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**(Laser, Atomic and Molecular Physics)**

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OF ELECTRONICALLY EXCITED  
POLYATOMIC MOLECULES**

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MOLECULAR DYNAMICS SIMULATION  
OF ELECTRONICALLY EXCITED POLYATOMIC MOLECULES

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ABSTRACT

A computer simulation method is proposed for MD study of the photoinduced intramolecular dynamics in polyatomic molecules electronically excited by ultrashort laser pulses. An efficient, partially analytical procedure for calculation of the absorption (emission) spectra is developed and used for determination of molecular potentials in accordance with the experimental supersonic jets spectra.

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## 1 Introduction

Many important processes in polyatomic molecules take place in excited electronic states or use them as transition states. Between these are photoinduced isomerization of retinal systems and photosynthetic bacteria, electron transfer in biological, interfacial, or electrochemical systems, vibrational relaxation in liquids, photodissociation. Typical are pico- and subpicosecond timescales and recent advances in generation of ultrashort laser pulses are highly promising for a deeper understanding of the basic mechanisms realized in Nature [1-4].

The complexity of the investigated objects, however, makes difficult a direct interpretation of the data obtained from different laser spectroscopies in time and frequency domains. Appropriate approximations and computer simulation methods are necessary.

Molecular Dynamics (MD) is a computer-based technique for modeling gases, fluids and solids at microscopic levels of distance and time, and is therefore an ideal technique for gaining a molecular appreciation of many physical processes [5-7]. The method is founded on the assumption that atomic motions are governed by classical mechanics subject to some appropriate multidimensional force-field. Limitations of the method are well known. A fundamental one results from the basic assumptions of the method, namely, quantum-mechanical behavior is neglected and a single potential energy surface governs the motion. The quantum nature of vibrational and electronic motion, however, is important and must generally be accounted for. Other problems are connected with practical difficulties in constructing accurate force-field, including large number of atoms, integrating for long times, or achieving accurate statistical sampling. All of these depend on the efficiency of the related computational procedure and models used.

A general statement of the problem is shown on Figure 1. A molecule being initially in a ground electronic state |1) after irradiation is excited to an upper electronic level |2). In the excited state different relaxation pathways to the ground state are possible: radiationless transition, spontaneous or stimulated emission. The enormous amount of data necessary to describe the evolution of the molecular wave function (or equivalently the density matrix) prevents a direct *ab initio* treatment of the problem. Adequate simulation, however, is possible using classical description of the dynamics in the limits of a single electronic state, but incorporating the quantal features of the electronic transitions [8-13].

## 2 Spectra Calculation and Potential Energy Surfaces

The interpretation of the vibrational structure of electronic spectra is usually done by calculating Frank-Condon factors for absorption-emission. The relative intensities  $I(m, n)$ , of the vibrational components of a given electronic transition are expressed in terms of the vibrational overlap integral:

$$I(m, n) = \left[ \int \psi_m^M(Q) \psi_n^N(Q) dQ \right]^2 \quad (1)$$

where for example  $\psi_n^N(Q)$  is the vibrational wave-function for the vibrational state  $n$  of the electronic state  $N$ , and  $Q$  represents the nuclear coordinates. For a precise evaluation

of the spectrum a large number of integrals should be calculated for pairs  $(m, n)$  including fundamental vibrational states and their combinations as well. Recently, Brumer and Gruner suggested effective algorithm and used it for calculation of stilbene ( $N = 26$  atoms) emission spectrum [14,15]. They evaluated Frank-Condon factors involving a typical number of  $\approx 130000$  states of the molecule with the computation implemented in PL/1, required 8 to 10MByte of virtual storage,  $\approx 20$ MByte of scratch disc space, and 10 to 12 minutes CPU time on an IBM 4361, including the computation of all the necessary matrices[14].

