

Calculation of Anharmonic Intensities in Vibrational Spectra of Raman Scattering and Full Interpretation of the Vibrational Spectrum of *trans*-1,3-Butadiene

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Abstract—The anharmonic model of vibrations of polyatomic molecule makes it possible, using the second-order perturbation theory, to interpret vibrational spectra in detail with resonances taken into account and to calculate the band intensities in spectra for fundamental frequencies, overtones, and combination frequencies. For molecules possessing a center of symmetry (to which *trans*-1,3-butadiene belongs), many vibration modes have zero intensities of absorption in IR spectra due to the mutual exclusion rule. For meaningful analysis of vibrations of such molecules, measurement of Raman scattering (RS) spectra is necessary, as is developing a theoretical model for calculating the anharmonic intensity. Perturbation theory (PT) in the form of contact transformations (CTs) has proven applicable for calculating the anharmonic intensities in RS spectra. The FORTRAN software program ANCO has been developed, which allows the calculation of vibration frequencies and IR–RS intensities of fundamental vibrations, overtones, and combination frequencies on the basis of second-order PT in form of CTs using the polynomial representation of potential energy, dipole moment and polarizability surfaces. The obtained frequencies and modes of anharmonic vibrations are provided, as well as interpretation of the experimental spectrum of the *trans*-1,3-butadiene molecule. A procedure for calculating the scale factors of the anharmonic force field is proposed. We also show that within the anharmonic vibration model, these factors are close to unity.

Key words: IR- and Raman spectra, anharmonic vibrations of molecules, anharmonic intensity, intensity of overtones and combination bands, perturbation theory, method of contact transformations, *trans*-1,3-butadiene, quantum-mechanical calculation, B3LYP.

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INTRODUCTION

Experimental study of the interaction between electromagnetic irradiation and matter allows us to measure the vibration–rotation spectra of absorption and scattering, which are characterized by their positions as well as intensities. The position of a spectral band is determined by the difference of energy values between the respective final and initial states of the molecule, while the intensity is determined by the integral, which contains the operator of the dipole moment of the molecule or the polarizability and wave functions regarding the states specified. In turn, the energy states are described by their eigenvalues and eigenfunctions of the Hamiltonian of the molecule (H). Hence, to complete the entire theoretical description of a molecular spectrum, it is necessary to know the type of operators specified, have a tool for determining the Hamiltonian's eigenvalues and func-

tions, and find the values of the matrix elements for the dipole moment or the polarizability operators.

In this work, we consider a theory corresponding to “semirigid” molecules [1], within which the operators of the potential energy, dipole moment, and polarizability of molecules are given as expansions in powers of internal coordinates at the point of the single energy minimum. If the consideration is limited to the quadratic potential function and linear terms of operators of dipole moments and polarizability, which corresponds to the simplest approximation “harmonic oscillator – rigid rotor,” the problem of frequencies and intensities can be solved precisely [2]. It is well-known that this approximation is too crude to describe a number of significant effects, for instance, the non-zero intensities of combination frequencies [3]. For more accurate reproduction of molecular spectra, it is necessary to consider an anharmonic problem where the operators listed are approximated by higher-order polynomials.

Despite the fact that the anharmonic problem cannot be solved analytically, we can find its numeric solution with high precision by virtue of the variational method (VM) [4]. Herein, the energy levels are determined by diagonalization of the matrix representation of the Hamiltonian, while the wave functions are sought in the form of linear combinations of basic functions of the “zero approximation,” i.e., the harmonic oscillator—rigid rotor functions. If the wave functions are known, there is a way to calculate the strength of lines too. As indicated in [5], for a triatomic molecule, the VM allows determination of all vibration—rotation levels of energy from the ground state to the dissociation limit. As the molecule under consideration becomes larger, the volume of calculations increases, which restricts the applicability of VM to only relatively small molecules. Since it is impossible to establish the functional correlation between the initial parameters of the Hamiltonian and spectroscopic constants, a solution of the inverse problem and construction of the so-called effective Hamiltonians are significantly complicated.

An alternative to VM for solving an anharmonic problem is another classical method of quantum mechanics: perturbation theory (PT) [6]. As one of the most efficient methods for solving an anharmonic problem in vibrational spectroscopy, an operator version of PT has been adopted that is called the method of contact transformations (CTs) [7–13]. There also exist other versions of PT [12] that yield similar results. The efficiency of the CT method has been convincingly proven in [14], where the vibration—rotation structure of the bands ν_1 and ν_3 for an H_2O molecule is predicted with a precision of $\sim 0.05 \text{ cm}^{-1}$.

The CT method also allows calculation of the integral intensity of vibrational bands in IR spectra in the anharmonic approximation, which has been considered in many publications (see, for example, [15–24]). However, for more adequate anharmonic analysis of vibrational spectra, it is also necessary to determine the intensities in the Raman spectra (RS), especially in the case of centrally symmetric molecules. There are just a few papers devoted to this point [25, 26]. Calculations of Raman intensity using the PT are also very rare [27]. In the present paper, we consider application of the CT method to calculate the Raman intensity and the creation of software for such calculations.

As an illustration of the method's possibilities, we present the results for a *trans*-1,3-butadiene molecule, which is interesting because of the presence of rotational isomerism. A half of its 24 fundamental frequencies are active only in the Raman spectra. A full analysis of experimental spectra is complicated by the presence of many overtones and combination frequencies. The possibility of theoretically predicting the values of their intensity would significantly simplify such an analysis.

For the anharmonic calculation of molecules similar to butadiene (ten atoms), the use of the most accurate quantum-mechanical methods (for example, CCSD(T)/aug-cc-pVnZ) makes no economical sense despite modern computing power. A more accessible method is B3LYP/6-31 + G(d,p), which recommends itself due to extensive calculations for organic molecules [28].

To achieve good agreement between the calculated and experimental fundamental frequencies, we used, in accordance with technique [29], a variation of harmonic frequencies that should make the prediction of overtones and combination tones more precise. The obtained harmonic frequencies make it possible to estimate scale factors of the force field, which can be used to calculate the spectra of 1,3-butadiene rotational isomers.

