Outline of data analysis

The alignment/orientation is described using the formalism developed by Rakitzis and Zare [1]. The starting point is to expand the spatial distribution of the photofragment angular momentum **J** in the molecular frame as a sum over modified spherical harmonics $C_q^k(\theta,\phi)$.

$$P(\theta,\phi) = \sum_{k=0}^{2J} \sum_{q=-k}^{k} A_q^{(k)} C_q^k(\theta,\phi) \tag{1}$$

Note that the modified spherical harmonics are related to the spherical harmonics by

$$C_q^k(\theta,\phi) = [4\pi/(2k+1)]^{1/2} Y_q^k(\theta,\phi) \tag{2}$$

In Equation (1), θ and ϕ are the polar angles relative to a z axis lying along the photofragment velocity vector **v** and an x axis lying in the plane of **v** and the photolysis polarisation vector $\epsilon_{\rm phot}$. It is therefore valid only for a fixed angle θ_ϵ between these two vectors. In order to obtain a general expression for the angular momentum polarisation that includes the angular scattering distribution of the photofragments, we can break up Equation (1) into a contribution from pure parallel transitions, a contribution from pure perpendicular transitions, and interference terms between the two. To achieve this separation we introduce a set of alignment parameters $a_q^{(k)}({\rm pol^n})$, which are related to the $A_q^{(k)}$ as follows:

$$A_0^{(k)} = [(1+\beta)\cos^2\theta_\epsilon a_0^{(k)}(\|) + (1-\beta/2)\sin^2\theta_\epsilon a_0^{(k)}(\perp)]/[1+\beta P_2(\cos\theta_\epsilon)] \tag{3}$$

$$A_1^{(k)} = \sin\theta_\epsilon\cos\theta_\epsilon a_1^{(k)}(\|,\perp)/[1+\beta P_2(\cos\theta_\epsilon)] \tag{4}$$

$$A_2^{(k)} = (1-\beta/2)\sin^2\theta_\epsilon a_2^{(k)}(\perp)/[1+\beta P_2(\cos\theta_\epsilon)] \tag{5}$$

with $A_q^{(k)} = (-1)^q A_{-q}^{(k)*}$.
The $a_q^{(k)}(\|)$ describe contributions to the alignment from processes involving pure parallel transitions from the ground state and the $a_q^{(k)}(\perp)$ from perpendicular transitions, with the $a_q^{(k)}(\|,\perp)$ arising from interference between the two types of process. For terms up to $k=2$, the details of this separation are all described in reference [1]. At this point we have an expression for the molecular frame angular momentum alignment (Equation (14) of reference [1] for moments up to $k=2$). To obtain an expression for the *measured* distribution, we need to correct each term in this equation for the detection sensitivity, which will depend on details of the experiment such as the REMPI transition chosen to detect the fragments and the polarisation of the probe light. For comparison with experimental data, we also need to transform the expression into a laboratory frame. For imaging experiments the most convenient lab frame has z lying along the time-of-flight direction, and x in the plane of z and the photolysis polarisation. We can then define three sets of angles:

$(\Gamma, 0)$ define the photolysis polarisation relative to the lab z axis.
(Δ, Φ) define the probe polarisation relative to the lab z axis.
(Ω, Θ) define the product velocity v relative to the lab z axis.

Four commonly-used geometries for measuring alignment are:

1. HHo, pump and probe lasers propagating at right angles, both polarised in image plane ($\Gamma = \pi/2$, $\Delta = \pi/2$, $\Phi = \pi/2$).

2. HVo, pump and probe lasers propagating at right angles, pump laser polarised in image plane, probe laser polarised perpendicular to image plane (along TOF axis) ($\Gamma = \pi/2$, $\Delta = 0$, $\Phi = 0$).

3. HHc, pump and probe lasers counterpropagating, both polarised in image plane ($\Gamma = \pi/2$, $\Delta = \pi/2$, $\Phi = 0$).

4. HVc, pump and probe lasers counterpropagating, pump laser polarised in image plane, probe laser polarised perpendicular to image plane ($\Gamma = \pi/2$, $\Delta = 0$, $\Phi = 0$)

