

**GEOMETRY STRUCTURE AND *IR* MULTIPHOTON  
EXCITATION SPECTRA OF  $\text{SiF}_2\text{H}_2$ . A THEORETICAL  
STUDY.**

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**Abstract**

A model for the collisionless infrared multiphoton excitation (IRMPE) has been developed for  $\text{SiF}_2\text{H}_2$ . In order to give an accurate description for infrared multiphoton absorption (IRMPA) spectra, the first four vibrational levels were considered. The geometry structure, harmonic vibrational frequencies and anharmonic frequency correction were calculated by density functional theory (DFT) using B3PW91 exchange-correlation functional and cc-pVTZ basis set. The theoretical spectra are compared with experimental results reported recently.

**Keywords:** infrared multiple photon excitation,  $\text{SiF}_2\text{H}_2$ , asymmetric top, geometry structure, induced dipole moment.

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## 1. Introduction

In the last few years, an increasing interest has been developed for  $SiF_2H_2$ , an asymmetric top which has been studied [1] as a prospective molecule for laser isotope ( $Si^{29}$  and  $Si^{30}$ ) separation. Both IR spectra and multiphoton absorption spectra were reported recently by Gorelik *et al.*[1] using both cw(continuum wave) and pulsed  $CO_2$  laser beams. Although the multiple-photon dissociation process is, in most cases, assisted by collisions, the absorption of the first few photons is coherent and modelling this part of the process could yield valuable information about the laser-molecule interaction. Moreover, in two frequency dissociation, the first pulse excites the desired isotopic species on the first vibrational levels of the pumped mode, while the second laser dissociates the excited molecules. Modelling the interaction of the first laser pulse with the molecular ensemble one can obtain information about how to establish the optimum conditions for the second pulse.

We describe in this paper a model for the infrared multiple photon excitation (IRMPE) of an asymmetric top. In particular, for  $SiF_2H_2$  we presented the basic algorithm used for selecting the vibration-rotation states involved in the excitation process. This was done by describing the vibration-rotation structure of the excited mode and imposing the appropriate selection rules for the infrared transitions. In order to simulate realistic IRMPA spectra, accurate molecular parameters (geometry structure, induced dipole moment, harmonic vibrational frequencies and anharmonic frequency correction) are necessary. Density functional theory (DFT) was used with (Becke exchange-, Pedrew-Wang correlation type functional) B3PW91 and (consistent correlated-polarized valence triple zeta) cc-pVTZ basis set. A similar *ab initio* calculation with a good approximation was made for  $CF_2HCl$  [2] and its  $^{13}C$  and  $^2H$  isotopic species.

In the next section a brief description of the employed methods is given. In section three the obtained results for  $SiF_2H_2$  are presented. The conclusions of the paper are given in the final section.

## 2. An IRMPE model

Collisionless IRMPE models and corresponding computer programs have been developed by us for spherical top molecules like  $SF_6$  [3] and  $UF_6$  [4], as well as for symmetric top molecules like  $Si_2F_6$  [5] and for asymmetric top molecules like  $CF_2HCl$  [6]. The main assumptions [3] in building the model are the following: (1) the excitation is coherent, *i.e.* the collision (if present during the laser pulse) do not influence the excitation; (2) the excitation starts from the ground state and is near-resonant to normal mode ( $\nu_3$  and  $\nu_4$  in this case) thus the rotating wave approximation is valid one; (3) after absorbing  $N$  photons the vibrational energy of the excited mode leak into a quasi-continuum. The model deals only with the absorption in the discrete region and the  $N=4$  case was considered; (4) the vibrational-rotational structure is assumed to be an anharmonic oscillator coupled to a rigid rotor.

Assuming a collision-less regime, the interaction molecule-laser field can be described by the time-dependent Schrödinger equation:

$$ih \frac{\partial \Psi(t)}{\partial t} = [H_0 + V(t)] \Psi(t), \quad (1)$$

where  $V(t) = \mu E \cos \omega t$  is the interaction term, and  $\Psi(t)$  can be expressed in terms of  $\phi_n$ , the eigenfunction of the molecular unperturbed vibrational-rotational Hamiltonian  $H_0$ :

$$\Psi(t) = \sum_n A_n(t) \phi_n. \quad (2)$$

The problem is to calculate  $A^*(t)A(t)$ , the time dependent population of the levels involved in the excitation path. By making the rotating wave approximation and using Laplace transform, the time-dependent problem reduces to a time-independent eigenproblem for an effective Hamiltonian:

