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# Calculation of absorption spectrum of the $1^1A_g \rightarrow 1^1B_u$ electronic transition of *trans*-1,3,5-hexatriene based on frequency-domain approach

**M. Miralinaghi*, F. Burbur and M. Abbaszadeh**

*Department of Chemistry, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran*

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## ABSTRACT

*The general expressions we previously derived for calculating of the vibronic structure in electronic absorption spectrum of a large polyatomic molecule based on frequency-domain approach (J. Molec. Spectrosc.**2013**, 286-287, 30-45) are applied to simulate the vibronic structure in the dipole-allowed* $1^1A_g \rightarrow 1^1B_u$ *electronic transition of trans-1,3,5-hexatriene molecule. The calculated results indicated that spectral profiles are primarily described by the Franck-Condon progression of four totally symmetric modes,* $\nu_5$, $\nu_{10}$, $\nu_{11}$ *and* $\nu_{13}$, *among which the* $\nu_5$ *(CC double bond stretch) and* $\nu_{10}$ *(CC single bond stretch) are the longest progression-forming modes, while the modes* $\nu_{11}$ *and* $\nu_{13}$ *have much less activities. The spectra also show combination bands (as* $5^1 11^1$, $5^1 10^1$, *etc.) produced by the* $a_g$ *modes.*

**Keywords:** molecular absorption, frequency-domain approach, hexatriene

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## INTRODUCTION

The highly versatile role of linear polyenes in several biological processes, such as vision, photosynthesis, and also their usefulness as computationally tractable models for more complex chromophores, retinal and carotenoids[1,2] make them as intriguing subject of experimental and theoretical investigations [3]. Optical experiments have established that linear polyenes with three or more conjugated double bonds have a dark $2^1A_g$ state between the $1^1A_g$ ground state and dipole allowed $1^1B_u$ excited state [3]. Unlike longer polyenes with four through six double bonds, 1,3-butadiene and 1,3,5-hexatriene have immeasurable emissions and their absorption spectra do not show well-resolved vibrational structures under supersonic jet absorption.

### 2. Theory

For molecular electronic absorption process in an isotropic medium, in which the transitions occur from the statistically equilibrated ground $\Phi_g(\mathbf{r},\mathbf{Q})\chi_v(\mathbf{Q})$ to the manifold of all final excited $\Phi_e(\mathbf{r},\mathbf{Q}')\chi_{v'}(\mathbf{Q}')$ adiabatic vibronic states, the thermally averaged absorption cross section $\alpha(\omega,T)$ is defined by [4-9]

$$\alpha(\omega,T)=\frac{4\pi^2\omega}{3\hbar c}\sum_{v}\rho_v\sum_{v'}\left|\langle gv|\hat{\boldsymbol{\mu}}|ev'\rangle\right|^2 D(\omega_{ev',gv}-\omega)\ , \tag{1}$$

where $c$ is the speed of light, $\rho_v$ is the Boltzmann distribution function for the initial vibronic states, $\hat{\boldsymbol{\mu}}$ is the electric dipole moment operator, $\omega_{ev',gv}$ is the vibronic transition angular frequency, and finally $D(\omega_{ev',gv}-\omega)$ is the normalized bandshapefunction which is considered to be Lorentzian with the same half-width $\gamma_{eg}$ for all vibronic bands:

$$D\left(\omega_{ev',gv}-\omega\right)=\frac{1}{\pi}\frac{\gamma_{eg}}{\left(\omega_{ev',gv}-\omega\right)^2+\gamma_{eg}^2} \tag{2}$$

In thelimit $\gamma_{mn}\to 0$, $D\left(\omega_{nm}-\omega\right)$ reduces to the Delta function. It was assumed that a Duschinsky transformation of the type $\mathbf{Q}'=\mathbf{J}\,\mathbf{Q}+\mathbf{D}$ relates the vibrational normal modes $\mathbf{Q}'$ of the excited electronic state to those $\mathbf{Q}$ of ground electronic state, where $\mathbf{J}$ is the Duschinsky rotation matrix which scrambles those normal modes which belong to the same irreducible representation $\Gamma_j$ of the molecular symmetry group, so it has block-diagonal form, and $\mathbf{D}$ is a column vector whose components are the shift of the equilibrium nuclear configuration of the excited with respect to that of the ground electronic state [10] . The transition dipole moment between the ground $\Phi_g(\mathbf{r},\mathbf{Q})\,\chi_v(\mathbf{Q})$ and an excited $\Phi_e(\mathbf{r},\mathbf{Q}')\,\chi_{v'}(\mathbf{Q}')$ adiabatic vibronicstate is given by

$$\langle gv|\hat{\boldsymbol{\mu}}|ev'\rangle=\int d\mathbf{Q}\,\chi_v^*(\mathbf{Q})\left(\int d^3\mathbf{r}\,\Phi_g^*(\mathbf{r},\mathbf{Q})\,\hat{\boldsymbol{\mu}}_{\mathrm{el}}(\mathbf{r})\,\Phi_e(\mathbf{r},\mathbf{Q}')\right)\chi_{v'}(\mathbf{Q}') \tag{3}$$

