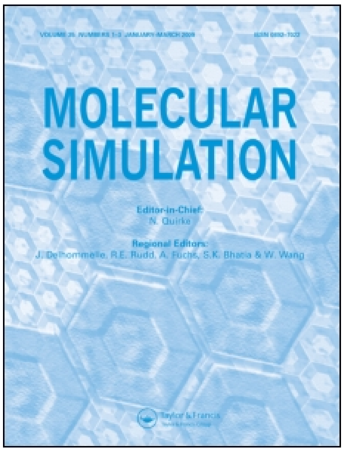

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Kukielski, J. I. and Sienkiewicz, J. E.(2001) 'Band Shape Analysis of Vibronic Spectra of Flexible Molecules in Solution', Molecular Simulation, 26: 2, 157 — 165
To link to this Article: DOI: 10.1080/08927020108023014
URL: http://dx.doi.org/10.1080/08927020108023014

Molecular Simulation, 2001, Vol. 26, pp. 157–165
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Printed in Malaysia.

BAND SHAPE ANALYSIS OF VIBRONIC SPECTRA OF FLEXIBLE MOLECULES IN SOLUTION

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(Received July 1999; accepted April 2000)

The absorption and emission spectra of biphenyl in cyclohexane are measured. Calculated Franck-Condon overlap integrals are used to simulate measured absorption and emission spectra of biphenyl in cyclohexane. The vibronic theory with the Born-Oppenheimer and Condon approximation is used.

Keywords: Absorption and emission spectra; Flexible molecule; Franck-Condon factors

1. INTRODUCTION

In the last few decades many papers have been devoted to the development of *ab initio* and semiempirical computational methods of computers vibronic spectra.

Many papers have taken into account considerations within the framework of the vibronic spectra [1–11, 14–16]. Among them, Hutchison [1] has reported an attempt to calculate the intensity of spectral lines for symmetrical diatomic molecules. This attempt is based on the Franck assumption [2] and Condon theory [3, 4]. Manneback [5] has formulated a simple recurrence procedure for computing the matrix elements for diatomic molecules leading to intensity. Further developments have been carried out by Keil [6]. Scherer *et al.* [7] have investigated the temperature dependence

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*Corresponding author. e-mail: fizjik@halina.univ.gda.pl of the electronic absorption spectrum. In turn, Gribov [8] has presented the calculation of vibronic spectra of polyatomic molecules in the most general form. Granville *et al.* [9] have analyzed vibronic intensity distribution for the series of linear polyenes and described absorption spectra by a least squares fitting procedure. Despite all this effort, the calculation of vibronic spectra still present significant problems. In particular, it is difficult to estimate the potential energy surfaces of the ground and excited states. Some early attempts use model potentials [10, 11] to describe potential energy surfaces. Other approaches take advantage of the relatively simple formulas of the Franck-Condon overlap integrals based on the harmonic oscillator approach *e.g.* [12, 13]. The approaches based on the model and harmonic oscillator potential energies allow the reproduction of absorption and emission molecular spectra within the frame work of the vibronic theory [16]. Measured vibronic spectra of two substituted biphenyl in 4- and 4′- position by pentyl and cyano group were presented in paper [17].

In this paper we apply and develop further the method proposed in the proceeding paper [16] where the Franck-Condon factors obtained from the harmonic oscillator wave functions were used to simulate absorption and emission spectra. A more detailed description of this method is presented in what follows.

2. MODEL OF THE EMISSION AND ABSORPTION SPECTRA

In this section we discuss the theory of the electronic emission and absorption spectra. Our aim is to outline the simple model which takes into account these two types of spectrum simultaneously.

Assuming the adiabatic approximation the total emission coefficient can be written as

$$I(\tilde{\nu}) = \sum_i P_i I_i(\tilde{\nu}) \tag{1}$$

where the index i indicates the vibrational levels in the electronic excited state S_i. Here, P_i is the thermal occupation probability of the state ψ_i and I_i is the emission coefficient of the spectrum coming from the one particular initial vibrational level i to all possible vibrational levels of the ground state S_g. Analogous formula for the total absorption coefficient can be written as

$$\varepsilon(\tilde{\nu}) = \sum_i P_i \varepsilon_i(\tilde{\nu}). \tag{2}$$

In this case the index i indicates the vibrational levels of the ground state S_g.