$$\left[ \hat{H}_0 + \hat{H}_I \right] \varphi = E \varphi, \quad (3)$$

where

$$\hat{H}_0 = \hat{H}_{harm.} + \hat{H}_{anharm.} + \hat{H}_{rot.} - n_v \nu_{laser}, \quad (4)$$

and

$$\hat{H}_I = \mu \cdot E \cdot F_{H-L}. \quad (5)$$

In eq.(4) and eq.(5) we note:  $\hat{H}_{harmonic}$ , the harmonic vibrational Hamiltonian,  $\hat{H}_{anharmonic}$ , the anharmonic approximation,  $\hat{H}_{rot}$ , the rotational Hamiltonian,  $n_v$  the vibrational quantum number,  $\nu_l$  the applied laser frequency,  $\mu$  the induced dipole moment,  $E$  the applied laser field, while  $F_{H-L}$  represent the Hönl-London coefficient. For a real vibration-rotation structure of polyatomic molecule, eq.(3) can be solved only numerically. At the same time the complexity of eq.(3) is given also by the fact that in case of asymmetric top the  $\hat{H}_{rot}$ , and the  $F_{H-L}$  expression can not be obtained immediately from analytical considerations.

The quantum mechanical description of the asymmetric rotor is obtained as a correction of the symmetric model [7, 8], which is defined as follows:

$$\begin{aligned} \langle J, K | \hat{H}_{rot} | J, K \rangle &= F (J(J+1) - K^2) - GK^2 \\ \langle J, K | \hat{H}_{rot} | J, K+2 \rangle &= \\ = \frac{1}{2}H \sqrt{[J(J+1) - (K+1)(K+2)][J(J+1) - K(K+1)]}, \end{aligned} \quad (6)$$

where  $J$  and  $K$  are the rotational quantum numbers, while  $F$ ,  $G$ , and  $H$  are functions of asymmetric parameter  $\sigma$  defined by the rotational constants  $A$ ,  $B$ , and  $C$ . Considering the foregoing statements, the rotational energy of asymmetric molecules can be obtained easily by solving the equation:

$$\hat{H}_{rot}\psi_{rot} = E_{rot}\psi_{rot}. \quad (7)$$

The Schrödinger equation as well as the  $F_{H-L}$  Hönl-London coefficient for asymmetric case can be expressed as:

$$F_{H-L}^{asymm} = \psi_{rot} F_{H-L}^{symm} \psi_{rot}. \quad (8)$$

The possible excitation paths are build considering the selection rules for vibrational and rotational transitions. While the vibrational transitions obey the well known selection rule:  $\Delta v = \pm 1$ , the rotational transitions for asymmetric top are more complicated. For the rotational selection rules we are able to define a simple analytic expression only for the quantum number  $J$ :  $\Delta J = 0, \pm 1$ , while for the quantum number  $K$  we have the following

rules:  $++ \leftrightarrow -+$  and  $+- \leftrightarrow --$  for band  $a$ ,  $++ \leftrightarrow --$  and  $+- \leftrightarrow -+$  for band  $b$  and  $++ \leftrightarrow +-$  and  $-+ \leftrightarrow --$  for band  $c$ , where  $a$ ,  $b$  and  $c$  corresponding to three principal axes each with its associated moment of inertia ( $I_a$ ,  $I_b$ , and  $I_c$ ), while “+” and “-” represent the symmetry of the rotational wave function during the rotation.

Building the excitation tree and solving eq.(3) for all quantum numbers  $v$ ,  $J$ , and  $K$  one can obtain the excitation probability for different laser frequencies. Moreover summing-up for several quantum numbers  $v$ , we can find the population probabilities of different vibrational levels up to  $v_{max}$ . We limited our calculation at  $v_{max} = 4$ , as a large number of vibration-rotation states are involved in the excitation due to the wide Maxwell-Boltzmann thermal distribution and the asymmetric rotor model taken into account.

### 3. Results and discussions

The standard harmonic and anharmonic frequency calculations were performed by the Gaussian03 computer code [9] by the DFT method using B3PW91 and cc-pVTZ basis set. We present the geometry parameters of  $SiF_2H_2$ , in Table 1., the theoretical and experimental harmonic vibrational frequencies in Table 2. , while Table 3. contains the anharmonic frequency corrections.

