

A MODEL FOR INFRARED MULTIPLE PHOTON EXCITATION OF CF_2HCl

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Abstract. A model for the collisionless infrared photon excitation has been developed for CF_2HCl . The large number of vibration-rotation states involved in the excitation led to the development of an algorithm to reduce the dimension of the eigenvalue problem to be solved. We define and estimate the cost of each excitation path in order to eliminate the high cost ones. To this end, the induced dipole moments for all normal modes are estimated by using the normal coordinate analysis, both for protonated and for deuterated molecule.

Key words: infrared multiple photon excitation, CF_2HCl , CF_2DCl , asymmetric top, dipole moments, computer model.

1. INTRODUCTION

In the last few years, an increasing interest has been developed for CF_2HCl , an asymmetric top which has been studied [1] as a prospective molecule for laser (^{13}C and D) isotope separation by infrared multiple-photon dissociation. Although the multiple-photon dissociation process is, in most cases, assisted by collisions, the absorption of the first few photons is coherent and modeling this part of the process could yield valuable information on molecule dissociation. Moreover, in two frequency dissociation, which has been applied also for CF_2HCl [2], the first just excite 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 ensemble of molecules with the first laser can help the researcher to establish the optimum conditions for the irradiation.

We describe in this paper a model for the infrared multiple photon excitation (IRMPE) of an asymmetric top. In particular, for CF_2HCl we present the basic algorithm used for selecting the vibration-rotation states involved in the excitation process. An essential preliminary step was to establish which kind of transitions are allowed in this molecule and their relative intensity. Therefore we also present the results obtained in calculating the induced dipole moments for the normal modes of the protonated and deuterated molecule.

2. AN IRMPE MODEL

Physical models and corresponding computer programs have been developed by us for spherical top molecules like SF₆ and UF₆ [3], as well as for symmetric top molecules like Si₂F₆ [4]. The main assumptions [2] in building this 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 (ν_3 in this case) thus the rotating wave approximation is a valid one: (3) after absorbing N photons the vibrational energy of the excited mode leak into a quasicontinuum. 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 eigenfunctions of the molecular unperturbed hamiltonian H_0 :

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

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, which, for a real vibration-rotation structure of a polyatomic molecule, can be solved only numerically.

However, unlike the cases of spherical top and symmetric top molecules, the structure of the vibration rotation-levels for an asymmetric top is more complicated. Therefore, if we consider all possible transitions from the ground state up to a certain vibrational level of the ν_3 ladder, the number of vibration-rotation states involved in the MP excitation is very high. The problem of reducing the number of states without affecting the quality of the description is crucial because the number of selected states will be also the dimension of the eigenproblem to be solved. Conventional approaches normally require full matrix diagonalization which, even for the large capacity of current supercomputers, is limited to problems with up to about 1000 basis functions. As in our case only personal computers are available, this figure will be drastically limited to about 100 basis functions. A useful observation in reducing the number of states is that, either because of the weak coupling or because of large detunings, some of these states are expected to contribute to a lesser extent to the multiphoton dynamics.

The fundamental ideas [5] originate from artificial intelligence in connection with techniques for finding a path or *most optimum* path between two points *via* some systematic exploration of alternatives in a "search tree" or, as it is also sometimes known "decision tree". The tree is represented with quantum states as nodal points and nonzero off-diagonal matrix elements as branches coupling the nodes. Although the ideas are applicable in general to any physical problem requiring the solution of coupled equations, the methods will be applied here to model the multiphoton dynamics of a general vibrating-rotating asymmetrical top molecules in an infrared laser field. For our model hamiltonian, the molecular eigenstates are known and it is clear that the transition between any two such states is determined by the magnitude of their coupling and the detuning of the laser from their resonance frequency. Hence, we define the criterion for picking the most important state $|a\rangle$, coupled to state $|b\rangle$, as the *performance quotient* (PQ),

$$PQ = \frac{|\langle a | \mu E | b \rangle|}{|E_a - E_b| - \hbar\omega_F}. \quad (3)$$

The numerator is the off-diagonal matrix element coupling $|a\rangle$ and $|b\rangle$, the denominator is the difference of their diagonal elements (molecular energies E_m plus the photon energy), and ω_F is the field frequency. It is not important to find a path or the most optimum path between a pair of initial and final modes, but rather to select the most important states for the multiphoton dynamics, while judiciously exploring the tree. By using the above criterion the paths can be ranked in order of their importance by defining a quantity named cost. The cost for a path leading from $|i\rangle$ to $|j\rangle$ is the sum of the reciprocal performance quotients:

$$\left| \frac{E_{j_1} - E_i}{\langle j_1 | \mu E | i \rangle} - \hbar\omega_F \right| + \left| \frac{E_{j_2} - E_{j_1}}{\langle j_2 | \mu E | j_1 \rangle} - \hbar\omega_F \right| + \dots + \left| \frac{E_f - E_{j_n}}{\langle f | \mu E | j_n \rangle} - \hbar\omega_F \right|, \quad (4)$$

where $|j_i\rangle$ are the intermediate (molecular) states coupling the initial and final ones in a $n + 1$ step path, and E_i , E_{j_i} and E_{j_m} are vibration-rotation energies. The above choice of the cost is meant to minimize the detuning and maximize the coupling of each one-photon transition along the IRMPE pathway. One should observe that, as ω_F is tuned over a frequency interval, different molecular states enter and exit the resonance zone so it is important to perform a search at each laser frequency to determine the most important states.

