

## Resonance Raman spectra interpretation by molecular coherent state representation

N. YU. TRIFONOV

42 Kommunisticheskaya St., Minsk, Byelorussia 220002, USSR

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**Abstract.** In this paper the problem of exact summation over vibrational states of intermediate electronic level excited by resonance Raman scattering in a molecular system with an arbitrary number of vibrational modes is solved with the help of the coherent state representation. For matrix elements of the resonance Raman (RR) amplitude the expressions in the form of an integral and multiple series as well as recurrence relations are obtained. The interpretation of RR spectra of linear-chain mixed-valence platinum complexes is given as an illustration.

### 1. Introduction

Resonance Raman (RR) band intensities in molecular systems are described, as a rule, by the second-order perturbation theory [1] that connects intensities with the polarizability tensor. The vast field of RR spectroscopy on crystals is usually described by the third-order perturbation theory [2] using a susceptibility tensor. Though historically the descriptions of RR experiments in molecules and solids have developed independently, the fundamental physical processes are identical. Hence, in [3], an attempt to apply the perturbation theory of the third order to molecular RR scattering was made. As shown in [4], the methods [1] and [3] are equivalent.

The RR intensity of the  $\nu$ - $w$  transition between vibrational levels of the ground electronic state  $g$  of the cold ( $T=0$  K) molecule under the influence of incident light of frequency  $\omega_0$  is connected with the dynamic polarizability tensor  $\alpha_{\nu w}$ . Hence we can put down

$$I_{\nu w} \sim (\omega_0 - \omega \nu)^4 |\alpha_{\nu w}|^2. \quad (1)$$

The vectors in this expression have  $n$  components according to a number of excited vibrational modes in the system. Thus,

$$\mathbf{v} = (v_1, v_2, \dots, v_n)$$

corresponds to excitation of  $v_1$  quanta in normal mode 1,  $v_2$  quanta of mode 2, etc., as a result of RR scattering in the ground electronic state. The initial molecular vibrational state is described by the vector

$$\mathbf{w} = (w_1, w_2, \dots, w_n);$$

the vector

$$\boldsymbol{\omega} = (\omega_1, \omega_2, \dots, \omega_n)$$

represents a set of excited normal vibration frequencies of the system. The scalar product is defined by the usual means:

$$\omega \mathbf{v} = \omega_1 v_1 + \omega_2 v_2 + \dots + \omega_n v_n.$$

In standard approximations of RR theory [1] (adiabatic Born–Oppenheimer for electron–nuclear motion, Condon for dipole electric momentum, harmonic for vibrational motion)† as well as in the suggestion of single resonant electronic state  $e$  (the rest excited electronic states are supposed to be removed), the polarizability tensor may be written as follows:‡

$$\alpha_{vw} = \text{const} \sum_{\mathbf{m}} \frac{\langle \mathbf{v} | \mathbf{m} \rangle \langle \mathbf{m} | \mathbf{w} \rangle}{\Delta E_{e\mathbf{g}} + \omega(\mathbf{m} - \mathbf{w}) - \omega_0 - i\Gamma_{e\mathbf{m}}}. \quad (2)$$

Here  $\Delta E_{e\mathbf{g}}$  is the electronic energy gap,  $\Gamma_{e\mathbf{m}}$  is the relaxation rate of the state  $e\mathbf{m}$ , i.e. the total damping constant, which is determined by all the homogeneous broadening mechanisms,§  $\langle . | . \rangle$  are overlap integrals for vibrational wave functions written in Fock space [5], and variables

$$\mathbf{m} = (m_1, m_2, \dots, m_n)$$

are numbers of vibrational quanta in the intermediate electronic state.

The expression (2) under review shows that in solving the problems of RR intensity calculation one should make a summation over the multidimensional vibrational space of the excited electronic state. The difficulty of this problem usually compels to solve it by fitting to the best coincidence with experimental data with regard to only some lower vibrational levels. One of the first attempts to take into account the contribution of all the intermediate vibrational states in one-mode molecular system was realized, evidently, in [6]. In the review [7] difficulties of summing-up over intermediate states in the case of multidimensional vibrational space as well as variants of getting them over with the help of a transform method (for example [8, 9]) were examined. This method was developed from the time-correlator formalism [10] on the basis of the theorem relating absorption and RR intensities as incident photon frequency functions.

All these approaches are rather good for calculating RR spectra on powerful computers, but are quite inconvenient for simple analysis. In this paper one can find solutions of the problem formulated above using the coherent state (CS) representation described in detail in [11]–[14]. CSs are used to describe a multidimensional harmonic oscillator modelling vibrations in a large molecular system—so-called molecular CSs. In contrast to the approaches noted above, which are good for calculating RR spectra with the help of powerful computers only, we develop an approach that is convenient both for computer calculations and for a simpler and more intuitive analysis.

† The object of interest is a large molecule, and so the effect of anharmonicity is insignificant.

‡ Herein and below, units in which  $c = \hbar = 1$  are used.

§ Vibrational levels of the ground electronic state are operating initial and final states in an act of RR scattering, while vibrational levels  $e\mathbf{m}$  of the excited electronic state are virtual. Thus, relaxation processes in the excited electronic state as well as inhomogeneous effects do not influence the RR band width. Therefore, for RR spectra, effectively,  $\Gamma_{e\mathbf{m}} = \Gamma$ .

In section 2, which is mainly methodical, a detailed description of the summation method for a case of excitation of a one-vibrational mode in molecule is given. In section 3, on the basis of the developed method, the overall intermediate-state sum in the common case of excitation of a multidimensional vibrational space is performed. Section 4 illustrates the use of the method for RR spectra interpretation.

