Line intensities of vibration-rotational transitions of acetylene molecule in the 1.5-μm region

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Within the framework of the method of effective operators, simultaneous fitting of line intensities of cold and hot bands of the acetylene molecule lying in the 1.5 μm region is performed. The fitting has resulted in a set of effective dipole moment parameters reproducing the intensities with the experimental accuracy.

Introduction

In the past decade we successfully developed a global approach to description of line intensities of vibration-rotational transitions in acetylene molecule by the method of effective operators. The effective Hamiltonian, globally describing vibration-rotation energy levels in the ground electron state of acetylene molecule and written accurately up to the forth order of magnitude in the Amat–Nielsen grouping scheme, was proposed in Ref. 1. In Ref. 2, main formulae for line intensity calculations of a four-atom molecule were derived for calculation by this method. Fitting the effective Hamiltonian's parameters to experimental line centers of the molecule was described in Refs. 3 and 4. The obtained effective Hamiltonian consists of 145 parameters and satisfactorily restores positions of up to 1000 spectral lines in the $1-10000$ cm^{-1} spectral range. Using the calculated wave functions of the effective Hamiltonian, we have managed to calculate the parameters of the effective dipole moment and describe line intensities of vibration-rotational transitions of acetylene molecule with an experimental accuracy in three spectral ranges.[5] In this work, we present calculation results for line intensities of acetylene molecule in the 1.5 μm spectral range.

Basic theory

The absorption coefficient $S_{b \leftarrow a}(T)$ for the vibration-rotational transition $b \leftarrow a$, cm^{-1}/(mol.·cm^{-2}), with the temperature T, in K, can be written by the well-known expression:

$$S_{b \leftarrow a}(T) = \frac{8\pi^3}{3hc} Cg_a v_{b \leftarrow a} \frac{\exp(-hcE_a / kT)}{Q(T)} \times$$

$$\times \left[1 - \exp\left(-hc v_{b \leftarrow a} / kT\right) \right] W_{b \leftarrow a}. \qquad (1)$$

Here c is the light speed; h is the Plank constant; k is the Boltzmann constant; C is the proportion of the given isotopic species in the sample; g_a is the statistical weight of the lower state; $Q(T)$ is the statistical sum; $v_{b \leftarrow a}$ is the transition frequency (wavenumber); $W_{b \leftarrow a}$ is the transition probability or line strength that can be defined as a square matrix element of the dipole moment operator.

In the frame of our method, for calculation of the line strength we took eigenfunctions of the effective Hamiltonian that can be found through calculation of line centers. The used effective Hamiltonian[4] is based on the assumption that there exists some cluster structure of vibration-rotational energy levels that can be deduced from relations for harmonic frequencies:

$$\omega_1 \approx \omega_3 \approx 5\omega_4 \approx 5\omega_5, \qquad (2)$$

$$\omega_2 \approx 3\omega_4 \approx 3\omega_5. \qquad (3)$$

One cluster or polyad, numbered by the integer P, consists of vibrational states satisfying the following relation for quantum numbers:

$$P = 5V_1 + 3V_2 + 5V_3 + V_4 + V_5. \qquad (4)$$

Effective Hamiltonian, in explicit form, consists of interactions only between vibrational states belonging to the same polyad. Other interactions are included as parameters of the effective Hamiltonian.

