# Notes on the simulation of aligned $\mathrm{CH}_{4}$ and $\mathrm{CHD}_{3}$ molecular beam 

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In these notes the experiments by Rainer Beck are discussed from a theoretical point of view, i.e. with the specific aim of developing quantum and quasi-classical schemes to reproduce the relevant experimental values.

For a detailed description of the theory of angular momentum, I refer to the book by Brink, Satchler "Angular Momentum" (Oxford University Press). For the detailed description of the experiment, I refer to Bruce Yoder's PhD Thesis "Steric Effects in the Chemisorption of Vibrationally Excited Methane on Nickel"

## 1 Wigner D-Matrix and rotations of the reference frame

As well known from the theory of angular momentum, in the rigid rotor approximation (i.e. neglecting coupling between rotations and vibrations) the eigenfuctions describing the angular part of a symmetric top molecule are the complex conjugate of Wigner Dmatrices ${ }^{1}$

$$
\begin{equation*}
\Psi(\alpha, \beta, \gamma)=\mathfrak{D}_{M K}^{J \star}(\alpha, \beta, \gamma) \tag{1}
\end{equation*}
$$

where $\alpha, \beta$ and $\gamma$ are the so-called Euler angles, one of the most common way to parametrize rotations of an object in 3 dimensions ${ }^{2}$. The quantum numbers $\mathrm{J}, \mathrm{M}$ and K correspond to the total angular momentum $(\hbar \sqrt{J(J+1)})$, the projection of the angular momentum along a fixed space axis, usually defined to be the Z axis ( $\hbar M$ ) and the projection of the angular momentum along the figure axis - the symmetry axis of the molecule ( $\hbar K$ ).

[^0]By definition (e.g. see Brink, Satchler "Angular Momentum" Oxford University Press), a Wigner D-matrix is a trasformation matrix of the angular momentum eigenstates due to rotations:

$$
\mathfrak{D}_{M K}^{J}(\alpha, \beta, \gamma)=\langle J M| \mathfrak{R}(\alpha, \beta, \gamma)|J K\rangle
$$

where $|J M\rangle$ and $|J K\rangle$ are angular momentum eigenstates of a linear rotor (spherical harmonics) and $\mathfrak{R}(\alpha, \beta, \gamma)$ is the Euler rotation corresponding to angles $\alpha, \beta, \gamma$.

In the experiments considered, the reacting methane molecules are prepared in a precise rotational state (or a statistical mixture of some of the states). The selection rule $\Delta M=0$ - that is used in the experiment to prepare aligned vibrational excited methane molecule - is valid in a reference system in which the Z axis lay along the direction of the laser linear polarization. Hence the initial state of the experiments has to be referred to such frame of reference. However, in our quantum simulations it is much more convenient to set the Z coordinate in a direction that is normal to the metal surface. For this reason we want to find the expression of the matrix of Eq. 1 in a new reference $\alpha^{\prime}, \beta^{\prime}, \gamma^{\prime}$ that is related to $\alpha, \beta, \gamma$ by a rotation $\mathfrak{R}(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma})$

$$
\mathfrak{D}_{M K}^{J}\left(\alpha^{\prime}, \beta^{\prime}, \gamma^{\prime}\right)=\langle J M| \mathfrak{R}\left(\alpha^{\prime}, \beta^{\prime}, \gamma^{\prime}\right)|J K\rangle=\langle J M| \mathfrak{R}(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}) \mathfrak{R}(\alpha, \beta, \gamma)|J K\rangle
$$

If we now introduce in the expression the identity over the J level $\sum_{M^{\prime}=-J}^{+J}\left|J M^{\prime}\right\rangle\left\langle J M^{\prime}\right|$ (other J values would not contribute since rotations do not couple states with different total angular momentum)

$$
\mathfrak{D}_{M K}^{J}\left(\alpha^{\prime}, \beta^{\prime}, \gamma^{\prime}\right)=\sum_{M^{\prime}=-J}^{+J}\langle J M| \mathfrak{R}(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma})\left|J M^{\prime}\right\rangle\left\langle J M^{\prime}\right| \mathfrak{R}(\alpha, \beta, \gamma)|J K\rangle
$$