where $\hat{\boldsymbol{\mu}}_{\mathrm{el}}(\mathbf{r})$ denotes electronic part of electric dipole moment operator $\hat{\boldsymbol{\mu}}$. Because of the parametric dependence of the electronic wavefunctions on the nuclear variables, the electronic transition moment

$$\boldsymbol{\mu}_{ge}(\mathbf{Q})=\int d^3\mathbf{r}\ \Phi_g^*(\mathbf{r},\mathbf{Q})\,\hat{\boldsymbol{\mu}}_{\mathrm{el}}(\mathbf{r})\ \Phi_e(\mathbf{r},\mathbf{Q}') \tag{4}$$

depends on $\mathbf{Q}$. Substituting for the transition dipole moment from equation (3), making use of equation (4), and assuming molecular vibrations in each of the electronic states can be described by *N* independent harmonic oscillators, we may then write equation (1) as

$$\alpha(\omega,T)=\frac{4\pi^2\omega}{3\hbar c}\left|\boldsymbol{\mu}_{ge}(\mathbf{Q})\right|^2\sum_{v}\rho_v\sum_{v'}\left|\langle v|v'\rangle\right|^2 D\left(\omega_{ev',gv}-\omega\right) \tag{5}$$

where $\left|\langle v|v'\rangle\right|^2$ is the Franck-Condon (FC) factor. Obviously, the absorption cross section $\alpha(\omega,T)$ is proportional to the FC factor. Note that in general, $\boldsymbol{\mu}_{ge}(\mathbf{Q})=\boldsymbol{\mu}_{ge}(\mathbf{0})+\sum_p\boldsymbol{\mu}_{ge}^{(1)}(p)Q_p+\ldots$ . In the Condon approximation, we have $\boldsymbol{\mu}_{ge}(\mathbf{Q})\approx\boldsymbol{\mu}_{ge}(\mathbf{0})$, that is, the transition dipole moment is assumed to be independent of nuclear coordinate.

Since the Duschinsky rotation matrix has block diagonal form, and each block corresponds to the vibrational modes that belong to the same symmetry species, the *N*-dimensional vibrational integrals appearing in equation (5) can be factorized as a product of vibrational integrals with lower dimensions

$$\langle \upsilon_1 \upsilon_2 \cdots \upsilon_N | \upsilon_1' \upsilon_2' \cdots \upsilon_N' \rangle = \langle \upsilon_1 \upsilon_2 \cdots | \upsilon_1' \upsilon_2' \cdots \rangle_{\Gamma_s} \langle \upsilon_1 \upsilon_2 \cdots | \upsilon_1' \upsilon_2' \cdots \rangle_{\Gamma_1} \cdots \tag{6}$$

where $\Gamma_s$ refers to the irreducible representation of totally symmetric modes and $\Gamma_1, \ldots$ refer to irreducible representations of nontotally symmetric modes. The vibrational modes of each category are renumbered as 1, 2, … . Equations (5,6) show that in all allowed electronic transitions the first band at low temperature is the $0-0'$ band followed by progressions in totally symmetric modes and combinations bands built on it. The length of each progression built on the true origin depends on the size of equilibrium geometry change from the lower to the upper electronic state in the direction of the corresponding totally symmetric mode.

Suppose the electronic transition occurs from the lowest vibrational level of the ground electronic state, and consider a combination band in which only *i*th, *j*th, and *l*th totally symmetric modes are excited with $\upsilon_i'$, $\upsilon_j'$, and $\upsilon_l'$ vibrational quanta of energy in the upper electronic state. Making use of equation (38) of ref. 11 the relative intensity of such a band with respect to a false (or the true) origin can be written as

$$\begin{aligned} I(\upsilon_i',\upsilon_j',\upsilon_l') = \Bigg| &(\upsilon_i'!\,\upsilon_j'!\,\upsilon_l'!)^{1/2} \sum_{k_1=0} \sum_{k_2=0} \sum_{k_3=0} \frac{(-\alpha_{ij})^{k_1}}{k_1!} \frac{(-\alpha_{il})^{k_2}}{k_2!} \frac{(-\alpha_{jl})^{k_3}}{k_3!} \times \\ &\frac{(\alpha_{ii}/2)^{(\upsilon_i'-k_1-k_2)/2}}{(\upsilon_i'-k_1-k_2)!} H_{\upsilon_i'-k_1-k_2}\left\{\alpha_{ii}^{-1/2}\left[(\mathbf{E}-\mathbf{P})\boldsymbol{\delta}\right]_i\right\} \times \\ &\frac{(\alpha_{jj}/2)^{(\upsilon_j'-k_1-k_3)/2}}{(\upsilon_j'-k_1-k_3)!} H_{\upsilon_j'-k_1-k_3}\left\{\alpha_{jj}^{-1/2}\left[(\mathbf{E}-\mathbf{P})\boldsymbol{\delta}\right]_j\right\} \times \\ &\frac{(\alpha_{ll}/2)^{(\upsilon_l'-k_2-k_3)/2}}{(\upsilon_l'-k_2-k_3)!} H_{\upsilon_l'-k_2-k_3}\left\{\alpha_{ll}^{-1/2}\left[(\mathbf{E}-\mathbf{P})\boldsymbol{\delta}\right]_l\right\} \Bigg|^2 , \end{aligned} \tag{7}$$

