TWO LASERS MULTIPHOTON EXCITATION AND DISSOCIATION OF SF_6: A COMPARISON BETWEEN EXPERIMENTS AND THE DENSITY MATRIX APPROACH.

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ABSTRACT

Multiphoton excitation and dissociation of SF_6 has been studied both theoretically and experimentally with the two lasers technique. The experiments are based on the opto-acoustic method, while the calculations have been performed by numerically solving a set of Bloch equations for the first few levels of the ν_3 IR active mode, coupled to a set of rate equations for the remaining levels. The results show a qualitative agreement between theory and experiments.

1.INTRODUCTION

Multiphoton excitation and dissociation of polyatomic molecules under IR laser irradiation consists of two different steps (1): in the first one the molecule is coherently excited through the first few levels of the IR active mode (discrete levels region), while in the second one, due to the high density of states, energy is effectively exchanged between mixed modes levels and the excitation becomes mainly incoherent (this region is the so-called quasi-continuum). The two frequencies technique, in which a molecule is irradiated with two laser IR sources, the first one tuned on the linear absorption frequency, the second one blue or red shifted with respect to the first one, helps to shed light on the two regions separately. In fact the first laser excites the molecule through the discrete levels, while the second one brings the excited molecule through the quasi-continuum. The calculations have been performed by extending the heat feed-back model, succesfully applied by Stone et al. (2) to the one laser excitation, in order to include the effect of the second laser. Even though we cannot expect at this stage a quantitative agreement between theory and experiments, we have found a qualitative agreement, which can be considered satisfying for the understanding of the process.

2. EXPERIMENTAL DETAILS AND METHOD OF CALCULATION

The experiments have been performed by irradiating a stainless-steel cell 30 cm. long, containing SF_6 at room temperature, with two pulsed T.E.A. CO_2 lasers (for details of the experimental apparatus see ref. (3)). This cell, sealed by two

Zn Se windows, was equipped with a capacitance microphone which is able to detect the acoustic wave originated by the V-T (vibration-translation) relaxation of the vibrationally excited molecules. The maximum of the opto-acoustical signal is proportional to the average vibrational energy absorbed by the molecules.

As for the theory, according to the heat feed-back model, the first few vibrational levels of the pumped ν_3 mode ($v\nu_3 \leq 3$) are treated by Bloch equations (the notation is the same as in ref. (2)):

$$\frac{d\rho_{jj}}{dt} = \frac{i}{\hbar}[\rho,H]_{jj} - (K^{VT}_{j,j-1} + K^{VT}_{j,j+1})\,\rho_{jj} + K^{VT}_{j+1,j}\,\rho_{j+1,j+1} +$$

$$+K^{VT}_{j-1,j}\,\rho_{j-1,j-1};\; j = 0,1,2 \qquad (1a)$$

$$\frac{d\rho_{jk}}{dt} = \frac{i}{\hbar}[\rho,H]_{j,k} - \frac{1}{T_{2\,j,k}}\,\rho_{j,k}\;;\; j\neq k;\; j,k = 0,1,2,3 \qquad (1b)$$

$$\frac{d\rho_{3,3}}{dt} = \frac{i}{\hbar}[\rho,H]_{3,3} - (K^{VT}_{3,2} + K^{VT}_{3,4} + T_{3,4})\,\rho_{3,3} +$$

$$+ (K^{VT}_{4,3} + T_{4,3})\,N_4 + K^{VT}_{2,3}\,\rho_{2,2} \qquad (1c)$$

were the elements of the hamiltonian are:

$$H_{nn} = \varepsilon_n \qquad (2a)$$

$$H_{n-1,n} = H_{n,n-1} = \alpha_{n,n-1}\,A \sin \omega t \qquad (2b)$$

These equations include the effect of dynamical evolution of the density matrix ($[\rho,H]$) and the effects of the V-T energy exchanges (K^{VT}) and of the intramolecular dephasing processes ($1/T_2$) (ε_n are the vibrational energies, $\alpha_{n,n-1}$ the dypole matrix elements between levels n and n-1, A the laser electric field intensity and ω the laser frequency; moreover T_{ij} are the transition rates which link the discrete region to the quasi-continuum). The second dynamical region is governed by a set of incoherent rate equations for the total populations of the vibrational levels:

$$\frac{dN_j}{dt} = (T_{j-1,j} + K^{VT}_{j-1,j})\,N_{j-1} + (T_{j+1,j} + K^{VT}_{j+1,j})\,N_{j+1} -$$

$$- (T_{j,j-1} + K^{VT}_{j,j-1} + T_{j,j+1} + K^{VT}_{j,j+1} + k_j) N_j; \quad 4 \leq j \leq 50 \qquad (3)$$

where k_j are specific rate constants for dissociation. The optical transition rate coefficients contain informations about the quanta in the not pumped modes through the dephasing times T_2 and have been calculated according to the prescriptions given in ref. (2), while the K^{VT} and k_i have been obtained by ref. (4). A simple anharmonic model has been used for the vibrational energies (2).

