



# Rotational dephasing of symmetric top molecules: Analytic expressions and applications

Oliver Schalk\*, Paul Hockett

Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6

## ARTICLE INFO

### Article history:

Received 22 September 2011

In final form 21 October 2011

Available online 29 October 2011

## ABSTRACT

An analytic expression for the rotational dephasing of an ensemble of symmetric top molecules excited by a short laser pulse is developed. This expression can be used to discern rotation from electronic and vibrational dynamics in polarization resolved studies and is computationally less demanding than numeric simulations used previously. The result agrees well with quantum mechanical treatment, both at room temperature and at cold rotational temperatures found in molecular beams. Applications to transient anisotropy and photoelectron angular distributions are given. Finally, we raise the possibility of combining transient anisotropy techniques with time-resolved photoelectron spectroscopy.

Crown Copyright © 2011 Published by Elsevier B.V. All rights reserved.

## 1. Introduction

Time-resolved polarization dependent pump–probe measurements such as transient anisotropy or photoelectron angular distributions (PADs) present powerful methods for obtaining information on excited state dynamics that cannot be obtained by population dependent measurements only. In anisotropy experiments based on transient absorption or fluorescence up-conversion, pump and probe pulses are polarized in two configurations: parallel or perpendicular with respect to each other [1,2]. The difference between the signals of these configurations is normalized by the signal under magic angle conditions, and is recorded in dependence of the time delay between pump and probe pulse. In time-resolved photoelectron spectroscopy, the observable may be the angle-integrated photoelectron yield or, in a more differential measurement, the angle-resolved yield. The latter observable, the PAD, contains detailed information on both the excited state dynamics [3–6] and the ionization dynamics [7–10] due to its sensitivity to the angular-momentum character of the photoelectron [10,11]. The angle-integration of the PAD to provide the total photoelectron yield necessarily obscures some detail, but much can still be learned from the time-resolved photoelectron spectrum (TRPES).

Disentangling the rotational, vibrational and electronic components of the excited state dynamics is a key challenge in the understanding of excited state processes. Various investigators have explored the effect of rotational dynamics on transient anisotropy [12–15], polarization resolved ion yield measurements [16–18],

and PADs by considering the effects of static alignments [9,10] or by the use of full numerical calculations for time-dependent alignment [3,4]. Here, we present an analytic expression for the reorientation of a symmetric top molecule, simplifying the treatment of collision induced rotational dephasing in liquids. This is also a convenient way to directly incorporate the rotational dynamics into a treatment of PADs, allowing the analytic separation of rotational dynamics from vibronic dynamics. Example calculations are presented and compared with the existing literature to stimulate progress in this direction.

## 2. The model

### 2.1. Excitation moments

In the absence of overlap between the pulses, a pump–probe experiment can be decomposed into three steps: pump, propagation and probe. For the pump step, we here consider the simple case of an isotropically distributed sample of molecules that is excited by a laser pulse linearly polarized along the laboratory fixed *z*-axis, the typical set-up in many time-resolved experiments (excitation with circular or elliptical polarized light can be implemented by applying the Jones-vector formalism [19] to the derivation in [15]). For a one photon pump the resulting distribution of transition dipole moments is  $\propto \cos^2\vartheta$ . More generally, for an *n*-photon process, the resulting distribution of excited molecules is given by [9,10,15,20]

$$\mathcal{P}^{(n)}(\vartheta) = \sum_{i=0}^n a_{n,i} P_{2i}(\cos \vartheta) \equiv \sum_{i=0}^n a_{n,i} Y_{2i,0}(\vartheta), \quad (1)$$

where *n* is the number of pump photons and  $\vartheta$  is the angle between the *z*-axis and the transition dipole moment along which a molecule

\* Corresponding author. Present address: Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität (LMU), Oettingenstraße 67, 80538 München, Germany. Fax: +49 89 2180 9202.