PERTURBATION THEORY IN THE FORM OF CONTACT TRANSFORMATIONS

The CT method, which is often called in the literature the canonical Van Vleck perturbation theory [7], is a modification of PT in terms of operators [8–13, 30–33]. It makes it possible to successfully solve many problems of molecular spectroscopy [12]. Let us consider its main aspects.

For the “unperturbed” problem (zero approximation), eigenvalues E_0 and eigenfunctions Φ_0 of Hamiltonian operator H_0 of harmonic oscillator are known in analytical form.

$$H_0\Phi_0 = E_0\Phi_0. \quad (1)$$

Despite the fact that the problem of a rigid rotor is also solved analytically, rotational corrections are ordinarily considered as perturbations [12]. Hence, it is necessary to find the eigenvalues E and eigenfunctions of the perturbed operator H that corresponds to the anharmonic oscillator—the nonrigid rotor, e.g., to solve the Schrödinger equation:

$$H\Phi = E\Phi. \quad (2)$$

Operator H is represented as the sum of H_0 and the perturbation operator V , which in turn can be represented as the sum of terms decreasing in order of magnitude.

$$H = H_0 + V = H_0 + \left(\sum_{n=1}^{\infty} H_n \right). \quad (3)$$

The operator H can be represented as a power series of parameter λ :

$$H(\lambda) = H_0 + V(\lambda) = H_0 + \sum_{n=1}^{\infty} \lambda^n H_n \equiv \sum_{n=0}^{\infty} \lambda^n H_n. \quad (4)$$

In this case, the eigenvalues and eigenfunctions of operator H will be functions of parameter λ .

$$H(\lambda)\Phi(\lambda) = E(\lambda)\Phi(\lambda). \quad (5)$$

Under the assumption that the respective derivatives exist, they can be expanded into series:

$$\begin{aligned} E(\lambda) &= E_0 + \sum_{n=1}^{\infty} \lambda^n E_n, \\ \Phi(\lambda) &= \Phi_0 + \sum_{n=1}^{\infty} \lambda^n \Phi_n. \end{aligned} \quad (6)$$

The key points of PT are the convergence of series (6) when parameter λ changes from zero to unity and the possibility of determining the expansion coefficients. There are different versions of PT [12] and, respectively, techniques for calculating the coefficients of series. Within the CT method, the Hamiltonian H is transformed using some unitary operator U that keeps the eigenvalues in (2) intact:

$$\tilde{H} = UHU^{-1}. \quad (7)$$

In this case, the Schrödinger equation (2) takes an equivalent form:

$$\begin{aligned} \tilde{H}\tilde{\Phi} &= E\tilde{\Phi}, \\ \text{where } \tilde{\Phi} &= U\Phi \text{ and } \Phi = U^{-1}\tilde{\Phi}. \end{aligned} \quad (8)$$

The operator U is chosen so that operator $\tilde{H}$ has as eigenfunctions the eigenfunctions of H_0 :

$$\tilde{\Phi} \equiv U\Phi = \Phi_0.$$

Since the operators with identical eigenfunctions commute, this condition means

$$[\tilde{H}, H_0] = 0. \quad (9)$$

Operator U is approximated by the product of operators converging to the unit one:

$$U = U_{\infty} \dots U_k \dots U_2 U_1, \quad (10)$$

which sequentially brings $\tilde{H}$ to the form of (9) in expansion according to the orders of smallness (4):

$$\begin{aligned} \tilde{H}^{(1)} &= U_1 H U_1^{-1}, \\ \tilde{H}^{(2)} &= U_2 \tilde{H}^{(1)} U_2^{-1}, \\ &\dots\dots\dots \\ \tilde{H}^{(k)} &= U_k \tilde{H}^{(k-1)} U_k^{-1}. \end{aligned} \quad (11)$$

The actual number of transformations (11) defines the order of PT. Operators U_k are represented in the form of an exponent:

$$\begin{aligned} U_k &= \exp(iS_k) \\ &= 1 + iS_k - \frac{1}{2}S_k^2 - i\frac{1}{6}S_k^3 + \dots = \sum_{n=0}^{\infty} \frac{i^n}{n!} S_k^n, \end{aligned} \quad (12)$$

i.e., a series in powers of some Hermitian operator S_k called the CT generator. The S_k generator does not contain a perturbation, and the latter is taken into account by its multiplication by λ^k :

$$U_k(\lambda) = \exp(i\lambda^k S_k) = \sum_{n=0}^{\infty} \frac{(i\lambda^k)^n}{n!} S_k^n. \quad (13)$$

Let us consider the case of the first contact transformation ($k = 1$). By inserting expansions (4) and (13) into (11) and combining terms of the same powers of λ , one can derive the following expression (the Campbell–Hausdorff formula):

$$\begin{aligned} \tilde{H}^{(1)} &= H + i\lambda[S_1, H] + \frac{(i\lambda)^2}{2!}[S_1, [S_1, H]] + \dots \\ &= H + \sum_{n=1}^{\infty} \frac{(i\lambda)^n}{n!} \underbrace{[S_1, [S_1, \dots [S_1, H] \dots]]}_n. \end{aligned} \quad (14)$$

If representation (4) of the operator H is inserted into (14) and the terms of identical powers of λ are combined, the transformed operator can be represented as a series in powers of λ :

$$\tilde{H}^{(1)}(\lambda) = \tilde{H}_0 + W(\lambda) = \tilde{H}_0 + \sum_{n=1}^{\infty} \lambda^n \tilde{H}_n. \quad (15)$$

To determine the expansion coefficients (15), let us put (15) into (14), transfer all terms to the right-hand side, and combine terms of the same powers of λ :

$$0 = H_0 - \tilde{H}_0^{(1)} + \sum_{n=1}^{\infty} \left(H_n - \tilde{H}_n^{(1)} + \sum_{m=0}^{n-1} \frac{i^{(n-m)}}{(n-m)!} \underbrace{[S_1, [S_1, \dots [S_1, H_m] \dots]]}_{n-m} \right). \quad (16)$$

