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THEORETICAL ASPECTS OF VIBRATIONAL SPECTROSCOPY OF CONDENSED SYSTEMS WITH IMPURITY PARTICLES

T. Marsagishvili, M. Machavariani

Ivane Javakhishvili Tbilisi State University,
R. Agladze Institute of Inorganic Chemistry and Electrochemistry.
Mindeli str. 11, 0186, Tbilisi, Georgia,
e-mail: tamaz.marsagishvili@gmail.com

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Abstract: *Some problems of vibrational spectroscopy of particles in condensed systems are considered in this work. One of the aspects of theoretical research is the study of the vibrational properties of individual particles in view of the nano-dimension of the molecules of the condensed system surrounding the particle. Using the apparatus of temperature, Green functions of the operators of polarization of condensed systems, two main mechanisms of influence on impurity particles from the medium, solvation and fluctuation, are distinguished. Theoretical results are obtained within the framework of these two mechanisms for calculating changes in the vibrational spectrum of individual particles. The theoretical results are used to analyze the experimental data on the vibrational spectra of the* N_2O *molecule in polar solvents: methanol, ethyl alcohol, acetone, and 1,2-dichloroethane.*

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Introduction

The modern development of studies in the complex condensed systems is increasingly approaching the level of the nanoscale. One of the aspects of research is the study of the vibrational properties of individual particles, taking into account the nano-dimension of the molecules of the condensed system surrounding the particle [1-3]. The condensed medium, depending on the polarity, significantly affects the vibrational spectrum of individual particles, causes a shift and broadening of the absorption peaks, and can even lead to the dissociation of particles into individual fragments. In this case, the influence of the condensed medium on the vibrational spectrum of impurity particles mainly occurs through two mechanisms of interaction - solvation and fluctuation mechanisms. The first of these two mechanisms assumes the solvation of the impurity molecule by the molecules of the medium; the second assumes the interaction of intramolecular vibrations of the impurity with fluctuations of the medium polarization.

Naturally, there is no exact theoretical solution to this kind of problem [4-13]. Real approximate methods assume the use of such models when describing the properties of a condensed medium, which allow one to describe the influence of the medium on the characteristics of an individual impurity particle with the help of measured quantities. The main effect of the influence of a non-regular polar condensed medium in calculating the vibrational spectrum of an impurity can be described using the temperature Green functions of the system's polarization operators. This makes it possible to take into account the effects of frequency and spatial dispersion of a condensed medium within the framework of various models when calculating the spectral characteristics of impurity particles.

1. Hamiltonian model of impurity particle in a condensed medium, solvation mechanism of interaction of an impurity particle with a polar medium.

Hamiltonian - an impurity particle in a condensed medium can be represented as:

$$H = H^0 + \sum a_s Q_s^0 + \sum h_{st} Q_s^0 Q_t^0 \qquad (1)$$

Here (and below) summation over repeated indices is assumed, H^0 is the Hamiltonian of the impurity particle in vacuum, Q_s^0 is the normal coordinate of the s-th intramolecular vibration of the impurity particle (it is assumed that we are working in a system in which the normal value of the coordinate Q_s^0 is zero), the elements a_s and h_{st} are determined by the relations:

$$a_s = \frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}' \left[E_i(\mathbf{r}) g_{ik}(\mathbf{r},\mathbf{r}',\omega=0) \frac{\partial E_k(\mathbf{r}')}{\partial Q_s^0} + \frac{\partial E_i(\mathbf{r})}{\partial Q_s^0} g_{ik}(\mathbf{r},\mathbf{r}',\omega=0) E_k(\mathbf{r}')\right], \qquad (2)$$

$$h_{st} = \frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}' \frac{\partial E_i(\mathbf{r})}{\partial Q_s^0} g_{ik}(\mathbf{r},\mathbf{r}',\omega=0) \frac{\partial E_k(\mathbf{r}')}{\partial Q_t^0}. \qquad (3)$$

Here, **E** is the strength of the electric field created by the polarized impurity particle, $g_{ik}(\mathbf{r},\mathbf{r}',\omega=0)$ is the Green function of the medium polarization operators **P(r,**t**)** at a finite temperature T [3]**:**

$$g_{ik}(\mathbf{r},\mathbf{r}',t-t') = -< T_t P_i(\mathbf{r},t) P_k(\mathbf{r}',t') > \qquad (4)$$

In general form, the calculation of the characteristic parameters of an impurity particle in a polar medium is rather cumbersome. It is more convenient to introduce some characteristic model functions, which can be used to study various aspects of the influence of the polar medium on the characteristic impurity parameters. For such problems, modeling of the Green functions of the medium polarization operators at a finite temperature is convenient.