E-mail address: [oliver.schalk@physik.uni-muenchen.de](mailto:oliver.schalk@physik.uni-muenchen.de) (O. Schalk).

is excited.  $P_{2i}(\cos \vartheta)$  are Legendre polynomials and  $Y_{k,l}(\vartheta)$  are spherical harmonics. For linear polarization there is no  $\varphi$  dependence, the decomposition into different basis functions are interchangeable, save for different normalization factors. Most generally there may also be a  $\varphi$  dependence to the distribution, requiring terms which are only described by  $Y_{2i,q \neq 0}$ ; this situation is discussed in Section 2.4. The  $a_{n,i}$  can be given analytically as [15]

$$a_{n,i} = \frac{\sqrt{4i+1}(2n)!}{2^{n-i-\frac{1}{2}}(n-i)!(2n+2i+1)!!}. \quad (2)$$

In the propagation step, the  $a_{n,i} = a_{n,i}(t)$  evolve in time. This time dependence is generally not known since it depends on various parameters such as the induced dynamics and the shape of a molecule. In the following, we will apply the following assumptions: (i) The molecule does not undergo collisions or electronic dynamics (although collisions may be modeled by free rotation between collision events [15]). (ii) The moments of inertia  $J_1$ ,  $J_2$  and  $J_3$  do not change in the course of an experiment. (iii) Two of the moments are equal ( $J_1 = J_2$ ). This final condition is only strictly fulfilled in symmetric tops, but many molecules possess two moments of inertia that are approximately equal.

In the remainder of this section, we will deal with the propagation step only. As described in the introduction, there are many ways to probe the evolution of the system. Some of these methods are discussed in Section 3.

The time dependence for the  $a_{n,i}(t)$  was previously solved for two special cases: linear ( $J_3 = 0$ ) and spherical ( $J_3 = J_1 = J_2 = J$ ) molecules. The solutions are given by [15,21]:

$$a_{n,i}(t) = a_{n,i}(0) \times \begin{cases} P_{2i}(\langle \cos \beta(t) \rangle) & \text{linear molecule} \\ \frac{1}{2i+1} P_{2i}^{1/2,-1/2}(\langle \cos \beta(t) \rangle) & \text{spherical molecule} \end{cases} \quad (3)$$

where  $P_i(\beta)$  are Legendre polynomials and  $P_i^{1/2,-1/2}(\beta)$  are Jacobi polynomials. The time dependence is governed by  $\beta(t) = \omega t$ . For a classical molecule, the averages are given by a Boltzmann distribution and are calculated via

$$\langle \cos^n \omega t \rangle = \int_0^\infty 2a\omega e^{-a\omega^2} \cos^n \omega t d\omega, \quad (4)$$

where  $a = J/2k_B T$  and  $T$  is the canonical temperature of the system. Eq. (4) can be solved analytically for different values of  $n$  [15].

## 2.2. Solution for the symmetric top

For a symmetric top molecule  $J_1 = J_2 \neq J_3$ . Let us define  $x = J_3/J_1$  ( $x \in [\frac{1}{2}, \infty]$ ) and  $\theta = \angle \vec{J}_3, \vec{d}$ , where  $\vec{d} = d(\theta)$  is the rotation axis of the molecule. According to Euler's formula, a rotation about  $\vec{d}$  can be described by [22]

$$\mathcal{F}(T(\beta))_{jk} = \delta_{jk} \cos \beta + d_j d_k (1 - \cos \beta) + \sin \beta \sum_{l=1}^3 \epsilon_{jkl} d_l, \quad (5)$$

where the probability for a rotation about a certain angle  $\theta$  is given by [23,15]

$$\mathcal{P}_{\parallel}(\theta) = \frac{\sqrt{x}}{2(1 + (x-1)\cos^2 \theta)^{3/2}}. \quad (6)$$

For the beginning, let the transition dipole moment be parallel to the principle axis of inertia as is often the case in symmetric tops. Contrarily to Ref. [15], the angle integration of  $(\mathcal{F}\vec{\mu})_z^{2n}$ , i.e., the rotated transition dipole moment,  $\theta$  has to include the probability defined in Eq. (6). The time dependent distribution then becomes, in the case of a one photon pump ( $n = 1$ ),

$$\begin{aligned} \mathcal{P}^{(1)}(\vartheta, t, x) \propto & \frac{1}{3} P_0(\cos \vartheta) \\ & + \left( \frac{\sqrt{x-1}(4+7x-2x^2) - 9\sqrt{x} \operatorname{arcsinh}(\sqrt{x-1})}{6(x-1)^{5/2}} \right. \\ & + \frac{-3x\sqrt{x-1} - \sqrt{x}(2x+1) \operatorname{arcsinh}(\sqrt{x-1})}{(x-1)^{5/2}} \langle \cos \beta \rangle \\ & \left. + \frac{x\sqrt{x-1}(2x+1) - \sqrt{x}(4x-1) \operatorname{arcsinh}(\sqrt{x-1})}{2(x-1)^{5/2}} \langle \cos^2 \beta \rangle \right) \\ & \times P_2(\cos \vartheta). \end{aligned} \quad (7)$$