Apparently, the right-hand side of the equation is equal to zero if each of the coefficients at powers of the perturbation parameter is also equal to zero. This gives us grounds to reformulate (16) in the form of a system of equations for an arbitrarily chosen n ($n > 0$):

$$\tilde{H}_n^{(1)} = H_n + \sum_{m=0}^{n-1} \frac{i^{(n-m)}}{(n-m)!} \underbrace{[S_1, [S_1, \dots [S_1, H_m] \dots]]}_{n-m}. \quad (17)$$

For a K -times transformed operator, one might derive the following expression (where $\delta = \text{mod}(n, K)$ is the remainder from division of n by K):

$$\begin{aligned} \tilde{H}_n^{(K)} = \tilde{H}_n^{(K-1)} + \sum_{m=0}^{\frac{(n-\delta)}{K}-1} \frac{i^{\frac{(n-\delta)}{K}-m}}{\left(\frac{(n-\delta)}{K}-m\right)!} \\ \times \underbrace{[S_K, [S_K, \dots [S_K, \tilde{H}_{Km+\delta}^{(K-1)}] \dots]}_{\frac{(n-\delta)}{K}-m}. \end{aligned} \quad (18)$$

An analogous formula from [30] contains an inaccuracy: the upper limit of summation is mistakenly specified as $(n - K - \delta)/2$. The operator S_K can be determined [12] from (17) at $n = K$ taking into account condition (9):

$$\tilde{H}_n^{(K)} = \tilde{H}_n^{(K-1)} + i[S_K, H_0]. \quad (19)$$

It is convenient to perform the calculation of S_K in the second quantization representation [12, 13, 34, 35]. As mentioned above, to solve a spectroscopic problem, it is necessary to know explicit forms of expressions for physically measurable parameters, e.g., the energies of vibration–rotation transitions and their intensities. The transition energy is determined by a matrix element of the Hamiltonian for wave functions, which corresponds to the initial and final states:

$$E_a - E_b = \langle \Phi^{(a)} | H | \Phi^{(b)} \rangle. \quad (20)$$

For the Hamiltonian of a harmonic oscillator H_0 , the wave functions and matrix elements are calculable analytically. In the case of the anharmonic oscillator due to the polynomial expansion of the Hamiltonian, wave functions (and, consequently, the matrix elements) are not determined analytically. The substitution of the contact-transformed Hamiltonian $\tilde{H}$ into (20), for which the wave functions coincide with the functions H_0 , makes it possible to solve the problem (20) analytically. For example, in the second order of CT, from the forms of generators S_1 and S_2 , it is possible to derive the explicit form of $\tilde{H}$ and find the formulas for matrix elements (20):

$$\langle \Phi^{(a)} | H | \Phi^{(b)} \rangle = \langle \Phi_0^{(a)} | \tilde{H} | \Phi_0^{(b)} \rangle. \quad (21)$$

In [8, 9], as well as in [1, 3, 4, 11, and 36], the formulas for effective Hamiltonians have been derived using CT. They are analytical functions of quantum numbers and the parameters of the Hamiltonian. The application of CT is not restricted to calculating the energies of states and transitions. If the analytical form of generators S is known, it is possible to obtain the representation of any other operator of a physical

quantity Ω in the basis of eigenfunctions of H_0 and, therefore, analytical formulas for matrix elements corresponding to the observable quantities:

$$\begin{aligned} \langle \Phi^{(a)} | \Omega | \Phi^{(b)} \rangle &= \langle (U^{-1} \Phi_0^{(a)}) | \Omega | U^{-1} \Phi_0^{(b)} \rangle \\ &= \langle \Phi_0^{(a)} | U \Omega U^{-1} | \Phi_0^{(b)} \rangle. \end{aligned} \quad (22)$$

The only requirement on the operator is the possibility of formulating it as the sum of terms of an increasing order of smallness, just like it is done for the initial Hamiltonian.

DIPOLE MOMENT OPERATOR AND INTENSITY OF IR ABSORPTION

For the Boltzmann distribution of molecules over states at absolute temperature T , the integral coefficient of absorption for the electric dipole transition $a \leftarrow b$ is determined by the formula [13, 33]

$$\begin{aligned} I^{(ab)} &= \int \varepsilon(\nu) d\nu \\ &= \frac{8\pi^3 N_A}{3hcQ} \nu^{(ab)} S^{(ab)} [e^{-E^{(b)}/kT} - e^{-E^{(a)}/kT}], \end{aligned} \quad (23)$$

which includes the Avogadro number (N_A), the Boltzmann constant k , the Planck constant (h), the speed of light in vacuum (c), the wave number of transition $\{\nu_{ab} = (E^{(b)} - E^{(a)})/hc\}$, and the sum of states (Q). In (23), the parameter $S^{(ab)}$ is the line strength for the electric dipole transition:

$$S^{(ab)} = \sum_{\alpha} |\langle \Psi^{(a)} | M_{\alpha} | \Psi^{(b)} \rangle|^2, \quad (24)$$

where $\Psi^{(a)}$ and $\Psi^{(b)}$ are total wave functions corresponding to nondegenerate eigenvalues $E^{(a)}$ and $E^{(b)}$, and M_{α} is the operator of the α -component of the molecule's electric dipole moment in a space-fixed coordinate system ($\alpha = X, Y, Z$). The form of M_{α} coincides with the classical expression for the function of the dipole moment:

$$M_{\alpha} = e \sum_{i=1}^N Z_i R_{i\alpha} - e \sum_{k=1}^n r_{k\alpha}, \quad (25)$$

where e is the value of elementary charge and Z_i is the charge of the i th nucleus, while $R_{i\alpha}$ and $r_{k\alpha}$ are the α -components of the coordinates of the i th nucleus and k th electron. Within the Born–Oppenheimer approximation, the full wave function of molecules is represented as the product of electron and nuclear wave functions, which allows independent integration over the coordinates of electrons and nuclei during calcula-

tion of matrix elements (24). In this case, (24) reduces to the form

$$S^{(ab)} = \sum_{\alpha} \left| \left\langle \Phi^{(a)} \left| \sum_{\beta} \varphi_{\alpha\beta} \mu_{\beta}(q) \right| \Phi^{(b)} \right\rangle \right|^2, \quad (26)$$

where the Φ are vibration–rotation wave functions; $\varphi_{\alpha\beta}(\rho)$ is the matrix of direction cosines, which connect the coordinate system of the center of mass ($\alpha = X, Y, Z$) with the coordinate system attached to the molecule ($\beta = \xi, \eta, \zeta$) determined by the Eckart conditions [13] and dependent on rotational operators; and $\mu_{\beta} = \mu_{\beta}(q)$ is an effective operator of the dipole moment dependent on normal coordinates q_i . According to [21, 27] let us consider pure vibrational transitions; thus the line strength for a dipole transition is

$$S^{(ab)} = \sum_{\alpha} \left| \langle \Phi^{(a)} | \mu_{\alpha} | \Phi^{(b)} \rangle \right|^2. \quad (27)$$