Here we suggest an efficient, partially analytical procedure for calculation of the absorption (excitation) or  $0^0$  dispersed fluorescence spectrum using harmonic approximation. For stilbene molecule the frequency matrices are calculated for  $\approx 30$  min. and the spectrum itself for  $\approx 4$  min, with spectral resolution of  $1\text{cm}^{-1}$  on a PC AT486, without special memory requirements. Another advantage of this method (using the density matrix formalism) is that, also, some characteristics of the excited state, relevant to a further MD analysis can be calculated.

## 2.1 Theory of the One-Photon Laser Pulsed Excitation

An excited state resulted from one-photon electronic transition  $|1\rangle \rightarrow |2\rangle$  can be described in the frame of the first order perturbation theory by the following formula for the quantum density matrix [16]:

$$\hat{\rho}_{22} = \frac{(d_{12})^2}{4\hbar^2} \int \int d\tau_1 d\tau_2 E_L(\tau_1) E_L^*(\tau_2) \hat{\rho}_{22}^0(\tau) \quad (2)$$

where  $d_{12}$  is the electronic dipole momentum,  $E_L$  is the complex strength of the laser field with frequency  $\omega_L$ ;

$$\hat{\rho}_{22}^0(\tau) = e^{-i\hat{d}_2\tau/2} e^{i\hat{d}_1\tau/2} \hat{\rho}_{11}^T e^{i\hat{d}_1\tau/2} e^{-i\hat{d}_2\tau/2} \quad (3)$$

is the generalized density matrix of a vibronic state, formed during time interval  $\tau$ , with  $s = (\tau_1 + \tau_2)/2$  being the starting time-point,  $\hat{\rho}_{11}^T$  is the density matrix of the initial ground equilibrium state with temperature  $T$ ,

$$\hat{\delta}_j = [\hat{p}^T m^{-1} \hat{p}/2 + U_j(\hat{x})]/\hbar \quad (4)$$

are the energy operators of the electronic terms ( $j = 1, 2$ ) in frequency units,  $\hat{p}$  is the vector of momentum,  $m$  is the mass matrix,  $U_j(\hat{x})$  are the corresponding potential energies. In this approach the delocalization of the wave packet is due to the uncertainty of the moments  $\tau_1$  and  $\tau_2$ , and to the quantum and thermal vibrational fluctuations as well.

Absorption and emission spectra are determined by the transition probability  $P(\omega) = T\tau\hat{\rho}_{22}$  of the process  $|1\rangle \rightarrow |2\rangle$  corresponding to absorption or emission of a photon with frequency  $\omega$  if the initial state  $|1\rangle$  and the final one  $|2\rangle$  are chosen appropriately. The spectrum is obtained calculating (2) for  $\hat{\rho}_{22}$  using a Gaussian laser pulse  $E_L(\tau)$  and integrating over a time period greater than all vibrational periods. In harmonic approximation Eq. (3) determines a Gaussian density matrix and using the corresponding technique, described elsewhere [11,12], any characteristic of the final state may be represented analytically by the frequency and mass matrices  $(\omega_1, \omega_2, m)$  and by the normal modes deviations of the

two electronic terms  $(x_1 - x_2)$ . We obtained the following expression for the transition probability:

$$P(\omega_L) = (\Omega_L^2/4) \int d\tau f_p(\tau) \exp[i(\omega_L - \omega_{12})\tau] \chi(\tau), \quad (5)$$

where  $f_p(\tau) = \int ds u_p(s - \tau/2) u_p^*(s + \tau/2)$  is the laser pulse autocorrelation function;  $\Omega = E_L d_{12}/\hbar$  is the Rabi frequency;  $\omega_{12}$  is the frequency of the electronic transition.

$$\chi(\tau) = \frac{\det[\sinh(\hbar\omega_1/kT)/(sh_1sh_2)]}{\det^{1/2}(cth_1/\omega_1 + cth_2/\omega_2) \det^{1/2}(cth_1\omega_1 + cth_2\omega_2)} \times \exp[-\frac{1}{\hbar}(x_2 - x_1)^T m^{1/2}(cth_1/\omega_1 + cth_2/\omega_2)^{-1} m^{1/2}(x_2 - x_1)], \quad (6)$$

$$sh_1 = \sinh[\omega_1(\hbar/kT - i\tau)],$$

$$sh_2 = \sinh(i\omega_2\tau/2),$$

$$cth_1 = \cotanh[\omega_1(\hbar/kT - i\tau)],$$

$$cth_2 = \cotanh(i\omega_2\tau/2);$$

$\omega_1, \omega_2$  are the vibrational frequency matrices of both electronic terms.

