

Global treatment of line intensities of vibrational-rotational transitions of acetylene molecule. Approach and design formulas

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A semiempirical method of global calculations of the vibrational-rotational line intensities of acetylene molecule developed within the framework of effective operator approach is presented.

Introduction

A series of our recent papers¹⁻¹⁴ has been devoted to the problem of global simulation of high-resolution spectra of linear triatomic molecules of CO₂ and N₂O. This simulation was made in the framework of the method of efficient operators. Two parameters of a spectral line, its center and integral intensity, were simulated. In these papers it was shown that the models, created by the authors, enabled us not only to reproduce, but also to predict both the centers and the intensities of spectral lines with an accuracy approaching that of the present-day experiment. In the subsequent papers^{15,16} the global simulation was extended to the line centers of tetratomic linear molecule of acetylene. The present paper is devoted to the global simulation of line intensities of the vibrational-rotational transitions of this molecule.

Line intensity. Line strength

The intensity of an absorption line $S_{b \leftarrow a}(T)$ due to the vibrational-rotational transition $b \leftarrow a$ in the units of cm⁻¹/(molecule cm⁻²) at the temperature T , K, is given by the well-known expression

$$S_{b \leftarrow a}(T) = \frac{8\pi^3}{3hc} C g_a \nu_{b \leftarrow a} \frac{\exp(-hcE_a/kT)}{Q(T)} \times [1 - \exp(-hc\nu_{b \leftarrow a}/kT)] W_{b \leftarrow a}, \quad (1)$$

here c is the speed of light, h is the Planck's constant, k is the Boltzmann constant, C is the content of a given isotope in a sample being studied, g_a is the statistical weight of the lower level, $Q(T)$ is the partition function, $\nu_{b \leftarrow a}$ is the frequency of the transition (wave number), E_a is the energy of lower state, $W_{b \leftarrow a}$ is the probability of the transition or the line strength.

In other units of the line intensity, namely, cm⁻¹/atm at T , K, an additional multiplier

$n \cdot 273.15/T$ appears in the formula (1), where n is the Loschmidt number. Thus, the relation between the two above-mentioned units is given by the expression:

$$1 \text{ cm}^{-1}/\text{mol} \cdot \text{cm}^{-2} \text{ at } T, \text{ K} = n \cdot 273.15/T \text{ cm}^{-1}/\text{atm at } T, \text{ K}. \quad (2)$$

A cumbersome procedure in the calculations of line intensities is connected with the calculation of the probability of the transition $W_{b \leftarrow a}$ or, as it is called in the literature, the line strength. In the sections below the schematic of semiempirical calculations of these probabilities will be given in the framework of the method of effective operators.

Operator of an effective dipole moment

In Ref. 15 we have proposed an effective vibration-rotation Hamiltonian describing fully the vibration-rotation energy levels of the acetylene molecule in its ground electronic state. In our next paper¹⁶ this effective Hamiltonian, earlier developed up to higher orders of the perturbation theory, was used for global processing of calculated results on the vibration-rotation energy levels of the acetylene molecule, being lower than 6000 cm⁻¹. As a result, this processing enabled us to reconstruct parameters of the effective Hamiltonian and to find the effective wave functions of vibration-rotation states, lying below 6000 cm⁻¹.

The effective Hamiltonian proposed is based on the assumption of cluster structure of the vibrational energy levels, following from the approximate relations between the harmonic frequencies

$$\omega_1 \approx \omega_3 \approx 5\omega_4 \approx 5\omega_5, \quad (3)$$

$$\omega_2 \approx 3\omega_4 \approx 3\omega_5. \quad (4)$$

One cluster or polyad, numbered by the integer P , contains the vibrational states, whose quantum numbers satisfy the relation

$$P = 5V_1 + 3V_2 + 5V_3 + V_4 + V_5. \quad (5)$$

The effective Hamiltonian describes only the interactions in an explicit form between the vibrational states of the same polyad. The remaining interactions are fully allowed for by the effective Hamiltonian parameters.

The effective Hamiltonian H^{eff} can be obtained from the vibrational-rotational Hamiltonian H_{VR} using contact transformations

$$H^{\text{eff}} = e^{iS} H_{VR} e^{-iS}, \quad (6)$$

and, hence, the corresponding operator of the effective dipole moment M^{eff} can be obtained from the operator M of dipole moment by the same contact transformations

$$M^{\text{eff}} = e^{iS} M e^{-iS}. \quad (7)$$

Within the framework of the method of effective operators the strength $N'J'\epsilon' \leftarrow NJ\epsilon$ of a line due to the transition between the vibration-rotation states numbered by the set of vibrational quantum numbers N , the quantum number of the angular momentum J , and the evenness $\epsilon = \pm 1$, are given by the following expression:

$$\begin{aligned} W_{N'J'\epsilon' \leftarrow NJ\epsilon} &= 3 \sum_{MM'} \left| \langle \Psi_{N'J'\epsilon'}^{\text{eff}} | M_Z^{\text{eff}} | \Psi_{NJ\epsilon}^{\text{eff}} \rangle \right|^2 = \\ &= 3 \sum_{MM'} \left| \sum_{\ell_4 \ell_5} \sum_{V_1 V_2 V_3 V_4 V_5} \sum_{V_1' V_2' V_3' V_4' V_5'} \times \right. \\ &\times J_{N\epsilon}^{V_1 V_2 V_3 V_4 V_5 \ell_4 \ell_5} J_{N'\epsilon'}^{V_1' V_2' V_3' V_4' V_5' \ell_4' \ell_5'} \times \\ &\left. \langle V_1' V_2' V_3' V_4' V_5' \ell_4' \ell_5' J' M' K' \epsilon' | M_Z^{\text{eff}} | V_1 V_2 V_3 V_4 V_5 \ell_4 \ell_5 J M K \epsilon \rangle \right|^2, \quad (8) \end{aligned}$$

here $J_{N\epsilon}^{V_1 V_2 V_3 V_4 V_5 \ell_4 \ell_5}$ are the mixing coefficients determining the wave eigenfunction of the effective Hamiltonian

$$\begin{aligned} \Psi_{NJM\epsilon}^{\text{eff}} &= \sum_{\ell_4 \ell_5} J_{N\epsilon}^{V_1 V_2 V_3 V_4 V_5 \ell_4 \ell_5} \times \\ &\times |V_1 V_2 V_3 V_4 V_5 \ell_4 \ell_5 J M K \epsilon\rangle. \quad (9) \end{aligned}$$