The general,  $n$ -photon, solution has the structure

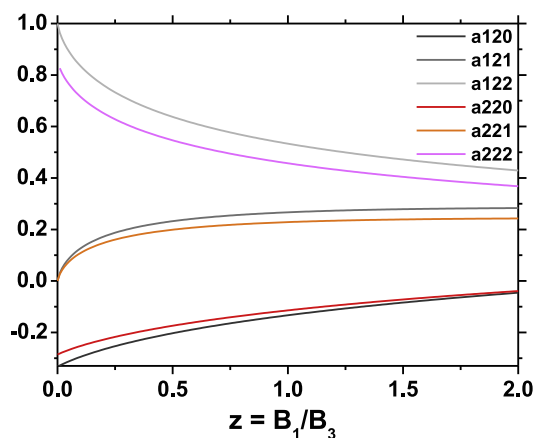
$$\begin{aligned} \mathcal{P}^{(n)}(\vartheta, t, x) \propto & \sum_{i=0}^n a_{n,i}(t, x) P_{2i}(\cos \vartheta) \quad \text{with} \\ a_{n,i}(t, x) = & \sum_{j=0}^{2i} a_{n,ij}(x) \langle \cos^j(\beta(t)) \rangle. \end{aligned} \quad (8)$$

The  $a_{n,ij}(x)$  for two photon excitation are shown in Appendix A. Eq. (7) is the solution for symmetric top molecules and correctly describes the time dependence for a linear ( $x = \infty$ ) and the spherical molecule ( $x = 1$ , see Eq. (3)) as well as the long time limit for the spherical top, as derived in Ref. [15], and represents the main result of this Letter. Figure 1 shows the dependence of  $a_{n,1,j}(z)$  from  $z \equiv x^{-1}$  ( $z \in [0, 2]$ ) for  $n = 1, 2$ . The structure of the  $z$ -dependence in both cases is similar. As required  $\sum_{j=0}^{2i} a_{n,ij} = a_{n,i} \forall x$ . For linear molecules  $a_{n,ij} = 0$  for odd  $i$  as required for even Legendre polynomials. Rotation about  $\beta$  can also be expressed as an eigenvalue equation in analogy to Eq. 28 of Ref. [15] as

$$\begin{aligned} \mathcal{D}_\beta(x) P_{2i}(\cos \vartheta) = & R_{2i}(\beta, x) P_{2i}(\cos \vartheta) \quad \text{with} \\ R_{2i}(\beta, x) = & \frac{\sum_{j=0}^{2i} a_{n,ij}(x) \langle \cos^j \beta \rangle}{\sum_{j=0}^{2i} a_{n,ij}(x)}. \end{aligned} \quad (9)$$

$\mathcal{D}_\beta(x, n)$  is the operator for a rotation about  $\beta$  and dependent on the molecular shape defined by ratio of the moments of inertia  $x$ . The  $R_{2i}(\beta, x)$  are normalized by  $\sum_{j=0}^{2i} a_{n,ij}$  and turn out not to be dependent on  $n$ , even though the  $a_{n,ij}$  are. The  $R_i(\beta, x)$  are the general form for the Legendre and Jacobi polynomials in Eq. 28 of Ref. [15] and Eq. (3) now reads:

$$a_{n,i}(t, x) = a_{n,i}(0) R_{2i}(\beta(t), x), \quad (10)$$



**Figure 1.** Comparison of the  $a_{n,1,j}$  parameter for  $n = 1, 2$  in dependence of the shape of a symmetric top molecule defined by the rotational constants about the two axes of inertia,  $B_1$  and  $B_3$ .

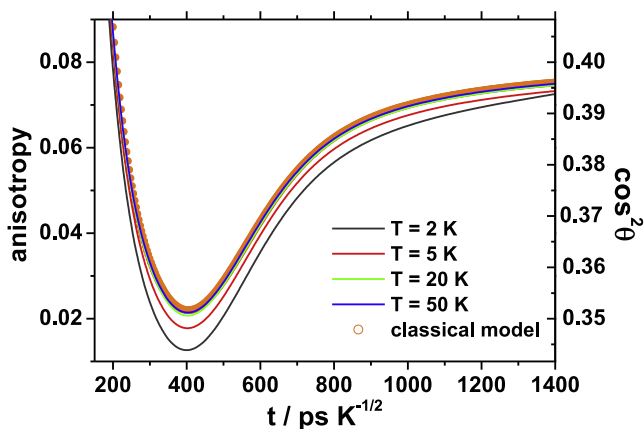
where the time dependence for the ensemble is given by

$$\beta(t) = \omega t \rightarrow \frac{\omega t}{(1 + (x^{-1} - 1)(\cos^2 \theta))^{1/2}} = \omega t \left( \frac{1}{3} (2 + x^{-1}) \right)^{-1/2}. \quad (11)$$

