

IR multiphoton absorption spectra of some freon molecules used in ^{13}C isotope separation

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A model calculation for the collisionless infrared multiphoton absorption (MPA) has been performed for some freon molecules (CF_2HCl , CF_2Cl_2 and CFCl_3) used in ^{13}C laser isotope separation. The harmonic vibrational frequencies and their anharmonic frequency corrections. The MPA spectra correlate well with experimental data for CF_2HCl and CF_2Cl_2 and reveal the excitation dynamics in collisionless regime.

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 lasers¹ besides the traditional 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 solution² to the chlorofluorocarbon contamination problem. The molecules in study are investigated both for their use in ^{13}C isotope separation (especially CF_2HCl) and for their implication in the destruction of stratospheric ozone layer (CF_2Cl_2 and CFCl_3).

In this paper we calculate the vibrational spectroscopic constants and infrared multiphoton absorption (MPA) spectra of CF_2HCl , CF_2Cl_2 and 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 us³⁻⁷.

2 The IRMPE model

Collisionless IRMPE models and corresponding computer programs have been developed by us for spherical top molecules³ SF_6 and UF_6 , for symmetric top molecules⁴ like Si_2F_6 as well as for asymmetric top molecules like CF_2HCl ⁵. 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 ϕ_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 Hamiltonian³.

Building the excitation tree and solving eq.(1) for all ν , J , and K quantum numbers one can obtain the excitation probability for different laser frequencies. Moreover summing-up for several ν quantum numbers we can find the population probabilities of different vibrational levels up to ν_{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 code⁹ considering the DFT method and using B3LYP exchange-correlation functional and cc-pVTZ basis set. A preliminary calculation¹⁰ 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 ν_8 normal mode of CF_2HCl the isotopic shift measured experimentally¹⁰ is 26 cm^{-1} , and in good agreement with our calculated value of 27.6 cm^{-1} . Also, the obtained normal mode frequencies are in good agreement with data from the literature for CF_2HCl ^{11,12} and CF_2Cl_2 ^{13,14}.

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	
	ω_i	x_{ij}	ω_i	x_{ij}	ω_i	x_{ij}	ω_i	x_{ij}	ω_i	x_{ij}	ω_i	x_{ij}
1	3129.3	-64.8	3116.7	-64.4	1093.6	-4.2	1065.3	-4.0	1089.3	-10.6	1061.5	-10.1
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	1125.6	-4.0	1083.5	-3.8	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	1128.8	-5.9	1101.2	-5.6	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			$CFCl_3$		
	μ_a	μ_b	μ_c	μ_a	μ_b	μ_c	μ_a	μ_b	μ_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 ν_3 and ν_8 normal modes of CF_2HCl have *a/c* type and *b* type bands respectively, CF_2Cl_2 ν_1 mode poses a *b* type band, while $CFCl_3$ ν_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 literature¹⁰⁻¹⁴, 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 ν_3 and ν_8 of CF_2HCl . Also given are experimental data⁷ of $\langle\langle E \rangle\rangle$, the average energy absorbed per CF_2HCl , by using an interferometric method⁸. One can see that the emission lines of the CO_2 laser fall in the red wing of the ν_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, ν_3 and ν_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 obtained¹ with a free electron laser. Excellent agreement

is obtained between the calculated MPA and measured dissociation data.

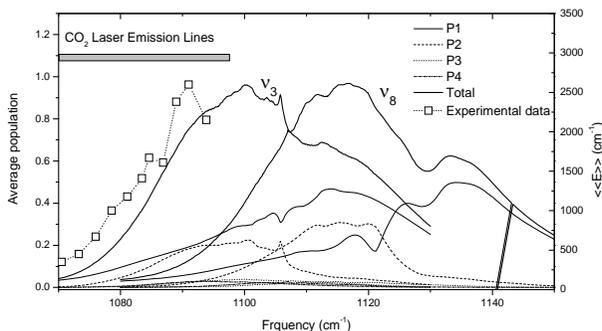


Fig. 1. MPA spectra of CF_2HCl , calculated for ν_3 and ν_8 normal modes at $\mu E = \Omega_3 = 0.779 \text{ cm}^{-1}$ and $\Omega_8 = 0.805 \text{ cm}^{-1}$ Rabi frequencies.

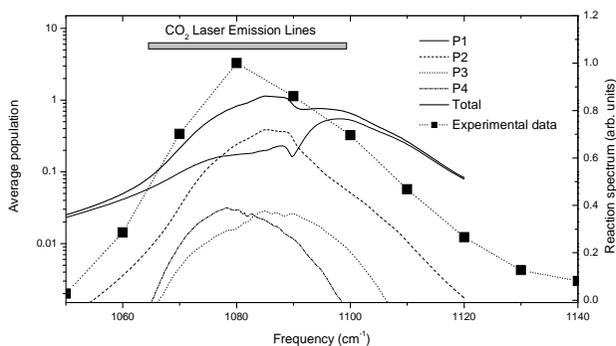


Fig. 2. MPA spectra of CF_2Cl_2 for ν_6 normal mode at $\Omega_6 = 0.688 \text{ cm}^{-1}$ Rabi frequency.

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 ν_6 normal mode, the molecule leaks into quasicontinuum. Absorbing more photons is therefore accomplished through the ν_6 normal mode which is connected to the quasicontinuum of the remaining normal modes at about 4000 cm^{-1} .

In Fig. 3 we give the MPA spectra of $CFCl_3$, also compared to the dissociation data¹ obtained with a free electron laser. The MPA spectrum exhibit 2-photon and 3-photon resonances, while the dissociation spectrum¹ 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 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.

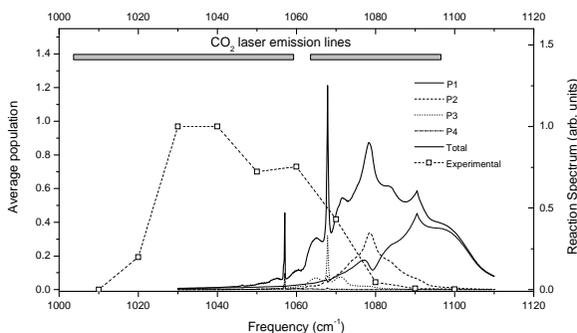


Fig. 3.

MPA spectra of $CFCl_3$ for ν_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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