Here Wang combinations are taken as the basis functions

$$\begin{aligned} |V_1 V_2 V_3 V_4 V_5 \ell_4 \ell_5 J M K \epsilon\rangle &= \\ &= \frac{1}{\sqrt{2}} (|V_1 V_2 V_3 V_4 V_5 \ell_4 \ell_5\rangle |J M K = \ell_4 + \ell_5\rangle + \\ &+ \epsilon |V_1 V_2 V_3 V_4 V_5 - \ell_4 - \ell_5\rangle |J M - K = -\ell_4 - \ell_5\rangle), \quad (10) \\ &|V_1 V_2 V_3 V_4 V_5 0 0 J M 0 \epsilon = 1\rangle = \end{aligned}$$

$$= |V_1 V_2 V_3 V_4 V_5 0 0\rangle |J M 0\rangle, \quad (11)$$

where $|V_1 V_2 V_3 V_4 V_5 \ell_4 \ell_5\rangle$ and $|J M K\rangle$ are the eigenfunctions of the energy operator of harmonic vibrations of C_2H_2 molecule and the eigenfunctions of a rigid symmetric top, respectively.

As noted above, the effective dipole moment operator, used in Eq. (8), can be obtained by contact transformations (7). However, in the present paper, we will not use contact transformations, but the operator of effective dipole moment can be constructed corresponding to the effective Hamiltonian^{15,16} from the symmetry considerations.

Transformation characteristics of the operator cyclic components of the effective dipole moment

The component M_Z of the dipole moment in the space-fixed coordinate system is connected with the components of dipole moment μ_x, μ_y, μ_z in the molecular-fixed coordinate system by the well-known relationship

$$\begin{aligned} M_Z &= D_{10}^{(1)}(-\theta, -\phi, -\chi) \mu_1 + D_{00}^{(1)}(-\theta, -\phi, -\chi) \mu_0 + \\ &+ D_{-10}^{(1)}(-\theta, -\phi, -\chi) \mu_{-1}, \quad (12) \end{aligned}$$

where $D_{m0}^{(1)}(-\theta, -\phi, -\chi)$ is the Wigner D -functions, and the cyclic components of the dipole moment μ_1, μ_0, μ_{-1} are expressed in terms of Cartesian components by the following equations:

$$\mu_1 = -\frac{1}{\sqrt{2}} (\mu_x + i\mu_y), \quad (13)$$

$$\mu_0 = \mu_z, \quad (14)$$

$$\mu_{-1} = \frac{1}{\sqrt{2}} (\mu_x - i\mu_y). \quad (15)$$

After applying the transform (7) to Eq. (12) the dipole moment components μ_1, μ_0, μ_{-1} become the vibration-rotation operators and, because no commutation between the above components and the Wigner D -functions exists, Eq. (12) should be rewritten in the anticommutation form. However, to simplify the presentation later on we shall use Eq. (12), and, when we are dealing with the calculation of matrix elements, we return to its anticommutator form.

We impose most general requirements of Hermitian character on the operator of effective dipole moment, namely, the realness as well as the requirements connected with its behavior relative to the transformations from a group of molecular symmetry. As a result, we obtain the transformation characteristics of cyclic components of the operator of effective dipole moment in the molecular-fixed coordinate system, which then will be used to construct the expansion of these components in terms of elementary vibrational and rotational operators.

Hermitian character

The requirement of Hermitian character $(M_Z^{\text{eff}})^+ = M_Z^{\text{eff}}$ results in the relationship

$$\begin{aligned} (D_{10}^{(1)})^* \mu_1^+ + (D_{00}^{(1)})^* \mu_0^+ + (D_{-10}^{(1)})^* \mu_{-1}^+ &= \\ = D_{-10}^{(1)} \mu_{-1} + D_{00}^{(1)} \mu_0 + D_{10}^{(1)} \mu_1, \end{aligned} \quad (16)$$

which can be performed under the following conditions:

$$\mu_1^+ = -\mu_{-1}, \quad (17)$$

$$\mu_{-1}^+ = -\mu_1, \quad (18)$$

$$\mu_0^+ = \mu_0. \quad (19)$$

Here and below + sign is used to denote the operation of Hermitian conjugation, and the * sign is used to denote the operation of complex conjugation. When deriving the conditions (17)–(19) we used the following characteristic of the Wigner D -functions:

$$(D_{MM'}^{(J)})^* = (-1)^{M-M'} D_{-M-M'}^{(J)}. \quad (20)$$

Realness

The requirement of realness $(M_Z^{\text{eff}})^T = M_Z^{\text{eff}}$ results in the relationship

$$\begin{aligned} (D_{10}^{(1)})^* \mu_1^T + (D_{00}^{(1)})^* \mu_0^T + (D_{-10}^{(1)})^* \mu_{-1}^T &= \\ = D_{-10}^{(1)} \mu_{-1} + D_{00}^{(1)} \mu_0 + D_{10}^{(1)} \mu_1, \end{aligned} \quad (21)$$

which can be performed only under the following conditions:

$$\mu_1^T = -\mu_{-1}, \quad (22)$$

$$\mu_{-1}^T = -\mu_1, \quad (23)$$

$$\mu_0^T = \mu_0. \quad (24)$$

The sign “T” is used in this paper to denote the operation of time inversion, which reduces to the change in sign of time and to complex conjugation of the coefficients in front of the operators.

