Global modeling of vibration-rotation spectra of the acetylene molecule

O.M. Lyulin [a,b], V.I. Perevalov [a,*]

[a] Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Academician Zuev Square, 634055 Tomsk, Russia
[b] National Research Tomsk State University, 36, Lenin av., 634050 Tomsk, Russia

A B S T R A C T

The global modeling of both line positions and intensities of the acetylene molecule in the 50–9900 cm^{-1} region has been performed using the effective operators approach. The parameters of the polyad model of effective Hamiltonian have been fitted to the line positions collected from the literature. The used polyad model of effective Hamiltonian takes into account the centrifugal distortion, rotational and vibrational ℓ-doubling terms and both anharmonic and Coriolis resonance interaction operators arising due to the approximate relations between the harmonic frequencies: $\omega_1 \approx \omega_3 \approx 5\omega_4 \approx 5\omega_5$ and $\omega_2 \approx 3\omega_4 \approx 3\omega_5$. The dimensionless weighted standard deviation of the fit is 2.8. The fitted set of 237 effective Hamiltonian parameters allowed reproducing 24,991 measured line positions of 494 bands with a root mean squares deviation 0.0037 cm^{-1}.

The eigenfunctions of the effective Hamiltonian corresponding to the fitted set of parameters were used to fit the observed line intensities collected from the literature for 15 series of transitions: $\Delta P = 0\text{-}13,15$, where $P = 5V_1 + 5V_3 + 3V_2 + V_4 + V_5$ is the polyad number (V_i are the principal vibrational quantum numbers). The fitted sets of the effective dipole moment parameters reproduce the observed line intensities within their experimental uncertainties 2–20%.

1. Introduction

The reference high temperature spectra of acetylene are of great importance for studying the atmospheres of carbon stars (see, for example, Ref. [1]) and exoplanets [2]. The respective spectra could be obtained experimentally or as a result of theoretical modeling. We know only two experimental papers [3,4] in which the laboratory high temperature spectra of acetylene were studied. The cited papers deal with the emission spectra of acetylene in the 3 μm rigion at temperatures from 870 K to 1455 K. The recorded spectra were theoretically modeled using the global effective rovibrational

Hamiltonian developed in Brussels [3]. To simulate the high temperature spectra, one has to know the effective dipole moment operator corresponding to the effective Hamiltonian used. The successful modeling of emission spectra of acetylene in 3 μm region performed in Ref. [4] was possible due to the fact that the absorption cross sections in this region are determined mostly by only one derivative of the dipole moment function $\frac{\partial \mu_z}{\partial q_3}$ [5]. For the simulation of high temperature spectra in other spectral regions it is necessary to develop the effective dipole moment operator corresponding to used effective Hamiltonian.

In this paper we present the results of the global modeling of both line positions and intensities performed using the global effective Hamiltonian and the corresponding dipole moment operator developed in Tomsk. These results will be used in the nearest future for the generation of high

* Corresponding author. Tel.: +7 3822491794; fax: +7 3822492086.
E-mail address: vip@lts.iao.ru (V.I. Perevalov).

temperature database for acetylene molecule in the spectral region from 0.6 cm^{-1} to 10000 cm^{-1}.

The global effective Hamiltonian used in Tomsk was formulated in our paper [6] about 20 years ago. It is a polyad model which takes into account the rotational and vibrational ℓ-doubling terms, the anharmonic and Coriolis resonance interaction operators arrising due to the following approximate relations between the harmonic frequences [7]

$$\omega_1 \approx \omega_3 \approx 5\omega_4 \approx 5\omega_5,$$

$$\omega_2 \approx 3\omega_4 \approx 3\omega_5. \tag{1}$$

To derive the above effective Hamiltonian we used the results obtained by Pliva [8], Hietanen [9], Huet et al. [10], Perevalov and Sulakshina [11], Abbouti Temsamani and Herman [12]. The preliminary results of the line position fitting with this effective Hamiltonian have been published in our papers [13–15].

The effective dipole moment operator corresponding to our global effective Hamiltonian [6] has been developed in our papers [16,17]. We have performed the parameterization of the effective dipole moment matrix elements in the basis of the product of the eigenfunctions of the harmonic oscillators and the rigid symmetric top eigenfunctions. The suggested aproach for the line intensity calculations has been successfully used in the modeling of the observed high resolution spectra of acetylene in different spectral regions [17–24].

The C_2H_2 spectra predicted with our models of effective Hamiltonian and effective dipole moment operator have also been successfuly used for the analysis of the experimental spectra in different spectral regions [25–27].

The global modeling of the acetylene vibrational energies within the framework of the method of effective operators was performed in Brussels (see [12,28] and the references therein). Later this team has performed the successfull global modeling of C_2H_2 line positions using effective Hamiltonian which is very similar to that we used (see [3,29,30] and the references therein). The comparison of the results of two global C_2H_2 line position fits is presented in Section 3.