The calculation of matrix elements in (27) for wave functions from (2) can be replaced for their calculation with a contact-transformed operator of the dipole moment on the basis of harmonic oscillator functions [15–21, 37]:

$$\begin{aligned} & \langle \Phi^{(a)} | \mu_{\alpha} | \Phi^{(b)} \rangle \\ &= \langle \Phi_0^{(a)} | U \mu_{\alpha} U^{-1} | \Phi_0^{(b)} \rangle = \langle \Phi_0^{(a)} | M_{\alpha} | \Phi_0^{(b)} \rangle. \end{aligned} \quad (28)$$

To complete the contact transformations, it is necessary to expand the operator μ_{α} into a series in powers of normal coordinates,

$$\begin{aligned} \mu_{\alpha}(q) &= \mu_{\alpha}^0 + \sum_r \frac{\partial \mu_{\alpha}}{\partial q_r} q_r + \frac{1}{2} \sum_{rs} \frac{\partial^2 \mu_{\alpha}}{\partial q_r \partial q_s} q_r q_s \\ &+ \frac{1}{6} \sum_{rst} \frac{\partial^3 \mu_{\alpha}}{\partial q_r \partial q_s \partial q_t} q_r q_s q_t + \dots \end{aligned} \quad (29)$$

and then to combine the terms in orders of smallness of PT:

$$\begin{aligned} \mu_{\alpha}^{[0]} &= \mu_{\alpha}^0 + \sum_r \frac{\partial \mu_{\alpha}}{\partial q_r} q_r \\ \mu_{\alpha}^{[1]} &= \frac{1}{2} \sum_{rs} \frac{\partial^2 \mu_{\alpha}}{\partial q_r \partial q_s} q_r q_s \\ \mu_{\alpha}^{[2]} &= \frac{1}{6} \sum_{rst} \frac{\partial^3 \mu_{\alpha}}{\partial q_r \partial q_s \partial q_t} q_r q_s q_t. \end{aligned} \quad (30)$$

Performing the double contact transformation, in accordance with (18), one can obtain the expression for the operator of the effective dipole moment:

$$\begin{aligned} M_{\alpha} &= \left(\mu_{\alpha}^{[0]} + i[S_1, \mu_{\alpha}^{[0]}] - \frac{1}{2}[S_1, [S_1, \mu_{\alpha}^{[0]}]] \right. \\ &\quad \left. + i[S_2, \mu_{\alpha}^{[0]}] \right) + (\mu_{\alpha}^{[1]} + i[S_1, \mu_{\alpha}^{[1]}]) + \mu_{\alpha}^{[2]}. \end{aligned} \quad (31)$$

Knowing the analytical form of operators S_1 and S_2 [10, 38], we can determine the form of operator M_{α} , and then, depending on the type of vibrational transition (fundamental, overtone, or combination), calculations by (28) and (30) reduce to the calculation of the matrix elements in the basis of the corresponding functions of the harmonic oscillator [21].

Since the expression for the intensity of the fundamental transition presented in [21] is rather cumbersome, we do not reproduce it here. For the matrix elements corresponding to overtones and combination frequencies, the following formulas are valid [21]:

$$\begin{aligned} & \langle \Phi(v_r, v_s, \dots) | M_{\alpha} | \Phi(v_r + 2, v_s, \dots) \rangle \\ &= \left(\frac{(v_r + 1)(v_r + 2)}{16} \right)^{1/2} \left[\frac{\partial^2 \mu_{\alpha}}{\partial q_r \partial q_r} + 2 \frac{\partial \mu_{\alpha}}{\partial q_r} \frac{K_{rrr}}{\omega_r} \right. \\ &\quad \left. + \sum_{s \neq r} \frac{\partial \mu_{\alpha}}{\partial q_s} K_{rrs} \left(\frac{1}{2\omega_r - \omega_s} - \frac{1}{2\omega_r + \omega_s} \right) \right], \end{aligned} \quad (32)$$

$$\begin{aligned} & \langle \Phi(v_r, v_s, v_t, \dots) | M_{\alpha} | \Phi(v_r + 1, v_s + 1, v_t, \dots) \rangle \\ &= \left(\frac{(v_r + 1)(v_s + 1)}{4} \right)^{1/2} \left(\frac{\partial^2 \mu_{\alpha}}{\partial q_r \partial q_s} + \frac{\partial \mu_{\alpha}}{\partial q_r} \frac{2K_{rrs}\omega_r}{\omega_s(2\omega_r + \omega_s)} \right. \\ &\quad \left. + \frac{\partial \mu_{\alpha}}{\partial q_s} \frac{2K_{ssr}\omega_s}{\omega_r(2\omega_s + \omega_r)} \right) + \left(\frac{(v_r + 1)(v_s + 1)}{4} \right)^{1/2} \\ &\quad \times \sum_{t \neq r, s} \left[\frac{\partial \mu_{\alpha}}{\partial q_t} \frac{K_{rst}}{2} \left(\frac{1}{\omega_r + \omega_s - \omega_t} - \frac{1}{\omega_r + \omega_s + \omega_t} \right) \right]. \end{aligned} \quad (33)$$