## 2. System with one vibrational degree of freedom

### 2.1. Notation

In this section we examine the case of excitation of one vibrational degree of freedom ( $n=1$ ) only. Hence, we rewrite (2) in the following form:

$$\alpha_{vw} = \text{const} \langle v|A(\sigma')|w\rangle, \quad (3)$$

$$A(\sigma') = \sum_{m=0}^{\infty} \frac{|m\rangle\langle m|}{\sigma' + m - w}, \quad (4)$$

$$\sigma' = (\Delta E_{eg} - \omega_0 - i\Gamma)/\omega. \quad (5)$$

Our first goal is the exact calculation (in the harmonic-oscillator approximation) of a sum in a matrix element of an operator (4).† For this purpose, let us use a Fock-Schwinger eigentime representation (see, for example, [15]). In the framework of this representation a matrix element of RR amplitude may be written as

$$\langle v|A(\sigma')|w\rangle = \sum_{m=0}^{\infty} \int_0^{\infty} d\beta \exp[-\beta(\sigma' + m - w)] \langle v|m\rangle \langle m|w\rangle. \quad (6)$$

The matrix element (6) will be the subject of our investigation. We shall study the matrix element with the help of CSs for a harmonic oscillator, modelling vibrations in a molecular system.

### 2.2. Expressions for amplitudes in coherent state representation

The matrix element

$$\langle \gamma|A(\sigma')|\alpha\rangle = \exp[-\frac{1}{2}(|\alpha|^2 + |\gamma|^2)] \sum_{v,w=0}^{\infty} \frac{\alpha^w \gamma^{*v}}{(v!w!)^{1/2}} \langle v|A(\sigma')|w\rangle, \quad (7)$$

is a generating function for  $\langle v|A(\sigma')|w\rangle$ . Replacing the expression (6) of the amplitude matrix element by the eigentime  $\beta$  into equation (7) we obtain the expansion

$$\langle \gamma|A(\sigma')|\alpha\rangle = \int_0^{\infty} d\beta \exp[-\frac{1}{2}|\alpha|^2(1 - e^{2\beta})] \sum_{m=0}^{\infty} e^{-\beta(\sigma+m)} \langle \gamma|m\rangle \langle m|e^{\beta}\alpha\rangle. \quad (8)$$

One can calculate the integral in equation (8) in several ways. It is more convenient to do this using a coordinate representation. We will model a vibrational mode excited in a molecule by a harmonic oscillator. We should remember that the wave functions of  $|\gamma\rangle$  and  $|e^{\beta}\alpha\rangle$  concern the initial electronic state,  $g$ , while the  $|m\rangle$  functions concern the excited one,  $e$ , the potential minimum position of which we will consider to be displaced on the value of  $R$ . Into the expansion of (8) we can substitute coherent states of harmonic oscillator, representing Gauss exponents [11]

† Note that the kernel of summation (4) is, in essence, the Green function of a one-dimensional quadratic system.

and standard normalized wave functions manifested (for example [16]) via Hermite polynomials,  $H_m$ , as well. In the obtained expression, we can accomplish the summation over quantum number  $m$  using Mehler's formula for a product of Hermite polynomials [17]. Then, having integrated over coordinate variables we obtain, for an amplitude generating function,

$$\langle \gamma | A(\tau) | \alpha \rangle = \exp \left[ -\frac{1}{2}(|\alpha|^2 + |\gamma|^2) - \delta^2 \right] \int_0^\infty d\beta e^{-\beta\sigma'} \exp \left[ (\alpha e^\beta - \delta)(\gamma^* - \delta)e^{-\beta} + \delta(\alpha e^\beta + \gamma^*) \right], \quad (9)$$

where  $\delta$  is a dimensionless displacement of the oscillator potential minimum under a transition into the excited state

$$\delta = R(\mu\omega/2)^{1/2}; \quad (10)$$

$\mu$  is a reduced mass of the modelling oscillator. The formula (9) is an integral expression for the matrix element (6) of an RR amplitude in the representation of coherent states of the molecular oscillator.

The described method of obtaining the integral expression (9) is not suitable for generalization in the case of excitation of an arbitrary number of vibrations in a system. So let us consider other ways.

First, we make some calculations of an auxiliary character. Proceeding from the notation of generating functions, we have

$$\langle \gamma | \zeta \rangle \langle \zeta | \alpha \rangle = \exp(-|\zeta|^2) \sum_{m=0}^{\infty} \frac{|\zeta|^{2m}}{m!} \langle \gamma | m \rangle \langle m | \alpha \rangle. \quad (11)$$

Now we use the results of [18]; hence the scalar product of CSs for harmonic oscillator can be transferred to

$$\langle \gamma | \alpha \rangle = \chi^{-1/2} \exp \left[ -\frac{1}{2}(|\alpha|^2 + |\gamma|^2 + \delta^2) \right] \exp \left[ \frac{\psi}{2\chi}(\alpha - \delta)^2 + \frac{1}{\chi}(\alpha - \delta)\gamma^* - \frac{\psi}{2\chi}\gamma^{*2} + \alpha\delta \right], \quad (12)$$

where the variables  $\chi$  and  $\psi$  are connected with the oscillator frequencies of  $\omega$  and  $\omega'$  in the states of  $|\alpha\rangle$  and  $|\gamma\rangle$ , respectively,

$$\chi = \frac{\omega + \omega'}{2(\omega\omega')^{1/2}}, \quad \psi = \frac{\omega - \omega'}{2(\omega\omega')^{1/2}}. \quad (13)$$