These resulting Eqs. (5), (6) provide the exact expression for the one-photon transition probability, including spectral shifts due to the energies at zero temperature  $\hbar\omega_1/2$ ,  $\hbar\omega_2/2$  and Boltzmann initial ground-state distribution. On the contrary, a semiclassical statistical approach gives only the exponential factor of (6).

For the average  $x$ -coordinate we have:

$$x_q = x_2 + \int p(\tau) \Delta x(\tau) d\tau / P(\omega_L), \quad (7)$$

where  $p(\tau)$  is the time density expression  $dP(\omega_L)/d\tau$  (see Eq. 5);

$$\Delta x(\tau) = -m^{-1/2} \omega_2^{-1} sh_2^{-1} (cth_1/\omega_1 + cth_2/\omega_2)^{-1} m^{1/2} (x_2 - x_1) \quad (8)$$

is the displacement relative to  $x_2$  at the moment  $\tau$ . For the average momenta we have  $p_q = 0$ . The energy of the  $k$ -th mode is given by:

$$E_k = 0.5\hbar\omega_k(x_2 - x_1)_k^2 P(\omega_L - \omega_k)/P(\omega_L). \quad (9)$$

## 2.2 Normal Mode Characteristics

In harmonic approximation the molecule is considered as  $3N - 6$  independent harmonic oscillators or normal modes ( $N$  is the number of atoms). If one neglects anharmonicities and Dushinski rotation each vibrational degree of freedom can be described by its frequencies in the ground and excited state, and by the displacement ( $\Delta$ ) between the minima of the two states. Actually, in the absorption spectrum only a small number of modes with sufficient  $\Delta$ -s appear with relevant intensity and are usually called optically active modes.

Using Eqs. (5) and (6) and the developed computer procedure we simulate *trans*-stilbene supersonic jet absorption spectrum using the characteristics of 12 optically active normal modes. Their frequencies in the ground and first excited singlet states are known

from supersonic-jets experimental spectra [17]. The simulation consists of varying the displacements along each mode until the relevant calculated intensities agree well with the experimentally obtained. The final result is presented in Figure 2 and Table 1. The simulation is straightforward, not surprisingly as the normal modes are independent, and the precision of the calculated characteristics is mainly determined by the precision of the experimental spectrum.

The obtained normal mode characteristics may be used for constructing the molecular Hamiltonian in applications where the harmonic approximation is valid, for instance ultrashort laser pulsed excitation.

### 3 Molecular Mechanics Method for the Ground and Excited state Potential Energy Surfaces

In many applications harmonic approximation is not adequate and a more general determination of the potential energy surfaces (PES) is necessary. In this section on the example of stilbene molecule we determine the PES of the ground and the electronically excited states by means of the Molecular Mechanics (MM) potential energy functions [18]. MM functions have been developed and parameterized on the basis of structural and thermodynamic experimental data. In this work on the example of stilbene molecule we parameterize our force field using the absorption spectrum obtained in supersonic jet experiments [17].

We use the following MM potential energy functions [19]:

$$U(r_1, \dots, r_N) = U_b + U_{va} + U_{tor} + U_{vw} \quad (10)$$

$$U_b = 0.5 \sum_b k_b (b - b_0)^2 \quad (11)$$

$$U_{va} = 0.5 \sum_\varphi k_\varphi (\varphi - \varphi_0)^2 \quad (12)$$

$$U_{tor} = 0.5 \sum_\theta V_\theta [1 - \cos(n_t \theta)] \quad (13)$$

$$U_{vw} = \sum f [-2.25/r_n^6 + 8.28 \times 10^5 \exp(-r_n/0.0736)] \quad (14)$$