3. RESULTS

Fig. 1a reports the experimental absorbed quanta per molecule after irradiation with two laser (n_{12}) as a function of the frequency of the second laser (ω_2), the frequency of the first laser (ω_1) being 948 cm^{-1}; the energy fluences are respectively $\phi_1 = 0.4\ J/cm^2$ and $\phi_2 = 0.8\ J/cm^2$, while the SF_6 pressure is 0.8 torr. In the same figure are reported also the absorbed quanta after irradiation with the second laser only (n_2) as a function of the frequency. One can note that there is a strong red shift as compared with the one laser frequency shift. In fig. 1b are reported the corresponding theoretical calculations, which also show a red shift, even through theoretical and experimental results are shifted in frequency. Fig. 2 reports the experimental dissociation yield (%) as a function of the frequency of the second laser (ω_2). Experimental conditions are: $\phi_1 = 1.0\ J/cm^2$, $\omega_1 = 948\ cm^{-1}$, $\phi_2 = 1.6\ J/cm^2$, $p = 0.3$ torr. One can note a completely different behaviour from the absorption curve, that is a decrease of the dissociation yield in going from red-shifted frequencies to blue shifted ones. Once again the theoretical calculations, reported in the same figure as a dashed line, confirm this trend, showing a decrease of the dissociation yield with increasing the frequency. However the experimental curve decreases faster than the theoretical one and the agreement is less satisfactory than for the absorption measurements. This is due to the difficulty of calculating the optical rate coefficients for the vibrational levels belonging to the tail of the distribution.

4. CONCLUSIONS

The results reported in the previous pages show that the heat bath feed-back model can be used with a fair amount of confidence to rationalize the two laser IR absorption measurements. The quantitative agreement needs of a series of improvements in the theory, which can be summarized as follows:

1) insertion of all rotational levels in the structure of the first few levels treated by the Bloch equations;
2) A better characterization of the vibrational energies of the first levels, which can be made by removing the degeneracy of the ν_3 pumped mode;
3) An estimation of the hot bands contribution.

All these points, which are at the present under investigation in our and other laboratories, would probably increase the agreement between theory and experiments. Despite these limitations we believe that the heath bath feed-back model can be considered as a first step for understanding the two lasers absorption measurements.

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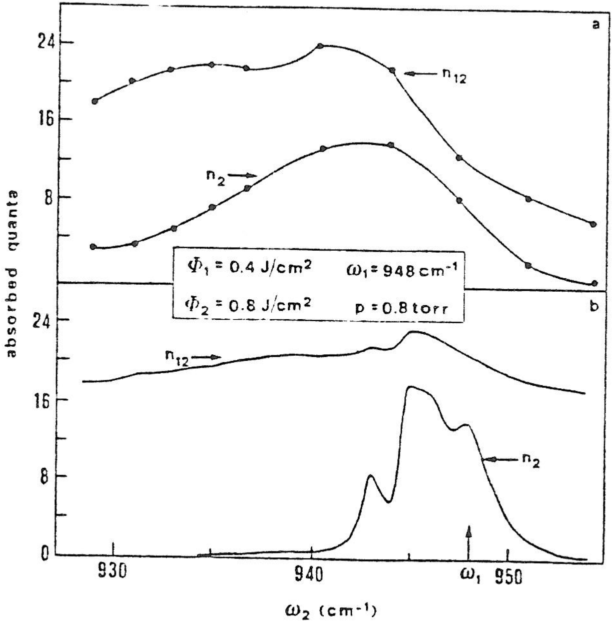

Fig. 1 - Absorption spectra with two lasers (n_{12}) and one laser (n_2). a) experimental; b) theoretical.

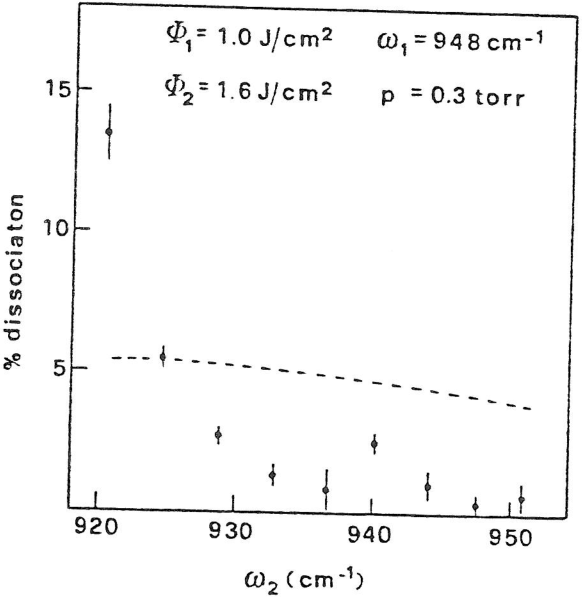

Fig. 2 - % dissociation yield as a function of the frequency of the second laser. ● experimental; --- theoretical.