*Table 1. The geometry parameter of  $SiF_2H_2$  obtained with DFT method using B3PW91 functional and cc-pVTZ basis set. The distance is given in Å, while the angle in degree.*

Coord.	Theo.	Exp.
$r_{Si-H}$	1.47646	1.471
$r_{Si-F}$	1.59757	1.577
$\alpha_{F-Si-F}$	107.900	107.9
$\alpha_{F-Si-H}$	108.504	—
$\alpha_{H-Si-H}$	114.727	112.8

The  $SiF_2H_2$  methane like system is an asymmetric top molecule having  $C_{2v}$  molecular symmetry with four non-degenerated ( $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$ )

symmetry elements and the asymmetric parameter:  $\sigma = -0.848$ . Due to the high symmetry ( $C_{2v}$ ) for an asymmetric top molecules the spectral shape is well resolved having only pure  $a$ ,  $b$ , and  $c$  band type.

*Table 2. The harmonic vibrational frequencies of  $SiF_2H_2$  obtained with DFT method using B3PW91 functional and cc-pVTZ basis set.*

*The values are given in  $cm^{-1}$ .*

Symm.	Mode	Theo.	Exp.
$A_1$	$\nu_1$	2276.6	2245.7
	$\nu_2$	971.6	981.7
	$\nu_3$	858.1	869.6
	$\nu_4$	312.8	322.0
$A_2$	$\nu_5$	723.5	730.0
$B_1$	$\nu_6$	2290.0	2250.5
	$\nu_7$	705.5	730.0
$B_2$	$\nu_8$	971.5	981.0
	$\nu_9$	892.1	903.4

Considering the results obtained for the molecular geometry (Table 1.) it can be stated that the theoretical parameters for bond lengths and bond angles are in a very good agreement with the experimental values [10]. Only in case of angle  $\alpha_{H-Si-H}$  can be observed a small difference between the theoretical value and the measured one. This leads us to conclude that the used basis set (cc-pVTZ) and theoretical method (DFT) with B3PW91 exchange-correlation functional gives an accurate description for our molecular system.

The calculated values for the harmonic vibrational frequency (Table 2.), are shifted with about  $10\text{ cm}^{-1}$  for most of the normal modes, when compared to the experimental values. This discrepancy can be explained by the global anharmonic effects of vibrations. In case of frequency values  $\nu_1$  and  $\nu_6$ , these shifts are very large. Both frequencies can be assigned to the stretching vibration mode (symmetric and antisymmetric) of hydrogen bond, in which case the large asymmetric effects of vibrations are well-known.

Table 3. The anharmonic vibrational frequencies of  $\text{SiF}_2\text{H}_2$  obtained with DFT method using B3PW91 functional and cc-pVTZ basis set. The values are given in  $\text{cm}^{-1}$ .

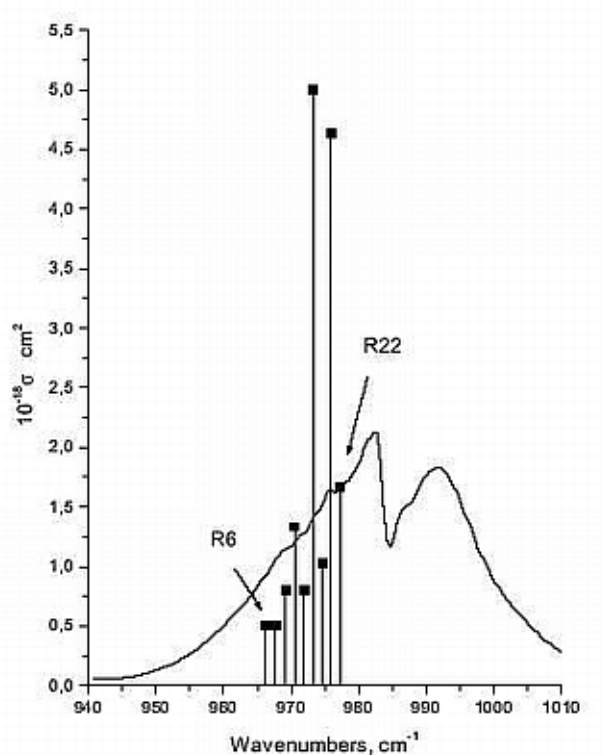
Mode	1	2	3	4	5	6	7	8	9
1	-12.1	-6.6	-0.5	-0.2	-6.3	-47.1	-4.5	0.7	-4.9
2		-1.1	-1.4	-1.2	0.0	-9.7	-3.7	0.2	2.0
3			-1.9	-1.9	-0.1	-0.2	-1.2	-4.0	-2.3
4				0.1	1.5	0.0	-0.7	-1.1	0.5
5					-1.0	-4.9	4.8	-4.2	-0.2
6						-11.8	-3.7	-0.7	-5.9
7							0.0	-0.1	1.5
8								-2.5	-4.1
9									-1.0