The respective integral intensities are

$$\begin{aligned} I(2\nu_r) &= \frac{4\pi^3 N_A}{3hc^2} 2\nu_r \\ &\times \sum_{\alpha} \left| \langle \Phi(v_r, v_s, \dots) | M_{\alpha} | \Phi(v_r + 2, v_s, \dots) \rangle \right|^2 \\ &\times \frac{1 + \exp(-h\nu_r/kT)}{1 - \exp(-h\nu_r/kT)}, \end{aligned} \quad (34)$$

$$I(\nu_r + \nu_s) = \frac{4\pi^3 N_A}{3hc^2} (\nu_r + \nu_s) \times \sum_{\alpha} |\langle \Phi(\nu_r, \nu_s, \nu_b, \dots) | M_{\alpha} | \Phi(\nu_r + 1, \nu_s + 1, \nu_b, \dots) \rangle|^2 \times \frac{1 + \exp(-hc(\nu_r + \nu_s)/kT)}{(1 - \exp(-hc\nu_r/kT))(1 - \exp(-hc\nu_s/kT))}. \quad (35)$$

Thus, to calculate the anharmonic intensity values by formulas (32)–(35), the information in the expansion coefficients (29) of the effective operator of the dipole moment in powers of normal coordinates is sufficient. To calculate the intensity for two-quantum transitions (first overtones and combination frequencies), it is sufficient to know first and second derivatives, while to calculate the intensity for fundamental frequencies, the third derivatives are also required [21].

POLARIZABILITY OPERATOR AND INTENSITY OF RAMAN SCATTERING

In the spectroscopy of Raman scattering [39], the vibrational transitions are determined by the dipole moment μ_i , which is induced by an external electric field E :

$$\mu_{ip} = \sum_{\sigma} \hat{\alpha}_{p\sigma} E_{\sigma}, \quad (36)$$

where $\hat{\alpha}_{p\sigma}$ is the polarizability operator of a molecule. By analogy with the operator of dipole moment M_{α} , $\hat{\alpha}_{p\sigma}$ is given by the operator $\hat{\alpha}_{p\sigma}(q)$ determined by the formula [27, 39]

$$\alpha_{p\sigma}(q) = \frac{2\pi}{h} \sum_{r \neq g} \left(\frac{\langle e_b | \mu_p | e_r \rangle \langle e_r | \mu_{\sigma} | e_a \rangle}{\omega_{ra} - \omega_0} + \frac{\langle e_b | \mu_{\sigma} | e_r \rangle \langle e_r | \mu_p | e_a \rangle}{\omega_{ra} + \omega_0} \right), \quad (37)$$

where ρ, σ are the axes of the molecular coordinate system; $|e_l\rangle$ are electronic wave functions; indices a, b, g, r refer to the initial, final, ground, and excited states, respectively; and ω_0 is the frequency of excitation radiation. The operator $\alpha_{p\sigma}(q)$, which is called the polarizability tensor, is calculated by the quantum-mechanical finite field method [40].

In the RS vibration spectra, a normalized absolute differential section of scattering is used as a quantity

characterizing the intensity of the i th band (in units of $10^{-48} \text{ cm}^6/\text{ster}$):

$$\frac{\partial \sigma_i}{\partial \Omega} (\omega_0 - \omega_i)^{-4} = \frac{(2\pi)^4}{45} \frac{hc}{8\pi^2 c^2 \omega_i} S(q_i) \left[1 - \exp\left(-\frac{hc\omega_i}{kT}\right) \right]^{-1}. \quad (38)$$

Here $S(q_i) = 45\bar{\alpha}_i^2 + 7\gamma_i^2$ is the coefficient of RS activity, in which invariants $\bar{\alpha}_i^2, \gamma_i^2$ (mean polarizability and anisotropy) have the form [39, 41]

$$\bar{\alpha}_i^2 = \frac{1}{9} [\langle v_a | \alpha_{xx} | v_b \rangle + \langle v_a | \alpha_{yy} | v_b \rangle + \langle v_a | \alpha_{zz} | v_b \rangle]^2, \quad (39)$$

$$\gamma_i^2 = \frac{1}{2} [\langle v_a | \alpha_{xx} | v_b \rangle - \langle v_a | \alpha_{yy} | v_b \rangle]^2 + \frac{1}{2} [\langle v_a | \alpha_{yy} | v_b \rangle - \langle v_a | \alpha_{zz} | v_b \rangle]^2 + \frac{1}{2} [\langle v_a | \alpha_{zz} | v_b \rangle - \langle v_a | \alpha_{xx} | v_b \rangle]^2 \quad (40)$$

$$+ 3[\langle v_a | \alpha_{xy} | v_b \rangle^2 + \langle v_a | \alpha_{yz} | v_b \rangle^2 + \langle v_a | \alpha_{zx} | v_b \rangle^2],$$

where the term $\langle \Phi^{(a)} | \alpha_{xy} | \Phi^{(b)} \rangle = \langle v_a | \alpha_{xy} | v_b \rangle$ is used to compact the formulas.

In full analogy with the operator of the dipole moment, the operator components of polarizability tensor in (37) can be expanded into a series in normal coordinates:

$$\alpha_{p\sigma}(q) = \alpha_{p\sigma}^0 + \sum_r \frac{\partial \alpha_{p\sigma}}{\partial q_r} q_r + \frac{1}{2} \sum_{rs} \frac{\partial^2 \alpha_{p\sigma}}{\partial q_r \partial q_s} q_r q_s + \frac{1}{6} \sum_{rst} \frac{\partial^3 \alpha_{p\sigma}}{\partial q_r \partial q_s \partial q_t} q_r q_s q_t + \dots \quad (41)$$

For a purely harmonic problem, the expansion (41) is limited to linear terms of q only. In such a case, only matrix elements of the following form will be nonzero:

$$\langle \Phi_0(\nu_r \pm 1, \nu_s, \dots) | \alpha_{p\sigma}(q) | \Phi_0(\nu_r, \nu_s, \dots) \rangle \approx \frac{\partial \alpha_{p\sigma}}{\partial q_r} \langle \Phi_0(\nu_r \pm 1, \nu_s, \dots) | | \Phi_0(\nu_r, \nu_s, \dots) \rangle. \quad (42)$$