where $H_j(x)$ is the Hermite polynomial, $\boldsymbol{\delta} = \boldsymbol{\Gamma}'^{1/2}\,\mathbf{D}$ is the *N*-dimensional vector of the reduced displacements $\{\gamma_j'^{1/2} D_j\}$, $\mathbf{E}$ is an $N \times N$ unit matrix, $\mathbf{P}$ is an $N \times N$ symmetric matrix defined by

$$\mathbf{P} = \boldsymbol{\Gamma}'^{1/2}\,\mathbf{J}\,\mathbf{G}^{-1}\,\mathbf{J}^T\,\boldsymbol{\Gamma}'^{1/2} , \tag{8a}$$

with

$$\mathbf{G} = \boldsymbol{\Gamma} + \mathbf{J}^T\,\boldsymbol{\Gamma}'\,\mathbf{J}, \tag{8b}$$

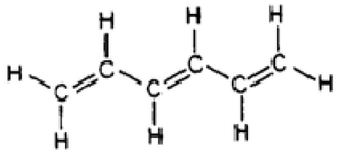
and $\alpha_{ij} = (\mathbf{E} - 2\mathbf{P})_{ij}$.

If only two totally symmetric vibrational modes *i*th and *j*th are excited with $\upsilon_i'$ and $\upsilon_j'$ quanta in the upper electronic state the corresponding relative intensity can be obtained by setting $\upsilon_l' = 0$ in equation (7), by which the summation indices $k_2$ and $k_3$ each takes only value of zero. Likewise, the relative intensity along the progression of a totally symmetric mode, e.g. *i*th mode, can be derived by setting $\upsilon_j' = \upsilon_l' = 0$ in equation (7), by which the summation indices $k_1, k_2$, and $k_3$ each takes only value of zero. Therefore, equation (7) permits us to calculate the relative intensities of most vibronic bands appearing in absorption spectra.

## RESULTS AND DISCUSSION

In this section, we shall apply the low-temperature limit versions of equations (5) and (7) to simulate absorption spectrum of the dipole allowed $1^1A_g \to 1^1B_u$ electronic transition of *trans*-1,3,5-hexatriene (simply called hexatriene hereafter). In the low temperature limit the absorption take place from the ground vibrational level of the ground electronic state. The procedure require the following quantities to be known: the zero-zero excitation frequency $\Omega_{eg}$, the vibrational frequencies of the ground $\{\omega_j\}$ and excited $\{\omega'_j\}$ electronic state, the shift of equilibrium nuclear configuration along $j$th totally symmetric mode $D_j$, and the extent of rotations of the vibrational modes upon the electronic excitation characterized by the Duschinsky rotation matrix $\mathbf{J}$. In the simulations, use is made of the experimental values of these quantities unless they are not available or the comparisons are aimed where the theoretical values are employed.

The 36 vibrational modes of *trans*-hexatriene molecule



are distributed among the irreducible representations of $C_{2h}$point group as 13 $a_g$ + 12 $b_u$ + 6 $a_u$ + 5 $b_g$ *;*

$a_g$ and $b_u$ are in-plane modes, while $a_u$ and $b_g$ are out-of-plane vibrations. The zero-zero excitation energy to the ionic $1^1B_u$ electronic state is 39786 cm$^{-1}$. Table 1 displays experimental and theoretical vibrational frequencies of the ground $1^1A_g$ and second excited $1^1B_u$ electronic states of molecule[12-16].

**Table 1.Vibrational frequencies (cm$^{-1}$) of $1^1A_g$ and $1^1B_u$ electronic states of hexatriene**$^a$

| $a_g$ modes | $1^1A_g$ | $1^1B_u$ |
|---|---|---|
| $\nu_1$ | 3089 | 3090 |
| $\nu_2$ | 3017 | 3078 |
| $\nu_3$ | 3000 | 3063 |
| $\nu_4$ | 2992 | 2983 |
| $\nu_5$ | 1626 | 1631$^*$ |
| $\nu_6$ | 1576 | 1513 |
| $\nu_7$ | 1399 | 1390 |
| $\nu_8$ | 1288 | 1349 |
| $\nu_9$ | 1283 | 1274 |
| $\nu_{10}$ | 1191 | 1224$^*$ |
| $\nu_{11}$ | 932 | 718$^*$ |
| $\nu_{12}$ | 443 | 449 |
| $\nu_{13}$ | 353 | 313$^*$ |

| $b_g$ modes | $1^1A_g$ | $1^1B_u$ |
|---|---|---|
| $\nu_{20}$ | 986 | 954 |
| $\nu_{21}$ | 903 | 930 |
| $\nu_{22}$ | 868 | 828 |
| $\nu_{23}$ | 615 | 544 |
| $\nu_{24}$ | 215 | 272 |