Using the definition of Wigner D-matrix we can write this expression as

$$
\begin{equation*}
\mathfrak{D}_{M K}^{J}\left(\alpha^{\prime}, \beta^{\prime}, \gamma^{\prime}\right)=\sum_{M^{\prime}=-J}^{+J} \mathfrak{D}_{M M^{\prime}}^{J}(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}) \mathfrak{D}_{M^{\prime} K}^{J}(\alpha, \beta, \gamma) \tag{2}
\end{equation*}
$$

If we identify with $\mathbf{R}^{\prime}=\alpha^{\prime}, \beta^{\prime}, \gamma^{\prime}$ the "laser" reference system (with Z oriented as the laser polarization) and with $\mathbf{R}=\alpha, \beta, \gamma$ the "surface" reference system (with Z normal to the surface), Eq. 2 tells us that in the "surface" reference frame the J,M,K initial state can be written as superposition of states in the "laser" frame with the same J and K. The coefficients of the superposition - $\mathfrak{D}_{M M^{\prime}}^{J}(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma})$ - are still Wigner D-matrices with the same J quantum number, evaluated for the angle of rotation that brings the "surface" reference system to the "laser" one.

If we assume that only the angle between the surface normal and the laser polarization is relevant, we further specialize our result by imposing that $\mathfrak{R}(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma})$ is a rotation through $\vartheta$ around the Y axis

$$
\mathfrak{R}(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma})=\mathfrak{R}(0, \vartheta, 0)
$$

In this assumption, the coefficient of Eq. 2 becomes equivalent to the so-called Wigner small D-matrix. Hence the initial rotational state of Eq. 1 becomes

$$
\begin{equation*}
\mathfrak{D}_{M K}^{J \star}\left(\mathbf{R}^{\prime}\right)=\sum_{M^{\prime}=-J}^{+J} d_{M M^{\prime}}^{J}(\vartheta) \mathfrak{D}_{M^{\prime} K}^{J \star}(\mathbf{R}) \tag{3}
\end{equation*}
$$

where we have dropped the complex conjugate from the Wigner small D-matrix since we adopt a convention such that $d_{M m}^{J}(\vartheta)$ are real functions of $\vartheta$ (i.e. the Z-Y-Z convention for the Euler angles, see Brink and Satchler's book).

On the other hand, if the experimental results are resolved also over the symmetric directions of the surface, Eq. 2 can still be used by retaining also the dependence on an azimuthal angle $\varphi$.

## 2 Two examples and a comparison with the experiments

In this section I will briefly discuss two cases, to explain how Eq. 3 can be used to simplify the problem of simulations of the scattering of aligned molecules.

## 2.1 $\mathrm{R}(0)$ transition in $\mathrm{CH}_{4}$

Consider the initial state of a vibrationally excited $\mathrm{CH}_{4}$ prepared by means of the $\mathrm{R}(0)$ transition (see Bruce Yoder's PhD thesis for details). This transition brings the rovibrational ground state $\nu_{3}=0, \mathrm{~J}=0$ to the excited state $\nu_{3}=1, \mathrm{~J}=1$ (here $\nu_{3}$ is the vibrational quantum number for the antisymmetric CH stretching mode). In the frame of reference of the laser polarization, such transition has the $\Delta M=0$ and $\Delta K=0$ selection rule. Since for $\mathrm{J}=0$, only $\mathrm{M}=0 \mathrm{~K}=0$ state is possible, we can conclude that the reacting $\mathrm{CH}_{4}$ is prepared in the rotational state $\mathrm{J}=1, \mathrm{M}=0, \mathrm{~K}=0$

$$
\begin{equation*}
\Psi_{0}\left(\mathbf{R}^{\prime}\right)=\mathfrak{D}_{00}^{1 \star}\left(\mathbf{R}^{\prime}\right) \tag{4}
\end{equation*}
$$

in the laser reference frame.
Using Eq. 3, we find that in the "surface" frame the initial state is expressed by

$$
\Psi_{0}(\mathbf{R})=\sum_{m=-1}^{+1} d_{0 m}^{1}(\vartheta) \mathfrak{D}_{m 0}^{1 \star}(\mathbf{R})
$$