Transforms from the group of molecular symmetry

The group of symmetry of the acetylene molecule C_2H_2 is $D_{\infty h}$ group having three forming elements, namely, the turn by an arbitrary angle ψ around a molecular axis $C(\psi)$, the reflection in the plane σ_{xz} passing through a molecular axis, and the inversion I . The molecular-fixed coordinate system is chosen in such a way that the molecule axis coincides with the axis z of the molecular-fixed coordinate system. According to the Hougen¹⁷ and Longe-Higgins¹⁸ scheme, with these operations of the point symmetry group the following operations can be compared from the extended commutation-inversion group¹⁹

$$C(\psi) \rightarrow E_\psi, \quad \sigma_{xz} \rightarrow E_0^*, \quad I \rightarrow (12)(34)_\pi^*, \quad (25)$$

where E is the identical commutation with a subsequent turn through the angle ψ around the axis of a molecule, E_0^* is the space inversion, and $(12)(34)_\pi^*$ is the commutation with the inversion and with the subsequent turn around the molecule axis through the angle π . Numeration of atoms is given in Fig. 1.

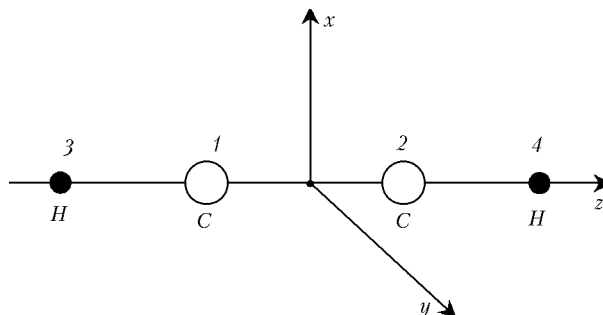


Fig. 1.

The dipole moment of the molecule is invariant relative to the commutation of identical kernels and reverses the sign at space inversion. Thus, the dipole moment of acetylene molecule is invariant relative to the operation $C(\psi)$ and reverses the sign at the operations σ_{xz} and I .

Operation $C(\psi) \rightarrow E_\psi$

The requirement of invariance of effective dipole moment relative to this operation $C(\psi)M_Z^{\text{eff}} = M_Z^{\text{eff}}$ results in the following law of transform for the cyclic components

$$C(\psi) \mu_\tau = e^{i\tau\psi} \mu_\tau, \quad (26)$$

where $\tau = -1, 0, 1$, since the Wigner D -functions under this operation are transformed as follows:

$$C(\psi) D_{\tau M'}^{(J)} = e^{-i\tau\psi} D_{\tau M'}^{(J)}. \quad (27)$$

Inversion operation $I \rightarrow (12)(34)_\pi^*$

As discussed above, the space-fixed component of effective dipole moment reverses the sign under the inversion operation $IM_Z^{\text{eff}} = -M_Z^{\text{eff}}$. The Wigner D -functions are invariant relative to the inversion

$$ID_{MM'}^{(J)} = D_{MM'}^{(J)}, \quad (28)$$

because in this operation the orientation of molecular-fixed coordinate system is the same, i.e., it does not act upon the Euler angles

$$I(\theta, \varphi, \chi) = (\theta, \varphi, \chi). \quad (29)$$

Hence, the components of effective dipole moment in the molecular-fixed coordinate system reverse sign under the inversion operation.

$$I\mu_\tau = -\mu_\tau. \quad (30)$$

From Eqs. (28) and (29) it follows that the rotational wave functions and the rotational operators are invariant relative to the inversion, i.e., are transformed by irreducible representations $\langle g \rangle$ of symmetry group of molecule $D_{\infty h}$. Thus, the inversion operation characteristic of the symmetry group of C_2H_2 molecule only yields the vibrational selection rules $g \leftrightarrow u$.

Operation $\sigma_{xz} \rightarrow E_0^*$

The space-fixed component of effective dipole moment reverses sign under this operation

$$E_0^* M_Z^{\text{eff}} = -M_Z^{\text{eff}}. \quad (31)$$

The orientation of molecular-fixed coordinate system under this operation varies as follows:

$$E_0^*(\theta, \varphi, \chi) = (\pi - \theta, \varphi + \pi, \pi - \chi), \quad (32)$$

and, hence, the Wigner D -function is transformed as

$$\begin{aligned} E_0^* D_{\tau_0}^{(1)}(\theta, \varphi, \chi) &= D_{\tau_0}^{(1)}(\pi - \theta, \varphi + \pi, \pi - \chi) = \\ &= -(-1)^\tau D_{-\tau_0}^{(1)}(\theta, \varphi, \chi). \end{aligned} \quad (33)$$