| $b_u$ modes | $1^1A_g$ | $1^1B_u$ |
|---|---|---|
| $\nu_{25}$ | 3091 | 3098 |
| $\nu_{26}$ | 3039 | 3083 |
| $\nu_{27}$ | 3008 | 3063 |
| $\nu_{28}$ | 2969 | 2983 |
| $\nu_{29}$ | 1624 | 1576 |
| $\nu_{30}$ | 1429 | 1466 |

| $a_u$ modes | | |
|---|---|---|
| | $1^1A_g$ | $1^1B_u$ |
| $\nu_{14}$ | 1009 | 988 |
| $\nu_{15}$ | 941 | 930 |
| $\nu_{16}$ | 900 | 836 |
| $\nu_{17}$ | 682 | 548 |
| $\nu_{18}$ | 248 | 200 |
| $\nu_{19}$ | 94 | 108 |

| | | |
|---|---|---|
| $\nu_{31}$ | 1294 | 1312 |
| $\nu_{32}$ | 1255 | 1248 |
| $\nu_{33}$ | 1128 | 1233 |
| $\nu_{34}$ | 964 | 955 |
| $\nu_{35}$ | 541 | 585 |
| $\nu_{36}$ | 152 | 169 |

[a]Vibrational frequencies in the ground electronic state $1^1A_g$ have been experimentally determined by infrared and Raman spectroscopic measurements at room temperature [13-15]. The direct absorption spectrum in jet cooled of the $1^1A_g \rightarrow 1^1B_u$ transition has been analyzed for determining the second excited state vibrational frequencies of $a_g$ modes which specified by asterisk sign [12]. Investigation of potential energy surface by an extended Pople-Pariser-Parr (PPP/CI) model has given adiabatic frequencies of other modes in $1^1B_u$ electronic state [16].

The displacement vectors $\mathbf{D}$, calculated from equation (45a) of ref. 17 using relative intensities of the first quanta of the progressions of $a_g$ modes in the $1^1A_g \rightarrow 1^1B_u$ transitions [12,16] collected in Table 2 and employing the Duschinsky matrix given in Table 3.

**Table 2. Relative intensities of the totally symmetric fundamental bands of the $1^1A_g - 1^1B_u$ spectrum ofhexatriene**

| | supersonic jet[a] | theory[b] |
|---|---|---|
| $I(1'_5)$ | 1.045 | 0.949 |
| $I(1'_6)$ | | 0.006 |
| $I(1'_7)$ | | 0.003 |
| $I(1'_8)$ | | 0.022 |
| $I(1'_{10})$ | 0.476 | 0.586 |
| $I(1'_{11})$ | 0.04 | |
| $I(1'_{12})$ | | 0.005 |
| $I(1'_{13})$ | 0.18 | 0.098 |

[a]*Ref. 12.* [b]*Ref. 16.*

**Table 3. Normalized Duschinsky matrices for the $a_g$ and $b_u$ modes of $1^1A_g - 1^1B_u$ electronic states of hexatriene**[a]

| $1^1B_u$ | $1^1A_g$ | $\nu_5$ | $\nu_6$ | $\nu_7$ | $\nu_8$ | $\nu_9$ | $\nu_{10}$ | $\nu_{11}$ | $\nu_{12}$ | $\nu_{13}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\nu_5$ | 0.93 | 0.09 | −0.09 | −0.27 | −0.10 | −0.01 | 0.05 | −0.03 | 0.01 | 0.93 |
| $\nu_6$ | −0.16 | 0.91 | −0.34 | −0.17 | 0.05 | −0.05 | 0.02 | −0.01 | 0.01 | −0.16 |
| $\nu_7$ | −0.01 | −0.3 | −0.92 | 0.23 | −0.12 | −0.01 | 0.0 | 0.0 | 0.0 | −0.01 |
| $\nu_8$ | −0.25 | 0.23 | −0.08 | −0.81 | −0.33 | −0.33 | 0.04 | −0.01 | −0.01 | −0.25 |
| $\nu_9$ | 0.01 | 0.16 | −0.15 | −0.32 | −0.92 | 0.01 | −0.03 | −0.01 | −0.02 | 0.01 |
| $\nu_{10}$ | 0.08 | −0.03 | 0.06 | 0.29 | 0.13 | −0.94 | 0.07 | −0.02 | 0.01 | 0.08 |
| $\nu_{11}$ | 0.03 | −0.02 | −0.01 | −0.01 | −0.04 | −0.08 | −0.96 | 0.03 | 0.01 | 0.03 |
| $\nu_{12}$ | 0.03 | 0.01 | 0.0 | 0.02 | 0.0 | 0.03 | −0.03 | 0.99 | 0.12 | 0.03 |
| $\nu_{13}$ | 0.01 | −0.02 | 0.0 | 0.01 | −0.01 | 0.0 | −0.01 | 0.12 | 0.99 | 0.01 |

[b]*Ref. 16.*

The Huang-Rhys factors corresponding to displacements $\mathbf{D}$, ($S'_j = \omega'_j D_j^2 / 2\hbar$, where $\omega'_j$ refers to the upper electronic state) are summarized in Table 4.