The transition dipole moment does not necessarily point in the same direction as the principle moment of inertia, but can lie perpendicular with respect to it. In true symmetric top molecules, the final state may be a degenerate state with transition dipole moments pointing along  $I_1$  and  $I_2$  which can lead to processes such as coherence decay and population transfer between these states [24,25] and can be included in the present ansatz [26]. However, the information obtained critically depends on the experiment and the applied conditions (e.g. the probe wavelength in transient absorption), where bleaching, excited state emission and excited state absorption already show a complicated behavior even without considering rotation. The effect on gaseous phase experiments will be shown in a later publication. In molecules with a lower symmetry, the transition dipole moment often points along an axis which is (nearly) perpendicular to the principal moment of inertia. We will discuss this more general case in Appendix B.

### 2.3. Validity of the model

It is evident that a classical model is only an approximation to a quantum mechanical treatment and is doomed to fail in describing coherent quantum effects such as alignment revivals which should be observed in the present case, provided the excited state lives long enough. However, regarding only the initial rotational dephasing, we can compare our classical solution with numeric quantum mechanical calculations. A simulation of the alignment/anisotropy for  $n = 1$  (and one photon probe in the case of anisotropy) is shown in Figure 2. We consider a spherical molecule with a moment of inertia of  $J = 6 \times 10^{-45}$  kg m<sup>2</sup> at different rotational temperatures ( $T = 2, 5, 20$ , and  $50$  K) for the quantum mechanical and the classical case. The quantum mechanical case was calculated with Eq. 29 from Ref. [15]. Plots of the anisotropy  $r = 1/5(3\cos^2\vartheta - 1)$  and the  $\cos^2\vartheta$ -distribution show that the classical model can be applied for a broad range of temperatures which are commonly achieved in molecular beam experiments where free rotation can be observed.



**Figure 2.** Comparison of the anisotropy/polarization of a spherical molecule with  $J = 6 \times 10^{-45}$  kg m<sup>2</sup> calculated with the classical ansatz and a quantum mechanical description.

### 2.4. Generalized $\mathcal{P}^{(n)}(\vartheta, \varphi, t)$ and frame transformations

In the literature on alignment and photoionization it is common to decompose  $\mathcal{P}^{(n)}(\vartheta, t)$  into a basis of spherical harmonics, as already shown in Eq. (1) for  $t = 0$ . Following this convention Eq. (8) can be rewritten as:

$$\mathcal{P}^{(n)}(\vartheta, \varphi, t) \propto \sum_{i=0}^n \sum_{q=-2i}^{2i} A_{2i,q}^{(n)}(t) Y_{2i,q}(\vartheta, \varphi), \quad (12)$$

The  $A_{2i,q}^{(n)}(t)$  are the  $n$ -photon, time dependent form of the  $A_{K,Q}$  axis distribution moments defined in Ref. [20] with  $2i \equiv K$  (hence only even  $K$  terms present, as appropriate for aligned, but unoriented, distributions) and  $q \equiv Q$ . In the simplest case where the pump and probe beam are parallel and cylindrical symmetry is not broken, only terms with  $q = 0$  are allowed:

$$A_{2i,q}^{(n)}(t) = \begin{cases} a_{n,i}(t) & q = 0 \\ 0 & q \neq 0 \end{cases}. \quad (13)$$

In this case there is no  $\varphi$  dependence of the distribution as  $Y_{2i,q=0}(\vartheta, \varphi) \propto P_{2i}(\cos\vartheta)$ .

In the general case  $\mathcal{P}^{(n)}(\vartheta, \varphi, t)$  may need to be transformed into a different reference frame. This is the case if the probe step involves a laser polarization which is not parallel to the pump step. Following Eq. (12), frame rotations can be written in terms of Wigner rotation matrix elements [27] which give the coefficients  $A_{2i,q'}^{(n)}(t)$  in the rotated frame defined by the Euler angles  $(\Phi, \Theta, \chi)$  [20]:

$$A_{2i,q'}^{(n)}(t) = \sum_q D_{q',q}^{2i}(\Phi, \Theta, \chi) A_{2i,q}^{(n)}(t). \quad (14)$$

This very general frame rotation can be applied as required to obtain  $\mathcal{P}^{(n)}(\vartheta, \varphi, t)$  in a given frame of reference.