where  $U_b$ ,  $U_a$ ,  $U_{tor}$ ,  $U_{vw}$  are contributions due to deviations from the equilibrium chemical bonds, valence and torsional (dihedral) angles, and due to Van-der-Waals interactions respectively (in Eq.14  $r_n = r/s$ , where  $r$  is the distance between atoms and  $s$  is the sum of van-der-Waals radii). All the equilibrium bond lengths, valence angles and Van-der-Waals radii are well known [19] and may be used directly. The transferability of the force constants has been proved for determination of the structure of a large number of molecules. For dynamical investigations, however, they should be adjusted additionally, as well as the equilibrium bond lengths and valence angles of the excited molecule. Using

the standard technique we calculate the frequency matrix of the ground state and vary the force constants of the MM PES (10–14) until a good fit to the available experimental data is obtained. As a result we characterize entirely the ground state PES and with the finally accepted parameters the calculated frequencies correspond to the experimental values with deviations less than 5 %.

For the excited state we accept the same potential energy functions as for the ground state (10–14) and look for the changes of the parameters accounting for the absorption and 0° dispersed fluorescence spectrum. Spectra are calculated using Eqs. (5) and (6). Although these analytical expressions are complex, it is clear, that the main features of the spectra are determined by the normal modes deviations of the two terms  $\Delta = (x_2 - x_1)$  and the differences of the frequency matrices  $\omega_1$  and  $\omega_2$  or, respectively, by the changes of the parameters of the MM PES. Spectra are most sensitive to changes in the equilibrium bond lengths. As a rule, bond lengths increase in an excited state. In stilbene, however, due to the delocalization of the double bond character from the ethylene  $C_e = C_e$  to  $C_e$ -phenyl bonds the former is expected to increase and the later to decrease. In our calculations we also find out that changes in bond lengths larger than 0.02Å lead to highly congested unresolved spectra, while it is known from the experiment that the spectra consist of well resolved lines. Consequently, we used an iterative procedure for calculating the parameters of the excited state PES, varying their values in thus obtained limits.

The spectrum calculated with the finally accepted parameters for the ground and the excited states is shown in Figure 3. It compares very favorably with the experimental data [17], showing the same trends for the dominant peaks and a similar background.

### 4 MD simulations of excited state dynamics

A general scheme of the computer experiments possible with the developed simulation programs is presented in Figure 4. Using a standard MM program or own-written minimization procedure and force field one obtain the equilibrium molecular structure. Then, as it has been described in Sect. 3 using Eqs. (5) and (6) it is possible to calculate the force field parameters in accordance with the available experimental data. We note, however, that the computer simulation is not straightforward. The spectrum is determined by the characteristics of the normal modes ( $\omega_1, \omega_2, \Delta$  – see Sect. 2) while in the simulation one varies the force field parameters. For a certain force field it may be not possible to obtain appropriate parameters.

Having determined the PES of the ground and excited states one use the standard technique [20] for obtaining the eigen values and vectors for the matrix of the potential energy second derivatives. The eigen values determine the frequency matrices, while the eigen vectors determine the basis for transformation of cartesian coordinates to normal coordinates. Using this initial basis and calculated MD trajectories it is possible to monitor the time evolution of the energy in all vibrational modes. The Fourier spectra of these time-dependencies reveal the typical frequencies of the energy exchange between the normal modes. For calculating MD trajectories in the excited state the initial coordinates should be determined by using the calculated average (along the excitation pulse duration) coordinates (Eq. 7) and their delocalization (Eq. 8).

We have used this procedure for modeling ultrashort laser pulsed excitation (a number

of modes with sufficient  $\Delta$ -s excited simultaneously) or single vibrational level excitation (SVL) and study of the processes of intramolecular vibrational energy redistribution (IVR) in anthracene ( $C_{14}H_{10}$ ) and p-difluorobenzene ( $C_6F_2H_4$ ) [21].