2. Effective Hamiltonian

Acetylene is a four atomic molecule which is linear in the ground electronic state and has $D_{\infty h}$ symmetry group. This molecule has five vibrational modes. Two of them $\omega_4(\Pi_g)$ and $\omega_5(\Pi_u)$ are degenerate bending modes, and the three others $\omega_1(\Sigma_g^+)$, $\omega_2(\Sigma_g^+)$ and $\omega_3(\Sigma_u^-)$, are nondegenerate stretching modes. Due to the approximate relations between the harmonic frequencies (1) the vibrational energy levels are grouped into clusters (polyads). A polyad can be numbered by a polyad number

$$P = 5V_1 + 3V_2 + 5V_3 + V_4 + V_5, \tag{2}$$

where V_i ($i = 1, 2, 3, 4, 5$) are the principal quantum numbers of the harmonic oscillators. Within the framework of the polyad model of effective Hamiltonian [6] its matrix in the basis of the product of the eigenfunctions of harmonic oscillators $\left|V_1 V_2 V_3 V_4^{\ell_4} V_5^{\ell_5}\right\rangle \equiv |V_1\rangle|V_2\rangle|V_3\rangle|V_4\ell_4\rangle|V_5\ell_5\rangle$ and the rigid symmetric top $|JMK\rangle$ is block-diagonal with respect to the polyad number P. Here ℓ_i ($i = 4, 5$) are the quantum numbers

of the projections of the vibrational angular momentum on the molecular-fixed axis z, connected with the double degenerate normal vibrations with the harmonic frequencies ω_i. We use the Wang combinations of the basis functions

$$|V_1 V_2 V_3 V_4 V_5 \ell_4 \ell_5 J M K \varepsilon\rangle$$
$$= \frac{1}{\sqrt{2}} (|V_1 V_2 V_3 V_4^{\ell_4} V_5^{\ell_5}\rangle |J M K = \ell_4 + \ell_5\rangle$$
$$+ \varepsilon |V_1 V_2 V_3 V_4^{-\ell_4} V_5^{-\ell_5}\rangle |J M - K = -\ell_4 - \ell_5\rangle), \tag{3}$$

with $\varepsilon = 1$ or -1 and

$$|V_1 V_2 V_3 V_4 V_5 00 J M \varepsilon = 1\rangle = |V_1 V_2 V_3 V_4^0 V_5^0 > |JM0\rangle. \tag{4}$$

Taking into account the symmetry properties of the basis functions each P block can be split into four isolated subblocks $\{P, q, \varepsilon\}$. Here

$$q = \begin{cases} g & V_3 + V_5 \quad even \\ u & V_3 + V_5 \quad odd. \end{cases} \tag{5}$$

The effective Hamiltonian can be presented by its matrix elements. For the sake of simplicity we present below the matrix elements of effective Hamiltonian in the multiplicative basis $|V_1 V_2 V_3 V_4^{\ell_4} V_5^{\ell_5} JK\rangle = |V_1 V_2 V_3 V_4^{\ell_4} V_5^{\ell_5}\rangle |JMK = \ell_4 + \ell_5\rangle$ but in our computer code the Wang combinations of the basis functions are used. In the case of free molecule, the magnetic quantum number M could be omitted. The diagonal on the principal vibrational quantum numbers matrix elements are given by the following equations:

$$\langle V_1 V_2 V_3 V_4^{\ell_4} V_5^{\ell_5} JK | H^{eff} | V_1 V_2 V_3 V_4^{\ell_4} V_5^{\ell_5} JK \rangle$$
$$= \sum_i \omega_i V_i + \sum_{ij} X_{ij} V_i V_j$$
$$+ \sum_{ab} g^{ab} \ell_a \ell_b + \sum_{ijl} Y_{ijl} V_i V_j V_l + \sum_{iab} Y_i^{ab} V_i \ell_a \ell_b$$
$$+ \sum_{ijlk} Z_{ijlk} V_i V_j V_l V_k + \sum_{ijab} Z_{ij}^{ab} V_i V_j \ell_a \ell_b$$
$$+ \sum_{abcd} Z^{abcd} \ell_a \ell_b \ell_c \ell_d + \sum_{ijklm} W_{ijklm} V_i V_j V_k V_l V_m$$
$$+ \sum_{ijkab} W_{ijk}^{ab} V_i V_j V_k \ell_a \ell_b + (B_e - \sum_i \alpha_i V_i + \sum_{ij} \gamma_{ij} V_i V_j$$
$$+ \sum_{ab} \gamma^{ab} \ell_a \ell_b + \sum_{ijk} \varepsilon_{ijk} V_i V_j V_k + \sum_{iab} \varepsilon_i^{ab} V_i \ell_a \ell_b)$$
$$\times [J(J+1) - K^2] - (D_e + \sum_i \beta_i V_i + \sum_{ij} \delta_{ij} V_i V_j$$
$$+ \sum_{ab} \delta^{ab} \ell_a \ell_b)[J(J+1) - K^2]^2; \tag{6}$$

Vibrational ℓ-doubling

$$\left\langle V_1 V_2 V_3 V_4^{\ell_4} V_5^{\ell_5} JK | H^{eff} | V_1 V_2 V_3 V_4^{\ell_4 \pm 2} V_5^{\ell_5 \mp 2} JK \right\rangle$$
$$= \left\{ r_{45} + \sum_i r_{i45} V_i + \sum_{ij} r_{ij45} V_i V_j + \sum_{ab} r_{45}^{ab} \ell_a \ell_b \right.$$
$$\left. + r_{45}^J J(J+1) + r_{45}^{JJ} [J(J+1)]^2 \right\}$$
$$\times \sqrt{(V_4 \mp \ell_4)(V_4 \pm \ell_4 + 2)(V_5 \pm \ell_5)(V_5 \mp \ell_5 + 2)}; \tag{7}$$

Rotational ℓ-doubling

$$\langle V_t^{\ell_t} JK | H^{eff} | V_t^{\ell_t \pm 2} JK \pm 2\rangle = \left\{ q_t + \sum_i q_{ti} V_i + \sum_{ij} q_{tij} V_i V_j \right.$$
$$\left. + \sum_{ab} q_t^{ab} \ell_a \ell_b + q_t^J J(J+1) \right\}$$
$$\times \sqrt{(V_t \mp \ell_t)(V_t \pm \ell_t + 2)[J(J+1) - K(K \pm 1)][J(J+1) - (K \pm 1)(K \pm 2)}. \tag{8}$$