## 3. Applications

### 3.1. Transient anisotropy

Transient anisotropy is defined as

$$r(t) = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}, \quad (15)$$

where

$$\begin{aligned} I_{\parallel} &= \langle \mathcal{P}^{(n)}(\vartheta, t, x) \cos^{2m} \vartheta \rangle_{\vartheta, \varphi} \\ I_{\perp} &= \langle \mathcal{P}^{(n)}(\vartheta, t, x) \sin^{2m} \vartheta \sin^{2m} \varphi \rangle_{\vartheta, \varphi} \end{aligned} \quad (16)$$

are integrated over a unit sphere and  $m$  is the number of probe photons.  $I$  can represent different observables such as the fluorescence yield in up-conversion experiments or excited state absorption, transient bleach or stimulated emission in transient absorption experiments. The result is [15]

$$r^{[n+m]}(t) = \frac{\sum_{i=0}^{\min(n,m)} a'_{n,i} \left( a'_{m,i} - \frac{(2m-1)!!}{(2m)!!} b'_{m,i} \right) R_{2i}(t, x)}{\sum_{j=0}^{\min(n,m)} a'_{n,i} \left( a'_{m,i} + 2 \frac{(2m-1)!!}{(2m)!!} b'_{m,i} \right) R_{2i}(t, x)} \quad (17)$$

where  $a'_{n,i} = \sqrt{\frac{2n+1}{2}} a_{n,i}$  and  $b'_{n,i} = \sqrt{\frac{2n+1}{2}} b_{n,i}$  with

$$b_{n,i} = \sum_{k=0}^n \binom{n}{k} (-1)^k a_{k,i} = (-1)^i \frac{\sqrt{4i+1} (2n)!! (2i-1)!! (2n)!!}{2^{n-1/2} i! (n-i)! (2n-1)!! (2n+2i+1)!!}. \quad (18)$$

$R_{2i}(t, x)$  is given by Eqs. (9) and (11). Eq. (17) is valid for the free rotation for a symmetric top molecule. Collision effects can be treated in the same way as described in Ref. [15].

### 3.2. Photoelectron angular distributions

As shown by Underwood and Reid [20], the lab frame (LF) PAD can be expressed as the convolution of  $\mathcal{P}^{(n)}(\vartheta, \varphi, t)$  with the molecular frame (MF) PAD. The  $\beta_{l,q}$  coefficients which parametrize the PAD are then given by:

$$\beta_{l,q}(t) = \sum_{i=0}^n A_{2i,q}^{(n)}(t) B_{l,2i,q}^{(m)}(t). \quad (19)$$

Here the  $\beta_{l,q}(t)$  are the expansion coefficients describing the PAD in a spherical harmonic basis, the  $A_{2i,q}^{(n)}(t)$  are the time-dependent axis distribution moments defined in Eq. (14), and the  $B_{l,2i,q}^{(m)}(t)$  describe the ionization dynamics for an  $m$ -photon ionization which, in turn, depend on the vibronic dynamics of the excited state [28], as well as the angular momentum coupling (including the polarization state of the ionizing radiation), and radial wavefunction overlap (for further discussion of the form of the  $B_{l,2i,q}^{(m)}(t)$  parameters see, for example, Refs. [5,8,20]). Hence the  $B_{l,2i,q}^{(m)}(t)$  can be considered as describing the MFPAD, and are convolved with the axis distribution moments to give the LFPAD. In the most general case the ionization dynamics are time-dependent, while in the case of purely rotational dynamics they are time-independent. The form of the  $B_{l,2i,q}^{(m)}(t)$  is quite complicated [5,20] and, although the angular momentum coupling can be calculated analytically, the full calculation of the  $\beta_{l,q}(t)$  requires the challenging *ab initio* computation of the radial part of

the ionization matrix elements; conversely, experimental  $\beta_{l,q}(t)$  combined with calculated  $A_{2i,q}^{(n)}(t)$  can provide a means to determine the ionization dynamics [4,29]. Even without knowledge of the  $B_{l,2i,q}^{(m)}(t)$ , deconvolution of the rotational and vibronic contributions to the measured  $\beta_{l,q}(t)$  provides insight into the vibronic dynamics of the excited state.