Taking into account Eqs. (31) and (33) we have

$$\begin{aligned} E_0^* M_Z^{\text{eff}} &= E_0^* \{D_{10}^{(1)} \mu_1 + D_{00}^{(1)} \mu_0 + D_{-10}^{(1)} \mu_{-1}\} = \\ &= -\{-D_{-10}^{(1)}(E_0^* \mu_1) + D_{00}^{(1)}(E_0^* \mu_0) - \\ &\quad - D_{10}^{(1)}(E_0^* \mu_{-1})\} = -M_Z^{\text{eff}}, \end{aligned} \quad (34)$$

from that follows the law of transform of cyclic components of the effective dipole moment in the molecular-fixed coordinate system:

$$E_0^* \mu_1 = -\mu_{-1}, \quad (35)$$

$$E_0^* \mu_{-1} = -\mu_1, \quad (36)$$

$$E_0^* \mu_0 = \mu_0. \quad (37)$$

Expansion of the effective dipole moment operator

A traditional method of contact transformations²⁰ results in a power series over elementary rotational and vibrational operators for molecular-fixed components of the effective dipole moment operator. Thus for a cyclic component μ_1 we have

$$\begin{aligned} \mu_1 &= \sum M_\eta^{(mn)(pq)(rs)(lkg)(efab)dct} (a_1^{+m} a_1^n) (a_2^{+p} a_2^q) \times \\ &\quad \times (a_3^{+r} a_3^s) ({}^4A_+^+)^l ({}^4A_+^+)^k ({}^4A_+^-)^g ({}^4A_+^-)^h \times \\ &\quad \times ({}^5A_+^+)^e ({}^5A_+^-)^f ({}^5A_+^-)^a ({}^5A_+^-)^b J^{2d} G_\eta^{ct}, \end{aligned} \quad (38)$$

where summation is performed over all indices of the parameter $M_\eta^{(mn)(pq)(rs)(lkg)(efab)dct}$, and G_η^{ct} is of the form

$$G_{+1}^{ct} = J_+^c (2J_z + c)^t \quad (39)$$

for $\eta = +1$,

$$G_0^t = J_z^t \quad (40)$$

for $\eta = 0$ and

$$G_{-1}^{ct} = (2J_z + c)^t J_-^c \quad (41)$$

for $\eta = -1$. In Eqs. (38)–(41) the following designations are used for elementary vibrational and rotational operators: a_i^+ and a_i are the operators of creation and annihilation of a vibrational quantum of nondegenerate vibration ($i = 1, 2, 3$) at the frequency ω_i ; the ladder operators for degenerate vibrations ($j = 4, 5$) are determined by the following expressions:

$${}^jA_\pm^+ = a_{ja}^+ \pm i a_{jb}^+, \quad (42)$$

$${}^jA_\pm^- = a_{ja}^- \pm i a_{jb}^-, \quad (43)$$

and the ladder operators of the angular momentum components are introduced as

$$J_\pm = J_x \mp i J_y, \quad (44)$$

where J_x, J_y, J_z are the Cartesian components of angular momentum in the molecular-fixed coordinate system. Matrix elements of the elementary vibrational and rotational operators are given in the Appendix, and their transformation characteristics are given in Table 1. Using these characteristics based on Eq. (26) we can obtain the following condition for powers of vibrational and rotational operators:

$$\begin{aligned} [(l + g) - (k + h)] + [(e + a) - \\ - (f + b)] - \eta c = 1. \end{aligned} \quad (45)$$

If, taking into account the matrix elements of elementary vibrational and rotational operators, as well as the condition

$$\Delta\ell_4 + \Delta\ell_5 = \Delta K, \quad (46)$$

that follows from the Hougén condition

$$\ell_4 + \ell_5 = K, \quad (47)$$

which is used when constructing the isomorphic vibration-rotation Hamiltonian of a linear molecule,²¹ Eq. (26) can be written in the following form:

$$- \eta c = 1 - (\Delta\ell_4 + \Delta\ell_5). \quad (48)$$

An expression for a cyclic component is derived from Eq. (38) using the relation (17)

$$\mu_{-1} = - \sum (M_\eta^{(mn)(pq)(rs)(lkg)(efab)dct})^* (a_1^{+n} a_1^m) \times$$

$$\begin{aligned} & \times (a_2^{+q} a_2^p) (a_3^{+s} a_3^r) ({}^4A_+^+)^h ({}^4A_+^-)^g ({}^4A_+^+)^k ({}^4A_+^-)^l \times \\ & \times ({}^5A_+^+)^b ({}^5A_+^-)^a ({}^5A_+^-)^f ({}^5A_+^-)^e J^{2d} G_{-\eta}^{ct}. \quad (49) \end{aligned}$$

Table 1. Transformation characteristics of elementary operators

Operator $j = 4, 5;$ $\tau = \text{"+"}, \text{"-"}"$	Hermitian conjugation	Time inversion	Turn $C(\psi)$	Inversion I	Reflection in a plane σ_{xz}
${}^jA_{\tau}^{\pm}$	${}^jA_{-\tau}^{\mp}$	${}^jA_{-\tau}^{\pm}$	$e^{-i\tau\psi} {}^jA_{\tau}^{\pm}$	$(-1)^j {}^jA_{\tau}^{\pm}$	${}^jA_{-\tau}^{\pm}$
$a_{\Sigma_g^+}^{\pm}$	$a_{\Sigma_g^+}^{\mp}$	$a_{\Sigma_g^+}^{\pm}$	$a_{\Sigma_g^+}^{\pm}$	$a_{\Sigma_g^+}^{\pm}$	$a_{\Sigma_g^+}^{\pm}$
$a_{\Sigma_u^+}^{\pm}$	$a_{\Sigma_u^+}^{\mp}$	$a_{\Sigma_u^+}^{\pm}$	$a_{\Sigma_u^+}^{\pm}$	$-a_{\Sigma_u^+}^{\pm}$	$a_{\Sigma_u^+}^{\pm}$
J_{τ}	$J_{-\tau}$	$-J_{-\tau}$	$e^{-i\tau\psi} J_{\tau}$	J_{τ}	$-J_{-\tau}$
J_z	J_z	$-J_z$	J_z	J_z	$-J_z$

$$\begin{aligned} \mu_{-1} &= (-1)^{c+t+1} \sum (M_{\eta}^{(mn)(pq)(rs)(lkg h)(efab)dct})^* \times \\ & \times (a_1^{+m} a_1^n) (a_2^{+p} a_2^q) (a_3^{+r} a_3^s) ({}^4A_+^+)^k ({}^4A_+^-)^l ({}^4A_+^-)^h ({}^4A_+^-)^g \times \\ & \times ({}^5A_+^+)^f ({}^5A_+^-)^e ({}^5A_+^-)^b ({}^5A_+^-)^a J^{2d} G_{-\eta}^{ct}. \quad (50) \end{aligned}$$