The anharmonic frequencies of different normal modes are presented in Table 3. We found significant corrections ( $\geq 10 \text{ cm}^{-1}$ ) for  $x_{11}$ ,  $x_{66}$ , and for their coupling  $x_{16}$ , though in the last case the  $47.09 \text{ cm}^{-1}$  value in our opinion is overestimated. From the point of view of multiphoton excitation process we are interested on the normal modes  $\nu_2$ , and  $\nu_8$ , because their frequencies fall in the spectral region of  $\text{CO}_2$  laser. The normal mode  $\nu_2$  is typical of  $\text{Si}-\text{F}$  antisymmetric stretching mode combined with the  $\text{Si}-\text{H}$  rocking, while  $\nu_8$  is characteristic of pure  $\text{H}-\text{Si}-\text{H}$  bending vibration. Their anharmonic corrections have small values:  $x_{22} = -1.06 \text{ cm}^{-1}$ , and  $x_{88} = -2.53 \text{ cm}^{-1}$ , but the most important finding is that their anharmonic coupling can be neglected ( $x_{28} = 0.19 \text{ cm}^{-1}$ ).

In order to simulate the IRMPA spectra, the following values are needed as input parameters: geometry parameters, harmonic and anharmonic vibrational frequencies, the quantum number of highest vibrational level, induced dipole moment of the given normal mode, laser frequency and intensity of the applied laser field. Based on the theory presented in the second section we developed a computer code which, using the above mentioned input parameters, is able to calculate the probability of the excitation for different vibrational level up to  $v_{max}$ . Considering  $v_{max} = 1$  one can obtain the conventional IR absorption spectra of the molecule. Comparing the theoretical and experimental absorption spectra we are able to estimate the

accuracy of our simulation. For the sake of comparison, the experimental and theoretical spectra are presented in Fig.1 and Fig.2, respectively.

The results show a good agreement between the experimental and theoretical spectral shapes. Both frequencies are *IR* active,  $\nu_2$  has pure *b* type band, while  $\nu_8$  present a pure *c* type band. Due to the coincidence of the frequency values the resulting spectral shape is more complicated, actually being a superposition of the two spectra.

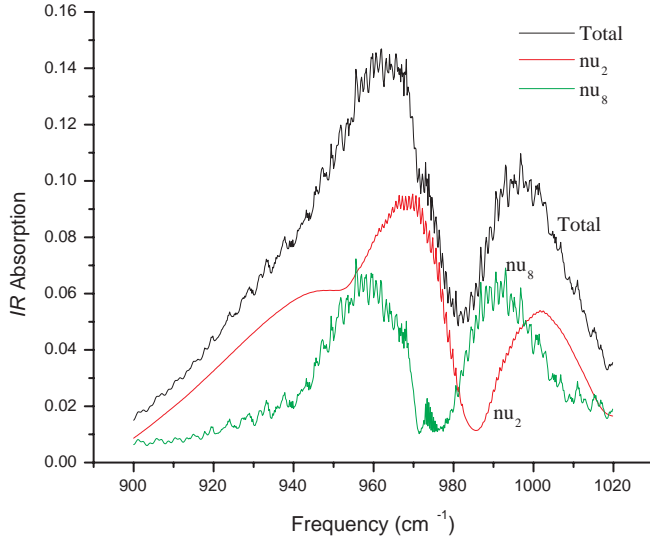


*Fig. 1. The experimental IR absorption spectrum of SiF<sub>2</sub>H<sub>2</sub>*

The multiphoton *IR* absorption spectra for the normal modes  $\nu_2$ , and  $\nu_8$  are presented in Fig.3 and Fig.4 respectively. The total absorption is computed