Substituting the expressions of the small D-matrix (see Tab. 1), we get

$$
\begin{equation*}
\Psi_{0}(\mathbf{R})=-\frac{1}{\sqrt{2}} \sin \vartheta \mathfrak{D}_{-10}^{1 \star}(\mathbf{R})+\cos \vartheta \mathfrak{D}_{00}^{1 \star}(\mathbf{R})+\frac{1}{\sqrt{2}} \sin \vartheta \mathfrak{D}_{10}^{1 \star}(\mathbf{R}) \tag{5}
\end{equation*}
$$

where $\vartheta$ is the angle between the surface normal and the direction of the laser polarization.
With two reasonable assumptions, this expression can be tested with the data reported by Bruce Yoder (see Fig. 4.10, page 128, Yoder's PhD thesis). First, we neglect quantum interference of the component of the initial state (see Appendix A). In this (reasonable)
approximation, the reaction probability of a superposition of states is the average of the reaction probability of the states, with weights that are given by the square of the superposition coefficients:

$$
P_{\text {react }}(\vartheta)=\left(-\frac{1}{\sqrt{2}} \sin \vartheta\right)^{2} P_{\text {react }}^{M=-1}+(\cos \vartheta)^{2} P_{\text {react }}^{M=0}+\left(\frac{1}{\sqrt{2}} \sin \vartheta\right)^{2} P_{\text {react }}^{M=+1}
$$

where $P_{\text {react }}^{M=m}$ is the reaction probability computed with the system in the initial $\mathrm{J}=1$, $\mathrm{K}=0$ and $\mathrm{M}=\mathrm{m}$ rotational state (in the "surface" reference).

Making the further assumption that the reaction probability does not change whether the molecule is rotating clockwise or counterclockwise along Z with the same angular velocity

$$
P_{\text {react }}^{M=-1}=P_{\text {react }}^{M=+1}=P_{\text {react }}^{\perp}
$$

In conclusion, we get

$$
\begin{equation*}
P_{\text {react }}(\vartheta)=\cos ^{2} \vartheta P_{\text {react }}^{\|}+\sin ^{2} \vartheta P_{\text {react }}^{\perp} \tag{6}
\end{equation*}
$$

Basing on a simple geometrical argument, in the thesis Yoder assumed a very similar model, i.e.

$$
\begin{align*}
P_{\text {react }}(\vartheta) & =\sqrt{\left(P_{\text {react }}^{\|}\right)^{2}-\sin ^{2} \vartheta\left[\left(P_{\text {react }}^{\|}\right)^{2}-\left(P_{\text {react }}^{\perp}\right)^{2}\right]}= \\
& =\sqrt{\cos ^{2} \vartheta\left(P_{\text {react }}^{\|}\right)^{2}+\sin ^{2} \vartheta\left(P_{\text {react }}^{\perp}\right)^{2}} \tag{7}
\end{align*}
$$

As shown in Fig. 1, the dependence on $\vartheta$ obtained in Eq. 6 is in agreement with the experimental results reported in the thesis.

## $2.2^{1} \mathrm{R}(1)$ transition in $\mathrm{CHD}_{3}$

Now consider the vibrationally excited $\mathrm{CHD}_{3}$ prepared with laser tuned at the ${ }^{1} \mathrm{R}(1)$ transition. This transition brings the rovibrational state $\nu_{1}=0, \mathrm{~J}=1, \mathrm{~K}=1$ to the excited state $\nu_{1}=1, \mathrm{~J}=2, \mathrm{~K}=1$ (here $\nu_{1}$ is the vibrational quantum number for the CH stretching normal mode). Again, in the frame of reference of the laser polarization, such transition has the $\Delta M=0$ selection rule. Since for $\mathrm{J}=1$, only the states $\mathrm{M}=0, \pm 1$ are possible, we can conclude that the reacting $\mathrm{CHD}_{3}$ will be a statistical mixture of rotational state $\mathrm{J}=2, \mathrm{~K}=1$ and $\mathrm{M}=0, \pm 1$