Comparing Eqs. (49) and (50), we find the following relation between the parameters M :

$$\begin{aligned} & (M_{\eta}^{(mn)(pq)(rs)(lkg h)(efab)dct})^* = \\ & = (-1)^{c+t} (M_{\eta}^{(nm)(qp)(sr)(ghlk)(abef)dct})^*. \quad (51) \end{aligned}$$

Finally, the cyclic component of the dipole moment in the molecular-fixed coordinate system μ_{-1} can be obtained from the cyclic component μ_1 using the operation E_0^* , Eq. (35)

$$\begin{aligned} \mu_{-1} &= (-1)^{c+t+1} \sum M_{\eta}^{(mn)(pq)(rs)(lkg h)(efab)dct} \times \\ & \times (a_1^{+m} a_1^n) (a_2^{+p} a_2^q) (a_3^{+r} a_3^s) ({}^4A_+^+)^k ({}^4A_+^-)^l ({}^4A_+^-)^h ({}^4A_+^-)^g \times \\ & \times ({}^5A_+^+)^f ({}^5A_+^-)^e ({}^5A_+^-)^b ({}^5A_+^-)^a J^{2d} G_{-\eta}^{ct}. \quad (52) \end{aligned}$$

Comparing Eqs. (49) and (52), we derive one more relationship between the parameters M :

$$\begin{aligned} & (M_{\eta}^{(mn)(pq)(rs)(lkg h)(efab)dct})^* = \\ & = (-1)^{c+t} M_{\eta}^{(nm)(qp)(sr)(ghlk)(abef)dct}. \quad (53) \end{aligned}$$

From the relationships (51) and (53) follows the realness of the parameters M . Finally, we have the following relation between these parameters:

$$\begin{aligned} & M_{\eta}^{(mn)(pq)(rs)(lkg h)(efab)dct} = \\ & = (-1)^{c+t} M_{\eta}^{(nm)(qp)(sr)(ghlk)(abef)dct}. \quad (54) \end{aligned}$$

Applying time inversion operation to the cyclic component μ_1 with the account of Eq. (22) results in one more expression for the cyclic component μ_{-1}

Taking into account the requirement of Hermitian property (19) of the cyclic component μ_0 of the effective dipole moment operator in the molecular-fixed coordinate system the expansion of this component can be presented as follows:

$$\begin{aligned} \mu_0 &= \sum [{}^{(0)}M_{\eta}^{(mn)(pq)(rs)(lkg h)(efab)dct} (a_1^{+m} a_1^n) (a_2^{+p} a_2^q) \times \\ & \times (a_3^{+r} a_3^s) ({}^4A_+^+)^l ({}^4A_+^-)^k ({}^4A_+^-)^g ({}^4A_+^-)^h \times \\ & \times ({}^5A_+^+)^e ({}^5A_+^-)^f ({}^5A_+^-)^a ({}^5A_+^-)^b J^{2d} G_{\eta}^{ct} + \\ & + ({}^{(0)}M_{\eta}^{(mn)(pq)(rs)(lkg h)(efab)dct})^* (a_1^{+n} a_1^m) \times \\ & \times (a_2^{+q} a_2^p) (a_3^{+s} a_3^r) ({}^4A_+^+)^h ({}^4A_+^-)^g ({}^4A_+^-)^k ({}^4A_+^-)^l \times \\ & \times ({}^5A_+^+)^b ({}^5A_+^-)^a ({}^5A_+^-)^f ({}^5A_+^-)^e J^{2d} G_{-\eta}^{ct}]. \quad (55) \end{aligned}$$

To fulfill the condition (26), it is necessary that

$$[(l + g) - (k + h)] + [(e + a) - (f + b)] = c, \quad (56)$$

or, what is the same,

$$\Delta\ell_4 + \Delta\ell_5 = \Delta K = c. \quad (57)$$

When performing the consideration, which is analogous to the preceding one, and using the conditions (24) and (37), we can show the realness of the parameters ${}^{(0)}M$ and the fulfillment of the following condition:

$$\begin{aligned} & {}^{(0)}M_{\eta}^{(mn)(pq)(rs)(lkg h)(efab)dct} = \\ & = (-1)^{c+t} {}^{(0)}M_{\eta}^{(nm)(qp)(sr)(ghlk)(abef)dct}, \quad (58) \end{aligned}$$

which coincides by its form with the condition (54). We shall use the relations (54) and (58) in what follows in calculating matrix elements of the effective dipole moment operator.