The stationary state of the linear molecule belonging to the ground electronic state, in the frame of the polyad approach, can be specified by five numbers: P, N, J, ε, and M, where P is the number of the polyad; N is the number of the vibrational state in the given polyad in increasing order of the energy; J is the quantum number of the angular momentum; $\varepsilon = \pm 1$ is the Wang symmetry coefficient; M is the projection of the angular momentum onto the Z axis in the laboratory system of coordinates. The effective Hamiltonian's eigenfunction, describing this stationary state, can be written as follows:

$$\Psi_{PNJM\varepsilon}^{\text{eff}} =$$

$$= \sum_{\substack{V_1V_2V_3V_4V_5 \\ \ell_4\ell_5}} {}^{J}C_{PN\varepsilon}^{V_1\ V_2\ V_3\ V_4\ V_5\ \ell_4\ \ell_5} |V_1V_2V_3V_4V_5\ell_4\ell_5 JMK\varepsilon\rangle,$$

(5)

where

$$|V_1V_2V_3V_4V_5\ell_4\ell_5 JMK\varepsilon\rangle =$$

$$= \frac{1}{\sqrt{2}}\big(|V_1V_2V_3V_4V_5\ell_4\ell_5\rangle |JMK = \ell_4 + \ell_5\rangle +$$

$$+\varepsilon|V_1V_2V_3V_4V_5 - \ell_4 - \ell_5\rangle|JM - K = -\ell_4 - \ell_5\rangle\big), \quad (6)$$

$$| V_1V_2V_3V_4V_5 0\, 0\, J\, M\, \varepsilon = 1 > =$$

$$= | V_1V_2V_3V_4V_5 0\, 0 > | JM0 > \qquad (7)$$

are the combinations of Wang eigenfunctions $|V_1V_2V_3V_4V_5\ell_4\ell_5\rangle$ of the energy operator of harmonic molecular vibrations and eigenfunctions $|JMK\rangle$ of the rigid symmetric rotor. The eigenfunction symmetry is usually lettered by «e» and «f», which corresponds to $\varepsilon = 1$ and $\varepsilon = -1$, respectively. Recall that in the absence of external electromagnetic fields, vibration-rotational energy levels are M times degenerated.

Using eigenfunctions of the effective Hamiltonian, the line strength for transition $P'N'J'\varepsilon' \leftarrow PNJ\varepsilon$ between two vibration-rotational states can be written as[2]:

Here ${}^{J}C_{PN\varepsilon}^{V_1V_2V_3V_4V_5\ell_4\ell_5}$ are mixing coefficients defining the eigenfunction of the effective Hamiltonian, that can be found when calculating line centers. Functions in Eq. (8) for $\Delta K = 0; \pm 1$ coincide with Clebsh–Gordon coefficients:

$$\Phi_{\Delta J\Delta K}(J,K) = (1\Delta K\ JK\,|\,J + \Delta J\ K + \Delta K). \quad (9)$$

Functions $F_{\Delta J\Delta K}(J,K)$ included in the coefficient of Herman–Wallis type at $\Delta K = 0$ for P- and R-branches have the form

$$F_{\Delta J\Delta K=0}^{\Delta V}(J,K) = b_J^{\Delta V}m + d_J^{\Delta V}[J(J + 1) + m - K^2]. \quad (10)$$

Here $m = -J,\ J + 1$ for P- and R-branches, respectively. We restrict ourselves in this work to expression (10) for Herman–Wallis factor. Other cases are described in Ref. 5. Functions $f_{\Delta V}^{\Delta\ell_4\Delta\ell_5}(V,\ell_4,\ell_5)$ under square root in Eq. (8) are given in Ref. 2. The combination of products of the Kronnecker symbols appears in Eq. (8) under square root as a consequence of using of the Wang basis functions. Parameters in the matrix elements of effective dipole moment operator $M_{\Delta V}^{\Delta\ell_4\Delta\ell_5} = M_{\Delta V}^{-\Delta\ell_4-\Delta\ell_5}$, $\kappa_i^{\Delta V}(i = 1, 2, 3, 4, 5)$, $a_i^{\Delta V}(i = 4, 5)$, $b_J^{\Delta V}$ and $d_J^{\Delta V}$ in Eq. (8) and (10) describe simultaneously the line intensities of "cold" and "hot" bands of the given series of transitions, with the given ΔP. In our semiempirical method, these parameters are fitted to experimental line intensities and then can be used for prediction of line intensities for transitions with high values of J, as well as for calculation of line intensities of "hot" bands of the given series.

