Helicity-induced shapes of resonant four-wave mixing responses from photofragments

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Abstract. Doppler profiles of the Degenerate Resonant Four-Wave Mixing (DFWM) spectral responses from rapidly recoiling products of photodecomposition by plane-polarized radiation are theoretically studied. Emphasis is placed on the shapes produced by rotational helicity when orientations of the angular momenta and the recoil velocities of nascent particles are correlated. Illustrations are provided for cases when a decay of resonating states tangibly affects the helicity-induced DFWM profiles.

1. Introduction

Reaction pathways are sharply imprinted on characteristics of the nascent particles \cite{1} typically born in non-equilibrium states. To read off these characteristics, linear spectroscopies have proved their unexcelled efficiency, especially in tandems with the mass spectrometric and ionization techniques. In particular, the laser-induced fluorescence (LIF) techniques have developed into the most useful means to study quantum properties of photofragments, i.e., in the case when a reaction itself is ignited by photons. In so doing, many photofragment properties as well as a number of correlations between them \cite{1, 2, 3, 4, 5, 6} have been investigated, both experimentally and theoretically. Subsequently, in a review of the day \cite{7} an advent of nonlinear optical methods to such studies, especially of the resonant four-wave mixing (RFWM) with its uniquely flexible polarization setup, was prognosticated. Yet, except the recent experiments \cite{8} performed at the Paul Scherrer Institute, the nonlinear optical tools have been never used for that aim despite the fact that RFWM had gained wide recognition as one of the most advanced all-optical means to track the quantum states of molecules at equilibrium \cite{9, 10}.

Photofragments produced by polarized laser beams have anisotropic distributions of their angular momenta \( \mathbf{j} \) and velocities \( \mathbf{v} \). To study the anisotropy of the OH radicals produced by the \( \text{H}_2\text{O}_2 \) photolysis by a plane-polarized laser radiation at 266 nm, the DFWM setup was established \cite{8}. Absorption of photons with the energy of about 37 600 cm\(^{-1} \) much exceeding the \( \text{H}_2\text{O}_2 \) dissociation threshold (17 300 cm\(^{-1} \)) creates pairs of rapidly recoiling OH radicals which are almost exclusively generated in the substates belonging to the ground vibronic level \cite{11}. Based on this fact, a quick estimation of the Doppler halfwidths of the DFWM frequency scanning the \( \text{A}^2\Sigma^+ - \text{X}^2\Pi(0,0) \) OH vibronic band around 32 300 cm\(^{-1} \) results in \( \approx 0.4 \) cm\(^{-1} \), approximately five times larger than the laser linewidth, thus allowing reliable resolution of the Doppler broadened profiles.
2. Third-order susceptibility of photofragments

Assuming that the laser line width is negligible, all four DFWM beams (three of the input and one of the generated signal) have the same frequency $\omega$ tuned close to a certain dipole-allowed transition $f \leftarrow i$. The latter circumstance allows us to consider only the on-resonance part ($\chi_{\text{res}}^{(3)}$) of the third-order susceptibility of nascent particles. To derive an expression for the induced polarization, one should average $\chi_{\text{res}}^{(3)}$ over the $j$- and $v$-distributions and then calculate $|\chi_{\text{res}}^{(3)}|^2$ that defines the useful signal. Taken together, these distributions define the form of the product density matrix $\rho$, the key consequence of the photolysis path. In so doing, we have extended classical Dixon’s expression [12] of $\rho$ to the case of a quantized linear rotator using the classical representation of the translational motion which is well justified for rapidly recoiling fragments. Another property to be introduced to $\rho$ is the (linear) polarization of a dissociation laser, namely, the orientation $(\Omega_D)$ of its polarization vector $\mathbf{e}_D$ which is a primary source of anisotropy. Derivation of such semiclassical form of $\rho$ was reported at the previous ICLS conference [13].

