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DETERMINATION OF CHARACTERISTIC OPTIC WAVELENGTHS FOR RELIABLE CONTROL OF SUBSTANCE COMPOSITION

The given paper suggests the method of selection of information and reference optic wave for measurement of substance composition applying optic methods, future trends concerning the usage of various optical ranges for express-measurement of substance composition are considered.

Key words: Schrödinger wave equation, Hamiltonian operator, spectrum, quantum number.

Introduction

One of the most complex technological problems, facing the enterprises of processing industry of agrarian branch of national economy is to provide automatic control of substance composition in initial products. First of all, it is stipulated by the lack of accurate measuring converters of non-electric values in electric ones, that could be used as means of measuring control over the systems of automatic control of technological processes. Such situation can be explained by non -ability to apply the direct methods for the solution of the given problem as a result of their low operation rate and dependence of measurements results of indirect control facilities (conductometric, dielcometric, thermophysical and other measuring methods) on non-information parameters, such as ambient temperature, illumination level of workshops, electrical and magnetic permeability of air layers that are located between measuring device and the object of control, as well as lack of adequate theoretical models [1, 2].

Taking into account the above-mentioned, it becomes evident that to provide highest possible level of control validity, it is necessary to apply basically new approaches for the solution of the given problem.

One of the approaches is the application of optical methods of comparative analysis, presented in [3]. However, as practical experience shows, their application is limited by practical obstacles, connected with the correct choice of reference and measuring channels frequency. This is stipulated by considerable complexity of molecular spectra, as compared with atomic ones, due to mutual overlapping of linear spectra of atoms, composing a molecule and spectra of interatomic interaction [4].

Problem set-up

While combining atoms into molecules, their electronic shells are united. Electromagnetic fields, appearing as a result of molecule formation in the process of approaching of electronic shells of the atoms, are not spheric and symmetrical, as in the atom [4-6]. Emerging of new degrees of molecule motion freedom influences the structure of its energy levels and, correspondingly on structure of molecule spectrum [5].

Presence of two or more positively charged nuclei in the molecule, considerably complicates the behaviour of charged particles system. If in atom, applying quantum mechanics, distribution of electron emergence probability in the field of only one nucleus is considered, then in the given case it is necessary to consider both the distribution of electrons emergence probability in the field of two or more nuclei, and location of nuclei in the space relatively the preset coordinate system [4, 6].

In the second half of the last century numerous research of radiation spectra were performed. It was established that radiation spectra of molecules consist of wide blurring bands without sharp boundaries [4]. This is determined by the complexity of internal motion in the molecule, as besides electrons motion around several nuclei in the molecule oscillatory motion of nuclei (together with

electrons orbiting around them) occurs around equilibrium position and rotary motion of the molecule as the whole. It follows, that electronic, oscillatory and rotational motion of the molecule,

correspond three types of energy levels $E_{el} E_{os} E_{rot}$ and, consequently, three types of molecular line spectra, which are overlapped. Since lines in spectra are arranged regularly [5] then, having established this regularity for the molecule of the substance, being the object of control, we can obtain the exact list of electromagnetic wavelengths of the optic region, that can be used as information waves.

Hence, knowing the laws of light absorption we can define theoretically the probability of absorption of optic energy quantum for any rather narrow wavelength range. Then, in accordance with the law of light distribution, light that passes through optic filter or is emitted by photodiode, the intensity of transmitted or reflected wave can be connected with the content of controlled substance.

Such approach enables to perform the transition from the system of experimental approximated static characteristics of the sensor to the possibility of theoretical deduction of the equation of measuring facility conversion by means of solution of quantum equation, which is of statistic character.

Analysis of methods of problem solution

Of all properties of atoms and molecules, the most important one is their internal energy E. Fundamental equation, that connects the energy of the system with its wave function ψ is stationary Schrodinger wave equation [8]:

$$\overline{\mathbf{H}} \cdot \boldsymbol{\psi} = \mathbf{E} \cdot \boldsymbol{\psi} \,, \tag{1}$$

where \overline{H} – is complete energy operator (Hamiltonian operator).



Fig. 1. Diagram of diatomatic molecule energy levels

To define theoretically stationary energy states of particles system (atom, molecule, ion) and further calculate spectra of thermodynamic functions, it is necessary to compose Hamiltonian operator \overline{H} for the system and solve equation (1). However, Schrodinger wave equation is solved only for the simplest model systems. For the molecule Schrodinger equation becomes so complicated, that its analytical solution is possible only for the simplest diatomic molecule-- ion H_2^+ at fixed location of nuclei. That is why, for the solution of practical problem it is expedient to use the approximated representation of complete wave function of the molecule in the form of the following product, that for the given case is rather accurate [5]:

$$\psi = \psi_{el} \cdot \psi_{osc} \cdot \psi_{rot} \,, \tag{2}$$

where multipliers $\psi_{el} \ \psi_{osc}$ and ψ_{rot} are related to the motion of electrons, oscillatory motion of nuclei and rotational motion of the molecule as a whole, correspondingly. This enables to solve Schrodinger wave equation separately for electronic, oscillatory and rotational wave function.

