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ABSTRACT: We report experimental and theoretical studies of the alignment effects produced in femtosecond time-resolved CH_3I predissociation in the *B* band at 201.2 nm. The experiment was of the pump-and-resonant probe type, coupled with velocity map ion imaging of the produced $CH_3(v)$ and $I^*(^2P_{1/2})$ photofragments. The measurements provide a detailed picture of the real-time *B*-band predissociation of CH_3I [1]. The experiments demonstrated highly-anisotropic time-dependent photofragment angular distributions which were satisfactory fitted by the expression:

$$I(t) = I_0(t)[1 + \beta_2(t)P_2(\cos\theta) + \beta_4(t)P_4(\cos\theta)] \qquad (1)$$

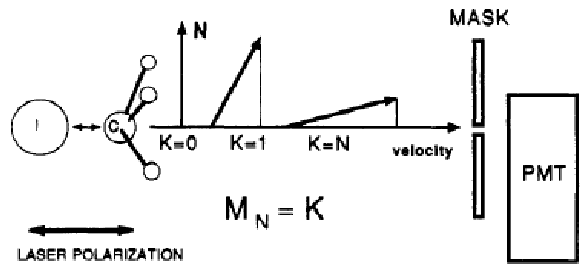
The experimental values of the total signal intensity $I_0(t)$ and the anisotropy parameters $\beta_2(t)$ and $\beta_4(t)$ are shown in Fig. 1 for the case of CH_3 fragments.
The obtained time-dependent anisotropy of the fragment distribution has been interpreted in terms of the theory describing the angular momentum alignment in photodissociation of rotating molecules [2]. The analysis made allowed for determination of the set of the anisotropy-transforming coefficients [3] which contain all information on the predissociation dynamics and give a new insight into the photolysis of CH_3I via the *B*-band.

THEORETICAL MODEL

$$I(\theta) = I(t)\left[1 + \beta P_2^K(\cos\theta)\right]\sum_{K=0}^{4}\tilde{P}_K A_0^{(K)} P_K^L(\cos\theta) = \sum_{K=0}^{4}\beta_K P_K^L(\cos\theta)$$

Correspondence between the phenomenological β_i coefficients and the alignment parameters

$$\begin{pmatrix}\beta_0\\ \beta_2\\ \beta_4\\ \beta_6\end{pmatrix} = \begin{pmatrix} 1 & \beta & 0 \\ \frac{1}{5}\beta & \left(1+\frac{2}{7}\beta\right) & \frac{2}{7}\beta \\ 0 & \frac{18}{35}\beta & \left(1+\frac{20}{77}\beta\right) \\ 0 & 0 & \frac{5}{11}\beta \end{pmatrix}\begin{pmatrix}\tilde{P}_0\\ \tilde{P}_2 A_0^{(2)}\\ \tilde{P}_4 A_0^{(4)}\end{pmatrix}$$



Lineal impulsive dissociation model

High J geometrical factors

$$\tilde{P}_0 = \frac{1}{3}\frac{1}{\sqrt{2J+1}}\left\{S_{00}^2 + \frac{2}{5}\frac{[3M^2 - J(J+1)]^2}{J(2J+3)(J+1)(2J-1)}S_{20}^2\right\}$$

$$\tilde{P}_2 = \frac{1}{3}\frac{1}{\sqrt{2J+1}}\left\{-2\sqrt{\frac{2}{5}}\frac{[3M^2 - J(J+1)]}{[J(2J+3)(J+1)(2J-1)]^{1/2}}S_{00}S_{20}\right\}$$
$$+\frac{1}{3}\frac{1}{\sqrt{2J+1}}\left\{\frac{4}{35}\frac{[3M^2 - J(J+1)]^2}{[J(2J+3)(J+1)(2J-1)]}S_{20}^2\right\}$$

$$\tilde{P}_4 = \frac{1}{\sqrt{2J+1}}\left\{\frac{4}{35}\frac{[3M^2 - J(J+1)]^2}{J(2J+3)(J+1)(2J-1)}S_{20}^2\right\}$$

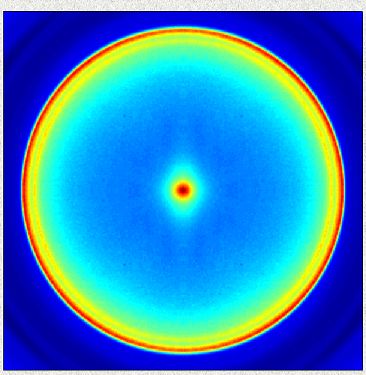
Alignment parameters

$$A_0^0 = 1$$
$$A_0^2 = \frac{3M^2 - J(J+1)}{J(J+1)^2}$$
$$A_0^4 = \frac{35M^4 - 30M^2J(J+1) + 3J^2(J+1) + 25M^2 - 6J(J+1)}{8J^2(J+1)^2}$$

Temporal evolution

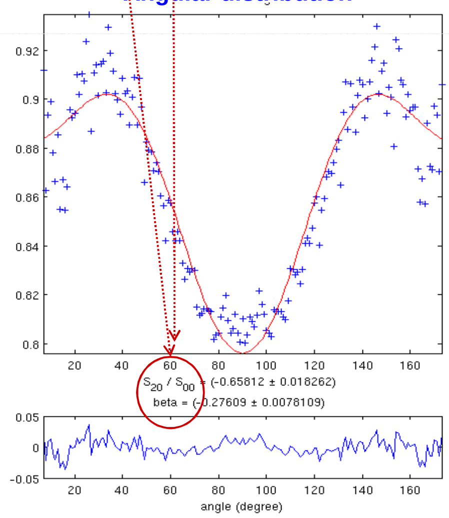
$$\beta_i(t) = \beta_i^{\infty} + I_{pr}(t)\otimes\Delta\beta_i\times\left(H(t-t_0)\,e^{-\frac{t-t_0}{\tau_{\beta_i}}} + H(t_0 - t)\right)$$

EXPERIMENTAL RESULTS

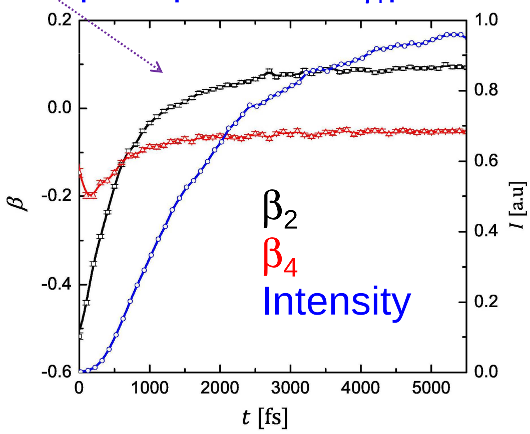


CH_3 (v = 0) produced at the onset of the CH_3I B band

Angular distribution



Temporal dependence of the β_i parameters



Time-dependent total intensity and anisotropy parameters for CH_3I predissociation in the *B*-band at 201.2 nm detecting $CH_3(n=0)$ fragments by 2+1 REMPI in femtosecond velocity map imaging experiments.

Discussion: The lineal impulsive model is able to reproduce the observed anisotropy in the B band photodissociation of methyl iodide. However, the validity of the model should be contrasted with a more complete theory where the depolarization depends on two angles: the angle of precession of the molecular axis around the total angular momentum **J** and the angle of self-rotation of the molecule around its symmetry axis. We have determined the explicit expressions for the rotational angular momentum depolarization of an anisotropy transforming $\mathbf{c}_{k_d q}^{K}$ coefficients as function of the involved. (Work in progress).

References
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