**Table 4. Huang-Rhys factors $S'_j$ for the $1^1B_u - 1^1A_g$ electronic states of hexatriene**[a]

| | |
|---|---|
| $S'_5$ | 1.042 |
| $S'_6$ | 0.011 |
| $S'_7$ | 0.003 |
| $S'_8$ | 0.051 |
| $S'_9$ | 0.009 |
| $S'_{10}$ | 0.471 |
| $S'_{11}$ | 0.024 |
| $S'_{12}$ | 0.007 |
| $S'_{13}$ | 0.177 |

[a]*Calculated using Duschinsky matrix from ref. 16.*

The vibronic structure of the $1^1A_g \rightarrow 1^1B_u$ electronic transition of hexatrienee in free jet expansion has been analyzed in details by calculating the relative intensities (relative to $0-0'$ origin) of the vibronic bands using equation (7). In order to investigate the effect of the normal mode scrambling on the vibronic structure, the relative intensities have been computed with and without the Duschinsky matrix for the $a_g$ modes given in Table 3. The fourth and fifth columns of Table 5 display the results. It is seen that the Duschinsky rotations does not have a considerable effect on vibronic bands. The discrepancies between the experimental and theoretical intensities may be attributed to the anharmonicities of the potential surfaces which are not considered in present work.

Figure 1a display the experimental absorption spectra due to the $1^1A_g \rightarrow 1^1B_u$ electronic transition of hexatriene in the jet-cooled [12]. Figure 1b represents the corresponding calculated spectra from extended Pople-Pariser-Parr with configuration interaction (PPP/CI) theory [16]. Stick spectrum is also shown and the main bands have been assigned as $n^x$, where $n$ is the excited normal mode and $x$ its quantum number.

**Table 5. Assignments, frequencies (cm$^{-1}$), and intensities associated with dipole allowed $1^1A_g \rightarrow 1^1B_u$ transition[a]**

| assignment | frequency | theory | | | experiment[d] |
|---|---|---|---|---|---|
| | | Hemley[b] | this work | | |
| $18^2$ | 200 | 0.2 | 0.5 | 0.5 | |
| $13^1$ | 313 | 9.8 | 19.9 | 18.0 | 18.0 |
| $12^1$ | 471 | | 0.7 | 0.5 | |
| $24^2$ | 544 | 0.3 | 0.4 | 0.4 | |
| $13^2$ | 626 | 0.4 | 1.0 | 0.5 | |
| $11^1$ | 718 | | 3.1 | 4.0 | 4.0 |
| $11^1 13^1$ | 1031 | | 0.6 | 0.9 | |
| $23^2$ | 1088 | 0.2 | 0.1 | 0.1 | |
| $10^1$ | 1224 | 58.6 | 45.8 | 47.6 | 47.6 |
| $9^1$ | 1274 | | 0.9 | | |
| $8^1$ | 1349 | 2.2 | 4.8 | 2.2 | |
| $7^1$ | 1390 | 0.3 | 0.3 | 0.3 | |
| $11^2$ | 1436 | | 0.5 | 0.8 | |
| $6^1$ | 1513 | | 1.1 | | |
| $6^1$ | 1513 | 0.6 | 1.1 | 0.6 | |
| $10^1 13^1$ | 1537 | 5.6 | 9.1 | 9.1 | |
| $5^1$ | 1631 | 94.9 | 103.9 | 104.5 | 104.5 |
| $8^1 13^1$ | 1662 | | 1.0 | 0.3 | |
| $11^2 13^1$ | 1749 | | | 0.1 | |
| $6^1 13^1$ | 1826 | | 0.2 | 0.2 | |
| $10^1 13^2$ | 1850 | | 0.4 | 0.3 | |
| $10^1 11^1$ | 1942 | | 1.4 | 1.8 | |
| $5^1 13^1$ | 1944 | 8.9 | 20.7 | 20.1 | |
| $5^1 12^1$ | 2102 | | 0.7 | 0.3 | |
| $11^3$ | 2154 | | | 0.1 | |
| $10^1 11^1 13^1$ | 2255 | | 0.3 | 0.4 | |
| $5^1 11^1$ | 2349 | | 3.2 | 3.3 | |
| $10^2$ | 2448 | 16.8 | 11.1 | 11.0 | 18.0 |
| $9^2$ | 2548 | | | 1.2 | |
| $8^1 10^1$ | 2573 | | 2.2 | 2.8 | |