$$
\begin{gather*}
\Psi_{-1}\left(\mathbf{R}^{\prime}\right)=\mathfrak{D}_{-11}^{2 \star}\left(\mathbf{R}^{\prime}\right) \\
\Psi_{0}\left(\mathbf{R}^{\prime}\right)=\mathfrak{D}_{01}^{2 \star}\left(\mathbf{R}^{\prime}\right)  \tag{8}\\
\Psi_{+1}\left(\mathbf{R}^{\prime}\right)=\mathfrak{D}_{11}^{2 \star}\left(\mathbf{R}^{\prime}\right)
\end{gather*}
$$

We now see how these states are trasformed into our space fixed "surface" reference. Using Eq. 3, we find that the state $\Psi_{0}\left(\mathbf{R}^{\prime}\right)$ transform to

$$
\Psi_{0}(\mathbf{R})=\sum_{m=-2}^{+2} d_{0 m}^{2}(\vartheta) \mathfrak{D}_{m 1}^{2 \star}(\mathbf{R})
$$



Figure 1: Dependence of the reactivity of $\mathrm{CH}_{4}-\mathrm{R}(0)$ beam with respect to the polarization angle of the laser. The green curve is the geometrical model by Yoder (Eq. 7), while the blue curve is the model described in this report (Eq. 6)

| J | M | K | $d_{M K}^{J}(\beta)$ |
| :---: | :---: | :---: | :---: |
| 1 | 1 | 1 | $\cos ^{2}(\beta / 2)$ |
|  | 1 | 0 | $-1 / \sqrt{2} \sin \beta$ |
|  | 1 | -1 | $\sin ^{2}(\beta / 2)$ |
|  | 0 | 0 | $\cos \beta$ |
|  | 2 | 2 | $\cos ^{4}(\beta / 2)$ |
|  | 2 | 1 | $-1 / 2 \sin \beta(1+\cos \beta)$ |
|  | 2 | 0 | $\sqrt{3 / 8} \sin ^{2} \vartheta$ |
|  | 2 | -1 | $1 / 2 \sin \beta(\cos \beta-1)$ |
|  | 2 | -2 | $\sin ^{4}(\beta / 2)$ |
|  | 1 | 1 | $1 / 2(2 \cos \beta-1)(\cos \beta+1)$ |
|  | 1 | 0 | $-\sqrt{3 / 2} \sin \beta \cos \beta$ |
|  | 1 | -1 | $1 / 2(2 \cos \beta+1)(1-\cos \beta)$ |
|  | 0 | 0 | $1 / 2\left(3 \cos ^{2} \vartheta-1\right)$ |

Table 1: Wigner small D-matrices for $J=1$ and $J=2$ (see Brink, Satchler "Angular Momentum" Oxford University Press). The elements that have not been reported can be found using the symmetry properties of Wigner small D-matrices: $d_{K M}^{J}(\beta)=(-)^{M-K} d_{M K}^{J}(\beta)$ and $d_{-M-K}^{J}(\beta)=(-)^{M-K} d_{M K}^{J}(\beta)$.
and analogous formulas for $\Psi_{1}(\mathbf{R})$ and $\Psi_{-1}(\mathbf{R})$. Substituting the small D-matrix, we get
$\Psi_{0}(\mathbf{R})=\sqrt{\frac{3}{8}} \sin ^{2} \vartheta\left[\mathfrak{D}_{-21}^{2 \star}(\mathbf{R})-\mathfrak{D}_{21}^{2 \star}(\mathbf{R})\right]-\sqrt{\frac{3}{2}} \sin \vartheta \cos \vartheta\left[\mathfrak{D}_{-11}^{2 \star}(\mathbf{R})-\mathfrak{D}_{11}^{2 \star}(\mathbf{R})\right]+\frac{1}{2}\left(3 \cos ^{2} \vartheta-1\right) \mathfrak{D}_{01}^{2 \star}(\mathbf{R})$
where $\vartheta$ is the angle between the surface normal and the direction of the laser polarization. Analogous expression can be obtained for the intial states $\Psi_{1}(\mathbf{R})$ and $\Psi_{-1}(\mathbf{R})$.