In our case the oscillator frequency in both states is constant,

$$\omega = \omega'. \quad (14)$$

Taking into account the equalities (12)–(14), the expression (11) can be put down in the form:

$$\begin{aligned} \exp \left[ -\frac{1}{2}(|\alpha|^2 + |\gamma|^2) - \delta^2 + (\alpha + \gamma^*)\delta \right] \frac{1}{2\pi} \int_0^{2\pi} d\theta \exp \left\{ [(\alpha - \delta)e^{-i\theta} + (\gamma^* - \delta)e^{i\theta}] |\zeta| \right\} \\ = \sum_{m=0}^{\infty} \frac{|\zeta|^{2m}}{m!} \langle \gamma | m \rangle \langle m | \alpha \rangle. \quad (15) \end{aligned}$$

An integral in this equality is a modified Bessel function of the first kind and zeroth order [17] with the following expansion in series:

$$I_0(x) = \sum_{m=0}^{\infty} \frac{(x^2/4)^m}{(m!)^2}. \quad (16)$$

Using this expansion in equation (15) we obtain another representation for a generating function of the amplitude matrix elements:

$$\begin{aligned} \langle \gamma | A(\sigma') | \alpha \rangle = & \exp \left[ -\frac{1}{2}(|\alpha|^2 + |\gamma|^2 - \delta^2 + (\alpha - \gamma^*)\delta) \right] \\ & \times [(\gamma^* - \delta)(\delta - \alpha)]^{-(\sigma' - w)} \gamma[\sigma' - w, (\gamma^* - \delta)(\delta - \alpha)]. \end{aligned} \quad (17)$$

In this formula  $\gamma[.,.]$  is the incomplete gamma function [19].

We may show that the expression (17) is equivalent to (9). Generalization of (9) and (17) is given in Appendix A1.

### 2.3. Expressions for amplitudes in the Fock representation

Now let us pass from the integral expression for matrix elements of  $\langle \gamma | A(\sigma') | \alpha \rangle$  amplitude in the representation of a harmonic oscillator CSs to the expression for  $\langle v | A(\sigma') | w \rangle$  matrix elements in the usual (Fock) representation. For this purpose, we shall use an expansion of the quadratic exponent into a Laguerre polynomial series [20]:

$$\begin{aligned} \exp(\gamma^* x + \alpha y + \gamma^* \alpha z) = & \sum_{v, w=0}^{\infty} C_{vw} \gamma^{*v} \alpha^w, \\ C_{vw} = & \left( \frac{v+w+|v-w|}{2} \right)^{-1} x^{(v-w+|v-w|)/2} y^{(w-v+|w+v|)/2} z^{(v+w-|v-w|)/2} L_{\binom{|v-w|}{v+w-|v-w|}/2} \left( -\frac{xy}{z} \right). \end{aligned}$$

Substituting this into (9) for the  $\langle \gamma | A(\sigma') | \alpha \rangle$  matrix element, we expand CSs into discrete (Fock) states. We obtain the integral representation for the  $\langle v | A(\sigma') | w \rangle$  matrix element of RR amplitude:

$$\begin{aligned} \langle v | A(\sigma') | w \rangle = & \left( \frac{\min(v, w)!}{\max(v, w)!} \right)^{1/2} \int_0^{\infty} d\beta \exp[\delta^2(e\beta - 1) - \beta\sigma'] \\ & \times \left( 2\delta e^{-\beta/2} \operatorname{sh} \frac{\beta}{2} \right)^{|v-w|} L_{\min(v, w)}^{|v-w|} \left( -4\delta^2 \operatorname{sh}^2 \frac{\beta}{2} \right), \end{aligned} \quad (18)$$

where  $\min(v, w)$  and  $\max(v, w)$  are the minimum and maximum values of  $v$  and  $w$ , respectively.

If one considers separately only Stokes or anti-Stokes processes, one can simplify equation (18). For example, if  $v \geq w$ , having replaced an integral variable, we calculate that

$$\langle v | A(\sigma') | w \rangle = \delta^{v-w} \left( \frac{w!}{v!} \right)^{1/2} \int_0^1 dt e^{-\delta^2 t} (1-t)^{\sigma'-1} L_w^{v-w} \left( -\frac{\delta^2 t^2}{1-t} \right). \quad (19)$$

Integrals of the (18) and (19) type can be calculated and they represent a sum of products of the gamma function  $\Gamma(\cdot)$  and confluent hypergeometric function  $\Phi(\dots)$  [19]. For example,

$$\langle v | A(\sigma') | 0 \rangle = \frac{\Gamma(\sigma')}{\Gamma(\sigma' + v + 1)} \delta^v (v!)^{1/2} \Phi(v + 1, \sigma' + v + 1, -\delta^2). \quad (20)$$

This formula coincides with the expression given in [6]. From the representation (17) one can obtain an expression equivalent to equation (20):

$$\langle v|A(\sigma')|0\rangle = \Gamma(\sigma') \frac{\delta^v}{(v!)^{1/2}} \sum_{n=0}^{\infty} \frac{\Gamma(n+v+1)}{\Gamma(\sigma'+n+v+1)} \cdot \frac{(-\delta^2)^n}{n!}.$$

