

## **IR multiphoton absorption spectra of some freon molecules used in $^{13}\text{C}$ isotope separation**

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A model calculation for the collisionless infrared multiphoton absorption (MPA) has been performed for some freon molecules ( $\text{CF}_2\text{HCl}$ ,  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$ ) used in  $^{13}\text{C}$  laser isotope separation. The harmonic vibrational frequencies and their anharmonic frequency corrections. The MPA spectra correlate well with experimental data for  $\text{CF}_2\text{HCl}$  and  $\text{CF}_2\text{Cl}_2$  and reveal the excitation dynamics in collisionless regime.

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### **1 Introduction**

The laser induced reaction in polyatomic molecules for the purpose of selective isotopic enrichment, continues to be an area of current interest. Research groups focus now on using free electron lasers<sup>1</sup> besides the traditional  $\text{CO}_2$  laser for dissociating selectively various molecules for separating carbon and silicon isotopes. Other possible applications of laser induced decomposition foresee an atmospheric engineering solution<sup>2</sup> to the chlorofluorocarbon contamination problem. The molecules in study are investigated both for their use in  $^{13}\text{C}$  isotope separation (especially  $\text{CF}_2\text{HCl}$ ) and for their implication in the destruction of stratospheric ozone layer ( $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$ ).

In this paper we calculate the vibrational spectroscopic constants and infrared multiphoton absorption (MPA) spectra of  $\text{CF}_2\text{HCl}$ ,  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$  molecules. The molecular structure and vibration-rotation parameters were calculated by DFT method using B3LYP exchange-correlation functional and cc-pVTZ basis set. These were used afterwards in the calculation of the MPA spectra, using a program originally developed by us<sup>3-7</sup>.

### **2 The IRMPE model**

Collisionless IRMPE models and corresponding computer programs have been developed by us for spherical top molecules<sup>3</sup>  $\text{SF}_6$  and  $\text{UF}_6$ , for symmetric top molecules<sup>4</sup> like  $\text{Si}_2\text{F}_6$  as well as for asymmetric top molecules like  $\text{CF}_2\text{HCl}$ <sup>5</sup>. The main assumptions of the model are: (1) the excitation is coherent, *i.e.* the collisions (if present during the laser pulse) do not influence the excitation; (2) the excitation starts from the ground state and is near-resonant to the excited normal mode 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 collisionless regime, the interaction molecule-laser field can be described by the time-dependent Schrödinger equation:

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

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  $A_n^*(t)A_n(t)$ , 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 of an effective Hamiltonian<sup>3</sup>.

Building the excitation tree and solving eq.(1) for all  $\nu$ ,  $J$ , and  $K$  quantum numbers one can obtain the excitation probability for different laser frequencies. Moreover summing-up for several  $\nu$  quantum numbers we can find the population probabilities of different vibrational levels up to  $\nu_{max}$ . We limited our calculation at  $\nu_{max}=4$ , as a large number of vibration-rotation states are involved in the excitation due to the wide Maxwell-Boltzmann thermal distribution.

### 3 Results and Discussion

The standard harmonic and anharmonic frequency calculations were carried out in Heidelberg on a Hewlett-Packard cluster by Gaussian03 computer code<sup>9</sup> considering the DFT method and using B3LYP exchange-correlation functional and cc-pVTZ basis set. A preliminary calculation<sup>10</sup> using B3LYP and B3PW91 exchange-correlation functionals and four different basis sets has shown that B3LYP and cc-pVTZ combination yields the best spectroscopic constants for  $CF_2HCl$ . This combination was further used also for  $CF_2Cl_2$  and  $CFCl_3$  related molecules. In Table I we give the symmetries, normal mode frequencies and the corresponding diagonal anharmonic constants for  $CF_2HCl$ ,  $CF_2Cl_2$ ,  $CFCl_3$ , calculated as described above. The modes of interest,

falling in the  $CO_2$  laser emission range are highlighted in bold. For  $\nu_8$  normal mode of  $CF_2HCl$  the isotopic shift measured experimentally<sup>10</sup> is  $26\text{ cm}^{-1}$ , and in good agreement with our calculated value of  $27.6\text{ cm}^{-1}$ . Also, the obtained normal mode frequencies are in good agreement with data from the literature for  $CF_2HCl$ <sup>11,12</sup> and  $CF_2Cl_2$ <sup>13,14</sup>.

Table 1. Symmetries, normal mode frequencies and the corresponding diagonal anharmonic constants for  $CF_2HCl$ ,  $CF_2Cl_2$ ,  $CFCl_3$ .