We show here model examples for one photon ionization of Rydberg orbitals following a one photon pump; the pump and probe pulses are parallel. Rydberg orbitals provide tractable model systems due to the small number of angular momentum components. Valence states can be treated with the same formalism, but require many more ionization matrix elements due to their more complicated angular momentum composition. The simplest case is ionization of an  $s$  Rydberg state, leading to only a  $p_z$  continuum state. Only a single ionization matrix element is required in this case. Ionization of a  $p_z$  Rydberg allows population of  $s$  and  $d_z$  continuum states, and the form of the PAD is determined by the phase difference between the  $s$  and  $d_z$  waves. Figure 3 shows these examples, in all cases the angular momentum coupling is calculated analytically (see Ref. [5], Eq. 45) and all the required radial ionization matrix elements have been set to unity. It is immediately clear that all the  $\beta_{l,q}$  respond to the alignment parameter  $A_{2,0}^{(n)}(t)$ , but the magnitude of this response is very different for the example cases shown here (note the different scales on Figure 3a and b). This reflects the changing sensitivity of the ionization to alignment, according to the  $B_{l,2i,q}^{(m)}(t)$ . The changes may be in-phase with the degree of alignment, for instance the  $\beta_{2,0}(t)$  in Figure 3a, or out-of-phase as shown by the  $\beta_{2,0}(t)$  in Figure 3b. Such effects have been experimentally observed, and also calculated using numerical methods, by Suzuki et al. for the case of picosecond photoelectron imaging of Rydberg states in pyrazine [29,30]. With knowledge of the radial part of the ionization dipole moments for ionization of pyrazine via the  $3s$  and  $3p$  Rydberg states, these results could be directly compared with those of Suzuki et al. Even without this knowledge, we see that the trends in the  $B_{l,2i,q}^{(m)}(t)$  agree well with their observations.

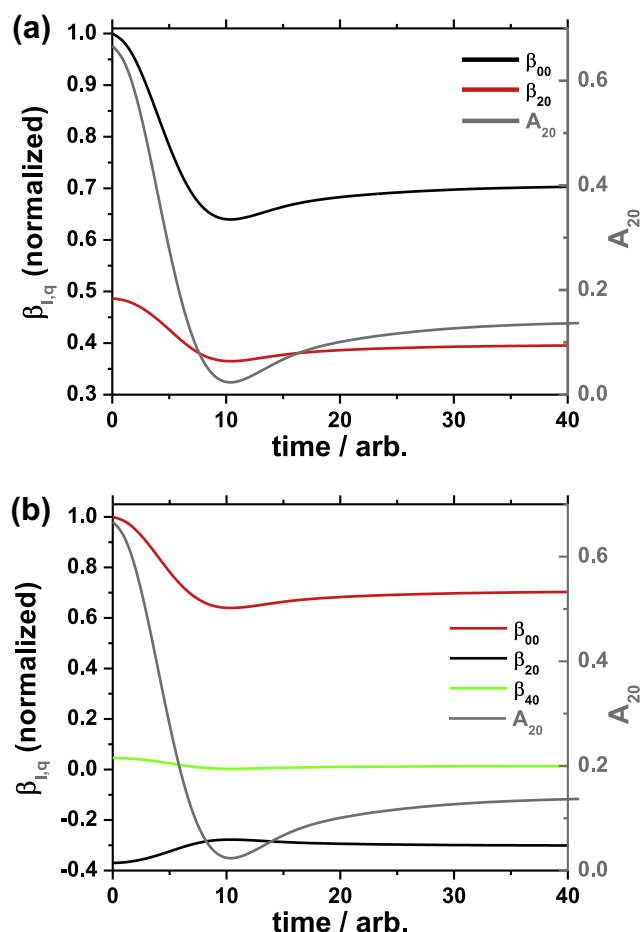
### 4. Conclusion

In conclusion, we have presented an analytic expression for reorientational dynamics of an ensemble of symmetric top molecules excited by one or more photons. Moreover, we have shown that this result is in line with expectations from existing work [4,9,15], but without the need for numerical methods in the solution of  $a_{n,i}(x, t)$ .