#### 2.4. Recurrence relations

Knowing the generating function  $\langle \gamma|A(\sigma')|\alpha\rangle$  gives us the opportunity to obtain recurrence relations for the  $\langle v|A(\sigma')|w\rangle$  matrix elements. Taking the derivative of this value with respect to the CS parameter  $\alpha$  we find

$$\frac{\partial}{\partial \alpha} \langle \gamma|A(\sigma')|\alpha\rangle = (\gamma^* - \delta) \langle \gamma|A(\sigma')|\alpha\rangle + \delta \langle \gamma|A(\sigma' - 1)|\alpha\rangle. \quad (21)$$

Expanding into  $\alpha$  and  $\gamma^*$  power series and equating coefficients of equal powers in the right and in the left sides of the expression, we obtain the recurrence relation

$$\begin{aligned} \langle v|A(\sigma')|w+1\rangle &= \left(\frac{v}{w+1}\right)^{1/2} \langle v-1|A(\sigma')|w\rangle \\ &+ \frac{\delta}{(w+1)^{1/2}} [\langle v|A(\sigma'-1)|w\rangle - \langle v|A(\sigma')|w\rangle]. \end{aligned} \quad (22)$$

Taking the derivative of the generating function with respect to  $\gamma^*$  we obtain by analogy:

$$\begin{aligned} \langle v+1|A(\sigma')|w\rangle &= \left(\frac{w}{v+1}\right)^{1/2} \langle v|A(\sigma')|w+1\rangle \\ &+ \frac{\delta}{(v+1)^{1/2}} [\langle v|A(\sigma')|w\rangle - \langle v|A(\sigma'+1)|w\rangle]. \end{aligned} \quad (23)$$

The recurrence relations (22) and (23) connect matrix elements between them when arguments  $\sigma'$  differ by 1. For matrix elements  $\langle v|A(\sigma')|0\rangle$ , with a vibrationless initial state, one can obtain recurrences connecting RR amplitudes with the same value  $\sigma'$ . For this purpose, it is necessary to use their evident expression via special functions.

For example, using the Gauss formula for contiguous relations between confluent hypergeometric functions [19] we obtain

$$\delta \langle \gamma|A(\sigma'+1)|0\rangle = \frac{\sigma'}{\gamma^* - \delta} \langle \gamma|A(\sigma')|0\rangle - \frac{\exp -\frac{1}{2}|\gamma|^2}{\gamma^* - \delta}.$$

Substituting this expression into (21), making differentiation procedures and equating again obtained coefficients of equal powers of CS parameters, we have

$$\langle v+1|A(\sigma')|0\rangle = -\left(\frac{v}{v+1}\right)^{1/2} \langle v-1|A(\sigma')|0\rangle + \frac{\delta^2 + \sigma' + v}{\delta(v+1)^{1/2}} \langle v|A(\sigma')|0\rangle - \frac{\delta_{v0}}{\delta}, \quad (24)$$

where  $\delta_{v0}$  is the Kronecker delta. This recurrence relation (24) coincides with one obtained by another method in [21].

### 3. System with a finite number of vibrational degrees of freedom

#### 3.1. Formulation of a problem

In this section we consider a case of excitation of several normal vibrations in a molecular system. A vibrational structure of the ground electronic state is modelled by a multidimensional harmonic oscillator with the Hamiltonian

$$\mathcal{H} = \frac{1}{2} \sum_{j=1}^n \omega_j (a_j a_j^\dagger + a_j^\dagger a_j), \quad (25)$$

where  $\omega_j$  is the frequency corresponding to the  $j$ -th normal mass-weighted coordinate  $x_j$ , through which the generation operators  $a_j^\dagger$  and annihilation operators  $a_j$  of vibrational quanta are expressed in the usual way:

$$a_j = \frac{1}{\sqrt{2}} (x_j(\omega_j)^{1/2} + i p_j / (\omega_j)^{1/2}),$$

$$a_j^\dagger = \frac{1}{\sqrt{2}} (x_j(\omega_j)^{1/2} - i p_j / (\omega_j)^{1/2}).$$

It is suggested that in excited electronic state the molecular Hamiltonian takes the form

$$\mathcal{H}' = \frac{1}{2} \sum_{j=1}^n \omega'_j (b_j b_j^\dagger + b_j^\dagger b_j), \quad (26)$$

where  $\omega'_j$  is the frequency corresponding to a normal mass-weighted coordinate

$$x'_j = x_j - R_j. \quad (27)$$

$R_j$  is the value of the molecular potential surface minimum shift in the excited state (relative to the ground state) along the  $j$ -th coordinate,  $b_j$  is annihilation operator of the  $j$ -th vibrational mode quantum in the excited electronic state, and  $b_j^\dagger$  is the adjoint of  $b_j$ . As in the one-dimensional case in the final formulae we suppose

$$\forall j \quad \omega_j = \omega'_j. \quad (28)$$

We consider, as usual, that the initial molecules are in a vibrationless state. This simplifies the obtained formulae. Then, we can rewrite the polarizability tensor (2) in the following form:†

$$\alpha_{\nu\sigma} = \text{const} \langle \nu | G(\sigma) | 0 \rangle, \quad (29)$$

$$G(\sigma) = \sum_m \frac{|m\rangle \langle m|}{\sigma + \omega m}, \quad (30)$$

$$\sigma = \Delta E_{e_g} - \omega_0 - i\Gamma. \quad (31)$$

Quantities in these formulae were explained earlier.

† The RR amplitude operator  $G(\sigma)$  is proportional to the operator  $A(\sigma')$  and, in contrast to the latter, it is not measured in units of any normal vibration frequency with symmetry preservation aim with respect to all  $n$  excited vibrations in the system.