To obtain evaluative values for a_s and h_{st}, one can perform calculations for a simple model of a homogeneous isotropic medium, not considering the effects of spatial dispersion. For the electric field strength of an impurity particle in the dipole approximation for a symmetric particle of radius r_o, we obtain:

$$a_s = -\frac{8\pi c_0\sqrt{\omega_{s0}}}{3r_0^3}\left(\frac{\partial d}{\partial q_s}\vec{d}\right), \qquad h_{st} = -\frac{4\pi c_0\sqrt{\omega_{s0}\omega_{t0}}}{3r_0^3}\left(\frac{\partial d}{\partial q_s}\frac{\partial d}{\partial q_t}\right) \qquad (5)$$

Where $\vec{d}$ is the dipole moment of the particle, ω_{s0} is the frequency of intramolecular oscillations of the particle in the gas phase (in vacuum), q_s the normal coordinate of the s-th intramolecular vibration of the impurity, with an equilibrium value equal to zero.

For a particle with one optically active degree of freedom, we obtain

$$a = -\frac{8\pi c_0\sqrt{\omega_0}}{3r_0^3}\left(\frac{\partial d}{\partial q}\vec{d}\right), \qquad h = -\frac{4\pi c_0\omega_0}{3r_0^3}\left(\frac{\partial \vec{d}}{\partial q}\right)^2 \qquad (6)$$

As can be seen from these formulas, taking into account the solvation mechanism of the interaction of an impurity particle with a polar medium led to an increase in the equilibrium length of the corresponding chemical bond (parameter a) and to a decrease in the frequency of the corresponding intramolecular vibration (parameter h).

2. Hamiltonian model of a condensed medium with impurity particles, fluctuation

mechanism of interaction of an impurity particle with a polar medium.

Taking into accountthe interaction of medium polarization fluctuations with intramolecular vibrations of impurity particles can be essential for the processes of intramolecular relaxation of polyatomic impurity particles. Information on the effect of medium polarization fluctuations on the frequencies of intramolecular vibrations of impurity particles can be obtained from an analysis of the frequency spectrum of the Green function of the operators of normal coordinates of intramolecular vibrations of particles. When it comes to uncharged impurity particles, the interaction of fluctuations of the medium polarization with the static field of the impurity can be neglected. In this case, for the Green functions of the operators of normal coordinates of intramolecular vibrations Q of an impurity, a system of linear inhomogeneous algebraic equations of the following form can be obtained:

$$G_{uv}(\omega_n) = G^0_{uv}(\omega_n) + G^0_{uu}(\omega_n)\, U_{uw}(\omega_n) G_{wv}(\omega_n), \qquad (7)$$

$$\omega_n = 2\pi nkT,\ n = 0, \pm 1, \pm 2, \pm 3,$$

Where $G^0_{uu}(\omega_n)$ is the temperature of the Green function of operators of a solvated polarized oscillator, $U_{uw}(\omega_n)$ is the renormalized interaction of intramolecular vibrations of a particle, taking into account the interaction of vibrations through a polar medium.

In formula (7) the renormalized interaction $U_{uw}(\omega_n)$ has the form:

$$U_{uw}(\omega_n) = \int d\mathbf{r}\, d\mathbf{r}' \frac{\partial E_u(\mathbf{r})}{\partial Q^0_l} g_{ik}(\mathbf{r}, \mathbf{r}', \omega_n) \frac{\partial E_w(\mathbf{r}')}{\partial Q^0_k}, \qquad \omega_n = 2\pi nkT,\ n = 0, \pm 1, \pm 2, \pm 3, \ldots. \qquad (8)$$

Obviously, the real frequency spectrum of an impurity particle will be determined by the vacuum frequency spectrum of the particle, so by the frequency spectrum of fluctuations of the medium and the interaction of intramolecular vibrations of the particle with fluctuations of the medium polarization.