## 3 Quantum and quasi-classical scattering simulations

The previous discussion shows how an angular momentum state aligned in ANY direction can be simply related to the full set of state of equal J and K in a space fixed frame of reference. From a theoretical point of view, this is extremely useful to define the proper initial conditions to simulate the aligned scattering experiments.

In terms of quasi-classical dynamics, we can develop a reasonable scheme to sample the initial conditions of all the M states for given $\mathrm{J}, \mathrm{K}$, in a given fixed frame of reference (e.g. with Z normal to the surface). One example of such scheme is described in Appendix B. Then we have at least two possibilities:

1. The simplest approach is to sample the initial conditions by fixing Z to be the axis of the laser reference of frame. In this case, to get results for different polarization angles is then necessary to repeat one set of trajectory for each orientation that we want to consider changing the sampling in agreement with the laser polarization direction (just two set of calculations are then needed if the two extreme polarization $\vartheta=0$ and $\vartheta=90^{\circ}$ are considered).
2. On the other hand, Eq. 3 tells us that if we know the reaction probability resolved for all the M states in a generic fixed frame of reference, we can compute the state resolved reaction probability for any laser polarization direction with the formula

$$
\begin{equation*}
P_{\text {aligned }}(J, M, K, \vartheta)=\sum_{M^{\prime}=-J}^{+J}\left|d_{M M^{\prime}}^{J}(\vartheta)\right|^{2} P_{\text {fixed }}\left(J, M^{\prime}, K\right) \tag{10}
\end{equation*}
$$

where $P_{\text {fixed }}\left(J, M^{\prime}, K\right)$ is the reaction probability of rovibrational state $\mathrm{J}, \mathrm{M}^{\prime}, \mathrm{K}$ (where m is the projection of the angular momentum along the given fixed reference) while $P_{\text {aligned }}(J, M, K, \vartheta)$ is the reaction probability of rovibrational state $\mathrm{J}, \mathrm{M}, \mathrm{K}$ (where M here is the projection along the laser polarization direction) and $\vartheta$ is the angle between the fixed frame and the polarization direction. The weights of the average $\left|d_{M m}^{J}(\vartheta)\right|^{2}$ have been chosen in agreement with Eq. 6, and represent the probability of finding the system in the state $\mathrm{J}, \mathrm{M}^{\prime}$ (with m projection along the fixed reference) for an initial state $\mathrm{J}, \mathrm{M}$ (with M projection along the polarization axis)

To decide which of the two approaches should be preferred, many elements should be taken into account: the number of orientations that we want to consider, the number of
$\mathrm{M}^{\prime}$ states to be included in the sum of Eq. 10, the different statistics of the two sampling methods.

In the case of quantum dynamics, again we have to possibilities.

1. Just like in the quasi-classical case, we can start from an initial state that is aligned in the laser polarization direction. To define such state, it may still be useful to employ Eq. 3 to define the correct initial condition with respect to a frame of reference than can be conveniently used in the quantum wavepacket calculations. In this case, one calculation is needed for each orientation $\vartheta$ that we want to consider.
2. As an alternative, we can start from a fixed frame of reference and repeat the calculation for all the allowed $\mathrm{M}^{\prime}$ states. Then the results for any laser frame of reference can be computed according to Eq. 3. Note however that here the average is more complicated than in Eq. 10 since we start from an initial state that is a superposition of states and quantum interference between those states should be considered. In detail, the quantity to be averaged is the (complex) S-matrix

$$
\begin{equation*}
S_{\text {laser }}(f \leftarrow J, M, K, \vartheta)=\sum_{M^{\prime}=-J}^{+J} d_{M m}^{J}(\vartheta) S_{\text {fixed }}\left(f \leftarrow J, M^{\prime}, K\right) \tag{11}
\end{equation*}
$$