For the RR amplitude matrix elements  $\langle \mathbf{v} | G(\sigma) | \mathbf{0} \rangle$ , by analogy with the one-dimensional case (6), one may pass to an eigentime representation, where

$$\langle \mathbf{v} | G(\sigma) | \mathbf{0} \rangle = \sum_{\mathbf{m}} \int_0^{\infty} d\beta e^{-\beta(\sigma - \omega \mathbf{m})} \langle \mathbf{v} | \mathbf{m} \rangle \langle \mathbf{m} | \mathbf{0} \rangle. \quad (32)$$

And again, these matrix elements are the main consideration.

### 3.2. Expressions for amplitudes in the coherent state representation

Matrix elements of RR amplitudes in the CS representation of a multi-dimensional harmonic oscillator should be written in the following form:

$$\langle \gamma | G(\sigma) | \mathbf{0} \rangle = \exp(-\frac{1}{2}|\gamma|^2) \sum_{\mathbf{v}} \frac{\gamma_1^{*v_1} \dots \gamma_n^{*v_n}}{(v_1! \dots v_n!)^{1/2}} \langle \mathbf{v} | G(\sigma) | \mathbf{0} \rangle.$$

To simplify similar expression by analogy with Bargmann [22], we must introduce the designations

$$\mathbf{v}! = v_1! \dots v_n!, \quad \gamma^{*\mathbf{v}} = \gamma_1^{*v_1} \dots \gamma_n^{*v_n},$$

in accordance with which we can rewrite the previous expression in the form of

$$\langle \gamma | G(\sigma) | \mathbf{0} \rangle = \exp(-\frac{1}{2}|\gamma|^2) \sum_{\mathbf{v}} \frac{\gamma^{*\mathbf{v}}}{(\mathbf{v}!)^{1/2}} \langle \mathbf{v} | G(\sigma) | \mathbf{0} \rangle, \quad (33)$$

and the generating function for (32) will be

$$\langle \gamma | G(\sigma) | \mathbf{0} \rangle = \sum_{\mathbf{m}} \int_0^{\infty} d\beta e^{-\beta(\sigma + \omega \mathbf{m})} \langle \gamma | \mathbf{m} \rangle \langle \mathbf{m} | \mathbf{0} \rangle.$$

In accordance with section 2, where the method of calculation for the one-vibrational mode was set forth, let us consider the product of the multidimensional overlap integrals

$$\langle \gamma | \zeta \rangle \langle \zeta | \mathbf{0} \rangle = \exp(-|\zeta|^2) \sum_{\mathbf{m}} \frac{|\zeta|^{2\mathbf{m}}}{\mathbf{m}!} \langle \gamma | \mathbf{m} \rangle \langle \mathbf{m} | \mathbf{0} \rangle. \quad (34)$$

The scalar product of two multidimensional CSs in the case of oscillator coordinate transformation under excitation according to the rule (27) can be presented in the form of a product of one-dimensional ones:

$$\langle \gamma | \zeta \rangle = \prod_{j=1}^n \langle \gamma_j | \zeta_j \rangle.$$

Having used for each of the one-dimensional scalar products the presentation similar to (13), we can rewrite the previous equality in the following way:

$$\begin{aligned} \langle \gamma | \zeta \rangle &= \exp[-\frac{1}{2}(|\zeta|^2 + |\gamma|^2 + \delta^2) + \zeta \delta] \\ &\times \prod_{j=1}^n \chi_j^{-1/2} \exp\left[\frac{\psi_j}{2\chi_j}(\zeta_j - \delta_j)^2 + \frac{1}{\chi_j}(\zeta_j - \delta_j)\gamma_j^* - \frac{\psi_j}{2\chi_j}\gamma_j^{*2}\right], \end{aligned}$$

where

$$\chi_j = \frac{\omega_j + \omega'_j}{2(\omega_j \omega'_j)^{1/2}}, \quad \psi_j = \frac{\omega_j - \omega'_j}{2(\omega_j \omega'_j)^{1/2}},$$



where  $\delta$  is a vector compounded of dimensionless displacements  $\delta_j$  along each normal coordinate:

$$\delta = (\delta_1, \dots, \delta_n)$$

Hence

$$\begin{aligned} \langle \gamma | \zeta \rangle \langle \zeta | 0 \rangle = & \exp \left[ -|\zeta|^2 - \frac{1}{2}|\gamma|^2 - \delta^2 + \gamma^* \delta \right] \prod_{j=1}^n \chi_j^{-1} \exp \left\{ \frac{\psi_j}{2\chi_j} [(\gamma_j^* - \delta_j)^2 + \delta_j^2] \right. \\ & \left. + \frac{1}{\chi_j} [(\gamma_j^* - \delta_j)\zeta_j - \zeta_j^* \delta_j] - \frac{\psi_j}{2\chi_j} (\zeta_j^2 + \zeta_j^{*2}) \right\}. \end{aligned}$$

Now let us fulfill the condition (28), i.e. let  $\forall j \chi_j = 1$ ,  $\psi_j = 0$ . Taking into account (34), we obtain

$$\sum_{\mathbf{m}} \frac{|\zeta|^{2\mathbf{m}}}{\mathbf{m}!} \langle \gamma | \mathbf{m} \rangle \langle \mathbf{m} | 0 \rangle = \exp \left[ -\frac{1}{2}|\gamma|^2 - \delta^2 + (\gamma^* - \delta)\zeta - \zeta^* \delta + \gamma^* \delta \right].$$