In the factorization approximation, the Green function of the operators of medium polarization can be represented as:

$$g_{ik}(\mathbf{r}, \mathbf{r}', \omega_n) = f(\omega_n) g_{ik}(\mathbf{r}, \mathbf{r}'), \qquad (9)$$

$$U_{uv}(\omega_n) = f(\omega_n) A_{uv}, \qquad (10)$$

$$A_{uv} = \int d\mathbf{r}\, d\mathbf{r}' \frac{\partial E_i(\mathbf{r})}{\partial Q^0_u} g_{ik}(\mathbf{r}, \mathbf{r}') \frac{\partial E_k(\mathbf{r}')}{\partial Q^0_v} \qquad (11)$$

The parameter A_{uv} depends on the shape of the particle, on the derivatives of the dipole moment of the particle with respect to the normal coordinates of the intramolecular vibrations of the impurity, and on the effects of the spatial dispersion of the condensed medium.

For spherically symmetric particles placed in a local homogeneous medium, the parameter A_{uv} is equal to

$$A_{uv} = A = -\frac{8\pi c_0 \omega_0}{3r_0^3} \left(\frac{\partial \vec{d}}{\partial q}\right)^2, \qquad (12)$$

Where r_o is the radius of the particle.

The simplest model for taking into account the effects of spatial dispersion of a condensed medium is the pole approximation for the function $f(\omega_n)$:

$$f(\omega_n) = \sum_{k=1}^{m} \frac{a_k}{\omega_k - \omega_n}, \qquad (13)$$

Where ω_k are the natural vibration frequencies of the medium, which can be complex, m is a number of poles, a_k are the intensities of the absorption peaks.

3. Green's function of operators of normal coordinates of intramolecular vibrations of an impurity particle with one optically active degree of freedom.

Above, a model was accepted within the framework of which the analytical form of the renormalized interaction is known. To analyze the vibration frequency spectrum of an impurity particle, it is necessary to carry out an analytic continuation from the discrete points $\omega_n = 2\pi nkT$ to the complex frequency plane.

As a result, for a particle with one optically active frequency, we obtain for the Green function

$$g_{QQ} = (\omega_s^2 + \omega_n^2 + U(\omega_n))^{-1} \tag{14}$$

where ω_s is the frequency of the intramolecular vibration of the impurity particle.

For the Laplacian image of the time retarded function of the operators of normal coordinates of intramolecular vibrations of an impurity, when using the pole approximation for renormalized interaction U in the form (13), the vibration spectrum is determined from the equation

$$(\omega_s^2 + p^2) \prod_{i=1}^{l}(\omega_i - p) + 2\sum_{i=1}^{l} a_i A \prod_{k=1,k\neq i}^{l}(\omega_k - p) = 0. \tag{15}$$

A special case of the pole approximation of the function f(ω) is the Debye function:

$$g(r, r'; \omega) = \frac{c_0}{4\pi}\frac{\gamma_0}{\gamma_0 + i\omega} \tag{16}$$

And for the $g_{QQ}(p)$ function at that, we have

$$g_{QQ}(p) = -\frac{\gamma_0 + p}{(p^2 + \omega_s^2)(p + \gamma_0) - \gamma_0\omega_s^2\kappa}, \tag{17}$$

Where κ is the bond strength coefficient

$$\kappa = -\frac{Ac_0}{4\pi}, \tag{18}$$

c_0 is a dimensionless constant equal to the difference between the reciprocal values of the dielectric constant of the medium to the right and left of the corresponding absorption peak. The frequency absorption spectrum of the system is determined from the solution of the equation

$$F(p) = (p^2 + \omega_s)(p + \gamma_0) - \gamma_0\omega_s^2\kappa = 0. \tag{19}$$

This equation always has one real root, and the other two are either real or complex conjugates, depending on the parameters in the equation (19).

The real root of this equation $p = p_0$ means the dissociation of the molecule if the polar medium is a liquid, or the transition of the molecule to another conformational state if the medium is a solid.