The squared modulus of the S-matrix gives the scattering probability to get to a final state $f$ starting from given initial conditions. Using this equation, it is possible to compute the reaction probability as the non-scattered probability. The dissociation probability then becomes

$$
\begin{gather*}
P_{\text {aligned }}(J, M, K, \vartheta)=\sum_{M^{\prime}=-J}^{+J}\left|d_{M M^{\prime}}^{J}(\vartheta)\right|^{2} P_{\text {fixed }}\left(J, M^{\prime}, K\right)- \\
2 \operatorname{Re}\left(\sum_{M_{1}} \sum_{M_{2}<M_{1}} d_{M M_{1}}^{J}(\vartheta) d_{M M_{2}}^{J}(\vartheta) \sum_{f}\left(S\left(f \leftarrow J, M_{1}, K\right)\right)^{\star} S\left(f \leftarrow J, M_{2}, K\right)\right) \tag{12}
\end{gather*}
$$

Further details about this can be found in Appendix A.
In conclusion, for both quantum and quasi-classical mechanics we are able to define correct initial condition to simulate the scattering of an aligned methan molecular beam.

This can be done a priori by setting a sampling method (for quasi-classical mechanics) or a initial wavefunction (for quantum mechanics) that properly describe a single (J,M,K) rotational state in the frame of reference defined by the polarisation axis of the laser.

As an alternative, the proper initial conditions can be enforced a posteriori. If the reaction probabilities (for classical mechanics) or the scattering matrix (for quantum mechanics) are known for all the M values in a particular space fixed frame of reference, the reaction probability can be computed for an initial state that has been aligned in ANY direction. Basing on Eq. 3 - i.e. the transformation that relates the alignment frame and the space fixed frame - we can find that the quasi-classical reaction probability is given by Eq. 10 and the quantum reaction probability is given by Eq. 12 .

## A Scattering of a superposition of states

Suppose we want to compute a dissociation probability for a molecule scattering on a surface. We choose an initial asymptotic state $|i\rangle$ of the molecule that is not a single state of the molecular hamiltonian (plus a free state for the scattering coordinates), but a superposition of orthonormal eigenstates $|\alpha\rangle$

$$
\begin{equation*}
|i\rangle=\sum_{\alpha}^{N} c_{\alpha}|\alpha\rangle \tag{13}
\end{equation*}
$$

From a classical point of view, if we think to the superposition of Eq. 13 as a statistical distribution with coefficients equal to the squared modulus of the $c_{\alpha}$, we would expect that the probability for the possible scattering or reactive events to be

$$
\begin{aligned}
P_{\text {react }}(i) & =\sum_{\alpha}^{N}\left|c_{\alpha}\right|^{2} P_{\text {react }}(\alpha) \\
P_{\text {scatter }}(f \leftarrow i) & =\sum_{\alpha}^{N}\left|c_{\alpha}\right|^{2} P_{\text {scatter }}(f \leftarrow \alpha)
\end{aligned}
$$

where $f$ labels the scattering final asymptotic states.
On the contrary, in a fully quantum approach the scattering probability to a given final state $f$ is the squared modulus of the S-matrix, which is the matrix element of the scattering operator $S$

$$
\left.P(f \leftarrow i)=|S(f \leftarrow i)|^{2}=|\langle f| S| i\right\rangle\left.\right|^{2}
$$

From the linearity of the scattering operator, we get

$$
\begin{equation*}
\left.\left.P(f \leftarrow i)=\left|\sum_{\alpha}^{N} c_{\alpha}\langle f| S\right| \alpha\right\rangle\left.\right|^{2}=\sum_{\alpha}^{N}\left|c_{\alpha}\right|^{2}|\langle f| S| \alpha\right\rangle\left.\right|^{2}+\sum_{\alpha}^{N} \sum_{\beta}^{N} c_{\alpha}^{\star} c_{\beta}(\langle f| S|\alpha\rangle)^{\star}\langle f| S|\beta\rangle \tag{14}
\end{equation*}
$$

