



Research of the Theory of the Form of the Circuits of Vibrational Spectra in a Liquid Phase

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ABSTRACT: In this article, when studying the processes occurring in aqueous solutions of surfactants, the greater importance of the forms of the line of Raman scattering is proved. The formulas for subtracting high-spectral moments are given for the shape of the oscillatory circuits, where in the second M (2), fourth M (4) high moments it is shown that they give more information.

KEY WORDS: relaxation, spectrum, approximant, satellite, correlation, probe, transformation.

I. INTRODUCTION

It is known that the form of vibrational Raman spectra contains valuable information about the structure of liquids and solutions. The study of the spectral forms makes it possible to determine the structural-dynamic processes in complex molecular systems, such as water-micellar ones.

The existence of structural features and conformational changes in alkyl chains in aqueous micellar solutions and lipid bilayers was established by RS (Raman scattering) by the ratio of the intensities of the ν (C-C) vibration bands in the 1100 cm^{-1} and ν (C-H) bands in the region of 3000 cm^{-1} [1]. However, an analysis of the intensities does not allow obtaining detailed microscopic information about the structure and dynamics of these systems contained in the contours of spectral lines.

The contours of the spectral lines are determined by the processes of vibrational and orientational relaxation of the molecules. The widely used parameters — the times of vibrational and orientational relaxation (correlation) and half-widths are slightly sensitive to structural transformations and changes in the conformation of the environment of the molecule [2] and are not directly comparable with theory, since the distribution functions in the system. The abundance of work on modeling the relationship between the shape of bands and TCF (temporal correlation functions) with the microscopic characteristics of the studied system (for example, review [3]) is an indication of the complexity of the problem, which is due to the fact that the shape of the lines and TCF depend on all many-particle distribution functions in system.

The determination of the second moment M [2], [4] already requires integration of about 50 line widths over the spectral section, which is practically feasible in rare cases. We have developed a method for determining the highest integral moments from the central part of the contour, based on the approximate line shape obtained on the basis of the Mori method [5]. In the widely used method, Mori approximates a memory function of any order by an a priori assumption about the nature of its temporal decline.

The most popular assumption is exponential decay, which leads to a line shape in the form of a superposition of a finite number of Lorentz contours. For such a form of lines, there are no higher integral moments:

$$M[n] = \int_{-\infty}^{+\infty} \frac{\Phi(\omega)}{2\pi} \omega^n d\omega \quad (1)$$

where $\Phi(\omega)$ is the shape of the lines

$$\Phi(\omega) = \int_{-\infty}^{+\infty} G(t) e^{-i\omega t} dt \quad (2)$$

where $G(t)$ is the temporal correlation function.

Useful information about the structure and dynamics of interacting molecules contains moments of line shape $M[n]$, defined as:

$$M[n] = \frac{\int_{-\infty}^{+\infty} \Phi(\omega)(\omega - \omega_0)^n d\omega}{\int_{-\infty}^{+\infty} \Phi(\omega) d\omega} \quad (3)$$

where ω_0 is the frequency at maximum.

Moments are expressed in terms of the Hamiltonian of the system as follows:

$$M[n] = \frac{\langle B^+ [H_1 [H_1 \dots [H_1 B]]] \dots \rangle}{\langle B^+ B \rangle} \quad (4)$$

where $[B]$ is the system operator responsible for the effect, which describes the interaction with electromagnetic radiation (the operator of the dipole moment or the polarizability tensor), B^+ is the Hermitian conjugate operator $[H, B] = HB - BH$, the sign $\langle \rangle$ means averaging over the equilibrium state of the system.

The value of the moments allows you to calculate the line shape and the corresponding TCF. Based on the representation of the Laplace transform of the TCF in the form of an infinite continued fraction, which is obtained by the Mori method or Lapshosh's equivalent algorithms [6], we have obtained the following general expression for the shape of a symmetric spectrum band:

$$\Phi(\omega) = \frac{(1 - B^2 \omega^2)^{\frac{1}{2}}}{1 + \sum_{n \geq 1} d_{2n} \omega^{2n}} \cdot \Phi(0) \quad (5)$$

where the frequency ω is measured from the center (maximum) of the strip, and the coefficients d_{2n} and B are known functions of the moments. Various approximations for the line shape are obtained from expression (5) by limiting the degree of the polynomial in the denominator.