As the analysis of equation (19) shows, if the bond strength coefficient $\kappa \leq 1$, then for the two roots of equation (19) p_1 and p_2 the relation $\mathrm{Re}p_1 < 0$, $\mathrm{Re}p_2 < 0$ is valid.

In this case, the time retarded Green function of the operators of normal coordinates of intramolecular vibrations of the impurity for the Debye approximation of the Green function of the operators of fluctuations of the medium polarization has the form

$$g_{QQ}(t) = -\theta(t)\Big(\frac{\omega_s(\gamma_0 + p_0)}{(p_0 - p_1)(p_0 - p_2)}\exp(p_0 t) + \frac{\omega_s(\gamma_0 + p_1)}{(p_1 - p_0)(p_1 - p_2)}\exp(p_1 t) \tag{20}$$

$$+ \frac{\omega_s(\gamma_0 + p_2)}{(p_2 - p_0)(p_2 - p_1)}\exp(p_2 t)\Big)$$

The first term on the right side of the relation characterizes the process of pure damping of oscillations in time, the next two terms are either oscillations (at κ = 0), or damping with oscillations, or pure damping. Decays with oscillations have a physical meaning at κ « 1.

For the resonance approximation of the Green function of the operators of fluctuations of the polarization of the medium, we have

$$g(\mathbf{r},\mathbf{r}';\,\omega_n) = \frac{c(\omega_r^2+\gamma^2)}{8\pi\omega_r}\left(\frac{1}{\omega-\omega_r+i\gamma} - \frac{1}{\omega+\omega_r+i\gamma}\right) \tag{21}$$

Where ω_r is the characteristic frequency of medium oscillations, γ is the attenuation of medium oscillations.

The renormalized interaction has the form as follows:

$$U(\omega_n) = \kappa\,\frac{\omega_r^2+\gamma^2}{(\omega_n+\gamma)^2+\omega_r^2} \tag{22}$$

The Laplasian image of the Green function of the operators of normal coordinates of intramolecular vibrations of an impurity has the form

$$G_{QQ} = -\frac{\omega_s((\gamma+p)^2+\omega_r^2)}{(p^2+\omega_s^2)((p+\gamma)^2+\omega_r^2-\kappa\omega_s^2(\omega_r^2+\gamma^2))}. \tag{23}$$

Where the Green function of poles g_{QQ} are determined from the equation

$$\varphi(p) = p^4 + 2\gamma p^3 + (\omega_r^2+\gamma^2+\omega_s^2)p^2 + 2\gamma\omega_s^2 p + \omega_s^2(\omega_r^2+\gamma^2)(1-\kappa) = 0. \tag{24}$$

It can be seen from the general analysis that this function can have either two real roots and two - complex conjugates or all roots complex (pair wise) conjugates. The study of the equation shows that if κ ‹1, then the real roots of the equation (24) are always negative, and the real parts of the complex conjugate roots vary from -γ to 0. Thus, the bond strength coefficient should not exceed the critical value κ =1. Equation (24) has real roots at the values of the bond strength coefficient $\kappa^* \le \kappa < 1$, where κ^* is the value at which the values of the real roots coincide, i.e. $p_1 = p_2 = \alpha$. For highly resonant media where the condition $\gamma \ll \omega_r$ is satisfied, the value of α is equal to

$$\alpha = -\gamma\omega_r^2/(\omega_r^2+\omega_s^2). \tag{25}$$

For the complex conjugate values of the roots of equation (24) we have

$$p_{3,4} = -\frac{\gamma\omega_s^2}{\omega_r^2+\omega_s^2} \pm i\sqrt{\omega_r^2+\omega_s^2}\left(1-\gamma^2\frac{\omega_r^2\omega_s^2}{(\omega_r^2+\omega_s^2)^3}\right). \tag{26}$$

In this case, the value of κ^* is equal to

$$\kappa^* = 1 - \frac{\gamma^2}{\omega_s^2}\,\frac{\omega_r^2+2\omega_s^2}{\omega_r^2+\omega_s^2}. \tag{27}$$