Transformations needed to explicitly present the functional dependence of $\chi_{\text{res}}^{(3)}$ on $\mathbf{e}_D$, unit polarization vectors $\mathbf{e}_k$ ($k = 1, 2, 3, 4$) of the RFWM beams and on the quantum numbers of the resonating states $f$ and $i$ require complicated algebra and will be published separately [14]. The line-space (Liouville) techniques [15] naturally combined with the angular momenta recoupling machinery [16] allows to decouple the field characteristics (i.e., tensors $G^{(K)}$ build on four unit vectors $\mathbf{e}_k$) from the photofragments properties. In accord with the conditions of measurements [8], one can assume the predominance of the Doppler broadening, or $\varepsilon \equiv c \Gamma f / \omega f v_0 \ll 1$, where $v_0$ is the mean recoil velocity and $\Gamma f$ denotes the decay rate which can be caused both by the collisional and natural lifetime effects. At the near-collinear geometry, when all five beams can be considered as copropagating along the common axis $\mathbf{k} \parallel OZ$, the decoupling procedure results in

$$\chi_{\text{res}}^{(3)} = \sum_{K,L,\lambda} \{ F^{(K)}(L, \lambda; f, i) \otimes C^{(\lambda)}(\Omega_D) \}_0^{(L)} S_L(\Delta \omega)$$

(1)

where $\otimes$ symbolizes contraction of two irreducible spherical tensors (IST) into a third one; the zero subscript denotes the OZ component of the resultant IST of rank $L$; $C^{(\lambda)}(\Omega_D)$ is an IST whose components are the Racah spherical harmonics [16]. In turn, $F^{(K)}$ is a linear combination of the polarization tensors $G^{(K)}$ and depends also on the quantum numbers of the combining states. We do not provide here its explicit form since it is of minor importance for the RFWM shape analysis.

The allowed values of $\lambda(=0, 2)$ are defined by the electric-dipole mechanism of photolytic decomposition [12] whereas $K$ runs from 0 up to 4 with the unity step. Finally, the rank $L$ characterizing the recoil anisotropy may vary from $|K - \lambda|$ up to $K + \lambda$. It is pertinent to note that the odd $K$ and $L$ values are forbidden in the LIF case implying that the correlations between odd powers of $\mathbf{j}$ and $\mathbf{v}$ remain silent in LIF. In contrast, RFWM opens a direct way to study such correlations, the leading one being the photofragment helicity for which $K = L = 1$. At $\lambda = 0$, the helicity suggests that the mean value of $(\mathbf{v}, \mathbf{j})$ is distinct from zero so that a certain part of photofragments has angular moments parallel (or antiparallel) to $\mathbf{v}$ and moves like bullets from a rifle’s barrel.

Remarking, the RFWM polarization setup allows to directly select the signals produced by helicity. This can be achieved by using the properties of the ISTs $G^{(K)}$ from which $F^{(K)}$ are built up. To annul all terms of $\chi_{\text{res}}^{(3)}$ with even $K$, we just set $\mathbf{e}_D = \mathbf{e}_1 = \mathbf{e}_2 = \mathbf{e}_3 = \mathbf{e}_X$ and use the perpendicular polarization ($\mathbf{e}_4 = \mathbf{e}_Y$) in the detection channel [8, 14].
3. Helicity-induced spectral distributions

The key objective of this study is the shape function $S_L(\Delta \omega)$ which corresponds to the translational anisotropy of rank $L$ and depends on the detuning $\Delta \omega$ from the resonance frequency $\omega_{fi}$. For rapidly recoiling fragments, the DFWM shape function can be written as a weighted sum of two terms

$$S_L(\Delta \omega) = \int f(v) dv \int_0^v \left[ \frac{a}{(\Delta \omega - kv)^2 + \Gamma^2} + \frac{b}{(\Delta \omega - kv)^2 + i\Gamma^2} \right] P_L(\kappa) dv_k$$

where $a$ and $b$ are certain real coefficients, $f(v)$ denotes the distribution of the absolute values of $v$ and $P_L(\kappa)$ is the Legendre polynomial of $\kappa = \cos(v, k) = vZ/v$.