Further, using the representation of the modified Bessel function  $I_0$  in the form of a series, we obtain

$$\langle \gamma | \mathbf{m} \rangle \langle \mathbf{m} | 0 \rangle = \exp \left( -\frac{1}{2}|\gamma|^2 - \delta^2 + \gamma^* \delta \right) \prod_{j=1}^n \frac{[(\delta_j - \gamma_j^*) \delta_j]^{m_j}}{m_j!}.$$

This enables us to write down the overall multidimensional sum (33) in CSs representation:†

$$\langle \gamma | G(\sigma) | 0 \rangle = \exp \left[ -\frac{1}{2}|\gamma|^2 - (\delta - \gamma^*) \delta \right] Q[(\delta_1 - \gamma_1^*) \delta_1, \dots, (\delta_n - \gamma_n^*) \delta_n; \omega_1, \dots, \omega_n; -\sigma]. \quad (35)$$

In the expression

$$Q[z_1, \dots, z_n; \omega_1, \dots, \omega_n; c] = \sum_{\mathbf{m}} \frac{z^{\mathbf{m}}}{\mathbf{m}! (\omega \mathbf{m} - c)}. \quad (36)$$

Some properties of the  $Q$ -function are given in Appendix A2.

### 3.3. Expressions for amplitudes in the Fock representation

The integral expression for generating functions of multidimensional RR amplitude matrix elements follows from that for the special  $Q$ -function (see Appendix A2):

$$\langle \gamma | G(\sigma) | 0 \rangle = \exp \left( -\frac{1}{2}|\gamma|^2 \right) \int_0^\infty d\beta e^{-\beta\sigma} \prod_{j=1}^n \exp \left[ -\delta_j^2 (1 - e^{-\beta\omega_j}) + \gamma_j^* \delta_j (1 - e^{-\beta\omega_j}) \right]. \quad (37)$$

Expanding the equality obtained into a series in powers of parameter  $\gamma_j^*$ , we deduce the integral expression for the RR amplitude matrix elements in Fock space:

$$\langle \mathbf{v} | G(\sigma) | 0 \rangle = \int_0^\infty d\beta e^{-\beta\sigma} \frac{[\delta(1 - e^{-\beta\omega})]^{\mathbf{v}}}{(\mathbf{v}!)^{1/2}} \prod_{j=1}^n \exp \left[ -\delta_j^2 (1 - e^{-\beta\omega_j}) \right]. \quad (38)$$

† The equality (35) can be deduced also by another method [23], by analogy with the method described in Appendix A1.

Calculating the integral (37) one can derive the amplitude matrix element representation in terms of a multiple series:

$$\langle \mathbf{v} | G(\sigma) | \mathbf{0} \rangle = \frac{\delta^{\mathbf{v}}}{(\mathbf{v}!)^{1/2}} \left[ \prod_{j=1}^n e^{-\delta_j} \sum_{k_j=0}^{\infty} \delta_j^{2k_j} (k_j!)^{-1} \sum_{l_j=0}^{v_j} (-1)^{l_j} \binom{v_j}{l_j} \right] \left[ 6 + \sum_{j=1}^n \omega_j (k_j + l_j) \right]^{-1}. \quad (39)$$

where  $\binom{v_j}{l_j}$  are binomial coefficients.

### 3.4. Recurrence relations

Recurrence relations for generating functions of RR amplitude matrix elements with different arguments result from the relation (A5) for a special  $Q$ -function with contiguous values of energy variable:

$$\sum_{j=1}^n (\delta_j - \gamma_j^*) \delta_j \omega_j \langle \gamma | G(\sigma + \omega_j) | \mathbf{0} \rangle + \sigma \langle \gamma | G(\sigma) | \mathbf{0} \rangle - \exp(-\frac{1}{2}|\gamma|^2) = 0.$$

Expanding matrix elements into a series in powers of the CSs parameter and equating terms of the same power, we obtain

$$\sum_{j=1}^n [\delta_j^2 \omega_j \langle \mathbf{v} | G(\sigma + \omega_j) | \mathbf{0} \rangle - \delta_j \omega_j (v_j)^{1/2} \langle v_j - 1 | G(\sigma + \omega_j) | \mathbf{0} \rangle] + \sigma \langle \mathbf{v} | G(\sigma) | \mathbf{0} \rangle - \frac{\delta_{\mathbf{v}, \mathbf{0}}}{(\mathbf{v}!)^{1/2}} = 0. \quad (40)$$

In this formula we use the designation

$$\langle v_j - 1 | G(\sigma + \omega_j) | \mathbf{0} \rangle = \langle v_1, \dots, v_{j-1}, v_j - 1, v_{j+1}, \dots, v_n | G(\sigma + \omega_j) | \mathbf{0} \rangle,$$

where  $\delta_{\mathbf{v}, \mathbf{0}}$  is an  $n$ -dimensional Kronecker delta.