When a strong connection with the medium is 1 – κ « 1 for arbitrary values of γ, one can find an approximate value of only one real root

$$p_1 = -(1-\kappa)\frac{\omega_r^2+\gamma^2}{2\gamma}. \tag{28}$$

If the medium is described by undamped oscillations with γ = 0, then the “beating” effect occurs in the system, at which

$$p_{1,2} = \pm\frac{i}{\sqrt{2}}(\omega_r^2+\omega_s^2-((\omega_r^2-\omega_s^2)^2+4\kappa\omega_r^2\omega_s^2)^{0.5})^{0.5},$$

$$p_{3,4} = \pm\frac{i}{\sqrt{2}}(\omega_r^2+\omega_s^2+((\omega_r^2-\omega_s^2)^2+4\kappa\omega_r^2\omega_s^2)^{0.5})^{0.5}. \tag{29}$$

It is easy to see that in the limit κ = 0 we obtain the frequencies of non-interacting oscillators with the characteristic frequencies of the impurity particle and the medium:

$$p_{1,2}^0 = \pm i\,\omega_s, \qquad p_{3,4}^0 = \pm i\,\omega_r. \tag{30}$$

Similarly to the calculations performed, one can also analyze systems in which an impurity particle has two optically active degrees of freedom.

4. Vibration spectra of a molecule N_2O in polar solvents: methyl alcohol, ethyl alcohol, acetone, 1.2-dichloroethane.

During the transition from the vacuum state to the condensed phase, the vibration spectra of the molecule N_2O undergo significant changes - there is a shift in the maximum of the absorption peak, broadening of the absorption peak, redistribution of intensities between different absorption peaks [14, 15]. Several solvents were chosen for quantitative processing of the experimental data. Methyl and ethyl alcohols, for the reason that they are the same type of solvents, however, the shifts in the absorption peak of the frequencies of the valence vibrations of the molecule N_2O occur in different directions. Such effects are observed in acetone - the frequency shifts towards an increase, and in 1.2 dichloroethane - the frequency decreases.

The frequency of the valence vibration of a bond ν_3 of N_2O molecule in vacuum is 2223 cm^{-1}.

Obviously, in this case, the frequency of the main level will be 1111.5 cm^{-1}, and the frequency of the first excited level will be 3334.5 cm^{-1}.

It is essential to take into account the effects of frequency and spatial dispersions of solvents phenomenologically.

The change in the square of the frequency of the valence vibration of the impurity, caused by the solvation of the impurity by the molecules of the medium, will take the form:

$$\Delta\omega^2 \approx -\frac{4\pi c_0}{3r_0^3}\left(\frac{\partial\vec{d}}{\partial q}\right)^2 = -\kappa\frac{\omega_g^2}{2}, \quad (31)$$

Where ω_g is the frequency of the vibration level, κ is a phenomenological parameter, the value of which can be estimated from experimental data.

The frequency dependence of the renormalized interaction can be presented in the form

$$U(\omega) = \kappa\delta\sum_{j=1}^{4}\frac{u_i}{(\omega-\omega_i)^2+\gamma_i^2}, \quad (32)$$

where δ is a dimensionless variable parameter, the values of the parameters u_i, γ_i and ω_i can be determined from the absorption spectra of the solvents [16]. Measurements were carried out on a Specord 75 IR infrared spectrophotometer (Table 1-4).

Table 1. Spectral parameters of the IR absorption spectrum o methyl alcohol

ω_i	γ_i	u_i
1030	60	0.85
1120	60	0.25
2850	60	0.75
3335	400	0.90

Table 2. Spectral parameters of the IR absorption spectrum of ethyl alcohol

ω_i	γ_i	u_i
1050	60	0.95
1085	60	0.80
2750	200	0.75
3325	380	0.90

Table 3. Spectral parameters of the IR absorption spectrum of Acetone

ω_i	γ_i	u_i
1100	30	0.23
1220	25	0.85
1365	35	0.83
3000	100	0.32

Table 4. Spectral parameters of the IR absorption spectrum of 1,2- dichloroethane

ω_i	γ_i	u_i
1015	25	0.45
1230	25	0.73
1315	25	0.70
2950	95	0.35

The energies of the vibration levels of an impurity can be easily calculated under the assumption that the valence vibration does not interact through the medium. In this case, to calculate the energy of vibration levels of the particle, we obtain the following equation:

$$\left(\omega^2 - \omega_s^2 + \kappa\frac{\omega_s^2}{2}\right)\prod_{j=1}^{4}\left((\omega - \omega_j)^2 + \gamma_j^2\right) + \omega_s^2\kappa\delta\sum_{i=1}^{4} u_i\gamma_i\prod_{j=1, j\neq i}^{4}\left((\omega - \omega_j)^2 + \gamma_j^2\right) = 0 \quad (33)$$

Based on this level, the values of the main level (frequency ω_0) and the first excited level (frequency ω_1) of the bond N - O are calculated at various values of the parameters of the bond strength with the medium κ and the dielectric properties of the solvent δ (see Table5).