$$W_{P'N'J'\varepsilon'\leftarrow PNJ\varepsilon} = (2J + 1)g_{PNJ\varepsilon} \left| \sum_{\substack{5V_1+3V_2+5V_3+V_4+V_5=P \\ \ell_4\ell_5}} \sum_{\substack{5\Delta V_1+3\Delta V_2+5\Delta V_3+\Delta V_4+\Delta V_5=\Delta P \\ \Delta\ell_4\Delta\ell_5}} {}^{J}C_{PN\varepsilon}^{V_1\ V_2\ V_3\ V_4V_5\ell_4\ \ell_5} \times \right.$$

$$\times {}^{J'}C_{P'N'\varepsilon'}^{V_1+\Delta V_1\ V_2+\Delta V_2\ V_3+\Delta V_3\ V_4+\Delta V_4\ V_5+\Delta V_5\ \ell_4+\Delta\ell_4\ \ell_5+\Delta\ell_5} \left\{ M_{\Delta V}^{\Delta\ell_4\ \Delta\ell_5}\Phi_{\Delta J\ \Delta K}(J,K)\times \right.$$

$$\times \sqrt{f_{\Delta V}^{\Delta\ell_4\ \Delta\ell_5}(\mathbf{V},\ell_4,\ell_5)\big(1 + \delta_{\ell_4,0}\delta_{\ell_5,0} + \delta_{\ell_4+\Delta\ell_4,0}\delta_{\ell_5+\Delta\ell_5,0} - 2\delta_{\ell_4,0}\delta_{\ell_5,0}\delta_{\ell_4+\Delta\ell_4,0}\delta_{\ell_5+\Delta\ell_5,0}\big)} \times$$

$$\times \left(1 + \sum_i \kappa_i^{\Delta V\,\Delta\ell_4\Delta\ell_5}V_i + \sum_{i=4,5} a_i^{\Delta V\Delta\ell_4\Delta\ell_5}(2\ell_i + \Delta\ell_i) + {}^{\Delta V}F_{\Delta J\Delta K}^{\Delta\ell_4\Delta\ell_5}(J,K)\right) +$$

$$+ \varepsilon'M_{\Delta V}^{2\ell_4+\Delta\ell_4\ 2\ell_5+\Delta\ell_5}\Phi_{\Delta J-[2(\ell_4+\ell_5)+\Delta\ell_4+\Delta\ell_5]}(J,K)\sqrt{f_{\Delta V}^{-(2\ell_4+\Delta\ell_4)-(2\ell_5+\Delta\ell_5)}(\mathbf{V},\ell_4,\ell_5)}\big(1 - \delta_{\ell_4,0}\delta_{\ell_5,0}\big)\big(1 - \delta_{\ell_4+\Delta\ell_4,0}\delta_{\ell_5+\Delta\ell_5,0}\big) \times$$

$$\left. \times \left(1 + \sum_i \kappa_i^{\Delta V\,2\ell_4+\Delta\ell_4\,2\ell_5+\Delta\ell_5}V_i + \sum_{i=4,5} a_i^{\Delta V\,2\ell_4+\Delta\ell_4\,2\ell_5+\Delta\ell_5}\Delta\ell_i + {}^{\Delta V}F_{\Delta J-[2(\ell_4+\ell_5)+\Delta\ell_4+\Delta\ell_5]}^{2\ell_4+\Delta\ell_4\,2\ell_5+\Delta\ell_5}(J,K)\right)\right\}\right|^2. \qquad (8)$$

Parameters of the operator of effective dipole moment for $\Delta P = 10$

In the framework of the above method, using the least-square method, we have fitted parameters of the operator of the effective dipole moment to the experimental line intensities of four bands[6] in the 6500 cm^{-1} range. These bands belong to a series of transitions with $\Delta P = 10$. Values of mixing coefficients $^{J}C_{PN\varepsilon}^{V_1V_2V_3V_4V_5\ell_4\ell_5}$ were obtained earlier as a result of global fitting of the effective Hamiltonian's parameters to experimental line centers lying below 10000 cm^{-1} (Ref. 4). The statistical sum $Q(T)$ was taken from Ref. 7. The proportion C of the isotopic species $^{12}C_2H_2$ is equal to 0.977828 (Ref. 6).