## 5 Conclusions

Frequency- and time-resolved absorption/emission spectra recorded in supersonic jets contain a large amount of information about the potential energy surfaces of the ground and electronically excited states, and about the purely intramolecular photoinduced dynamics. Using the usual first order perturbation theory for the quantum density matrix and local quadratic approximation of the PES near the ground state equilibrium coordinates we find out exact expression for the one-photon quantum transition probability  $P(\omega)$ , giving its dependence on the frequency matrices and the normal modes displacements of the both electronic terms (Eqs. 5, 6). If, then, one use any appropriate way of determining the PES, spectra calculation based on these equations can be used for adjusting the parameters of the PES. Otherwise, if only experimental spectra are available, the frequency matrices are determined to some extent and in a computer simulation (Sect. 2.2) the dimensionless normal modes displacements can be calculated. We choose to determine the PES by means of the MM potential energy functions. They are relatively simple and widely used in structural studies of organic molecules. Therefore, some analogy is possible for dynamical studies and some of the parameters are well determined.

After the PES or equivalently (in harmonic approximation) the frequency matrices and the dimensionless displacements of normal modes are determined, some characteristics of the excited state can be calculated and used for an accurate MD or wave packet analysis of the molecule dynamics after excitation (Eqs. 7, 8). As a first guess, the averaged over the pulse duration coordinates  $x_q$  (Eq. 7) may be used as initial conditions for the equations of motion. For a more precise statistical treatment, the delocalization during the excitation (Eq. 8) should also be taken into account.

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## Figure captions

Figure 1. MD simulation of electronically excited polyatomic molecules: a general scheme.

Figure 2. Stilbene absorption spectrum calculated using Eqs. (5, 6) and characteristics of 12 normal modes, given in Table 1. The temperature is 5K.

Figure 3. Stilbene absorption spectrum calculated using Eqs. (5, 6) and potential energy surfaces determined by MM method (Eqs. 10–14). The temperature is 5K.

Figure 4. General scheme of computer experiments on photoinduced (by ultra-short laser pulse) intramolecular excited state dynamics.

Table 1. Characteristics of 12 optically active stilbene modes: frequencies  $\omega_2$  and  $\omega_1$  in the ground and first excited singlet states (taken from experimental data [17]), dimensionless displacement of the two electronic terms  $\Delta$  (determined in computer simulation described in text), calculated and experimental (in brackets) values of the intensities of the relevant fundamental lines in the absorption spectrum

$\omega_2$ ( $cm^{-1}$ )	$\omega_1$ ( $cm^{-1}$ )	$\Delta$	I(a.u)
0	0		
204	197.6	1.21	78.5 (79)
290	280.3	0.75	30.0 (30)
624	590.7	0.32	10.0 (10)
870	850	0.56	16.9 (17)
1006	972.7	0.70	25.8 (26)
1072	1069.8	0.26	4.9 (5)
1031	1249.3	0.38	10.3 (10.6)
1340	1332.4	0.34	6.8 (7.5)
1495	1464	0.12	1.8 (1.7)
1584	1548.4	0.20	3.0 (3.5)
1607	1553	0.16	1.7 (1.9)
1654	1637.8	0.17	2.2 (2.3)