The emission and absorption coefficients of a molecule in the initial vibrational states can be written in the following forms [10, 11, 16].

$$I_i(\tilde{\nu}) = \frac{1}{3} C_I \mu^2 \sum_f \chi_{if} \tilde{\nu}^4 g(\tilde{\nu} - \tilde{\nu}_{if}) \tag{3}$$

$$\varepsilon_i(\tilde{\nu}) = \frac{1}{3} C_\varepsilon \mu^2 \sum_f \chi_{if} \tilde{\nu} g(\tilde{\nu} - \tilde{\nu}_{if}) \tag{4}$$

where μ is the dipole moment of the electronic transition, χ is the Franck-Condon factor, $g(\tilde{\nu} - \tilde{\nu}_{if})$ is the line shape function centered at the appropriate value of the transition frequency from the initial vibration state i to the final state f, C_I and C_ε are respectively the constant factors of the emission and absorption.

In our approach the line shape function is assumed to be equal for all transitions and has the Gaussian form

$$g(\tilde{\nu} - \tilde{\nu}_{if}) = \frac{1}{\sqrt{\pi}\,\delta} \mathrm{e}^{-(\tilde{\nu} - \nu_{if})^2/\delta^2} \tag{5}$$

with the width (FWHM)

$$\delta_{\frac{1}{2}} = 2\sqrt{ln\,2}\,\delta. \tag{6}$$

The Franck-Condon factor is the following product

$$\chi_{if} = \prod_l \langle i_l | f_l \rangle \tag{7}$$

where $\langle i_l | f_l \rangle$ are the overlaps of the one-dimensional harmonic oscillator wave functions. For transitions from the vibrational initial state $i_l = 0$ to the final state $f_l = n$ this overlap is given by

$$\langle 0 | n \rangle = \frac{\Delta_l^n}{\sqrt{n!}} \mathrm{e}^{-\delta_l^2/2} \tag{8}$$

where Δ_l is the fitting parameter. This parameter is proportional to the displacement between the equilibrium inter-nuclear distance of the vibration in the ground state ψ_g and the excited state ψ_e. Here, we have the symmetry relation

$$\langle 0 | n \rangle = \langle n | 0 \rangle. \tag{9}$$

3. RESULTS

3.1. Experimental Results

The absorption and emission spectra of biphenyl were measured in cyclohexane. This sample has been chosen because it has distinctively different shapes of absorption and emission spectra. The concentration of the solution was 10^{-5}M. The absorption spectra were measured using the SPECORD M-40 spectrophotometer (Carl Zeiss Jena). In turn, fluorescence spectra were recorded by a conventional apparatus using an exciting and collecting monochromator. The fluorescence emitted from the sample was focused on a photo-multiplier and the fluorescence spectra were collected on

TABLE I Calculated parameters Δ_l

l	Δ_l *of absorption*	Δ_l *of emission*
1	0.5	2.1
2	2.4	0.0
3	1.2	0.0

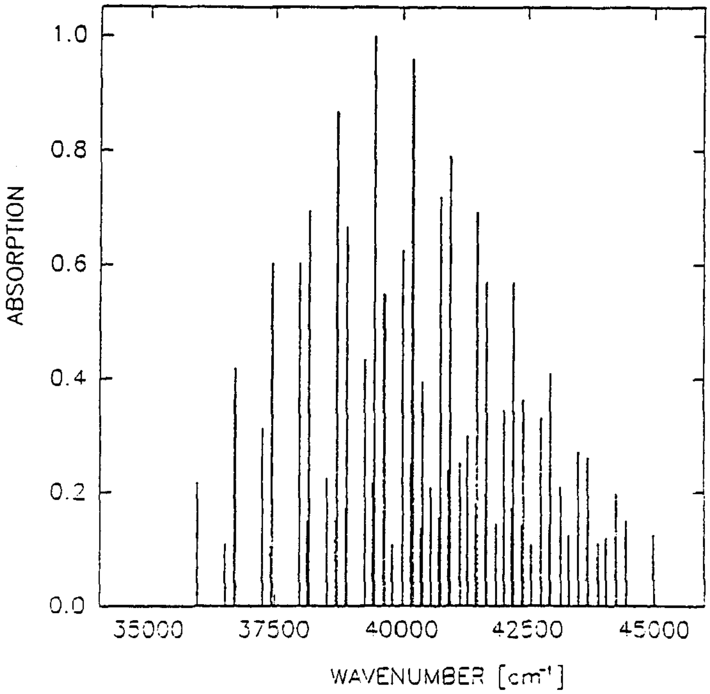

FIGURE 1 Calculated Franck-Condon factors for the absorption spectrum represented by the stick diagram.

the computer and fully corrected. Infrared absorption spectra of biphenyl in cyclohexane were obtained on the BRUKER 113v-FT Fourier transform spectrometer operating at the resolution of $2\,\mathrm{cm}^{-1}$. The solvent was spectroscopically pure. All these measurements were carried out at room temperature. The measured absorption and emission spectra were normalized to unity taking the highest value of the spectrum as equal to one.