| | | | | | |
|---|---|---|---|---|---|
| $7^1 10^1$ | 2614 | | 0.1 | 0.4 | |
| $10^1 11^2$ | 2660 | | 0.2 | 0.4 | |
| $8^2$ | 2698 | | 0.3 | 0.7 | |
| $6^1 10^1$ | 2737 | | 0.5 | | |
| $10^2 13^1$ | 2761 | 4.0 | 2.2 | 2.2 | |
| $6^1 9^1$ | 2787 | | | 0.1 | |
| $5^1 10^1$ | 2855 | 54.9 | 47.6 | 49.7 | 57.3 |
| $5^1 9^1$ | 2905 | | | 1.3 | |
| $5^1 8^1$ | 2980 | 1.4 | 5.0 | 3.0 | |
| $8^2 13^1$ | 3011 | | | 0.1 | |
| $5^1 7^1$ | 3021 | | 0.3 | 0.2 | |
| $6^2$ | 3026 | | | 0.1 | |
| $5^1 11^2$ | 3067 | | 0.5 | 1.0 | |
| $5^1 6^1$ | 3144 | | 1.2 | | |
| $5^1 6^1$ | 3144 | | 1.2 | 0.6 | |
| $10^2 11^1$ | 3166 | | 0.3 | 0.4 | |
| $5^1 10^1 13^1$ | 3168 | 5.5 | 9.5 | 10.1 | |
| $5^2$ | 3262 | 44.5 | 54.2 | 52.9 | 67.1 |
| $5^1 8^1 13^1$ | 3293 | | 1.0 | 0.4 | |
| $10^2 11^1 13^1$ | 3479 | | | 0.1 | |
| $5^1 10^1 13^1$ | 3481 | | 0.5 | 0.4 | |
| $5^1 10^1 11^1$ | 3573 | | 1.5 | 1.5 | |
| $5^2 13^1$ | 3575 | 4.0 | 10.8 | 10.8 | |
| $10^3$ | 3672 | 3.1 | 1.9 | 1.6 | |
| $5^1 8^1 11^1$ | 3698 | | 0.2 | | |
| $5^2 12^1$ | 3733 | | 0.4 | | |
| $8^1 10^2$ | 3797 | | | 1.2 | |
| $7^1 10^2$ | 3838 | | | 0.2 | |
| $8^2 10^1$ | 3922 | | 0.1 | 0.2 | |
| $6^1 10^2$ | 3961 | | 0.1 | | |
| $5^2 11^1$ | 3980 | | 1.7 | 1.3 | |
| $10^3 13^1$ | 3985 | | 0.4 | 0.4 | |
| $5^1 10^2$ | 4079 | 15.5 | 11.6 | 11.4 | 16.0 |
| $5^1 9^2$ | 4179 | | | 1.2 | |
| $5^1 8^1 10^1$ | 4204 | 1.2 | 2.3 | 3.4 | |
| $5^1 8^2$ | 4329 | | 0.3 | 0.6 | |

| | | | | | |
|---|---|---|---|---|---|
| $5^1 10^2 13^1$ | 4392 | 1.6 | 2.3 | 2.5 | |
| $5^2 10^1$ | 4486 | 25.4 | 24.8 | 25.1 | 18.0 |
| $5^2 9^1$ | 4536 | | | 2.7 | |
| $5^2 8^1$ | 4611 | | 2.6 | 1.9 | |
| $5^1 8^2 13^1$ | 4642 | | | 0.1 | |
| $5^2 7^1$ | 4652 | | 0.1 | | |
| $5^2 11^2$ | 4698 | | 0.3 | 0.6 | |
| $5^1 10^2 13^2$ | 4705 | | 0.1 | 0.1 | |
| $5^2 6^1$ | 4775 | | 0.6 | 0.3 | |
| $5^1 10^2 11^1$ | 4797 | | 0.4 | 0.3 | |
| $5^2 10^1 13^1$ | 4799 | 2.6 | 4.9 | 5.5 | |
| $5^3$ | 4893 | 13.8 | 18.9 | 17.3 | 15.0 |
| $10^4$ | 4896 | 0.4 | 0.3 | 0.2 | |
| $5^2 8^1 13^1$ | 4924 | | 0.5 | 0.3 | |
| $8^1 10^3$ | 5021 | | | 0.3 | |
| $5^2 10^1 11^1$ | 5204 | | 0.8 | 0.6 | |
| $5^3 13^1$ | 5206 | 1.2 | 3.8 | 3.8 | |
| $5^1 10^3$ | 5303 | 2.8 | 2.0 | 1.7 | |
| $5^3 12^1$ | 5364 | | 0.1 | | |
| $5^1 8^1 10^2$ | 5428 | | | 1.5 | |
| $5^1 10^2 11^2$ | 5515 | | | 0.1 | |
| $5^1 8^2 10^1$ | 5553 | | 0.1 | 0.2 | |
| $5^3 11^1$ | 5611 | | 0.6 | 0.3 | |
| $5^1 10^3 13^1$ | 5616 | | 0.4 | 0.4 | |
| $5^2 10^2$ | 5710 | 7.1 | 6.0 | 5.8 | |
| $5^2 9^2$ | 5810 | | | 0.6 | |
| $5^2 8^1 10^1$ | 5835 | | 1.2 | 2.0 | |
| $5^2 10^1 11^2$ | 5922 | | 0.1 | 0.3 | |
| $5^2 8^2$ | 5960 | | 0.1 | 0.3 | |
| $5^2 10^2 13^1$ | 6023 | | 1.2 | 1.3 | |
| $5^3 10^1$ | 6117 | 7.7 | 8.6 | 8.2 | |
| $5^3 8^1$ | 6242 | | 0.9 | 0.8 | |
| $5^3 11^2$ | 6329 | | | 0.2 | |
| $5^3 6^1$ | 6406 | | 0.2 | | |
| $5^2 10^2 11^1$ | 6428 | | 0.2 | 0.1 | |
| $5^3 10^1 13^1$ | 6430 | | 1.7 | 1.9 | |