Line strength. Design equations

Using the expansions (38) and (55) for the cyclic components of effective dipole moment in the molecular-

fixed coordinate system, as well as the relations (54) and (58) between the coefficients of these expansions, the matrix elements, in Eq. (8), were calculated. In the calculation we used the matrix elements of elementary vibrational and rotational operators given in the Appendix as well as the relationship

$$\langle J'K'M' | D_{00}^{(1)} | JKM \rangle = \sqrt{\frac{2J+1}{2J'+1}} (1\tau JK | J'K') (10 JM | J'M'), \quad (59)$$

where $(J_1 m_1 J_2 m_2 | Jm)$ is inserted for the Clebsch–Gordan coefficients. After summing over magnetic quantum numbers M and M' in Eq. (8), when we used the relationship

$$\sum_{MM'} (10 JM | J' M')^2 = \frac{2J'+1}{3}, \quad (60)$$

an expression was derived in the first orders by the perturbation theory for the line strength of the vibration-rotation transition $N'J'\epsilon \leftarrow NJ\epsilon$:

$$W_{N'J'\epsilon \leftarrow NJ\epsilon} = (2J+1) \left| \sum_{\substack{V_1 V_2 V_3 V_4 V_5 \\ \ell_4 \ell_5}} \sum_{\substack{5\Delta V_1 + 3\Delta V_2 + 5\Delta V_3 + \Delta V_4 + \Delta V_5 = \Delta P \\ \Delta \ell_4 = 0, \pm 1, \pm 2, \dots \\ \Delta \ell_5 = 0, \pm 1, \pm 2, \dots}} J C_{N\epsilon}^{V_1 V_2 V_3 V_4 V_5 \ell_4 \ell_5} \times \right. \\ \left. \times J' C_{N'\epsilon'}^{V_1 + \Delta V_1 V_2 + \Delta V_2 V_3 + \Delta V_3 V_4 + \Delta V_4 V_5 + \Delta V_5 \ell_4 + \Delta \ell_4 \ell_5 + \Delta \ell_5} \left\{ M_{\Delta V}^{\Delta \ell_4 \Delta \ell_5} \Phi_{\Delta J \Delta K}(J, K) \times \right. \right. \\ \left. \left. \times \sqrt{f_{\Delta V}^{\Delta \ell_4 \Delta \ell_5}(V, \ell_4, \ell_5)} \left(1 + \delta_{\ell_4, 0} \delta_{\ell_5, 0} + \delta_{\ell_4 + \Delta \ell_4, 0} \delta_{\ell_5 + \Delta \ell_5, 0} - 2\delta_{\ell_4, 0} \delta_{\ell_5, 0} \delta_{\ell_4 + \Delta \ell_4, 0} \delta_{\ell_5 + \Delta \ell_5, 0} \right) \times \right. \right. \\ \left. \left. \times \left(1 + \sum_i \kappa_i^{\Delta V} V_i + \sum_{i=4,5} a_i^{\Delta V} (2\ell_i \Delta \ell_i + 1) + F_{\Delta J \Delta K}^{\Delta V}(J, K) \right) \right\} \right|^2. \quad (61)$$

The functions $\Phi_{\Delta J \Delta K}(J, K)$ in Eq. (61) for $\Delta K = 0, \pm 1$ coincide with the Clebsch–Gordan coefficients

$$\Phi_{\Delta J \Delta K}(J, K) = (1\Delta K JK | J + \Delta J K + \Delta K), \quad (62)$$

and for $\Delta K = \pm 2$ the functions are given by the following expressions:

$$\Phi_{1\pm 2}(J, K) = (1 \pm 1JK | J + 1K \pm 1) \times \sqrt{(J \mp K)(J \pm K + 3)}, \quad (63)$$

$$\Phi_{0\pm 2}(J, K) = (1 \pm 1JK | J K \pm 1) \times \sqrt{(J \mp K - 1)(J \pm K + 2)}, \quad (64)$$

$$\Phi_{-1\pm 2}(J, K) = (1 \pm 1JK | J - 1K \pm 1) \times \sqrt{(J \mp K - 2)(J \pm K + 1)}. \quad (65)$$

The functions $F_{\Delta J \Delta K}(J, K)$ involved in the factor of Hermann-Wallis type, for $\Delta K = 0, \pm 1$ are given below and they coincide with those we have used for triatomic linear molecules, excluding specific case of tetratomic linear molecules $\Delta K = 0, \Delta \ell_4 \neq 0, \Delta \ell_5 \neq 0$. If $\Delta K = \pm 1$, these functions are the following:

Q-branch:

$$F_{\Delta J \Delta K}^{\Delta V}(J, K) = -\frac{1}{2} b_J^{\Delta V} (2K\Delta K + 1) + d_{JQ}^{\Delta V} \left[J(J+1) - K^2 - \Delta K \left(K + \frac{\Delta K}{2} \right) \right]; \quad (66)$$

P- and R-branches:

$$F_{\Delta J \Delta K}^{\Delta V}(J, K) = -\frac{1}{4} (d_{JQ}^{\Delta V} - d_J^{\Delta V}) - \frac{1}{2} (b_J^{\Delta V} + d_{JQ}^{\Delta V}) (2K\Delta K + 1) - d_{JQ}^{\Delta V} K^2 + b_J^{\Delta V} m + d_J^{\Delta V} m^2 + (d_{JQ}^{\Delta V} - d_J^{\Delta V}) m \left(K\Delta K + \frac{1}{2} \right). \quad (67)$$

Here $m = -J, 0, J + 1$ for P, Q and R-branches, respectively.

For $\Delta K = 0, \Delta \ell_4 = 0, \Delta \ell_5 = 0$, as in the case of triatomic linear molecules we have

$$F_{\Delta J \Delta K=0}^{\Delta V}(J, K) = b_J^{\Delta V} m + d_J^{\Delta V} [J(J+1) + m - K^2]. \quad (68)$$

It should be noted that in this case at $\ell_4 = \ell_5 = 0$ Q-branch is lacking.

For a specific case $\Delta K = 0, \Delta \ell_4 \neq 0, \Delta \ell_5 \neq 0$ it is necessary to consider two possibilities: a) $K = 0$, b) $K \neq 0$.

a) $K = 0$.