In accordance with quantum mechanics and above mentioned approximation (2) energy of all kinds of motion in the molecule may obtain only quantized values [4,6,7]. In this case full energy of molecule can be presented in the form of quantized values of energy, which correspond to three kinds of its internal motion (Fig. 1) [5]. Thus:

$$E = E_{el} + E_{osc} + E_{rot}$$
(3)

the above indicated values are interrelated in the following manner [5]:

$$E_{el}: E_{osc}: E_{rot} = 1: \sqrt{\frac{m}{M}}: \frac{m}{M}$$
(4)

where m – is the mass of electron, and M has the order of nuclei mass in the molecule, i. e.

$$\frac{m}{M} = 10^{-3} \div 10^{-5}$$
(5)

correspondingly:

$$E_{el} \gg E_{osc} \gg E_{rot}$$
(6)



Fig. 2. Two low potential curves of hydrogen molecules

As a rule, E_{el} has the order of several eV (visible and near-ultra-violet region), $E_{osc} = 10^{-2} \div 10^{-1} \text{ eV}$ (and near-ultra-red region), $E_{rot} = 10^{-5} \div 10^{-3} \text{ eV}$ (deep-infra-red region) [5]. In accordance with (6), equation system of molecules energy is characterized by the system of spaced energy levels. In the Fig 1 a and b correspond to electron levels, V' and V'' – correspond to quantum number of oscillatory levels, J' and J'' correspond to quantum numbers of rotation levels.

But while considering certain problems of molecular spectrometry we cannot help taking into

account the interaction of various kinds of motion in the molecule. For instance, one of the symptoms of such interaction between the motion of electrons and nuclei is the dependence of electron energy on relative location of nuclei, that leads to the notion regarding the curves and surfaces of potential energy in the molecule [5, 8]. While approaching of two atoms from infinity to small distances, their potential energy U(r) passes across minimum or constantly increases (repulsive potential curve) – Fig 2 [5]. In the first case stable molecule with interatomic distance r_e that corresponds to minimum potential energy is formed. In the second case, stable molecule is not formed. Each molecule corresponds to a family of potential energy curves (including repulsive curves), their relative location and shape are characterized for the system of nuclei and electrons, forming the molecule [6, 7].

Fig 2 shows two low-potential lines for the simplest diatomic molecule of hydrogen. From traditional point of view, the potential curve can be treated as geometric place of amplitude locations of harmonic oscillator, depending on its energy. The form of real potential curves is obtained from spectroscopic experimental data [8]. For their analytical description various approximated expressions are used. However, in case of stable potential curve, irrespective of type of function U(r) it can be decomposed into a series in circumference of the point $r_e[5]$:

$$U(\mathbf{r}) = U(r_e) + \left(\frac{dU}{dr}\right)_{r=r_e} (r - r_e) + \frac{1}{2} \left(\frac{d^2 U}{dr^2}\right)_{r=r_e} (r - r_e)^2 + \dots$$
(7)

For the minor deviations of nuclei from equilibrium state we can neglect other components, and s minimum we may assume $\left(\frac{dU}{dr}\right)_{r=r_e} = 0$. Having taken the value U(r_e) as the starting point of count, we may assume, accordingly, that U(r_e)=0. As a result [8]

$$U(r) = \frac{1}{2} \left(\frac{d^2 U}{dr^2}\right)_{r=r_e} (r-r_e)^2 = \frac{1}{2} K(r-r_e)^2 \text{ where } K = \left(\frac{d^2 U}{dr^2}\right)_{r=r_e}$$
(8)

The expression (8) has the same form as the expression for the energy of harmonic oscillator with elasticity factor K. Substitution (8) for oscillator energy Ev in Schrödinger equation yields the following expression for oscillating energy of harmonic oscillator

$$E_{\nu} = (\nu + \frac{1}{2})\omega_e hc \tag{9}$$

where $\nu = 1,2,3...$ – oscillating quantum numbers; ω_e – frequency of oscillations cm⁻¹; h – Plank constant ; c – light speed. The expression (9) can be used for approximated calculations of oscillatory energy of molecules at minor deviations form equilibrium. In accordance with the statement regarding the short stay of the molecule in exited state [6] and on condition of the lack of strong external excitations, the accuracy of values, obtained by means of (9), completely satisfy the specified technical requirements

For simplified case, when the object of control is diatomic molecule of the substance, using Morse function, we obtain [8]:

$$U(r - r_e) = D_e \{1 - \exp[-\beta(r - r_e)]\}^2,$$
(10)

where D – is the energy of dissociation into molecule, calculated from the minimum of potential curve (Fig.2), where β coefficient is defined as

$$\beta = \omega_{\rm e} \left(\frac{2\pi^2 \mu c}{D_e h}\right)^{1/2} \tag{11}$$

and μ is the given mass of the molecule .