The main aim of fitting by the least-square method is the minimization of the standard deviation functional defined as follows:

$$\chi = \sqrt{\left.\sum_{i=1}^{N}\left(\frac{S_i^{obs} - S_i^{calc}}{\delta_i}\right)^2 \right/ (N_{obs} - n)}, \qquad (11)$$

where S_i^{obs} and S_i^{calc} are the experimental and calculated intensities of i-th line; $\delta_i = \dfrac{S_i^{obs}\sigma_i}{100\%}$, σ_i is the experimental deviation of ith line, %; N_{obs} is the number of lines included in the fitting; n is the number of fitted parameters. At the standard deviation close to unity, the main part of the fitted parameters has an experimental accuracy. To estimate the fitting quality, it is preferable to use the root mean square deviation (RMS) defined as:

$$RMS = \sqrt{\left.\sum_{i=1}^{N}\left(\frac{S_i^{obs} - S_i^{calc}}{S_i^{obs}}\right)^2 \right/ N_{obs}} \cdot 100\%. \quad (12)$$

Useful information about the quality of fitting is also contained in the mean deviation for band (MR) between the calculated and experimental line intensities, defined by

$$MR = \frac{1}{N_{band}}\sum_{i=1}^{N}\frac{S_i^{obs} - S_i^{calc}}{S_i^{obs}} \cdot 100\%, \qquad (13)$$

where N_{band} is the number of fitted lines for the band.

When fitting line intensities, their experimental values were weighted with the factor $\sigma = 2\%$. Just this accuracy for line intensity calculation is pointed in Ref. 6. The fitting has resulted in the values: $\chi = 0.65$ and RMS = 1.3%, which indicate that experimental intensities are reproduced with the experimental accuracy. The values of the obtained effective dipole moment parameters are given in Table 1, and the results of fitting are summarized in Table 2.

Table 1. Parameters of effective dipole moment operator for C$_2$H$_2$ molecule, $\Delta P = 10$

Parameter*	Value	Parameter	Value
M_{10100}	0.010519(9)**	M_{11011}	0.0009086(8)
κ_4	−0.044(1)	b_J	−0.00028(4)
κ_5	−0.018(1)	d_J	−0.000056(2)
b_J	−0.00026(2)	−	−

     * Values of parameters $M_{\Delta V}$ are given in Deby, other parameters are dimensionless.
     ** The error corresponding to the standard deviation is given in parenthesis.

Line intensities of the $(\nu_1 + \nu_2 + \nu_4 + \nu_5)^0$ band are mainly stipulated by intensity transfer from the $\nu_1 + \nu_3$ band due to anharmonic resonance interactions between these bands. Therefore, El Hachtouki and Vander Auwera[6] have included four coefficients of Herman−Wallis factor to describe the rotational dependence of line intensities of the weaker band $(\nu_1 + \nu_2 + \nu_4 + \nu_5)^0$ in the frame of the nonresonance model. In our model, the rotational dependence of line intensities is mainly included as the rotational dependence of mixing coefficients. As a consequence, we can satisfactorily reproduce experimental intensities of all four bands even with a single main parameter M_{10100}. Values of this parameter and statistical results of fitting for different bands are given in Table 3.