The first term of the right hand size corresponds to the classical scattering probability

$$
\left.\sum_{\alpha}^{N}\left|c_{\alpha}\right|^{2}|\langle f| S| \alpha\right\rangle\left.\right|^{2}=\sum_{\alpha}^{N}\left|c_{\alpha}\right|^{2} P_{\text {scatter }}(f \leftarrow \alpha)
$$

hence the expression of Eq. 14 contains a non-classical interference term

$$
\begin{equation*}
\sum_{\alpha}^{N} \sum_{\beta}^{N} c_{\alpha}^{\star} c_{\beta}(\langle f| S|\alpha\rangle)^{\star}\langle f| S|\beta\rangle \tag{15}
\end{equation*}
$$

in which we also have to consider the phase of the S-matrix and not just its amplitude.

Due to quantum interference, we could have in general that

$$
\begin{gathered}
P_{\text {react }}(i) \neq \sum_{\alpha}^{N}\left|c_{\alpha}\right|^{2} P_{\text {react }}(\alpha) \\
\sum_{f} P_{\text {scatter }}(f \leftarrow i) \neq \sum_{\alpha}^{N}\left|c_{\alpha}\right|^{2} \sum_{f} P_{\text {scatter }}(f \leftarrow \alpha)
\end{gathered}
$$

Equality strictly holds only when we neglect quantum effects, hence in the classical limit.
By means of the full $S$ matrix we get the quantum expression for the reaction probability. For any normalized state, the unitarity of $S$ operator implies that

$$
\sum_{f} P_{\text {scatter }}(f \leftarrow i)+P_{\text {react }}(i)=1
$$

So, we can compute the reaction probability as

$$
\left.P_{\text {react }}(i)=1-\sum_{f} P_{\text {scatter }}(f \leftarrow i)=1-\sum_{f}|\langle f| S| i\right\rangle\left.\right|^{2}
$$

Substituting the expression for the state $|i\rangle$ as a superposition of states (Eq. 13) we get

$$
\begin{gathered}
P_{\text {react }}(i)=1-\sum_{\alpha}^{N} \sum_{\beta}^{N} c_{\alpha}^{\star} c_{\beta} \sum_{f}(\langle f| S|\alpha\rangle)^{\star}\langle f| S|\beta\rangle= \\
\left.=1-\sum_{\alpha}^{N}\left|c_{\alpha}\right|^{2} \sum_{f}|\langle f| S| \alpha\right\rangle\left.\right|^{2}-\sum_{\alpha}^{N} \sum_{\beta \neq \alpha}^{N} c_{\alpha}^{\star} c_{\beta} \sum_{f}(\langle f| S|\alpha\rangle)^{\star}\langle f| S|\beta\rangle
\end{gathered}
$$

We can recognize $\left.1-\sum_{\alpha}^{N}\left|c_{\alpha}\right|^{2} \sum_{f}|\langle f| S| \alpha\right\rangle\left.\right|^{2}$ as the weighted sum of the $|\alpha\rangle$ states reaction probability. Using the symmetry of the expression in the sum with respect to exchange of $\alpha$ and $\beta$, we get

$$
\begin{equation*}
P_{\text {react }}(i)=\sum_{\alpha}^{N}\left|c_{\alpha}\right|^{2} P_{\text {react }}(\alpha)-2 \operatorname{Re}\left(\sum_{\alpha}^{N} \sum_{\beta<\alpha}^{N} c_{\alpha}^{\star} c_{\beta} \sum_{f}(\langle f| S|\alpha\rangle)^{\star}\langle f| S|\beta\rangle\right) \tag{16}
\end{equation*}
$$

hence the term $\left(\alpha^{\prime}, \beta^{\prime}, \gamma^{\prime}\right)$

$$
2 R e\left(\sum_{\alpha}^{N} \sum_{\beta<\alpha}^{N} c_{\alpha}^{\star} c_{\beta} \sum_{f}(\langle f| S|\alpha\rangle)^{\star}\langle f| S|\beta\rangle\right)
$$

determine the interference effect in the reaction probability.

