuracy of about 5%. The use of formula (14) to calculate frequencies in IR spectra of liquids with different molecular structure and crystals has demonstrated that complex spectra of such objects always contain spectral lines that correspond to cluster formations with the number of the particles corresponding to a Fibonacci series.
Table 1. Libration oscillation frequencies of dimers (cm\(^{-1}\)) in the cluster structure of liquid benzene and its Raman.

| Calc. (10) | [20,21] | Calc. (10) | [20,21] | Calc. (10) | [20,21] |
|------------|--------|------------|--------|------------|--------|
| 11.57 \(\omega_{\text{4min}}\) | 11.57 | 277 \(\omega_{\text{4min}}\) \(\sqrt{3}\) | 275.77 | 1605 \(\omega_{\text{3min}}\) \(\sqrt{610}\) | 1606.8 |
| 20.0 \(\omega_{\text{1max}}\) \(\sqrt{3}\) | 286 \(\omega_{\text{1max}}\) \(\sqrt{610}\) | 2042 \(\omega_{\text{3min}}\) \(\sqrt{987}\) | 2045 |
| 25.9 \(\omega_{\text{4max}}\) \(\sqrt{5}\) | 20.25 | 298 \(\omega_{\text{4max}}\) \(\sqrt{21}\) | 301.6 |
| 32.7 \(\omega_{\text{1max}}\) \(\sqrt{8}\) | 31.4 | 341 \(\omega_{\text{2min}}\) \(\sqrt{55}\) | – | 2338 \(\omega_{\text{2min}}\) \(\sqrt{2584}\) | 2325 |
| 41.7 \(\omega_{\text{1max}}\) \(\sqrt{13}\) | – | 363 \(\omega_{\text{3min}}\) \(\sqrt{987}\) | 374.12 | 2974 \(\omega_{\text{3min}}\) \(\sqrt{4181}\) |
| 46.0 \(\omega_{\text{2min}}\) | – | 380 \(\omega_{\text{3min}}\) \(\sqrt{34}\) | 388.8 | 2950 |
| 53.0 \(\omega_{\text{min}}\) \(\sqrt{21}\) | 53.5 | 434 \(\omega_{\text{2min}}\) \(\sqrt{89}\) | 462 | 3063 \(\omega_{\text{4min}}\) \(\sqrt{610}\) | 3044 |
| 65.0 \(\omega_{\text{3min}}\) | 61.0 | 482 \(\omega_{\text{3min}}\) \(\sqrt{55}\) | – | 3304 \(\omega_{\text{3min}}\) \(\sqrt{2584}\) |
| 67.5 \(\omega_{\text{4min}}\) \(\sqrt{34}\) | 70 | | | 3309 |
| 79.7 \(\omega_{\text{2min}}\) \(\sqrt{3}\) | 79.06 | 552 \(\omega_{\text{2min}}\) \(\sqrt{144}\) | 3783 \(\omega_{\text{2min}}\) \(\sqrt{6765}\) |
| | | 568 \(\omega_{\text{2min}}\) \(\sqrt{21}\) | | 3788 |
| | | 588 \(\omega_{\text{3min}}\) \(\sqrt{2584}\) | | 600 |
| 85.8 \(\omega_{\text{3min}}\) \(\sqrt{55}\) | 86.6 | 613 \(\omega_{\text{3min}}\) \(\sqrt{89}\) | 626.3 | 3895 \(\omega_{\text{4min}}\) \(\sqrt{987}\) | 3893 |
| 92.0 \(\omega_{\text{3min}}\) \(\sqrt{2}\) | | | | |
| 102.8 \(\omega_{\text{2min}}\) \(\sqrt{5}\) | 100 | 702 \(\omega_{\text{2min}}\) \(\sqrt{233}\) | 690 | 4203 \(\omega_{\text{3min}}\) \(\sqrt{4181}\) |
| 109 \(\omega_{\text{3min}}\) \(\sqrt{89}\) | – | 723 \(\omega_{\text{4min}}\) \(\sqrt{34}\) | 713.5 | 4208 |
| 124 \(\omega_{\text{4min}}\) | 128 | 780 \(\omega_{\text{3min}}\) \(\sqrt{144}\) | 790 | 4955 \(\omega_{\text{4min}}\) \(\sqrt{1597}\) | 4959 |
| 130.1 \(\omega_{\text{2min}}\) \(\sqrt{8}\) | 128 | 893 \(\omega_{\text{2min}}\) \(\sqrt{377}\) | 952 | 5346 \(\omega_{\text{3min}}\) \(\sqrt{6765}\) |
| 139 \(\omega_{\text{4min}}\) \(\sqrt{144}\) | – | | | 5346 |
| 145 \(\omega_{\text{4min}}\) \(\sqrt{5}\) | 144.63 | 992 \(\omega_{\text{3min}}\) \(\sqrt{233}\) | 992.5 |
| 166 \(\omega_{\text{2min}}\) \(\sqrt{13}\) | 168 | 1136 \(\omega_{\text{2min}}\) \(\sqrt{610}\) | 1148.5 |
| 175 \(\omega_{\text{2min}}\) \(\sqrt{2}\) | 171 | 1170 \(\omega_{\text{2min}}\) \(\sqrt{89}\) | 1176.8 |
| 211 \(\omega_{\text{2min}}\) \(\sqrt{21}\) | 210 | 1262 \(\omega_{\text{3min}}\) \(\sqrt{377}\) | 1249 | 6303 \(\omega_{\text{4min}}\) \(\sqrt{2584}\) |
| 215 \(\omega_{\text{4min}}\) \(\sqrt{3}\) | 213.9 | 1445 \(\omega_{\text{2min}}\) \(\sqrt{987}\) | | |
| 268 \(\omega_{\text{2min}}\) \(\sqrt{34}\) | 264 | 1488 \(\omega_{\text{4min}}\) \(\sqrt{144}\) | 1479 | 8018 \(\omega_{\text{3min}}\) \(\sqrt{4181}\) |
Conclusion

The distribution of clusters by the number of particles in their composition suggests the existence of clusters with a most stable configuration and with the number of particles determined by a Fibonacci series. Successive collapse of a selected cluster having the corresponding to a Fibonacci series takes place according to the rule saying that a newly emerged cluster also has the number of particles corresponding to a Fibonacci series with the preserved ratio between the number of particles in two successively transformed clusters, which is equal to the "golden section" $\phi = 0.618...$. A change in the dimer 's libration oscillation frequency with the change of the number of particles in the cluster structure is accompanied by emission of a photon having the frequency that is proportional to the square root of the number of particles in the cluster.

Mathematical construction of the adopted model is based on the assumption that there is an effective potential of inter- particle interaction and it is possible to calculate the most probable number of particles in the structure of the cluster by the Erlang distribution.

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