In the anharmonic case, it is also necessary to take into account terms of greater orders, up to the third derivative in the second order of PT. If the operator $\alpha_{p\sigma}(q)$ is subjected to a double CT (see (31)), we can derive a transformed operator of the polarizability component for a molecule $A_{p\sigma}$, whose matrix elements in the basis of the harmonic oscillator's eigenfunctions

are equal to the matrix elements of the initial operator for anharmonic functions:

$$\begin{aligned}\langle \Phi^{(a)} | \alpha_{\rho\sigma} | \Phi^{(b)} \rangle &= \langle \Phi_0^{(a)} | U \alpha_{\rho\sigma} U^{-1} | \Phi_0^{(b)} \rangle \\ &= \langle \Phi_0^{(a)} | A_{\rho\sigma} | \Phi_0^{(b)} \rangle.\end{aligned}\quad (43)$$

Since the effective operators of the dipole moment and polarizability tensor are represented by series (29) and (41), the contact-transformed operator $A_{\rho\sigma}$ is determined by an equation of the same form as the operator of the effective dipole moment M_α (31). Therefore, for the matrix elements $A_{\rho\sigma}$, which correspond to fundamental frequencies, overtones, and combination frequencies, formulas (32) and (33) are correct if M_α is replaced by $A_{\rho\sigma}$. Thus, to calculate the values for the anharmonic intensities of overtones and combination frequencies in Raman spectra, the second derivatives in (41) are sufficient, while in the case of fundamental frequencies, the third derivatives are required as well.

THE METHOD OF CALCULATION

To calculate the frequencies for fundamental vibrations, overtones and combination frequencies, and their intensities in IR and Raman spectra of polyatomic molecules in the anharmonic approximation by the method described above, the FORTRAN software program ANCO was created based on a previous version [42]. Along with reproduction of main features of the analogous SPECTRO program [43], ANCO incorporates novel possibilities including that of coordination with the GAUSSIAN'03 package [44] to calculate the potential energy surfaces for molecules.

The capabilities of the method and program have been validated with the example of a butadiene molecule. Following recommendations [28], the quantum-mechanical part of calculations is done by the B3LYP/6-31+G(d,p) technique. The coefficients of a polynomial expansions for the surfaces of potential energy, dipole moment, and polarizability are calculated analytically and by numerical differentiation using GAUSSIAN'03 output [44].

In a frame of the harmonic problem for fitting frequencies, the Pulay method of scaling of force field is widely used [45]. As for anharmonic calculations, the differences of experimental and calculated frequencies are ordinarily smaller. The anharmonic force field can also be scaled by various techniques [42]. Since the quantum-mechanical approach less accurate for prediction of the harmonic field [46], in our opinion, it is reasonable to use Handy's method of harmonic frequency variation [29], which allows to adjust fundamental frequencies to experimental ones, and also improves the precision of predicting overtones and combination tones. The latter is especially important for more accurate determination of their intensities, since even a minor shift in resonance frequencies may cause the substantial redistribution of intensities.

Handy's method of harmonic frequency variations [29] is as follows:

1) Calculation of harmonic ω_0 and fundamental frequencies ν_0 from the quantum-mechanical force field.

2) Evaluation of experimental harmonic frequencies:

$$\omega_{\text{exp}} = \nu_{\text{exp}} - (\nu_0 - \omega_0).$$

3) Recalculation of anharmonic constants and frequencies ν_0 on the basis of estimating ω_{exp} .

4) Repeat calculation of ω_{exp} , checking for convergence (otherwise return to step (2)).

The values of optimized harmonic frequencies make it possible to determine the scale factors for the harmonic part of the force field [42]:

$$C_i = [(L^{-1})^+ \omega_{\text{exp}} L^{-1}]_{ii} / (F_0)_{ii}, \quad (44)$$

where L is the matrix of vibration modes and F is the matrix of force constants. The results of calculations for butadiene molecule are presented in Tables 1 and 2.

DISCUSSION AND CONCLUSIONS

The butadiene molecule is particularly interesting due to the presence of the conjugated double bonds C=C and rotational isomerism. A significant number of papers have been devoted to investigating its vibration spectra and rotational isomerism, including very recent ones (see [47] and references therein). In [47] one of the best quantum-mechanical methods, CCSD(T)/aug-cc-pVTZ, has been used to calculate the structure and fundamental frequencies of butadiene. On the basis of our study, one may conclude that [47] and a number of earlier works (see, for example, [48, 49]) did not escape some inaccuracies in assigning bands to fundamentals, in particular, where resonance effects strongly affect the frequencies of C—H vibrations in the region of 3000 cm⁻¹. These work could not also fully interpret bands corresponding to overtones and combination frequencies. The anharmonic calculation of frequencies and intensities of butadiene vibrations performed by us with ANCO based on B3LYP/6-31+G(d,p) technique allowed us to eliminate many remaining questionable assignments.

The predicted values of fundamental frequencies (see Table 1) deviate from experimental ones with an average error 8 cm⁻¹; the biggest errors correspond to the frequencies C=C (ν_4, ν_{20}). The frequencies of C—H-vibrations ν_1 (A_g) and ν_{19} (B_u), which do not participate in resonances, are predicted with high precision at a level near 1 cm⁻¹. The assignment of the frequencies of other C—H-vibrations is interesting too: ν_2, ν_3, ν_{18} , and ν_{19} . As is seen in Table 1, they all participate in complex resonances forming polyads. To ascertain the assignment of these frequencies by the Handy method, we adjusted the other 20 frequencies to the experimental ones. The obtained values of $\nu_2 = 3018$,

Table 1. Calculated and experimental fundamental vibration frequencies for *trans*-1,3-butadiene