According to this Table, the solvation and fluctuation mechanisms of the interaction of a molecule N_2O with solvents leads to a shift of the ground and excited vibration levels towards higher energies. The energy of the vibration transition from the ground level to the energy level, in which all vibrations of the molecule, except ν_3, are in the ground state, the valence vibration of the N-O bond in the first excited state was determined as the difference $\omega_1 - \omega_0$.

When choosing the parameters κ and δ, it must be taken into account that the parameter κ is dimensionless, see formula (31). For this reason, it is natural that when calculating for the frequencyω_0, the parameter κ will be 3 times larger than for ω_1.When it comes to the parameter δ in acetone and 1,2-dichloroethane it can be chosen to be approximately the same for the frequencies ω_0 and ω_1, since the absorption spectra of these solvents are separate peaks against a uniform background (input of the parameter δ is associated with the presence of this background).

Table 5. Vibration bond levels of the molecule of the ground and first excited state in methyl, ethyl alcohols, acetone and 1.2-dichloroethane.

	ω_0					ω_1				
Solvent	κ	δ_0				κ	δ_1			
		0.1	0.3	0.5	1.0		0.1	0.3	0.5	1.0
Methyl alcohol	0.02	1105	1104	1103	1099	0.01	3324	3321	3318	3309
	0.03	1102	1100	1098	1093	0.015	3319	3314	3309	3296
						0.02	3314	3308	3301	3284
Ethyl alcohol	0.02	1104	1101	1098	1089	0.01	3325	3321	3318	3310
	0.03	1101	1096	1091	1076	0.015	3320	3315	3310	3297
						0.02	3314	3308	3301	3285
Acetone	0.02	1106	1105	1104	1103	0.01	3322	3322	3322	3321
	0.03	1103	1102	1102	1098	0.015	3318	3317	3317	3317
						0.02	3326	3326	3326	3326
1,2-dichloroethane	0.02	1106	1106	1106	1105	0.01	3326	3326	3326	3325
	0.03	1103	1103	1103	1102	0.015	3322	3322	3322	3322
						0.02	3318	3318	3318	3318

For methyl and ethyl alcohols, the IR spectra have a more complex structure with an uneven background, and when calculating $\Omega = \omega_1 - \omega_0$, the parameters δ_0, , δ_1 for ω_0 and ω_1 can have different values for the ground and first excited energy levels.

The best agreement between the calculated frequency shift $\Delta\Omega_{calc}$ and the experimental data $\Delta\Omega_{exp}$ for all solvents was obtained at κ_0 = 0.003 for ω_0 and κ_1 = 0.001 for the level ω_1. For parameters δ - choice from a wider range (Table 6).

Table 6. Theoretical and experimental values of the shift of absorption peaks of the N_2O molecule in methyl, ethyl alcohols, acetone and 1.2-dichloroethane.

Solvent	κ_0	κ_1	δ_0	δ_1	Ω cm^{-1}	$\Delta\Omega_{calc}$, cm^{-1}	$\Delta\Omega_{exp}$, cm^{-1}
Methyl alcohol	0.03	0.01	0.3	0.1	2224	-1	-0.9
			0.5	0.3	2223	0	
	0.03	0.01	0.1	0.3	2220	3	0.8
			0.3	0.5	2222	1	
Ethyl alcohol	0.03	0.01	0.1	0.1	2223	0	-2.6
			0.3	0.3	2224	-1	
			0.5	0.5	2224	-1	
			1.0	1.0	2228	-5	
1,2-dichloroethane	0.03	0.01	0.1	0.1	2223	0	0.9
			0.3	0.3	2223	0	
			0.5	0.5	2223	0	
			1.0	1.0	2223	0	

Conclusion

The mechanisms of the influence of a condensed medium on the vibration spectrum of individual impurity particles are considered. It shows that the condensed medium causes a shift and broadening of the absorption peaks of impurity particles and can lead to the dissociation of particles into separate fragments.