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Morse function for H_2 for the molecule is shown in Fig 2 by dashed line. Quantum values of oscillation energy of anharmonic oscillator (10) correspond to potential curve [8, 7].

$$\mathbf{E}_{\nu} = hc \left[\omega_e \left(\nu + \frac{1}{2} \right) - \omega_e x_e \left(\nu + \frac{1}{2} \right) \right], \tag{12}$$

where $\omega_e x_e$ – inharmonicity coefficient, cm⁻¹.

It should be noted, that (12) rather accurately describes the system of oscillation energy level of diatomic molecule. Only with small inharmonicity. For description of the molecules with strongly expressed inaharmonicity (for instance, H2), the second $(\omega_e y_e)$, third etc, inaharmonicity coefficients are used.

For rotation energy, the solution of Schrödinger equation for the simplest case of diatomic molecule, taking into account the above-mentioned considerations, can be written as:

$$E_{r} = hc[B_{\nu}J(J+1)],$$
(13)

where B_{ν} – is rotational constant (cm⁻¹) for the given oscillating state ν ; J – is rotational quantum number.

While transition of the molecule from one level of rotation energy into another level, at stable electron and oscillation levels purely rotational spectra are observed. As it was already mentioned above, these spectra are in far infrared region. Infra-red oscillation rotational spectra have the form of band, with rotational structure. Arrangement and intensity of lines in emission and absorption spectra are defined by the rules of selection; probabilities of transition and population upper (U', J') and lower (U'', J'') states of molecule. It should be noted that purely rotational and oscillation rotational transitions are possible only if electric dipole moment is available in the molecule. This fact considerably facilitates the identification of clearly expressed polar molecules as it enables to use for their identification information wave of smaller frequency.

Absorption and emission spectra while transition of molecule from one electronic state into another are referred to as electronic ones, although it would be more correctly speak about electronic-oscillating-rotational transitions, as simultaneously with electronic state oscillating and rotational state of the molecule changes. Hence, using (3), (12), (13), the system of all possible energy states of diatomic molecule can be presented as:

$$E = E_{e} + E_{v} + E_{r} = E_{e} + hc \left[\omega_{e} \left(v + \frac{1}{2} \right) - \omega_{e} x_{e} \left(v + \frac{1}{2} \right) \right] + hc \left[B_{v} J (J + 1) \right]$$
(14)

or, using the notion of therms, applied in spectrometry (i. e. energy, expressed in units cm⁻¹)

$$T = T_{e} + G(v) + F(J) = T_{e} + \left[\omega_{e}\left(v + \frac{1}{2}\right) - \omega_{e}x_{e}\left(v + \frac{1}{2}\right)\right] + \left[B_{v}J(J+1)\right]$$
(15)

where G(v) = F(J) generally accepted designations for oscillating and rotational therms; T_{e-} therm of purely electronic excitation, that is assumed to be equal zero for basic electronic state.

Wave numbers of possible electronic-oscillating-rotational transitions are expressed by the equations [8]:

$$v = T' - T'' = T_e + \left[\omega'_e \left(v + \frac{1}{2}\right) - \omega'_e x'_e \left(v' + \frac{1}{2}\right)\right] + \left[\omega''_e \left(v'' + \frac{1}{2}\right) - \omega''_e x''_e \left(v'' + \frac{1}{2}\right)\right] + \left[B'_v J'(J'+1)\right] - \left[B''_v J''(J''+1)\right]$$
(16)

where all the values with one prime are referred to the state with larger energy (upper state), values with two primes- to lower state, v = T' - T'' wave number of electron transition, $B'_v \neq B''_v$ Наукові праці ВНТУ, 2010, № 2

and the fact that rotational constant changes while variation of inter – nucleus distance is taken into account.

Rotational-oscillation absorption and emission spectra are observed for all the molecules. The totality of spectra lines, available at electron-oscillation-rotational transition is called system of bands, and the spectrum itself – band spectrum, number of lines, corresponding to certain difference of oscillating quantum numbers v' - v'' is called band. With each band we can distinguish (at sufficient resolution of the device) rotational structure that is superposition of three branches, which unambiguously correspond to the rules of selection for rotational quantum number: $\Delta J = 0,+1,-1$ [6]. Corresponding branches are called P, Q, and R – branches.