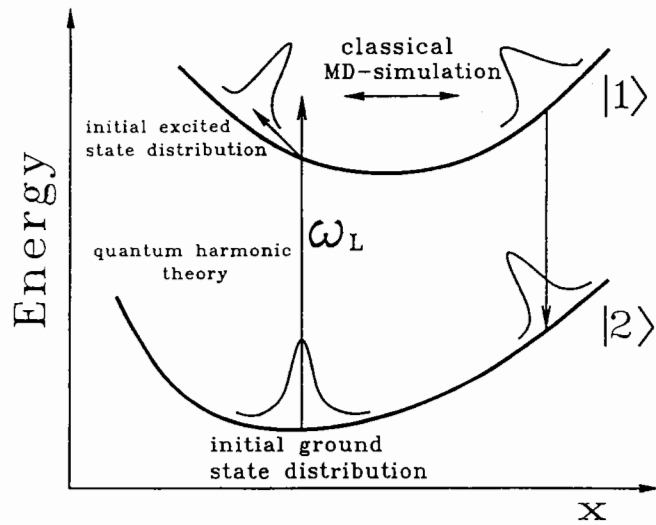


Fig.1

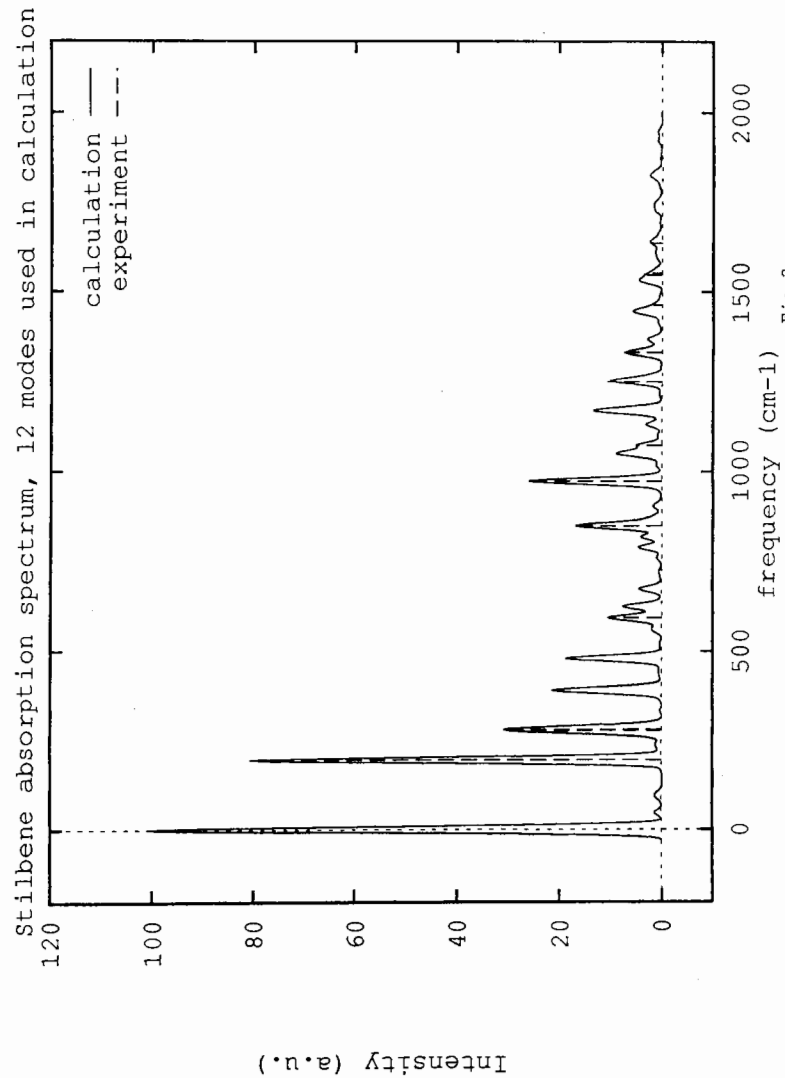


Fig.2