ν	Assignment, symmetry	Harmonic frequency ω (shift $\omega - \omega_0$)	Shift $\Delta(\nu' - \omega)$	Anharmonic unperturbed frequency ν'	Shift $\Delta(\nu - \nu')$	Anharmonic perturbed frequency (shift $\nu - \nu_0$)	Experimental (IR, gas)	Experimental (RS, gas)	Resonance polyades
A_g									
ν_1	$\nu(\text{CH}_2)\text{asym.str.}$	(2.28) 3243.96	-143.91	3100.04	-0.04	(1.57) 3100.00	—	3100.0	—
ν_2	$\nu(\text{C}-\text{H})\text{str.}$	(-10.51) 3143.76	-143.97	2999.79	12.21	(-16.69) 3012.00	—	3012.0	$\{\nu_2, \nu_{20} + \nu_{21}, \nu_4 + \nu_6, 2 \times \nu_5\}$
ν_3	$\nu(\text{CH}_2)\text{sym.str.}$	(-14.82) 3126.57	-146.02	2980.55	20.45	(-21.11) 3001.00	—	3001.0	$\{\nu_3, \nu_{20} + \nu_{21}, \nu_4 + \nu_6, \nu_4 + \nu_5\}$
ν_4	$\nu(\text{C}=\text{C})\text{sym.str.}$	(-18.27) 1691.39	-41.42	1649.98	-5.98	(-18.93) 1644.00	—	1644.0	$\{\nu_4, \nu_{15} + \nu_{16}\}$
ν_5	$\delta(\text{CH}_2)\text{sciss.}$	(-2.28) 1476.90	-35.47	1441.43	0.57	(-3.10) 1442.00	—	1442.0	—
ν_6	$\delta(\text{C}-\text{H})\text{deform.}$	(-3.02) 1312.35	-22.56	1289.79	-11.79	(-5.10) 1278.00	—	1278.0	$\{\nu_6, \nu_{23} + \nu_{24}\}$
ν_7	$\nu(\text{C}-\text{C})\text{str.}$	(-2.94) 1227.44	-23.46	1203.97	0.03	(-3.83) 1204.00	—	1204.0	—
ν_8	$\rho(\text{CH}_2)\text{rock.}$	(-0.61) 901.16	-13.56	887.60	1.40	(-0.76) 889.00	—	889.0	—
ν_9	$\delta(\text{C}-\text{C}=\text{C})\text{def.}$	(-3.56) 512.43	1.38	513.81	-0.81	(-3.66) 513.00	—	513.0	—
A_u									
ν_{10}	$\tau(\text{C}=\text{O})\text{twist.}$	(-10.05) 1041.55	-26.54	1015.01	-1.21	(-10.50) 1013.80	1013.80	—	—
ν_{11}	$\chi(\text{CH}_2)\text{wag.}$	(-8.92) 923.80	-15.73	908.07	0.00	(-9.03) 908.07	908.07	—	—
ν_{12}	$\chi(\text{C}-\text{H})\text{wag.}$	(-1.50) 535.08	-9.21	525.87	-1.30	(-1.76) 524.57	524.57	—	—
ν_{13}	$\tau(\text{C}-\text{C})\text{tors.}$	(-5.29) 168.38	-5.96	162.42	0.00	(-5.72) 162.42	162.42	—	—
B_g									
ν_{14}	$\chi(\text{C}-\text{H})\text{wag.}$	(-6.17) 987.84	-21.84	966.00	0.00	(-6.38) 966.00	—	966.0	—
ν_{15}	$\chi(\text{CH}_2)\text{wag.}$	(-9.79) 924.13	-16.13	908.00	0.00	(-9.91) 908.00	—	908.0	—
ν_{16}	$\chi(\text{C}=\text{C})\text{twist.}$	(-11.36) 763.02	-14.02	749.00	0.00	(-11.60) 749.00	—	749.0	—
B_u									
ν_{17}	$\nu(\text{CH}_2)\text{asym.str.}$	(2.15) 3244.21	-144.39	3099.83	0.80	(-0.15) 3100.63	3100.63	—	—
ν_{18}	$\nu(\text{C}-\text{H})\text{str.}$	(-7.07) 3147.73	-142.60	3005.13	6.27	(-14.24) 3011.40	3011.40	—	$\{\nu_{18}, \nu_4 + \nu_{21}, \nu_4 + \nu_{22}\}$
ν_{19}	$\nu(\text{CH}_2)\text{sym.str.}$	(3.55) 3154.45	-139.28	3015.17	-31.18	(-9.20) 2984.00	2984.00	—	$\{\nu_{19}, \nu_5 + \nu_{20}, \nu_4 + \nu_{21}, \nu_{18}\}$
ν_{20}	$\nu(\text{C}=\text{C})\text{asym.str.}$	(-23.52) 1631.89	-37.08	1594.81	1.64	(-22.99) 1596.45	1596.45	—	$\{\nu_{20}, \nu_6 + \nu_{24}\}$
ν_{21}	$\delta(\text{CH}_2)\text{sciss.}$	(-7.47) 1411.11	-30.34	1380.77	-0.17	(-7.96) 1380.60	1380.60	—	—
ν_{22}	$\delta(\text{C}-\text{H})\text{def.}$	(-3.54) 1316.42	-23.09	1293.34	0.76	(-4.60) 1294.10	1294.10	—	$\{\nu_{22}, \nu_{12} + \nu_{16}\}$
ν_{23}	$\rho(\text{CH}_2)\text{rock.}$	(-3.79) 1000.36	-10.06	990.30	0.00	(-3.88) 990.30	990.30	—	—
ν_{24}	$\delta(\text{C}-\text{C}=\text{C})\text{def.}$	(-3.33) 292.89	6.21	299.10	0.00	(-3.28) 299.10	299.10	—	—

Table 2. Assignment of combination frequencies and overtones in spectrum of *trans*-1,3-butadiene