Nr. mod	$CF_2HCl$ ( $C_3v$ )				$CF_2Cl_2$ ( $C_{2v}$ )				$CFCl_3$ ( $C_{3v}$ )			
	$^{12}C$		$^{13}C$		$^{12}C$		$^{13}C$		$^{12}C$		$^{13}C$	
	$\omega_i$	$x_{ij}$	$\omega_i$	$x_{ij}$	$\omega_i$	$x_{ij}$	$\omega_i$	$x_{ij}$	$\omega_i$	$x_{ij}$	$\omega_i$	$x_{ij}$
1	3129.3	-64.8	3116.7	-64.4	<b>1093.6</b>	<b>-4.2</b>	<b>1065.3</b>	<b>-4.0</b>	<b>1089.3</b>	<b>-10.6</b>	<b>1061.5</b>	<b>-10.1</b>
2	1319.5	-9.4	1312.7	-9.1	661.0	-0.14	655.7	-0.13	798.8	-3.3	771.0	-3.0
3	<b>1125.6</b>	<b>-4.0</b>	<b>1083.5</b>	<b>-3.8</b>	443.4	-0.2	443.3	-0.17	798.0	-2.9	770.1	-2.7
4	794.2	-2.5	754.5	-2.4	255.3	-0.06	254.9	-0.06	522.3	-0.62	518.9	-0.64
5	600.4	0.0	589.4	-0.03	317.2	-0.24	317.2	-0.28	391.9	-0.74	391.8	0.22
6	400.9	1.1	398.9	0.4	1159.6	-7.1	1126.9	-6.7	391.7	-0.74	391.7	0.25
7	1374.0	-10.4	1366.9	-9.8	430.4	-0.01	427.5	-0.01	343.9	-0.12	342.5	-0.11
8	<b>1128.8</b>	<b>-5.9</b>	<b>1101.2</b>	<b>-5.6</b>	862.0	-1.7	831.7	-1.6	239.8	-1.7	239.7	-1.7
9	359.2	0.0	357.1	0.02	425.1	-0.24	425.1	-0.24	239.5	-1.7	239.3	-1.7

Table 2. Calculated induced dipole moments [in Debye units] for the molecules containing  $^{12}C$  isotope

Nr. mod	$CF_2HCl$			$CF_2Cl_2$			$CFCl_3$		
	$\mu_a$	$\mu_b$	$\mu_c$	$\mu_a$	$\mu_b$	$\mu_c$	$\mu_a$	$\mu_b$	$\mu_c$
1	-0.197	0.0	-0.014	0.0	-1.669	0.0	-1.070	0.0	0.0
2	-0.336	0.0	-0.273	0.0	-0.753	0.0	0.0	0.115	1.057
3	-1.444	0.0	1.218	0.0	0.118	0.0	0.0	-1.057	0.115
4	-1.252	0.0	-1.612	0.0	0.118	0.0	0.206	0.0	0.0
5	-0.849	0.0	0.475	0.0	0.0	0.0	0.0	0.0	-0.297
6	-0.254	0.0	-0.288	1.736	0.0	0.0	0.0	0.297	0.0
7	0.0	-0.355	0.0	-0.595	0.0	0.0	-0.153	0.0	0.0
8	0.0	1.952	0.0	0.0	0.0	1.818	0.0	0.0	0.019
9	0.0	0.600	0.0	0.0	0.0	-0.264	0.0	-0.019	0.0

The induced dipole moments were calculated using the fractional Mullikan charge approach, and the calculated vibrational amplitudes for

the given normal mode. The dipole moments are listed in Table 2 for the normal modes of  $CF_2HCl$ ,  $CF_2Cl_2$ ,  $CFCl_3$ , in Debye units. From this table one can see that  $\nu_3$  and  $\nu_8$  normal modes of  $CF_2HCl$  have *a/c* type and *b* type bands respectively,  $CF_2Cl_2$   $\nu_1$  mode poses a *b* type band, while  $CFCl_3$   $\nu_1$  mode has a parallel type band. The type of band will determine the selection rules for the vibration-rotation transitions, during MPA process.

We also calculated the rotational constants and centrifugal distortion constants. From these data we estimated that, for a rotational quantum number, for example  $J=30$ , which is significantly populated at 300 K, the contribution to the rotational energy is chiefly given by the terms corresponding to the rigid rotor, thus the centrifugal distortion terms in rotational energy were neglected.

The calculated spectroscopic parameters were used as input data in modeling the MPA spectra, as described in Sec. II. We must mention at this point that, by limiting the absorption at  $N=1$ , we obtained the conventional IR spectra, which were compared to the spectra in the literature<sup>10-14</sup>, and obtained reasonable agreement. In the following we will present the results obtained with  $N=4$ , therefore allowing in the model the multiple absorption of IR photons up to the fourth vibrational level.

We give in Fig. 1 the MPA spectra corresponding to the two infrared active modes  $\nu_3$  and  $\nu_8$  of  $CF_2HCl$ . Also given are experimental data<sup>7</sup> of  $\langle\langle E \rangle\rangle$ , the average energy absorbed per  $CF_2HCl$ , by using an interferometric method<sup>8</sup>. One can see that the emission lines of the  $CO_2$  laser fall in the red wing of the  $\nu_3$  mode, which is particularly advantageous for the IR multiphoton decomposition of this molecule. The Rabi frequencies indicated in Fig. 1, are slightly different because we calculated the spectra at the same pulse energy for both normal modes. The agreement of the calculated MPA spectra with experimental data is satisfactory, if one keeps in mind the simplifying assumptions of the model. In particular the two IR active modes,  $\nu_3$  and  $\nu_8$  have very closed values of normal frequencies, and therefore the two MPA spectra are overlapped to a good extent. Therefore one can assume strong couplings between the high vibration-rotation levels of the two modes involved in the excitation, which may enhance the multiphoton process.