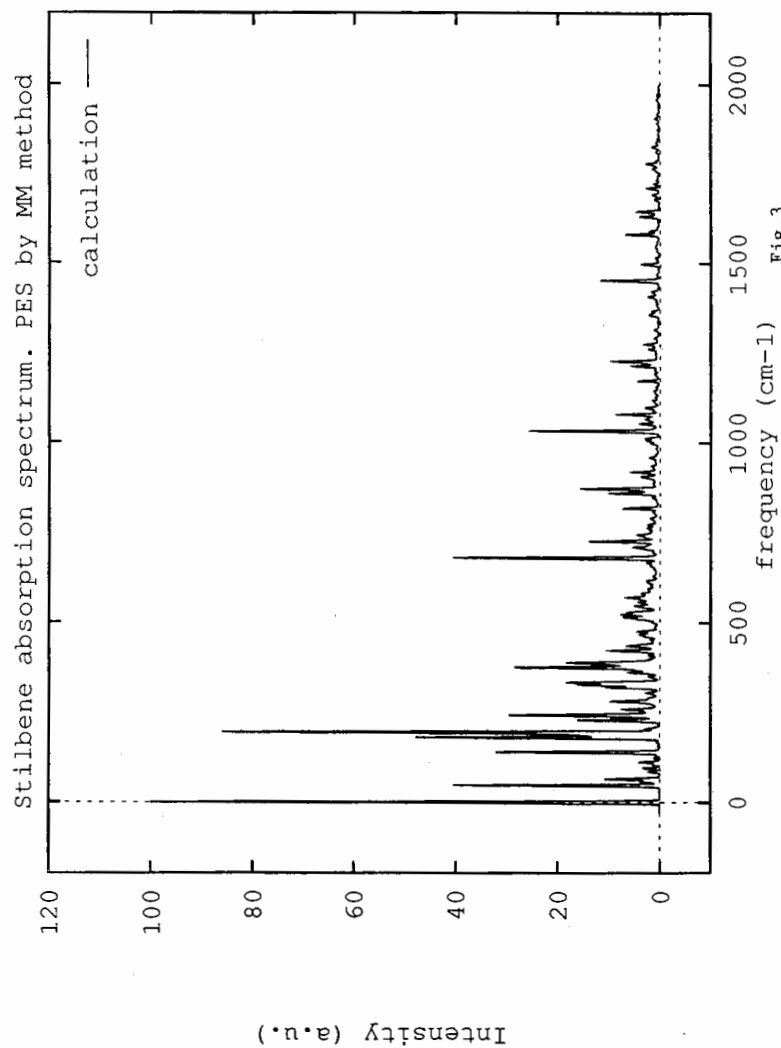


Fig.3

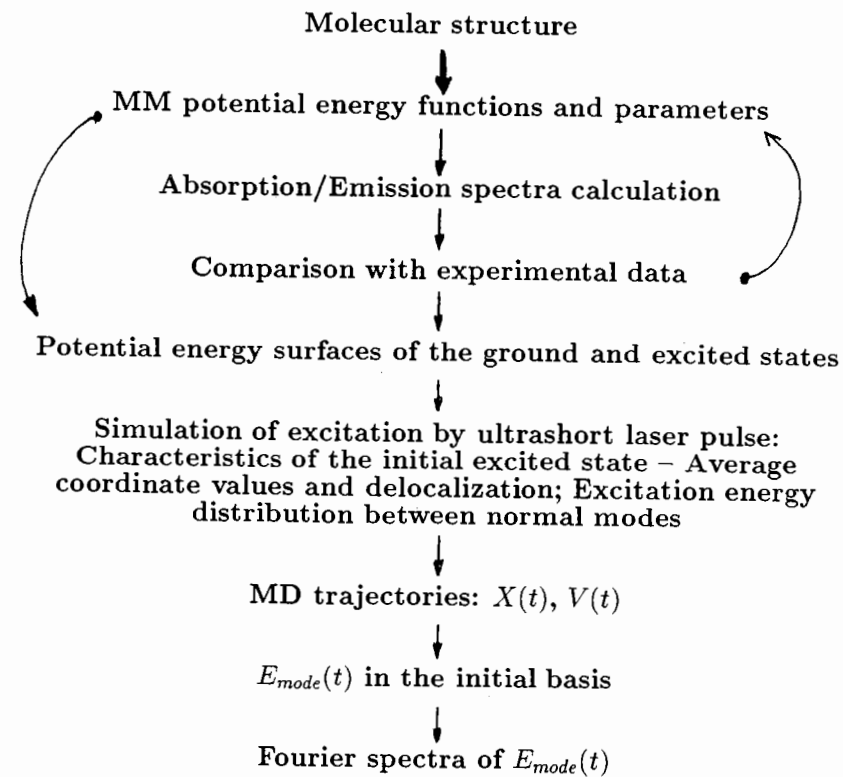


Fig.4