It should be noted that the effect of a condensed medium on the vibration spectrum of impurity particles occurs through two interaction mechanisms - solvation and fluctuation. Each mechanism was studied in detail, and analytical results were obtained that allow one to take into account the effects of the solvation of an impurity molecule by the molecules of the medium, as well as the interaction of intramolecular vibrations of the impurity with fluctuations of the medium polarization.

Theoretical results are applied to analyze the vibration spectra of the N_2O molecule in polar solvents: methanol, ethyl alcohol, acetone, 1.2-dichloroethane.

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ТЕОРЕТИЧЕСКИЕ АСПЕКТЫ КОЛЕБАТЕЛЬНОЙ СПЕКТРОСКОПИИ КОНДЕНСИРОВАННЫХ СИСТЕМ С ПРИМЕСНЫМИ ЧАСТИЦАМИ

Т. Марсагишвили, М. Мачавариани

Тбилисский государственный университет им. И.Иванишвили,
Институт неорганической химии и электрохимии им. Р. Агладзе
Ул. Миндели, 11, 0186, Тбилиси, Грузия
e-mail: tamaz.marsagishvili@gmail.com

Аннотация: В работе рассмотрены некоторые проблемы колебательной спектроскопии частиц в конденсированных системах. Один из аспектов теоретических исследований представляет собой изучение колебательных свойств отдельных частиц с учетом нано-размерности окружающих частицу молекул конденсировааной системы. С использованием аппарата температурных функций Грина операторов поляризации конденсированных систем выделены два основных механизма влияния на примесные частицы со стороны среды – сольватационный и флуктуационный. Получены теоретические результаты в рамках этих двух механизмов для расчета изменения колебательного спектра отдельных частиц. Теоретические результаты использованы для анализа экспериментальных данных по колебательным спектрам молекулы N_2O в полярных растворителях: метиловом спирте, этиловом спирте, ацетоне, 1.2-дихлорэтане.

Ключевые слова: колебательная спектроскопия, конденсированные системы, сольватация, примесные частицы, пространственная дисперсия, функции Грина.

QARIŞIQLARIN HİSSƏCİKLƏRİ İLƏ KONDENSASİYA OLUNMUŞ SİSTEMLƏRİN VİBRASİON SPEKTROSKOPİYASININ NƏZƏRİ ASPEKTLƏRİ

T. Marsaqişvili, M. Maçavariani

İ. İvanişvili adına Tbilisi Dövlət Universiteti
R. Aqladze adına Qeyri-üzvi və Elektrokimya İnstitutu
Mindeli küçəsi 11, 0186, Tbilisi, Gürcüstan
e-mail: tamaz.marsagishvili@gmail.com

Xülasə: Bu işdə kondensasiya olunmuş sistemlərdə hissəciklərin vibrasiya spektroskopiyasının bəzi problemləri nəzərdən keçirilir. Nəzəri tədqiqatın aspektlərindən biri də hissəciyi əhatə edən kondensasiya olunmuş sistemin molekullarının nanoölçüsü nəzərə alınmaqla ayrı-ayrı hissəciklərin vibrasiya xassələrinin öyrənilməsidir. Mühitin hissəciklərə təsirinin iki əsas mexanizmi fərqləndirilib - solvatasiya və fluktuasiya. Ayrı-ayrı hissəciklərin vibrasiya spektrinin dəyişməsini hesablamaq üçün bu iki mexanizm çərçivəsində nəzəri nəticələr əldə edilib. Nəzəri nəticələr polyar həlledicilərdə: metanol, etil spirti, aseton və 1,2-dixloretanda N_2O molekulunun vibrasiya spektrləri üzrə eksperimental məlumatların təhlili üçün istifadə olunur.

Açar sözlər: vibrasiya spektroskopiyası, kondensasiya olunmuş sistemlər, həlletmə, qarışıqlı hissəciklər, fəza dispersiyası, Qrin funksiyaları.