Bearing in mind the above considerations, we built a computer program which, by using the selection rules for infrared transitions in an asymmetric top, identifies all possible excitation paths, either for *a/c* type bands or for *b* type bands (see below). The costs of the paths are estimated by using Eq. (4) then a desired number of paths with lowest costs are picked and the corresponding matrix

elements of the effective hamiltonian are calculated. After solving the eigenvalue problem for this matrix the program computes the populations of the excited levels.

3. CALCULATION OF THE INDUCED DIPOLE MOMENTS

To build the excitation paths and to calculate their costs one need to know the values and directions of the induced dipole moments which will determine the selection rules and intensities in the vibration-rotation transitions. If one knows the values of the dipole moments along x axis (c), y axis (b) and z axis (a), induced during the vibration of a given normal mode, one can derive the selection rules then build all the possible excitation paths, and calculate their costs. The symmetry group of the molecule (C_s) allows normal modes to have either totally symmetric or totally asymmetric vibrations. The ν_1 to ν_6 modes have an a/c hybrid type band and the ν_7 to ν_9 modes have a b type band. As we are interested in the ν_3 mode for CF_2HCl and ν_8 mode for CF_2DCl , it was necessary to calculate the values of the induced dipole moments in all three directions and for all modes.

The induced dipole moments can be written as follows:

$$\mu_{01}^\alpha = \sum_i q_i l_{i\alpha}, \quad (5)$$

where $\alpha = x, y, z$. Also, q_i represents the effective charges of the atoms of the molecule, and $l_{i\alpha}$ are the elements of the displacements matrix, which we obtained from a G-F normal mode analysis of the molecule. By using the force constants reported in [8] we obtained the elements of the displacement matrix. To calculate the four effective charges we derived a system of four algebraic equations as follows. The first two equations were derived from the values of the permanent dipole moments, $\mu_a = 0.12D$, and $\mu_c = 1.43D$ [6], measured from Stark effect in microwave spectra. The ratio

$$\left| \frac{\Delta\mu_{6a}}{\Delta\mu_{6c}} \right| = 1.5 \quad (6)$$

reported [7] for the induced dipole moments in the ν_6 band was used to derive the third equation. Finally the charge conservation law represents the fourth equation.

The values obtained for the effective charges are:

$$\begin{aligned} q_C &= 0.7117e, \\ q_H &= 0.6905e, \\ q_{Cl} &= -0.3869e, \\ q_F &= -0.5077e, \end{aligned}$$

and were used to calculate the values of the induced dipole moments for all normal modes, both for protonated and for deuterated molecule. The results are shown in Table 1. As a check for our calculation we also listed in Table 1 the values obtained for the normal mode frequencies, which are in agreement with the already reported frequencies [8].

Table 1

Harmonic frequencies and induced dipole moments (units in Debye), for protonated and deuterated chlorodifluoromethane, calculated as described in the text

<i>i</i>	CF ₂ HCl				CF ₂ DCI			
	ω_i [cm ⁻¹]	μ_c	μ_b	μ_a	ω_i [cm ⁻¹]	μ_c	μ_b	μ_a
1	3028.96	-.453	.000	-.050	2234.44	-.315	.000	-.052
2	1312.04	.264	.000	-.364	1105.88	-.494	.000	.628
3	1105.81	.684	.000	-.727	1001.83	.737	.000	-.296
4	810.48	-.681	.0000	-.805	746.87	-.526	.000	-.891
5	591.34	-.495	.0000	.117	587.72	-.549	.000	.093
6	422.22	.222	.0000	.333	419.04	.243	.000	.385
7	1353.47	.000	.348	.000	1159.77	.000	-.724	.000
8	1127.14	.000	1.06330	.000	970.29	.000	.819	.000
9	365.31	.000	.335	.000	360.21	.000	.382	.000

As one can see from Table 1, the values of the induced dipole moments obey the rules imposed by the molecule symmetry, as mentioned above. Indeed, the normal modes ν_1 to ν_6 will exhibit hybrid *a/c* type bands (as μ_b vanish for these modes), while ν_7 to ν_9 modes have only *b* type bands. This will influence both the selection rules thus the multiphoton excitation paths, and the intensity of the transitions, because of different direction cosine factors.

The usefulness of these data is twofold: first, a basic one for the molecule and its deuterated isotopic species. They can be used, for example, in simulating and fitting the intensities of the lines obtained in a high resolution spectroscopy measurement. Second, they are necessary as starting data to model the infrared multiphoton process in this molecule.

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