The recurrence relation (40) connects the amplitudes with arguments differed on a quantity of normal frequencies. It is interesting to get a connection of matrix elements of RR amplitudes with exciting only any one normal coordinate. Having differentiated the integral expression for the matrix element  $\langle \gamma | G(\sigma) | \mathbf{0} \rangle$  (37) with respect to the chosen  $\gamma_j^*$ , and having done the same with expansion of this matrix element with respect to the Fock states (33), let us equate the series obtained. We find [24] that

$$\forall j \quad (v_j + 1)^{1/2} \langle v_j + 1 | G(\sigma) | \mathbf{0} \rangle = \delta_j (\langle \mathbf{v} | G(\sigma) | \mathbf{0} \rangle - \langle \mathbf{v} | G(\sigma + \omega_j) | \mathbf{0} \rangle), \quad (41)$$

where the following designation is accepted:

$$\langle v_j + 1 | G(\sigma) | \mathbf{0} \rangle = \langle v_1, \dots, v_{j-1}, v_j + 1, v_{j+1}, \dots, v_n | G(\sigma) | \mathbf{0} \rangle.$$

Using (41) in common relations (40) we can get rid of expressions with displaced arguments of the  $\sigma + \omega_j$  type. As a result, we obtain the following symmetrical relations connecting the RR operator  $G(\sigma)$  matrix elements:

$$\sum_{j=1}^n [\delta_j \omega_j (v_j)^{1/2} \langle v_j - 1 | G(\sigma) | \mathbf{0} \rangle - (v_j + 1)^{1/2} \langle v_j + 1 | G(\sigma) | \mathbf{0} \rangle] + (\delta_j^2 + v_j) \omega_j \langle \mathbf{v} | G(\sigma) | \mathbf{0} \rangle + \sigma \langle \mathbf{v} | G(\sigma) | \mathbf{0} \rangle - \delta_{\mathbf{v}, \mathbf{0}} = 0. \quad (42)$$

In these relations all the matrix elements depend upon one and the same argument and differ by an excitation number of different normal vibrations. In the case of only one normal coordinate, the relations (42) are coming to recurrence relations (24) obtained earlier.

#### 4. Illustration

Linear-chain mixed-valence platinum complexes are solid crystal salts under standard conditions. The platinum exists in the ground state of these molecules in two different environments, square planar and octahedral with formal oxidation states, +2 and +4 respectively. Platinum ions are bridged by halogens. A molecule formed in this way is a linear chain with alternate valences of chain-making platinum ions. Physical properties of such compounds are highly anisotropic, and they may be treated as quasi-one-dimensional semiconductors [25].

RR spectra of complexes of interest [26] are observed if molecules are irradiated by light with frequencies in the absorption band. Electron transition is electrically allowed, and RR spectra are characterized by long intense progression  $\omega_1 v_1$ , where  $\omega_1$  is the totally symmetric stretching vibration of the  $\text{Pt}^{+4}\text{-X}$  chain; X is the halogen. The anharmonicity constants for such modes are on the average  $-1.0 \text{ cm}^{-1}$  for chlorides, and about  $-0.3 \text{ cm}^{-1}$  for bromides. This is in agreement with the general observation that the vibration-forming long progression of RR overtones is harmonic. The intense progression of the main vibration  $\omega_1$  is accompanied by other weak progressions, the enabling mode of which is another Raman-active mode, while the progression-forming mode is, as for the main progression,  $\omega_1$ .

With respect to equation (1), from the ratio of intensities of the RR bands corresponding to different sets  $\mathbf{v}_1$  and  $\mathbf{v}_2$  of vibrational quanta, we obtain

$$\frac{I_{\mathbf{v}_2 0}}{I_{\mathbf{v}_1 0}} = \left( \frac{\omega_0 - \omega \mathbf{v}_2}{\omega_0 - \omega \mathbf{v}_1} \right)^4 \frac{|\langle \mathbf{v}_2 | G(\sigma) | 0 \rangle|^2}{|\langle \mathbf{v}_1 | G(\sigma) | 0 \rangle|^2}, \quad (43)$$

where matrix elements  $\langle \mathbf{v} | G(\sigma) | 0 \rangle$  are given by (38) and (39) and are dependent on dimensionless displacements  $\delta$  of the molecule potential surface minimum.

From experimentally measured values of the RR intensities of the first overtone and the fundamental of the main progression-forming mode  $\omega_1$ , with the help of equation (43), we found the magnitudes of the dimensionless displacement. The displacements and the corresponding axial  $\text{Pt}^{+4}\text{-X}$  bond length changes  $R$  (10) on excitation from the ground to the resonant excited state for the compounds investigated are listed in table 1. Displacements along other excited normal coordinates were obtained in the same way. So we have extracted the excited-state geometry of such molecules from the RR spectra [27].

With the help of displacement magnitudes by recurrence relations of section 3.4 we computed relative overtone and combination band intensities, i.e. intensities with respect to the intensity of the main progression-forming mode  $\omega_1$ . Calculated RR spectra of these complexes are in good agreement with experimental ones. This testifies to the reliability of the obtained excited-state geometry parameters.

Table 1. Computed excited-state geometry changes for linear-chain mixed-valence platinum complexes.

Complex	$\delta$	$R$ (Å)
$[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$	2.54	0.21
$[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Br}_2](\text{ClO}_4)_4$	1.77	0.15
$[\text{Pt}(\text{en})\text{Cl}_2][\text{Pt}(\text{en})\text{Cl}_4]$	2.00	0.17
$[\text{Pt}(\text{en})\text{Br}_2][\text{Pt}(\text{en})\text{Br}_4]$	1.99	0.17

$\text{en} = 1,2\text{-diaminoethane } \text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH}_2$ .

The author of [26], who did not succeed in extracting such information from RR spectra of these platinum complexes using other methods, suggested, in terms of chemistry, that the  $\text{Pt}^{+4}\text{-X}$  bond length changes on excitation, perhaps by some tenths of an angstrom; this agrees with the magnitudes we obtained.

## 5. Conclusion

We now consider the principal results obtained in this paper. With the help of the CS method, we carried out the exact summation of the contributions from all the multidimensional vibrational diversity of the intermediate electronic state into the polarizability tensor of RR scattering in a polyatomic system. For the RR amplitude matrix elements, closed expressions, using molecular system parameters and experimental conditions, were obtained. Amplitude matrix elements are expressed using a  $Q$  special function. Recurrence relations for  $Q$ -functions and some types of recurrence relations for matrix elements of RR amplitudes are deduced. In the case of the excitation of one normal mode, the expressions obtained are as previously achieved by other methods.