In Fig. 2 we give the MPA spectra of  $CF_2Cl_2$ , compared to the dissociation data obtained<sup>1</sup> with a free electron laser. Excellent agreement

is obtained between the calculated MPA and measured dissociation data.

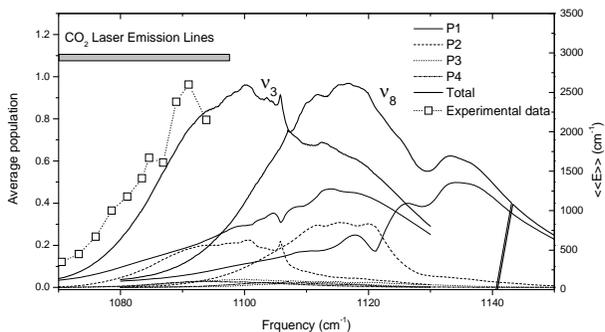


Fig 1. MPA spectra of  $CF_2HCl$ , calculated for  $\nu_3$  and  $\nu_8$  normal modes at  $\mu E = \Omega_3 = 0.779 \text{ cm}^{-1}$  and  $\Omega_8 = 0.805 \text{ cm}^{-1}$  Rabi frequencies.

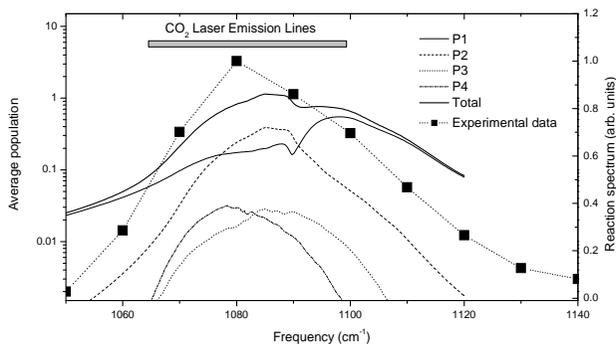


Fig. 2. MPA spectra of  $CF_2Cl_2$  for  $\nu_6$  normal mode at  $\Omega_6 = 0.688 \text{ cm}^{-1}$  Rabi frequency.

The maximum of the population  $P_4$  of the fourth vibrational level coincides with the maximum of the measured data. One might conclude therefore that after absorbing three or four photons in the  $\nu_6$  normal mode, the molecule leaks into quasicontinuum. Absorbing more photons is therefore accomplished through the  $\nu_6$  normal mode which is connected to the quasicontinuum of the remaining normal modes at about  $4000 \text{ cm}^{-1}$ .

In Fig. 3 we give the MPA spectra of  $CFCl_3$ , also compared to the dissociation data<sup>1</sup> obtained with a free electron laser. The MPA spectrum exhibit 2-photon and 3-photon resonances, while the dissociation spectrum<sup>1</sup> is broad and red-shifted. The possible reason might be neglecting the hot band absorption as the molecule (see Table 1) has one normal mode with vibrational frequency around  $240\text{ cm}^{-1}$ , a value which is close to the thermal energy at 300 K, therefore significantly populated. However we roughly recover the shape of the experimental data, namely an abrupt variation in the red wing and a smoother one in the blue side. We conclude that also in this case the two-photon and three-photon resonances are important dissociation channels.

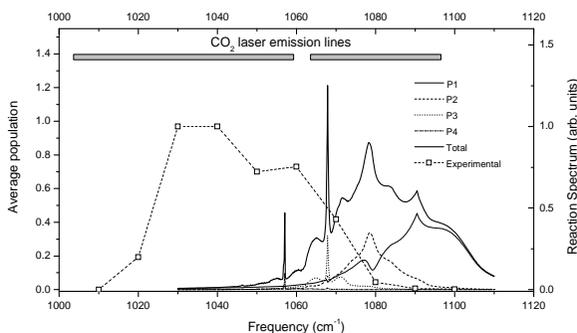


Fig. 3.

MPA spectra of  $CFCl_3$  for  $\nu_1$  normal mode at  $\Omega_I=0.853\text{ cm}^{-1}$  Rabi frequency.

In conclusion we calculated the MPA spectra of  $CF_2HCl$ ,  $CF_2Cl_2$  and  $CFCl_3$  molecules, and compared them with experimental data from the literature. The agreement is not good for  $CFCl_3$  but good for  $CF_2HCl$  and excellent for  $CF_2Cl_2$  molecule. The results enabled us to derive information about the excitation dynamics, which cannot be obtained otherwise. This information can be useful for developing more sophisticated excitation schemes by using for example two or more laser frequencies or chirped pulses.

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