Our methodology can be used to treat the more complex case of ionization by convolving  $a_{n,i}(x, t)$  with the ionization dynamics. Our model results for Rydberg orbital ionization show good agreement with existing angle-resolved measurements and numerical calculations. Furthermore, by allowing for frame rotations between pump and probe steps, our formalism suggests the possibility of transient anisotropy measurements in angle-integrated ionization experiments. Such measurements, analogous to the existing transient anisotropy measurements mentioned in Section 3.1, could be obtained by recording time-resolved photoelectron spectra (TRPES) for two orthogonal polarization geometries. The additional information provided could be sufficient to uniquely assign the electronic character of states giving rise to different bands in the TRPES, which is often not possible from data recorded at a single polarization geometry.

### Acknowledgment

O.S. thanks the Humboldt Foundation for financial support.



**Figure 3.** (a)  $\beta_{l,q}$  and for  $s \rightarrow p_z$  ionization. (b)  $\beta_{l,q}$  and for  $p_z \rightarrow s + d_z$  ionization. In both cases the alignment parameter  $A_{2,0}^{(1)}$  (1-photon pump process) is shown.

## Appendix A. Two photon excitation

The parameters for the two photon excitations are

$$\begin{aligned}
 a_{2,0,0} &= \frac{1}{5} \\
 a_{2,1,0} &= \frac{\sqrt{x-1}(4+7x-2x^2) - 9\sqrt{x}\operatorname{arcsinh}(\sqrt{x-1})}{7(x-1)^{5/2}} \\
 a_{2,1,1} &= \frac{-18x\sqrt{x-1} - 6\sqrt{x}(2x+1)\operatorname{arcsinh}(\sqrt{x-1})}{7(x-1)^{5/2}} \\
 a_{2,1,2} &= \frac{3x\sqrt{x-1}(2x+1) - 3\sqrt{x}(4x-1)\operatorname{arcsinh}(\sqrt{x-1})}{7(x-1)^{5/2}} \\
 a_{2,2,0} &= \frac{1}{1680(x-1)^5} \left( (144x^5 - 1160x^4 + 550x^3 + 5095x^2 - 4245x - 384) + 105\sqrt{x(1-x)}(4x^3 + 18x^2 + 12x + 1) \arccos(\sqrt{x}) + 30\sqrt{-x(x-1)^3}(14x^2 + 149x + 47)\operatorname{arcsinh}(\sqrt{x-1}) \right) \\
 a_{2,2,1} &= \frac{1}{84(x-1)^5} \left( (x(x-1)(244x^2 - 628x - 351)) - 21\sqrt{x(1-x)}(4x^3 + 18x^2 + 12x + 1) \arccos(\sqrt{x}) - 6\sqrt{x(x-1)^3}(38x^2 + 65x + 2)\operatorname{arcsinh}(\sqrt{x-1}) \right) \\
 a_{2,2,2} &= \frac{1}{56(x-1)^5} \left( (x(x-1)(48x^3 - 128x^2 - 658x + 48)) - 3\sqrt{x(1-x)}(4x^3 + 18x^2 + 12x + 1) \arccos(\sqrt{x}) - 18\sqrt{x(x-1)^5}(10x + 1)\operatorname{arcsinh}(\sqrt{x-1}) \right) \\
 a_{2,2,3} &= \frac{1}{12(x-1)^5} \left( (x(x-1)(92x^2 + 16x - 3)) + 3\sqrt{x(1-x)}(4x^3 + 18x^2 + 12x + 1) \arccos(\sqrt{x}) - 18x\sqrt{x(x-1)}(2x^2 + x - 3)\operatorname{arcsinh}(\sqrt{x-1}) \right) \\
 a_{2,2,4} &= \frac{1}{48(x-1)^5} \left( (x(x-1)(48x^3 + 104x^2 - 62x + 15)) + \sqrt{x(1-x)}(4x^3 + 18x^2 + 12x + 1) \arccos(\sqrt{x}) + 18\sqrt{x(x-1)}(-10x^3 + 11x^2 - 2x + 1)\operatorname{arcsinh}(\sqrt{x-1}) \right)
 \end{aligned}
 \tag{A.1}$$

## Appendix B. Excitation perpendicular to the principal moment of inertia

Calculating the  $\mathcal{P}(\vartheta, t)$  for a transition dipole moment perpendicular to the principal axis of inertia (for example the  $y$ -axis) requires transformation of the probability in Eq. (6). This probability can be calculated analogously to the case of parallel transition moments via [15,23]

$$\begin{aligned}
 \mathcal{P}_{\perp}(\vartheta, \varphi) &= \int_0^{\infty} dj \frac{2j}{Q} \exp \left\{ -\frac{j^2}{k_B T} \left[ B_1 \cos^2 \vartheta_{\perp} + \sin^2 \vartheta_{\perp} (B_1 \cos^2 \varphi_{\perp} + B_3 \sin^2 \varphi_{\perp}) \right] \right\} \\
 &= \frac{\sqrt{x}}{2 \left( \cos^2 \vartheta_{\perp} + \sin^2 \vartheta_{\perp} (x \sin^2 \varphi_{\perp} + \cos^2 \varphi_{\perp}) \right)^{3/2}}.
 \end{aligned}
 \tag{B.1}$$