Table 2. Statistical results of fitting for different bands

State *		Range, cm^{-1}	J_{max}	Line number	MR, %	RMS, %
Upper state	Lower state					
1010000	0000000	6452.6–6626.5	37	57	0.01	0.74
110111−1	0000000	6564.1–6685.3	30	47	0.01	1.11
1011010	0001010	6448.3–6587.3	30	84	0.02	1.32
1010101	0000101	6459.2–6591.6	28	81	0.02	1.63

     * Vibrational states are labeled by $V_1V_2V_3V_4V_5\ell_4\ell_5$ quantum numbers.

Table 3. Results of fitting of experimental line intensities of C$_2$H$_2$ molecule with a single parameter for the 1.5 μm region

State*		Range, cm^{-1}	J_{max}	Number of lines	MR, %	RMS, %
Upper state	Lower state					
1010000	0000000	6452.6–6626.5	37	57	2.00	2.45
110111−1	0000000	6564.1–6685.3	30	47	2.41	3.03
1011010	0001010	6448.3–6587.3	30	84	−4.49	4.83
1010101	0000101	6459.2–6591.6	28	81	2.27	2.77
$\chi = 1.77$		RMS = 3.5%		$M_{10100} = 0.01066(1)$D		

     * Vibrational states are denoted by $V_1V_2V_3V_4V_5\ell_4\ell_5$ quantum numbers.
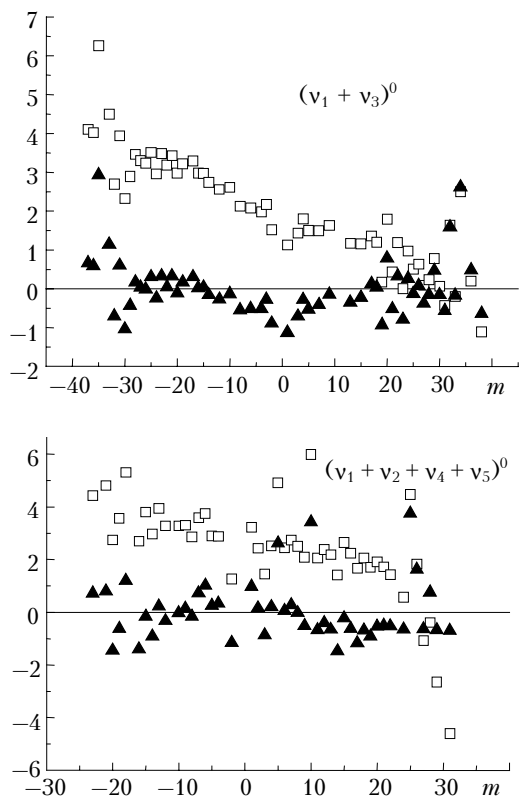
Fig. 1. Relative deviations of experimental line intensities for $(\nu_1 + \nu_3)^0$ and $(\nu_1 + \nu_2 + \nu_4 + \nu_5)^0$ bands from calculated ones. Squares denote relative deviations of line intensities for fitting with a single parameter; triangles denote relative deviations of line intensities for fitting with full set of parameters

In the figure, standard deviations between experimental and calculated line intensities for two "cold" bands are shown. The linear dependence of the standard deviations on m for a single-parameter fitting is clearly seen, although standard deviations

themselves only slightly exceed the experimental uncertainty of line intensities.

Conclusions

A set of parameters for the effective dipole moment operator of the acetylene molecule is calculated, which satisfactorily reproduces line intensities of the molecule in the 1.5 μm range. The set reproduces experimental line intensities[6] for four bands $\nu_1 + \nu_3$, $(\nu_1 + \nu_2 + \nu_4 + \nu_5)^0$, $\nu_1 + \nu_3 + \nu_4 - \nu_4$, and $\nu_1 + \nu_3 + \nu_5 - \nu_5$ with the experimental accuracy. It can be used for intensity calculation of other "hot" bands lying in the 1.5 μm range, i.e., for generation of a high-temperature spectrum of acetylene molecule in the given range of wavelengths.

Acknowledgments

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