After some manipulation, which involves using results from above, determining expressions for transforming between the lab frame and molecular frame coordinates, and extending the expressions in Reference 1 to include terms up to $k = 4$, the final expression for the measured signal intensity in terms of the $a_q^{(k)}(\mathrm{pol^n})$ parameters is:

$$
\begin{aligned}
I =& 1 + c\beta C_{20}(\gamma) + \\
& s_1\Big\{(1-\beta/2)a_0^{(1)}(perp)C_{10}(\delta)C_{10}(\gamma) + \sqrt{2}\mathrm{Re}[a_1^{(1)}]C_{11}(\delta)C_{11}(\gamma)cos\phi + c\sqrt{8/3}\mathrm{Im}[a_1^{(1)}]C_{11}(\delta)C_{21}(\gamma)\sin\phi\Big\} + \\
& s_2\Big\{(1/3)(1+\beta)a_0^{(2)}(\|) + 2(1-\beta/2)a_0^{(2)}(\perp)C_{20}(\delta) + c(2/3)[(1+\beta)a_0^{(2)}(\|) - (1-\beta/2)a_0^{(2)}(\perp)]C_{20}(\delta)C_{20}(\gamma) \\
& + c\sqrt{8/3}\mathrm{Re}[a_1^{(2)}]C_{21}(\delta)C_{21}(\gamma)\cos\phi + \sqrt{8/3}\mathrm{Im}[a_1^{(2)}]C_{21}(\delta)C_{21}(\gamma)\sin\phi + c\sqrt{32/3}(1-\beta/2)a_2^{(2)}(\perp)C_{22}(\delta)C_{22}(\gamma) \\
& s_3\Big\{(1-\beta/2)a_0^{(3)}(\perp)C_{30}(\delta)C_{30}(\gamma) + \sqrt{2}\mathrm{Re}[a_1^{(3)}]C_{31}(\delta)C_{11}(\gamma)\cos\phi + c\sqrt{8/3}\mathrm{Im}[a_1^{(3)}]C_{31}(\delta)C_{21}(\gamma)\sin\phi \\
& + c\sqrt{32/3}(1-\beta/2)a_1^{(3)}(\perp)C_{32}(\delta)C_{32}(\gamma)\cos 2\phi\Big\} + \\
& s_4\Big\{(1/3)[(1+\beta)a_0^{(4)}(\|) + 2(1-\beta/2)a_0^{(4)}(\perp)]C_{40}(\delta) + c(2/3)[(1+\beta)a_0^{(4)}(\|) - (1-\beta/2)a_0^{(4)}(\perp)]C_{40}(\delta)C_{20}(\gamma) \\
& + c\sqrt{8/3}\mathrm{Re}[a_1^{(4)}]C_{41}(\delta)C_{21}(\gamma)\cos\phi + \sqrt{8/3}Im[a_1^{(4)}]C_{41}(\delta)C_{21}(\gamma)\sin\phi + c\sqrt{32/3}(1-\beta/2)a_2^{(4)}(\perp)C_{42}(\delta)C_{22}(\gamma)
\end{aligned}
\tag{6}
$$

A number of quantities appearing in this equation require explanation:

1. The angles γ, δ, and ϕ are determined from

$$
\begin{aligned}
\cos\gamma =& \cos\Omega\cos\Gamma + \sin\Omega\sin\Gamma\cos\Theta \\
\cos\delta =& \cos\Omega\cos\Delta + \sin\Omega\sin\Delta\cos(\Theta - \Phi) \\
\cos\phi =& \big\{\sin^2\Omega\cos\Gamma\cos\Delta + \sin\Gamma\sin\Delta\cos\Phi - \sin\Omega\cos\Omega(\sin\Delta\cos\Gamma\cos(\Phi-\Theta) + \sin\Gamma\cos\Delta\cos\Theta) - \\
& \sin^2\Omega\sin\Gamma\sin\Delta\cos(\Phi-\Theta)\cos\Theta\big\}/(\sin\gamma\sin\delta) \\
\sin\phi =& \big\{\cos\Omega\sin\Gamma\sin\Delta\sin\Phi - \sin\Omega(\sin\Delta\cos\Gamma\sin(\Phi-\Theta) + \sin\Gamma\cos\Delta\sin\Theta)\big\}/(\sin\gamma\sin\delta)
\end{aligned}
\tag{7}
$$

2. The s_k are REMPI sensitivity parameters that depend on the J values of the initial, intermediate and final states in the REMPI transition used to ionize the photofragments. References to papers describing how to calculate these are given in [1] on page 3345.

3. c is a constant equal to 1 for experimental geometries in which the pump laser is linearly polarised, and -1/2 for geometries in which the pump laser is circularly polarised.