3.2. Theoretical Results

We have simulated optical line shapes of absorption and emission spectra of biphenyl in cyclohexane. These simulations are based on the model presented in Ref. [16]. After analysis of vibration and vibronic spectra, suitable modes and parameters were chosen.

All calculations were carried out choosing from 60 vibration modes only the three most active modes from vibration FTIR and Raman spectra: $698.8\,\mathrm{cm}^{-1}$, $736.5\,\mathrm{cm}^{-1}$ and $1280.0\,\mathrm{cm}^{-1}$. Additionally to those three active modes, overtones and combinations (mixing) lines were taken into account and calculated. We also assume a Gaussian shape Eq. (5) of the bands with

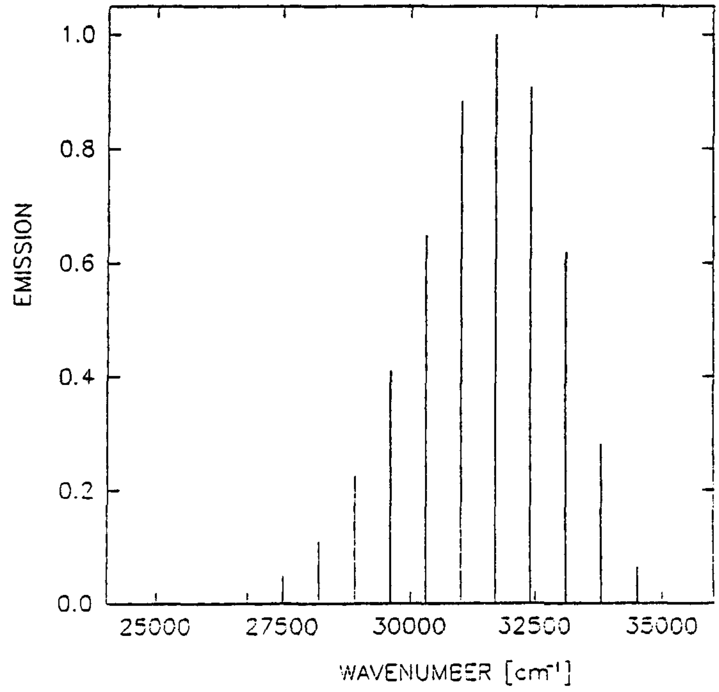

FIGURE 2 Calculated Franck-Condon factors for the emission spectrum represented by the stick diagram.

the width (FWHM) $\delta_{1/2}$ from Eq. (6) equals to 700 cm^{-1} and the electronic transition frequency equal to 34500 cm^{-1}.

Our task was to find values of parameters Δ_l for $l = 1$, 2 and 3 by fitting the simulated spectra (Eqs. (3) and (4)) to the measured ones by the means of the least-square method. We did this separately for absorption and emission spectra. The found values of Δ_l are presented in Table I.

Having obtained the best fit, we drew the intermediate results of the Franck-Condon factors (Eq. (7)) in Figures 1 and 2 for absorption and emission, respectively. These are so called "stick spectra" showing the relative intensity of particular transitions in molecule.

4. DISCUSSION

The experimental and calculated absorption spectrum is shown in Figure 3. In turn, Figure 4 shows the experimental and calculated emission spectrum. The experimental absorption spectrum is structureless with one global

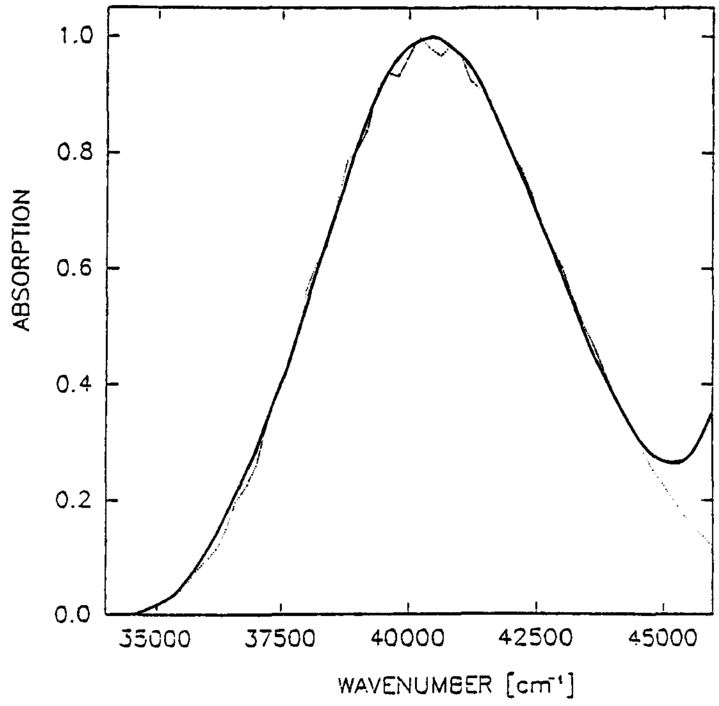

FIGURE 3 Measured (solid line) and simulations (dotted line) absorption spectra.