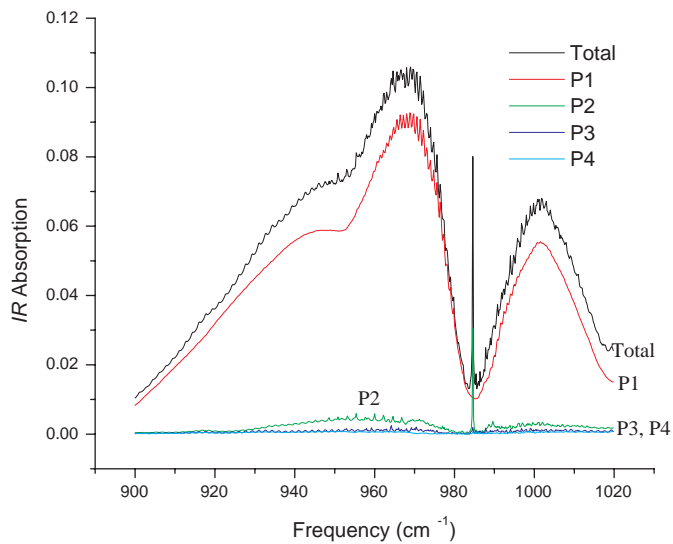


as a sum of different vibrational level population (labelled as P1, P2, P3, and P4 for the corresponding vibrational levels). In both cases we observe an important two photon contribution (see P2 in the figures), but with a different spectral structure.



*Fig. 2. The theoretical IR absorption spectrum of SiF<sub>2</sub>H<sub>2</sub>*

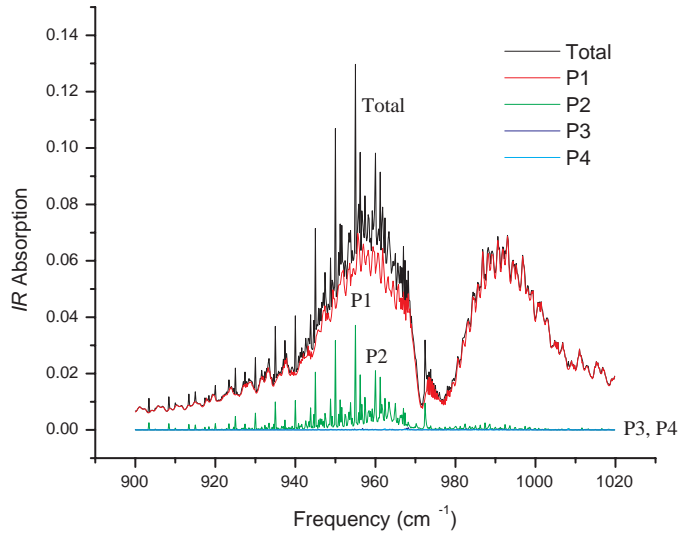
The P2 shape of  $\nu_2$  present a single pronounced peak (shifted with the magnitude of  $x_{22}$  according to the band origin), while in case of  $\nu_8$  we have more smaller peaks (as a multiple of  $x_{88}$ ). The P3 and P4 populations are very small in comparison with P1 and P2, therefore the total absorption is mainly given by the contribution of the first two levels. With respect to the efficiency of laser field absorption it can be said that in the course of laser excitation in both cases the two photon absorption is very important with the observation that for  $\nu_2$  we have a smooth spectral shape, while  $\nu_8$  shows a much more isotope selective band.



*Fig. 3. The theoretical IR multiphoton absorption spectra of  $\nu_2$  for the total and the different vibrational level (P1, P2, P3, and P4) excitation.*

#### 4. Conclusions

The geometry structure, harmonic vibrational frequencies and anharmonic frequency correction for  $SiF_2H_2$  have been calculated by the density functional theory (DFT) using B3PW91 exchange-correlation functional and cc-pVTZ basis set. For the geometry structure we found a very good agreement between the theoretical and experimental results. The calculated frequencies of different normal modes are analysed in pursuance of the harmonic and anharmonic approximation and are compared with the experimental results.



*Fig. 4. The theoretical IR multiphoton absorption spectra of  $\nu_8$  for the total and the different vibrational level (P1, P2, P3, and P4) excitation.*

The shape of IR absorption spectra for frequencies  $\nu_2$ , and  $\nu_8$  is interpreted as a superposition of the two different bands, while in case of multiphoton absorption spectra we found an important two photon contribution besides of the one photon effects. It also can be noted that the third and fourth level populations are small in comparison with the first two level contributions. This suggests that the bottleneck for the multiphoton process is very strong for both modes, which make us to assume that further photon absorption is possible only if assisted by collisions.

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