| | | | | |
|---|---|---|---|---|
| $5^4$ | 6524 | 3.1 | 4.9 | 4.1 |
| $5^3 8^1 13^1$ | 6555 | | 0.2 | 0.1 |
| $5^3 10^1 11^1$ | 6835 | | 0.3 | 0.1 |
| $5^2 10^3$ | 6934 | 1.3 | 1.0 | |
| $5^2 10^3$ | 6934 | | 1.0 | 0.9 |
| $5^2 8^1 10^2$ | 7059 | | 0.3 | 0.8 |
| $5^2 10^3 13^1$ | 7247 | | 0.2 | 0.2 |
| $5^3 10^2$ | 7341 | 2.1 | 2.1 | 1.9 |
| $5^3 9^2$ | 7441 | | | 0.2 |
| $5^3 8^1 10^1$ | 7466 | | 0.4 | 0.8 |
| $5^3 10^1 11^2$ | 7553 | | | 0.1 |
| $5^3 10^2 13^1$ | 7654 | | 0.4 | 0.5 |
| $5^4 10^1$ | 7748 | 1.7 | 2.3 | 1.9 |
| $5^4 9^1$ | 7798 | | | 0.9 |
| $5^4 8^1$ | 7873 | | 0.2 | 0.2 |
| $5^4 10^1 13^1$ | 8061 | | 0.5 | 0.5 |
| $5^5$ | 8155 | | 1.0 | 0.7 |
| $5^2 8^1 10^3$ | 8283 | | | 0.2 |
| $5^3 10^3$ | 8565 | | 0.4 | 0.3 |
| $5^3 8^1 10^2$ | 8690 | | 0.1 | 0.3 |
| $5^4 10^2$ | 8972 | | 0.5 | 0.4 |
| $5^4 8^1 10^1$ | 9097 | | 0.1 | 0.2 |
| $5^4 10^2 13^1$ | 9285 | | 0.1 | 0.1 |
| $5^6$ | 9786 | | 0.2 | 0.1 |

[a] *Intensities are relative to the* $0-0'$ *band .Bands with intensities smaller than 0.1 arenot listed.* [b]*Ref. 16.* [c]*Including Duschinsky matrix from ref. 16.* [d]*Ref. 12.*

The absorption spectrum is composed of the vibronic bands involving four totally symmetric modes, $\nu_5$, $\nu_{10}$, $\nu_{11}$ and $\nu_{13}$, among which the $\nu_5$ (CC double bond stretch) and $\nu_{10}$ (CC single bond stretch) are the longest progression-forming modes, while the modes $\nu_{11}$ and $\nu_{13}$ have much less activities. The spectra also show combination bands (as $5^1 11^1$, $5^1 10^1$, etc.) produced by the $a_g$ modes. Therefore, the spectrum is primarily described by the progressions in totally symmetric modes $\nu_5$ and $\nu_{10}$ (which have the highest Huang-Rhys factors; 1.042 and 0.471, respectively) and their combinations. Figure 1c and 1d display the calculated absorption spectrum of the $1^1A_g \to 1^1B_u$ transition of hexatriene at $T = 0\,\mathrm{K}$ by considering a 9-mode model consisting of nine totally symmetric $a_g$ modes ($\nu_5 - \nu_{13}$)for displaced-distorted and displaced-distorted-rotated models, respectively. The normal mode rotations have minor effect on the simulated spectral profile in Figure 1d.The Lorentzian half-width of $\gamma_{eg} = 100\ \mathrm{cm}^{-1}$ has been used in the simulations.