Equation 6 describes the full 3D distribution of the detected photofragments. To obtain an expression for a velocity-map image, we simply substitute in the appropriate values of the angles Γ, Δ and Φ to describe the experimental geometry, and then integrate the distribution over the z (TOF) axis. This can generally be done analytically (though using Mathematica is *far* preferable to trying to do it by hand!) by using one or other of the Jacobians

$$\begin{aligned} dz =& - v \sin\Omega d\Omega \\ dz =& v/(v^2 - r^2)^{1/2} dv \end{aligned} \tag{8}$$

where v is the product speed and r is its projection on to the image plane. For a sliced image no integral is required; we simply set $\Omega = \pi/2$. The good news is that evaluating Equation 6 for a specific geometry generally leads to a greatly simplified expression. In the current study, involving the 157 nm dissociation of O_2, the situation is further simplified by the fact that a pure parallel transition is involved, such that only the $a_0^{(2)}(\|)$ and $a_0^{(4)}(\|)$ alignment parameters are non-zero. For example, the resulting expressions for sliced images using the four experimental geometries defined above are:

$$\begin{aligned} I_{\mathrm{HHo}}\Big[\mathrm{sliced}) =& (\frac{3}{2} - \frac{3}{16} s_2 a_0^{(2)}(\|) - \frac{3}{128} s_4 a_0^{(4)}(\|)\Big] + \Big[\frac{3}{2} - \frac{3}{4} s_2 a_0^{(2)}(\|) + \frac{39}{256} s_4 a_0^{(4)}(\|)\Big] \cos 2\Theta + \\ & \Big[-\frac{9}{16} s_2 a_0^{(2)}(\|) + \frac{75}{128} s_4 a_0^{(4)}(\|)\Big] \cos 4\Theta + \frac{105}{256} s_4 a_0^{(4)}(\|) \cos 6\Theta \\ I_{\mathrm{HVo}}(\mathrm{sliced}) =& \Big[\frac{3}{2} - \frac{3}{4} s_2 a_0^{(2)}(\|) + \frac{9}{16} s_4 a_0^{(4)}(\|)\Big] + \Big[\frac{3}{2} - \frac{3}{4} s_2 a_0^{(2)}(\|) + \frac{9}{16} s_4 a_0^{(4)}(\|)\Big] \cos 2\Theta \\ I_{\mathrm{HHc}}(\mathrm{sliced}) =& \Big[\frac{3}{2} + \frac{15}{16} s_2 a_0^{(2)}(\|) + \frac{57}{128} s_4 a_0^{(4)}(\|)\Big] + \Big[\frac{3}{2} + \frac{3}{2} s_2 a_0^{(2)}(\|) + \frac{279}{256} s_4 a_0^{(4)}(\|)\Big] \cos 2\Theta + \\ & \Big[\frac{9}{16} s_2 a_0^{(2)}(\|) + \frac{135}{128} s_4 a_0^{(4)}(\|)\Big] \cos 4\Theta + \frac{105}{256} s_4 a_0^{(4)}(\|) \cos 6\Theta \\ I_{\mathrm{HVc}}(\mathrm{sliced}) =& I_{\mathrm{HVo}}(\mathrm{sliced}) \end{aligned} \tag{9}$$

Now that we have analytical expressions for the images measured in each experimental geometry used, we can determine the alignment parameters $a_q^{(k)}()$ by carrying out a best-fit to the experimental data. To speed up computation, we reduce the 2D fit to a series of 1D fits. This is achieved by recognising the fact that for images measured with linearly polarised pump and probe light, the angular dependence may be expanded as a Fourier cosine series. Only even terms are non-zero.

$$\mathcal{I}(r,\phi) = c_0(r) + c_2(r)\cos 2\phi + c_4(r)\cos 4\phi + c_6(r)\cos 6\phi \tag{10}$$

For $O(^1D_2$ detected via (2+1)REMPI, only terms in the sum up to $n = 6$ need be retained. The Fourier coefficients $c_n(r)$, which are functions of the radial coordinate r of the image (i.e. the projection of the photofragment velocity onto the image plane), may be extracted directly from the experimental images $\mathcal{I}(r,\phi)$ by carrying out the appropriate integrals over the angular coordinate ϕ.

$$c_n(r) = N \int_0^{2\pi} \mathcal{I}(r,\phi) \cos(n\phi) v_p \, \mathrm{d}\phi \tag{11}$$

where the normalization constant N is equal to 1 when $n = 0$ and 2 when $n > 0$. For the geometries employed, it is straightforward to identify the Fourier coefficients from the analytical expressions for the images given in Equation (9) by matching terms with Equation (10). By

carrying out a simultaneous fit of these analytical expressions for the Fourier coefficients to the corresponding experimentally measured quantities $c_n(r)$, with the $a_q^{(k)}$ as fitting parameters, the alignment parameters may be determined.

References

1. T. P. Rakitzis and R. N. Zare, *J. Chem. Phys.*, **110(7)** 3341 (1999)