To proceed, we may consider $vZ$ as a complex variable and close the integration path by adding a semicircle of radius $v$ in the upper half plane. In the fast-recoil limit when $\varepsilon = \Gamma/kv \to 0$ the integral along the semicircle vanishes. By taking the residues inside the thus closed integration loop we immediately conclude that the $b$-term disappears whereas the first integral over $vZ$ equals

$$I_1 = \frac{a\pi}{k\Gamma} P_L(\Delta \omega/kv) \theta(1 - (\Delta \omega/kv)^2)$$

where $\theta(x)$ the Heaviside step function. In this limit, the Doppler shape (2) drops to zero when the pole crosses the integration loop at $(\Delta \omega/kv)^2 > 1$ and the residue contribution vanishes. The result (3) exactly corresponds to that of the LIF theory when decay processes are discarded. The only difference is that, to obtain a measurable DFWM profile, we must finally square the spectral function while this operation is unnecessary for LIF. Therefore, when the helicity ($L = 1$) is the sole mechanism of Doppler broadening, the DFWM profile $|S_1(\Delta \omega)|^2$ reduces to a parabola ($x^2$) with the intensity dropping to zero both at the center and at $|\Delta \omega| \geq kv$.

However, for small but finite decay rates the DFWM and LIF shape expressions differ since the first one (2) is complex whereas the LIF shape is a real part of $I_1$. Here, illustrations are provided for the spectral behaviour of the helicity ($L = 1$) shape at finite $\varepsilon$. Both $I_1$ and $I_2$ integrals (the factor standing at $b$ coefficient in Eq. (2), correspondingly) can be expressed via elementary functions. For brevity sake, we do not provide the explicit bulky expressions but plot on Figs. 1 and 2 $I_1$ and $I_2$ as functions of dimensionless detuning $x = \Delta \omega/kv$ at different values of $\varepsilon$. The functions are normalized by the factor $\pi/k\Gamma$ (see Eq. (3)) that makes the maximal value of $I_1$ close to unity. We see that the effect of the relaxation rate increasingly smoothes the sharp edges at $x = \pm 1$ and induces the intensity in the "forbidden" range in which $|\Delta \omega| > kv$.

The $I_2(x)$ component is entirely due to the finite decay rate; moreover, its real part behaves as

Figure 1. $I_1(x)$ shape transformation with reduced decay rate $\varepsilon$: $\varepsilon = 0.01$ (black line), $\varepsilon = 0.05$ (blue line), $\varepsilon = 0.1$ (red line).
an odd function of $x$ whereas the imaginary part is even. It means that - since $a$ and $b$ are real multipliers - the interference between the odd and even components is absent and the observed Doppler DFWM helicity profile is therefore an even function of the frequency detuning.

The observable (modulus squared) shapes are plotted on Fig. 3 for $a = b = 1$ and for different values of $\varepsilon$. Because of squaring, the periphery intensity is somewhat dampered but peaks near $x = \pm 1$ survive. The main peak produced by the sum of $I_1$ and $\Re I_2$ is broadened and shifted towards the line center. As seen from Fig. 2, the positions of the $\Im I_2$ component maxima are weakly affected by $\varepsilon$ and remain close to $x = \pm 1$. Finally, because of the increasing role of $|\Im I_2|^2$, new maxima at $x = \pm 1$ appear at $\varepsilon \approx 0.1$ (Fig. 3). However, we should note that in the practically important cases the collisional relaxation is inevitably accompanied by the velocity-changing collisions which also affect the Doppler shapes and therefore the theory should be refined.

4. Synopsis

The DFWM profiles caused by the rotational helicity of photofragments are derived for the case of inhomogenous Doppler broadening accompanied by decay processes of resonating states. The results reveal the difference between the DFWM and LIF spectral distributions which becomes more pronounced at faster decays.
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