In this case the function $F_{\Delta J \Delta K=0}^{\Delta V}(J, K)$ is given by Eq. (68) for P- and R-branches. However, Q-branch

occurs only in the first order by the perturbation theory and therefore the expression for a corresponding matrix element (the expression in braces of Eq. (61)) is replaced by the expression

$${}^Q M_{\Delta V}^{\Delta \ell_4 \Delta \ell_5} \sqrt{f_{\Delta V}^{\Delta \ell_4 \Delta \ell_5}(V, \ell_4, \ell_5)} \sqrt{J(J+1)}. \quad (69)$$

Note that this case was discussed by Watson²² using as an example the bands $(\nu_4 + \nu_5) \Sigma_u^+ - (0) \Sigma_g^+$ and $(\nu_4 + \nu_5) \Sigma_u^- - (0) \Sigma_g^-$ of C_2H_2 molecule.

b) $K \neq 0$.

In this case the function $F_{\Delta J \Delta K}^{\Delta V}(J, K)$ is given again by Eq. (68) for P - and R -branches, and for Q -branch we have

$$F_{\Delta J \Delta K}^{\Delta V}(J, K) = \left[\frac{\Delta V d_{JQ}^{\Delta \ell_4 \Delta \ell_5}}{K} + d_J^{\Delta V} \right] [J(J+1) - K^2]. \quad (70)$$

Note that the parameter $\Delta V d_{JQ}^{\Delta \ell_4 \Delta \ell_5}$ has the same order of smallness as the parameter $b_J^{\Delta V}$. Hence, in the special case considered strong dependence of the function $F_{\Delta J \Delta K}^{\Delta V}(J, K)$ on the quantum number of angular momentum J is observed.

The functions $f_{\Delta V}^{\Delta \ell_4 \Delta \ell_5}(V, \ell_4, \ell_5)$ under the radical sign in the relation (61) can be obtained as the products of elementary functions given in Appendix. The combination of products of the Kronecker symbols appears under the square root in expression (61) because of the Wang basis used. The parameters of matrix elements of the operator of effective dipole moment

$$M_{\Delta V}^{\Delta \ell_4 \Delta \ell_5} = M_{\Delta V}^{-\Delta \ell_4 - \Delta \ell_5}, \quad {}^Q M_{\Delta V}^{\Delta \ell_4 \Delta \ell_5} = -{}^Q M_{\Delta V}^{-\Delta \ell_4 - \Delta \ell_5},$$

$$\kappa_i^{\Delta V} (i = 1, 2, 3, 4, 5), \quad a_i^{\Delta V} (i = 4, 5), \quad b_J^{\Delta V}, \quad d_J^{\Delta V},$$

$$d_{JQ}^{\Delta V} \text{ and } \Delta V d_{JQ}^{\Delta \ell_4 \Delta \ell_5} = -\Delta V d_{JQ}^{-\Delta \ell_4 - \Delta \ell_5}$$

$$\left({}^Q M_{\Delta V}^{\Delta \ell_4 \Delta \ell_5} = M_{\Delta V}^{\Delta \ell_4 \Delta \ell_5} \Delta V d_{JQ}^{\Delta \ell_4 \Delta \ell_5} \right),$$

involved in the expression (61) and expressions for the functions $F_{\Delta J \Delta K}^{\Delta V}(J, K)$, describe simultaneously the line intensities of cold and hot bands belonging to a given series of transitions determined by the value of ΔP . In the semiempirical approach used these parameters are fitted to the experimental values of line intensities, and then serve for predicting line intensities with large values of quantum number of the angular momentum J as well as lines of hot bands belonging to the series being considered.

Classification of vibration-rotation states. Selection rules

To collect all data, necessary for calculating the line intensities of acetylene molecule, we give in this section reference data on the symmetry classification of vibration-rotation states of this molecule as well as the selection rules determining the processes of dipole absorption and emission.

Owing to the condition $K = \ell_4 + \ell_5$ the vibration-rotation states of acetylene molecule can have only the Σ symmetry type.

The evenness of vibration-rotation state is determined by the value $\varepsilon(-1)^J$. When denoting the type of symmetry of vibration-rotation state, the evenness is denoted by the upper indices “+” or “-“:

$$\varepsilon(-1)^J = \begin{cases} 1 \rightarrow \Sigma^+ \\ -1 \rightarrow \Sigma^- \end{cases}. \quad (71)$$

The behavior of vibration-rotation state relative to the inversion operation from the point group of molecule $D_{\infty h}$ is determined by the value $(-1)^{V_3+V_5}$. Symmetric states are denoted by the subscript “ g ”, and antisymmetric states are denoted by the subscript “ u ”.

$$(-1)^{V_3+V_5} = \begin{cases} 1 \rightarrow \Sigma_g \\ -1 \rightarrow \Sigma_u \end{cases}. \quad (72)$$

The nuclear statistical weights are given in Table 3. The selection rules for spectra of dipole absorption of molecule C_2H_2 are given in Table 2.

**Table 2. Selection rules for spectra
of dipole absorption of C_2H_2 molecule**

Vibration	
ΔV_5 is odd number ($\Delta \ell_5 = \pm 1, \pm 3, \dots$),	ΔV_3 is even number
ΔV_5 is even number ($\Delta \ell_5 = 0, \pm 2, \pm 4, \dots$),	ΔV_3 is odd number
Vibration-rotation	
Group $D_{\infty h}$	
$+ \leftrightarrow -$	
$g \leftrightarrow u$	
Group $SO(3)$	
ΔJ	$\varepsilon \leftrightarrow \varepsilon'$

$\Delta J = 0$	$1 \leftrightarrow -1$
$\Delta J = \pm 1$	$\begin{cases} 1 \leftrightarrow 1 \\ -1 \leftrightarrow -1 \end{cases}$

Table 3. Nuclear statistical weights of acetylene molecule

Type of symmetry	g
Σ_g^+, Σ_u^-	1
Σ_g^-, Σ_u^+	3

Conclusion

In this paper we described the approach and general pattern of global calculations of line intensities of vibration-rotation transitions in the spectra of dipole absorption of acetylene molecule. The approach developed is based on the method of effective operators. In our next paper this approach will be used for simultaneously describing line intensities of cold and hot bands in the range of 13.6; 7.8, and 5 μm .