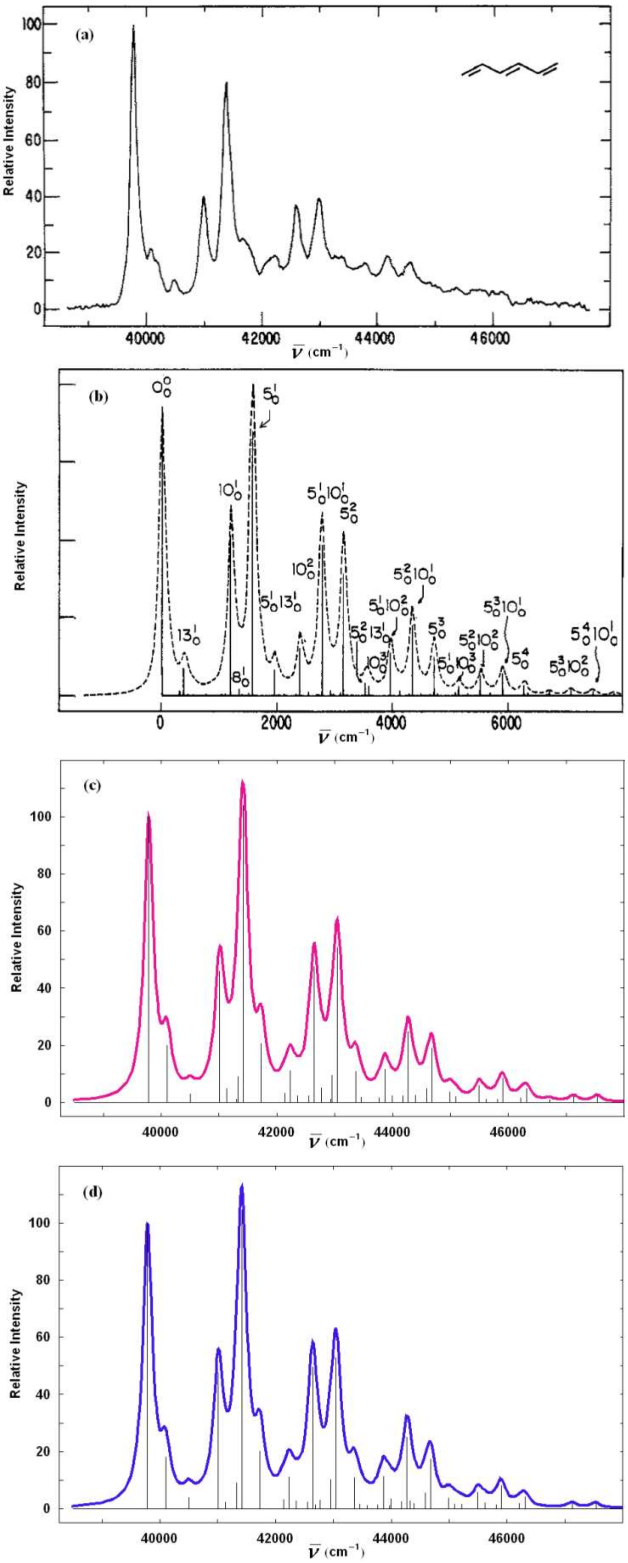


**Figure 1.The $1^1A_g \rightarrow 1^1B_u$ absorption spectrum of hexatriene. (a) experimental spectrum in jet- cooled from ref. 12, (b) calculated spectrum using PPP/CI theory from ref. 16, (c) calculated spectrum using displaced-distorted model, and (d) calculated spectrum using displaced-distorted-rotated model**

## CONCLUSION

The general expressions which previously derived for calculating of the vibronic structure in electronic absorption spectrum of a large polyatomic molecule based on frequency-domain approach [10], equations 5 and 7, have been usedsuccessfully to simulate the vibronic structure in the dipole-allowed $1^1A_g \rightarrow 1^1B_u$ electronic transition of *trans*-1,3,5-hexatriene molecule. The detailed analysis of the vibronic structure in the spectrum are presented in Table 5, and the simulated spectrumis displayed in Figure 1, and comparison has been made with the experimental and theoretical data.

## REFERENCES

[1] A. V.Mane, B. A. Karadge, J. S. Samant, *J. Chem. Pharm. Res*.,**2010**, 2(3), 338-347.
[2] G. Vijayalakshmi1, M. Adinarayana, P. JayaprakashRao, *J. Chem. Pharm. Res*.,**2012**, 4(7), 3574-3582.
[3] B. E. Kohler, *Chem. Rev.,***1993**, 93, 41-54.
[4] M. Ramegowda, *J. Chem. Pharm. Res*., **2013**, 5(5),182-186.
[5] C.-K. Lin, M.-C. Li, M. Yamaki, M. Hayashi, S.H. Lin, *Phys. Chem. Chem. Phys.*,**2010**,12, 11432-11444.
[6] T. Petrenko, F. Neese, *J. Chem. Phys.,***2007**,127, 164319/1-164319/15.
[7] J. Li, C. -K. Lin, X. Y. Li, C.Y. Zhu, S. H. Lin, *Phys. Chem. Chem. Phys*.,**2010**,12, 14967-14976.
[8] R. He, L. Yang, C. Zhu, M.Y. Yamaki, Y.-P. Lee, S.H. Lin, *J. Chem. Phys*.**2011**,134, 094313/1-094313/12.
[9] R. Islampour, A. Khavaninzadeh, M. Miralinaghi, *J. Molec.Spectrosc.*,**2013**, 286, 30-45.
[10] F. Duschinsky, *ActaPhysicochim.*,**1937**,URSS 7, 551-556.
[11] R. Islampour, M. Dehestani, S.H. Lin, *J. Molec. Spectrosc.,***1999**,194, 179-184.
[12] D. G.Leopold, R. D. Pendley, J. L. Roebber, R. J. Hemley, V. Vaida, *J. Chem. Phys.*,**1984**, 81, 4218-4229.
[13] H.Torri, M. Tasumi, *Vib. Spect.,***1995**,8, 205-214.
[14] F. W.Langkilde, R . Wilbrandt, O. H. Nielsen, F. M. Nicolaisen, *SpectrochimActa,***1987**, 43A, 1209-1230.
[15] H.Yoshida, Y. Furukaua, M.Tasumi, *J. MolStruct.*,**1989**, 194, 279-299.
[16] R. J. Hemley, A. C. Lassaga, V. Vaida, M. Karplus, *J. Chem. Phys.,***1988**, 92, 945-954.
[17] R. Islampour, M. Miralinaghi, A. Khavaninzadeh, *J. Phys. Chem. A*,**2011**,115, 8860-8869.