The developed formalism enables one to solve the problem of extracting excited-state geometry parameter according to RR spectroscopy data as well as RR band intensity calculation.

Application of the method to the spectra of concrete species has been carried out. For illustration, we chose linear-chain mixed-valence platinum complexes, the calculations for which cannot be provided by other methods.

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## Appendix

### A1. Generalization of equation (9)

In view of possible subsequent generalizations we obtain an expression for matrix elements in the coherent state representation without the condition (14). Remembering [17] that the exponent  $\exp [2xz - x^2]$  is a generating function for the Hermite polynomials  $H_m(x)$  and taking into account that the scalar product  $\langle \gamma | \alpha \rangle$  is a generating function for the product  $\langle m | \alpha \rangle$  in a mixed basis we obtain from equation (12) the necessary expression for the product  $\langle m | \alpha \rangle$  included in equation (8):

$$\langle m | \alpha \rangle = \exp \left[ -|\alpha|^2 + \frac{\psi}{2\chi} (\alpha - \delta)^2 + \alpha\delta - \frac{1}{2}\delta^2 \right] \frac{(\psi/\chi)^{m/2}}{(2^m m! \chi)^{1/2}} H_m \left( \frac{\alpha - \delta}{(2\chi\psi)^{1/2}} \right). \quad (\text{A } 1)$$

Substituting the equality (A 1) into the initial expansion (8) and using, as it was done above, the Mehler formula for the Hermite polynomials product, we obtain an integral expression for the matrix elements of RR amplitude in the coherent state representation in the following form:

$$\begin{aligned} \langle \gamma | A(\sigma') | \alpha \rangle = & \exp \left[ -\frac{1}{2}(|\alpha|^2 + |\gamma|^2) - \delta^2 \right] \\ & \times \int_0^\infty d\beta \frac{\exp(-\beta\sigma')}{(\chi^2 - \psi^2 e^{-2\beta})^{1/2}} \exp \left\{ \frac{\chi\psi \operatorname{sh} \beta}{\chi^2 e^\beta - \psi^2 e^{-\beta}} [(\alpha e^{\beta(x+\psi)^2} - \delta^2) + (\gamma^* - \delta)^2] \right. \\ & \left. + \frac{[\alpha e^{\beta(x+\psi)^2} - \delta](\gamma^* - \delta)}{\chi^2 e^\beta - \psi^2 e^{-\beta}} + \delta[\alpha e^{\beta(x+\psi)^2} + \gamma^*] \right\}. \quad (\text{A } 2) \end{aligned}$$

This integral expression (A 2) has a more common nature than (9) because deducing the first one it was suggested that frequencies of the normal mode in the initial and in the excited states are different. If one takes a condition (14) of frequencies equality, i.e.  $\chi=1$  and  $\psi=0$ , one will come back from (A 2) to the expression (9).

### A 2. Special $Q$ -function

The  $Q$ -function like (36) appeared [12] in connection with investigations of various systems in the CS representation of quadratic Hamiltonians. The function depends on  $2n+1$  variables. It is convenient to name the first  $n$  variables,  $z_j$ , as the main variables, the second group of variables,  $\omega_j$ , as frequency variables, and the last variable as energy.

Somehow this function is one of the natural generalizations of a confluent hypergeometric function in a multidimensional case. Namely, with the identical frequency variables  $\omega_1 = \dots = \omega_n = \omega$  the  $Q$ -function comes to a confluent hypergeometric one:

$$Q[z_1, \dots, z_n; \omega, \dots, \omega; -\sigma] = \frac{1}{\sigma} \exp\left(\sum_{j=1}^n z_j\right) \Phi\left(1, 1 - \frac{\sigma}{\omega}, -\sum_{j=1}^n z_j\right).$$

In the case of a one vibrational mode the expression (35) comes to (20). If one rewrites (36) in eigentime  $\beta$  representation and sums over states  $m$ , one can obtain the integral representation for the  $Q$ -function:

$$Q[z_1, \dots, z_n; \omega_1, \dots, \omega_n; -\sigma] = \int_0^\infty d\beta \exp\left[-\beta\sigma + \sum_{j=1}^n z_j \exp(-\beta\omega_j)\right]. \quad (\text{A } 3)$$

Hence, we immediately have a formula for a  $Q$ -function differentiation along any main variable:

$$\frac{\partial}{\partial z_j} Q[z_1, \dots, z_n; \omega_1, \dots, \omega_n; -\sigma] = Q[z_1, \dots, z_n; \omega_1, \dots, \omega_n; -\sigma - \omega_j]. \quad (\text{A } 4)$$

Integrating the representation (A 3) by parts, one obtains the recurrence relation connecting the  $Q$ -function with different energy variables; that is,

$$\sum_{j=1}^n \omega_j z_j Q[z_1, \dots, z_n; \omega_1, \dots, \omega_n; -\sigma - \omega_j] + \sigma Q[z_1, \dots, z_n; \omega_1, \dots, \omega_n; -\sigma] = \exp\left(\sum_{j=1}^n z_j\right). \quad (\text{A } 5)$$

If we consider the one-dimensional function  $Q[z; \omega; -\sigma]$ , there remains only three terms in recurrence relation (A 5) and we come to Gauss relations for contiguous confluent hypergeometric functions [19].

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