IR (gas), contour	RS (gas)	RS (liquid)	Calculation	Intensity	Assignment
w, Q 1067.0	wm 1300	w 322	322.30	2.06	$2 \times \nu_{13}$
w, A/B 1267.5			1070.23	1.08	$\nu_{13} + \nu_{15}$
			1270.73	1.07	$\{\nu_{12} + \nu_{16}, \nu_{22}\}$
		wm 1300	1302.40	18.63	$\{\nu_{23} + \nu_{24}, \nu_6\}$
		w 1400	1398.75	0.62	$\{\nu_8 + \nu_9, \nu_5\}$
vw, Q 1414.4			1412.88	0.17	$\nu_8 + \nu_{12}$
vw, B 1432.4			1434.00	1.10	$\nu_{12} + \nu_{15}$
vw, A/B 1490.4			1492.42	0.80	$\nu_{12} + \nu_{14}$
w, A/B 1655.4			1656.87	0.50	$\nu_{11} + \nu_{16}$
		wm 1659	1657.91	14.83	$\{\nu_{15} + \nu_{16}, \nu_4\}$
	wm 1659	w 1656	1657.91	14.83	$\{\nu_{15} + \nu_{16}, \nu_4\}$
		w 1679	1680.59	3.45	$\nu_{21} + \nu_{24}$
vw, sh 1740.2			1741.15	0.37	$\nu_5 + \nu_{24}$
vw, A/B 1764.3			1763.58	0.53	$\nu_{10} + \nu_{16}$
		w 1777	1774.70	3.46	$2 \times \nu_8$
ms, A 1819.6			1818.56	17.45	$\nu_{11} + \nu_{15}$
vw, B 1873.3			1873.55	0.61	$\nu_{11} + \nu_{14}$
vw, B 1901.0			1895.33	0.07	$\nu_9 + \nu_{21}$
vvw, Q 1914.0			1921.35	0.10	$\nu_{10} + \nu_{15}$
vw, Q 1956.6			1947.86	0.25	$\nu_4 + \nu_{24}$
vw, A 1971.0	wm 1659		1974.59	0.61	$\nu_{10} + \nu_{14}$
vvw, Q 2046.6			2042.23	0.01	$\nu_{16} + \nu_{22}$
		w 2088	2088.21	0.91	$\nu_7 + \nu_8$
vvw, A/B 2107.4			2106.99	0.10	$\nu_9 + \nu_{20}$
vvw, Q 2167.0			2174.90	0.09	$\nu_4 + \nu_{12}$
vvw, Q 2216.4			2217.49	0.05	$\nu_7 + \nu_{10}$
vw, B 2266.2			2266.86	0.16	$\nu_8 + \nu_{21}$
vvw, Q 2295.6			2279.86	0.16	$\nu_6 + \nu_{23}$
vvw, Q 2346.0			2342.36	0.07	$\nu_{16} + \nu_{20}$
vvw, B 2424.5			2427.96	0.11	$\nu_5 + \nu_{23}$
vw, A 2494.6	wm 1659		2494.31	0.27	$\nu_7 + \nu_{22}$
vvw, Q 2566.7			2558.59	0.02	$\nu_{14} + \nu_{20}$
vw, A 2583.1			2579.00	0.09	$\nu_6 + \nu_{22}$
vvw, A 2732.6			2732.19	0.07	$\nu_5 + \nu_{22}$
		vw 2751	2758.65	0.18	$2 \times \nu_{21}$
vvw, B 2798.8			2795.86	0.03	$\nu_7 + \nu_{20}$
vvw, B 2818.4			2815.60	0.03	$\nu_5 + \nu_{21}$
		w 2870	2872.66	3.20	$\{2 \times \nu_5, \nu_{20} + \nu_{22}, \nu_2\}$
vw, B 2924.3			2923.08	2.96	$\{\nu_4 + \nu_{22}, \nu_{18}, \nu_{19}\}$
	w 2906		2923.81	2.98	$\{\nu_4 + \nu_6, \nu_3, \nu_{20} + \nu_{22}\}$
		w 2953	2954.05	2.98	$\{\nu_{20} + \nu_{21}, \nu_3, \nu_2, \nu_4 + \nu_6\}$
m, A/B 3031.4			3033.36	1.24	$\{\nu_4 + \nu_{21}, \nu_5 + \nu_{20}, \nu_{18}\}$
m, A/B 3055.2			3066.59	16.27	$\{\nu_5 + \nu_{20}, \nu_{19}, \nu_4 + \nu_{21}\}$
		w 3180	3186.21	1.45	$2 \times \nu_{20}$
vw, A 3235.7			3237.77	0.30	$\nu_4 + \nu_{20}$
vw, B 3398.9			3398.97	0.11	$\nu_1 + \nu_{24}$

Note: The units of intensity for IR and Raman spectra are km/mol and 10^{-48} cm⁶/sr.

$\nu_3 = 3010$, $\nu_{18} = 3016$, and $\nu_{19} = 2983$ made the assignment of experimental bands 3012, 3001, 3011.4, and 2984.0 cm^{-1} more certain. Then, matching was performed for all experimental frequencies; the results are summarized in Table 1. The calculation of frequencies and intensities of combination frequencies and overtones in IR and Raman spectra made it possible to reliably assign the majority of experimental bands (see Table 2). We also confirmed certain Fermi resonances that had been proposed empirically [48].

The specified fundamental frequencies allowed determination of the scale factors of the harmonic part of force field within the anharmonic problem (the scale factors for harmonic calculation are in parentheses): C–C str.: 0.994 (0.945); C=C str.: 0.983 (0.913); CH_2 str.(trans): 1.000 (0.921); CH_2 str.(cis): 0.998 (0.895); C–H str.: 0.994 (0.915); C=C–C def.: 0.985 (0.998); =C–H rock.: 0.993 (0.949); CH_2 sciss.: 0.990 (0.954); CH_2 rock.: 0.994 (0.983); C–C tors.: 0.952 (0.878); C–H wag.: 0.980 (0.968); CH_2 wag.: 0.980 (0.947); C=C tors.: 0.982 (0.914). The small deviation from unity of the scale factors obtained in the anharmonic calculation confirms that the method used provides sufficient calculation precision even when such an economical quantum-mechanical technique as B3LYP/6-31+G(d,p) is used. Apparently, the scale factors mainly correct the absence of anharmonicity effects within the harmonic problem. The obtained scale factors can be utilized to calculate structurally related molecules including rotational isomers. Perturbation theory in the form of CT along with the theory of Raman scattering make it possible to go beyond the traditional double harmonic approximation to calculate the Raman scattering and determine intensities for fundamental vibrations, overtones, and combination frequencies with account of polynomial representation of the polarizability of molecules.

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