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APPENDIX

Matrix elements of elementary vibrational and rotational operators in the case of tetratomic linear molecules

Nondegenerate vibrations

$$\begin{aligned} \langle V_i + 1 | a_i^+ | V_i \rangle &= \sqrt{V_i + 1}, \\ \langle V_i - 1 | a_i^- | V_i \rangle &= \sqrt{V_i}, \end{aligned}$$

where $i = 1, 2, 3$ numbers nondegenerate vibrations.

Degenerate vibrations

$$\begin{aligned} \langle V_t + 1 \ell_t \pm 1 | A_{\pm}^{\pm} | V_t \ell_t \rangle &= \mp \sqrt{V_t \pm \ell_t + 2}, \\ \langle V_t - 1 \ell_t \pm 1 | A_{\pm}^{\mp} | V_t \ell_t \rangle &= \pm \sqrt{V_t \mp \ell_t}, \end{aligned}$$

where $t = 4, 5$ numbers the degenerate vibrations.

Components of the angular momentum

$$\langle J K \pm 1 | J_{\pm} | J K \rangle = \sqrt{(J \mp K)(J \pm K + 1)}.$$

Vibration phases and wave functions are selected according to our calculations.²³

Functions $f_{\Delta V_1 \Delta V_2 \Delta V_3 \Delta V_4 \Delta V_5}^{\Delta \ell_4 \Delta \ell_5}(V_1, V_2, V_3, V_4, V_5, \ell_4, \ell_5)$.

These functions consist of the product of elementary functions for each mode which are determined by the following matrix elements:

$$\begin{aligned} \sqrt{f_{\Delta V_i}(V_i)} &= \langle V_i + \Delta V_i | (a_i^+)^{\Delta V_i} | V_i \rangle = \\ &= \sqrt{\frac{(V_i + 1)(V_i + 2) \dots (V_i + \Delta V_i)}{\Delta V_i}}, \\ \sqrt{f_{-\Delta V_i}(V_i)} &= \langle V_i - \Delta V_i | a_i^{\Delta V_i} | V_i \rangle = \\ &= \sqrt{\frac{V_i(V_i - 1) \dots (V_i - \Delta V_i + 1)}{\Delta V_i}}, \end{aligned}$$

where $i = 1, 2, 3$.

$$\begin{aligned} \sqrt{f_{\Delta V_i}^{\pm \Delta \ell_t}(V_t, \ell_t)} &= (-1)^{\frac{1}{2}(\Delta V_i \pm \Delta \ell_t)} \times \\ &\times \langle V_t + \Delta V_t \ell_t \pm \Delta \ell_t | (A_+^+)^{\frac{1}{2}(\Delta V_i \pm \Delta \ell_t)} (A_-^+)^{\frac{1}{2}(\Delta V_i \mp \Delta \ell_t)} | V_t \ell_t \rangle = \\ &= \sqrt{(V_t + \ell_t + 2)^{\frac{1}{2}(\Delta V_i \pm \Delta \ell_t)} (V_t - \ell_t + 2)^{\frac{1}{2}(\Delta V_i \mp \Delta \ell_t)}}, \\ \sqrt{f_{-\Delta V_i}^{\pm \Delta \ell_t}(V_t, \ell_t)} &= (-1)^{\frac{1}{2}(\Delta V_i \mp \Delta \ell_t)} \times \\ &\times \langle V_t - \Delta V_t \ell_t \pm \Delta \ell_t | (A_+^-)^{\frac{1}{2}(\Delta V_i \pm \Delta \ell_t)} (A_-^-)^{\frac{1}{2}(\Delta V_i \mp \Delta \ell_t)} | V_t \ell_t \rangle = \\ &= \sqrt{(V_t + \ell_t)^{\frac{1}{2}(\Delta V_i \mp \Delta \ell_t)} (V_t - \ell_t)^{\frac{1}{2}(\Delta V_i \pm \Delta \ell_t)}}, \\ \sqrt{f_{\Delta V_i=0}^{\Delta \ell_t}(V_t, \ell_t)} &= (-1)^{\frac{1}{2} \Delta \ell_t} \langle V_t \ell_t + \Delta \ell_t | (A_+^+ A_-^-)^{\frac{1}{2} \Delta \ell_t} | V_t \ell_t \rangle = \\ &= \sqrt{(V_t + \ell_t + 2)^{\frac{1}{2} \Delta \ell_t} (V_t - \ell_t)^{\frac{1}{2} \Delta \ell_t}}, \\ \sqrt{f_{\Delta V_i=0}^{-\Delta \ell_t}(V_t, \ell_t)} &= (-1)^{\frac{1}{2} \Delta \ell_t} \langle V_t \ell_t - \Delta \ell_t | (A_-^+ A_+^-)^{\frac{1}{2} \Delta \ell_t} | V_t \ell_t \rangle = \\ &= \sqrt{(V_t - \ell_t + 2)^{\frac{1}{2} \Delta \ell_t} (V_t + \ell_t)^{\frac{1}{2} \Delta \ell_t}}, \end{aligned}$$

where $t = 4, 5$. In the above expressions we used the following designations:

$$\begin{aligned} x^{\{n\}} &= \underbrace{x(x+2) \dots [x+2(n-1)]}_n, \quad n > 0, \\ x^{\{-n\}} &= \underbrace{x(x-2) \dots [x-2(n-1)]}_n, \quad n > 0. \end{aligned}$$

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