In the point, where the lines of rotational structure become more concentrated the boundary of the band is located. The emergence of the boundary is caused by the difference of values of rotational constants $B'_{\nu} \ \pi \ B''_{\nu}$ in the equation (16). Absolute difference $|B'_{\nu} - B''_{\nu}|$ for the majority of electron transitions is considerably greater, than for oscillating ones (which occur without change of electron state). That is why, the presence of quantum bands is characteristic feature of electron-oscillation-rotational spectra, where as in oscillating rotational IR spectra the boundaries are not observed.

As the example we will consider the algorithm of investigation of electronic- oscillatingrotational absorption spectrum of diatomic molecule of iodine. Investigated absorption spectrum corresponds to electron transition ${}^{1}\sum_{g}^{+} \rightarrow {}^{3}\prod_{0u}^{+}$ and is located in the area of long waves 490 < v < 650 M (15400 < v < 20400 cm⁻¹) [5, 8]. At temperatures, close to room temperature and if other external sources of excitation are missing, greater part of molecules (<<65%) are in low oscillation state v'' = 0 of basic electron state ${}^{1}\sum_{g}^{+}$ [5, 8], then internuclei distance r'_{e} is 0,4 A greater than r''_{e} [5]. That is why, transitions, being observed, arrived at left ("slope") branch of potential curve. In absorption spectrum intensive v'' – progression with v'' = 0. In spite of the fact that the positions from v'' = 1,2,... in accordance with Boltsman distribution law less populated, the probability of transitions from these positions is rather high [4], and progressions from v'' = 1,2,...

While dissociation from the basic electron state ${}^{1}\sum_{g}^{+}$ non-excited atoms in states ${}^{2}P_{\frac{3}{2}}$. are

formed. Excitation energy of iodine atom $\left({}^{2}P_{\frac{1}{2}} - {}^{2}P_{\frac{3}{2}}\right) E_{A} = 7603 \,\mathrm{cm}^{-1}.$

If we perform the analysis of oscillation structure of the given electronic transition, i. e. if we measure the values of wave numbers of bands and perform their distribution by indefinite values of oscillating quantum numbers v'' and v' bottom and upper electronic states, then we can define the coefficient of the equation (4), neglecting the oscillating term and, thus, define experimental value of molecular constants T_e , ω'_e , $\omega''_e x'_e$, $\omega''_e x''_e$. Statistical analysis of the experimental data, computing the dependencies of (4) kind, taking into account the above-mentioned simplification, is rather complicated and requires computer processing, that is why its presentation in the given research is not expedient. For determination of basic oscillating frequency ω_e and constant non-harmonic $\omega_e x_e$ simple method is used. First differences given electronic state that numerically are equal to the differences of wave numbers of neibouring bands of the given progression are defined and analyzed depending on v.

From the above-mentioned simplification at fixed value of v'' we obtain [5]:

$$V(v'+1) - V(v') = \Delta G_{v+\frac{1}{2}} = \omega_e' - 2\omega_e' x_e'(v'+1)$$
(17)

Linear dependence $\Delta G_{\nu+\frac{1}{2}}$ on ν allows to determine graphically molecular constants ω_e and

 $\omega_e x_e$. To improve accuracy of the obtained values it is expedient to perform regressive analysis (17) and define coefficient $2\omega'_e x'_e$.

Since progressions by v'' can be allocated in the spectrum, then, in such a way molecular constants can be defined for lower electronic state, in which, on condition of absence of active external exciting factor, the majority of molecules of the substance is [4, 6, 7].

Conclusions

From the above-mentioned it is obvious, that in general case determination of wavelength of reference and information waves can be realized by the solution of the system of Schrödinger equations for each of substance, available in controlled product. This enables to define the most efficient areas of absorption spectrum of controlled object, as well as provides the possibility to determine the number of absorption lines, occurring in the range of information wave. In accordance with the law of light absorption for spectrum lines and the law of distribution by the wavelength of information wave there appears the possibility of reduction of equation of conversion of such measuring device to statistic expression, that on condition of sufficient intensity of light flux (sufficient amount of light quanta per unit of time) provides high accuracy of measurements.

We can make a conclusion that the most efficient portion of spectrum for information wave while determining the amount of the substance, that consists of clearly expressed polar molecules is near infra red region. It is connected with the presence in such molecules of great electric dipole moment, which makes possible purely rotational and rotational-oscillating energy transistors.

For measurement of the amount of substance that consists of non-polar molecules the most promising wavelength of information wave are wavelengths that correspond to the boundaries of rotational lines of spectrum. It enables, at the expense of the amount of absorption lines, which are concentrated in the interval of information wave, to reach high intensity of light absorption that results in increase of sensitivity of measuring device.

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