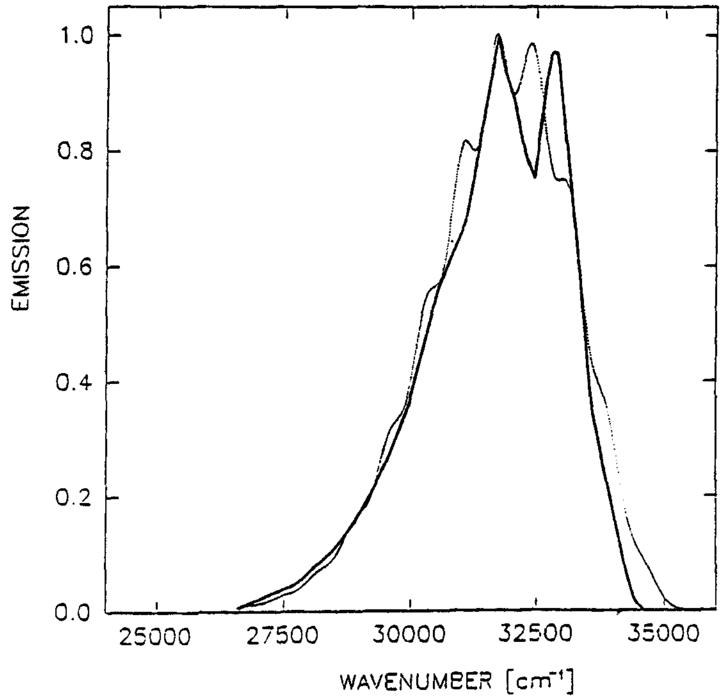

FIGURE 4 Measured (solid line) and simulations (dotted line) emission spectra.

maximum at 40400 cm^{-1}. The experimental emission spectrum displays some structure with the one global maximum at 31746 cm^{-1} and two local maxima at 31050 cm^{-1} and 32786 cm^{-1}.

The presented model assumes the symmetry transition relation between absorption and emission spectra (see Eq. (9)). According to the Kasha rule [18], emission takes place from the first (lowest) vibrational level of the excited electronic state. In our approach we assumed that the electronic potential surfaces are presented by harmonic oscillators which are identical for both the ground and excited singlet states. It means that the normal modes of the ground and excited states are the same. As mentioned above, the most active three modes were taken into account to calculate the Franck-Condon factors of absorption and emission spectra. Our calculations show that for the absorption spectrum all three modes are important. While in the case of the emission spectrum only one mode 698.9 cm^{-1} is accepted. It means that the two remaining modes with the exactly taken values from FTIR and Raman spectra do not play any role in the emission spectrum. In addition, it can be very useful tool to identify modes which play important role in experimentally obtained spectrum. This can be seen in Table I and Figures 3, 4.

The fact that chosen here three mode play different roles in the absorption and emission spectra is connected with the different geometry of molecule in the ground and excited states. This is experimentally confirmed by different shapes of absorption and emission spectra.

The experimental absorption $\varepsilon(\nu)_{\text{exp}}/\nu$ and emission $I(\nu)_{\text{exp}}/\nu^4$ spectra are compared with the theoretical results $\varepsilon(\nu)_{\text{calc}}/\nu$ and $\mathrm{I}(\nu)_{\text{calc}}/\nu^4$, where ν is the transition frequency. It seen that generally the experimental spectra are reproduced in the calculated spectra. The emission spectrum is reproduced to a satisfactory level while the absorption spectrum is very well reproduced.

5. CONCLUSION

We have shown that the proposed model allows for efficient calculation of Franck-Condon factors. In turn, these factors are treated as input data to simultaneous simulation of the absorption and emission spectra. It is found from the chosen three active modes in the Franck-Condon absorption and emission analysis that they play different roles in the simulation of each spectrum. It is seen that generally the theoretical absorption and emission spectra are in a satisfactory agreement with measured spectra. This means that numerical calculations based on the proposed model generally work well in the case of low lying vibrational levels. This model should be useful where *ab initio* potential energy surfaces are unavailable. That is the case for the biphenyl studied in this paper. It is very difficult to calculate potential energy surfaces, especially in excited states for polyatomic molecules. We hope that the proposed model will be useful in other investigations of vibronic spectra of molecules. Further work is in progress.

Acknowledgements

This work has been supported by Komitet Badań Naukowych under BW/5200-5-0300-0 project. The numerical calculations have been performed in TASK.

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