The direct determination of the moment $M[n]$ ($n > 2$) from the experimental line shape in the vast majority of cases is impossible due to noise on the wings of the spectral bands, the presence of satellites, insufficient sensitivity of the device, etc. Therefore, we propose a method for determining experimental values $M[n]$ based on expression (5) for the line shape.

For this, the central part of the vibrational band, in the region of which the signal-to-noise ratio is greatest and the influence of satellites is least significant, is approximated by the inverse polynomial:

$$\Phi(\omega) = \frac{\Phi(0)}{1 + \sum_{n \geq 1} A_{2n} \omega^{2n}} \quad (6)$$

where the coefficients A_{2n} are unknown moment functions. Determination of quantities A_{2n} by fitting the experimental circuit, it is then possible to calculate the moments.

In the case we realized, when in (5) $d_{2n} = 0$ for $n > 2$, the calculation of the experimental moments is based on the following equations

$$A_2 = \frac{\tau_2}{\tau_1} \tau^2 + \tau^2 - 2\tau_1^2 + \frac{\tau_2^2}{8\tau_1^2} \tau^2, \quad (7)$$

$$A_4 = \frac{\tau_2^3}{8\tau_1^3} \tau^4 + \frac{\tau_2^2}{8\tau_1^2} \tau^4 - \frac{1}{2} \tau_1^2 \tau^2 + \tau_1^4 - \tau_1 \tau_2 \tau + \frac{3\tau_2^4 \tau^4}{64\tau_1^4}. \quad (8)$$

The second and fourth moments are expressed through relaxation times:

$$M[2] = \frac{1}{\tau_1^2}; \quad M[4] = M[2]^2 + \frac{M[2]^3}{\tau^2}, \quad (9)$$

where:

$$\tau = \frac{\Phi(0)}{\int_{-\infty}^{+\infty} \Phi(\omega) d\omega}. \quad (10)$$

From the analysis of the second and fourth spectral moments we obtain the factor of the forms of the spectral band:

$$f = \frac{M[4]}{3M[2]^2}. \quad (11)$$

The parameter f is a fundamental characteristic of the contours of vibrational bands and it is equal to unity for the Gaussian contour and grows to infinity when the form approaches the Lorentzian:

$$\Phi_{\text{гаусс}}(\omega) = \Phi(0) \exp\left(-\frac{\omega^2}{2\Delta\nu_{\frac{1}{2}}^2}\right), \quad (12)$$

$$\Phi_{\text{лоренц}}(\omega) = \frac{\Phi(0)}{1 + \frac{\omega^2}{\Delta\nu_{\frac{1}{2}}^2}}, \quad (13)$$

where $\Delta\nu_{\frac{1}{2}}$ is the half-width of the true contour.

In principle, relation (4) for the well-known Hamiltonian of system H allows one to calculate the quantity $M[n]$. However, with many different contributions to H (leading practically to the uncertainty of the Hamiltonian H). Such a calculation for real systems is hardly possible. Therefore, a calculation method is proposed in comparison with experiment, not the quantities $M[n]$ themselves, but their changes when the state of the system changes with respect to some suitable basic system. These changes can be associated, for example, with the transition of a probe molecule from a solution to a bilayer (in our case, it is convenient as a basic probe system in a liquid hydrocarbon whose molecules are close in length to a lipid molecule. This approach emphasizes the differences between the studied system and the specific interaction molecules — the probe with the environment from the basal. A comparison of the experimental and theoretical changes in the moments at different basic states allows us to draw conclusions about the nature of the interaction of probe molecules in the studied system, about the vibrational and orientational relaxation of the probes, and ultimately provides valuable information about the aggregation mechanisms and the microscopic structure of membrane systems.

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