$Q = (\pi k_B^3 T^3 / B_1^2 B_3)^{1/2}$  is the rotational partition function and  $B_i = 1/J_i$ . The angle  $\vartheta_{\perp}$  is now the angle between the  $y$ -axis and the rotational axis and the integration has to be performed including  $\vartheta_{\perp}$  and  $\varphi_{\perp}$ . Unfortunately, no analytical solution could be found in this case.

## References

[1] G.R. Fleming, Chem. Appl. Ultrafast Spectroscopy (1986).

[2] A. Kowski, Crit. Rev. Anal. Chem. 23 (1993) 459.  
 [3] Y. Suzuki, T. Seideman, J. Chem. Phys. 122 (2005) 234302.  
 [4] T. Suzuki, Annu. Rev. Phys. Chem. 57 (2006) 555.  
 [5] A. Stolow, J.G. Underwood, Adv. Chem. Phys. 113 (2008) 497.  
 [6] C.Z. Bisgaard, O.J. Clarkin, G. Wu, A.M.D. Lee, O. Geßner, C.C. Hayden, A. Stolow, Science 323 (2009) 1464.  
 [7] J. Cooper, R.N. Zare, J. Chem. Phys. 48 (1968) 942.  
 [8] D. Dill, J. Chem. Phys. 65 (1976) 1130.  
 [9] K.L. Reid, J.G. Underwood, J. Chem. Phys. 112 (2000) 3643.  
 [10] K.L. Reid, Annu. Rev. Phys. Chem. 54 (2003) 397.  
 [11] T. Seideman, Annu. Rev. Phys. Chem. 53 (2002) 41.  
 [12] P.M. Felker, A.H. Zewail, J. Chem. Phys. 86 (1987) 2460.  
 [13] J.S. Baskin, M. Chachisvilis, M. Gupta, A.H. Zewail, J. Phys. Chem. A 102 (1998) 4158.  
 [14] V.M.F. Gelin, J. Phys. Chem. A 104 (2000) 6150.  
 [15] O. Schalk, A.N. Unterreiner, Phys. Chem. Chem. Phys. 12 (2010) 655.  
 [16] N.F. Scherer, J.F. Shepanski, A.H. Zewail, J. Chem. Phys. 81 (1984) 2181.  
 [17] Y.J. Lee, S.H. Cho, N.J. Kim, S.K. Kim, J. Chem. Phys. 115 (2001) 739.  
 [18] S. Sato, Y. Fujimura, Chem. Phys. Lett. 140 (1987) 169.  
 [19] R.C. Jones, J. Opt. Soc. Am. 31 (1941) 488.  
 [20] J.G. Underwood, K.L. Reid, J. Chem. Phys. 113 (2000) 1067.  
 [21] R.G. Gordon, J. Chem. Phys. 43 (1965) 1307.  
 [22] J.F. Cornwell, Group Theory in Physics I and II, Academic Press, London, 1984.  
 [23] G.M. Nathanson, G.M. McClelland, J. Chem. Phys. 81 (1984) 629.  
 [24] K. Wynne, R.M. Hochstrasser, Chem. Phys. 171 (1993) 179.  
 [25] D.A. Farrow, W. Qian, E.R. Smith, A.A. Ferro, D.M. Jonas, J. Chem. Phys. 129 (2008) 174509.  
 [26] O. Schalk, A.-N. Unterreiner, Z. Phys. Chem. 225 (2011) 927.  
 [27] R.N. Zare, Angular Momentum, Wiley, New York, 1988.  
 [28] P. Hockett, C.Z. Bisgaard, O.J. Clarkin, A. Stolow, Nature Phys. 7 (2011) 612.  
 [29] T. Suzuki, L. Wang, M. Tsubouchi, J. Phys. Chem. A 108 (2004) 5764.  
 [30] M. Tsubouchi, B.J. Whitaker, T. Suzuki, J. Phys. Chem. A 108 (2004) 6823.