## B Quasi-classical sampling of the aligned initial state

I briefly sketch the idea behind one reasonable way to make a quasi-classical sampling of the initial condition of $\mathrm{CHD}_{3}$. Especially for this part, I have to thank Francesco Nattino, whose collaboration has been invaluable and greatly appreciated.

In a space fixed reference frame, the three quantum numbers J, M, K corresponds to three constants of motion (which are conserved when the molecule is moving in the vacuum). J corresponds to the total angular momentum, M to its projection on the space fixed Z axis and K to its projection along the figure axis (that in a symmetric top is the symmetry axis of order $>2$, in our case the $\mathrm{CH}_{3}$ umbrella axis)

$$
\begin{array}{ccc}
J & \rightarrow & |\mathbf{L}|^{2}=\hbar \sqrt{J(J+1)} \\
M & \rightarrow & L_{Z}=\hbar M \\
K & \rightarrow & L_{\text {axis }}=\hbar K
\end{array}
$$

This three conditions can be conveniently visualized as in Fig. 2. If we fix the Z axis in the space, the angular momentum is a vector lying in the cone defined by the angle

$$
\cos \rho=\frac{M}{\sqrt{J(J+1)}}
$$

The length of the vector is $\hbar \sqrt{J(J+1)}$ and then by generating a random number $\xi \in$ $[0,2 \pi]$ we can fix the other components of the angular momentum

$$
\begin{aligned}
L_{X} & =\hbar \sqrt{J(J+1)} \cos \xi \\
L_{Y} & =\hbar \sqrt{J(J+1)} \sin \xi
\end{aligned}
$$

Now we have to fix the orientation of the molecule. To obey the quantization rule of $L_{\text {axis }}$, we have to orient the figure axis $\vec{\omega}$ in a cone of angle $\beta^{\prime}$ with respect to the angular momentum

$$
\cos \beta^{\prime}=\frac{K}{\sqrt{J(J+1)}}
$$

Note that $\beta^{\prime}$ is the second Euler angle describing the orientation of the molecule in the reference defined by the angular momentum. The other two Euler angles $\alpha^{\prime}$ and $\gamma^{\prime}$ can be chosen randomly in the correct definition interval [ $0,2 \pi$ ] (possibly reduced by additional symmetry of the molecule, such as the $C_{3 v}$ symmetry of the umbrella).

So we have fully specified

- the cartesian components $\left(L_{X}, L_{Y}, L_{Z}\right)$ of the angular momentum with respect to the space fixed frame
- the euler angles $\left(\alpha^{\prime}, \beta^{\prime}, \gamma^{\prime}\right)$ defining the orientation of the molecule with respect to the angular momentum

Composing the rotation $\left(\alpha^{\prime}, \beta^{\prime}, \gamma^{\prime}\right)$ with a rotation to bring the angular momentum from the z axis to its absolute orientation, we can find the ( $\alpha, \beta, \gamma$ ) angles describing the orientation of the molecule in the space fixed frame.

Note that in total we have 6 degree of freedom, 3 for the angular momentum and 3 for the orientation. We have 3 constraints coming from quantization rules and 3 additional values that should be randomly sampled in an interval $[0,2 \pi]$.


Figure 2: Relative orientation of the Z axis, the angular momentum $\vec{L}$ and the figure axis $\vec{\omega}$, with indetermination represented as is customary with two cones.


[^0]:    ${ }^{1}$ More precisely, a normalization factor dependent on J is required to get properly normalized eigenstates.

    $$
    \Psi(\alpha, \beta, \gamma)=\frac{\sqrt{2 J+1}}{2 \pi \sqrt{2}} \mathfrak{D}_{M K}^{J \star}(\alpha, \beta, \gamma)
    $$

    For the sake of clarity in this discussion these normalization factors will be dropped.
    ${ }^{2}$ More precisely, different sets of Euler angles arise from different conventions. In this notes, we use the Z-Y-Z convention, with counterclockwise rotations and an active point of view.

