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The quantitative determination of laser-induced molecular axis alignment

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Experiments in the gas phase usually involve averaging observables over a random molecular axis alignment distribution. This deleterious averaging limits insights gained by probes of molecular dynamics, but can be overcome by prealigning molecular axes using laser-alignment methods. However, the transformation from the laboratory frame to the molecular frame of reference requires quantitative knowledge of the axis alignment distribution. The latter is often hard to obtain directly from experimental data, particularly for polyatomic molecules. Here we describe a general maximum-likelihood classification procedure for non-adiabatic numerical alignment simulations with free parameters that employs experimental data from an alignment-dependent probe. This method delivers (i) the most probable molecular frame angular dependence of the probe, and (ii) the most likely laboratory frame axis alignment distribution of the sample, each with a confidence interval. This procedure was recently used for studies of angle- and channel-resolved strong field ionization of 1,3-butadiene in the molecular frame [Mikosch *et al.*, Phys. Rev. Lett. **110**, 023004 (2013)], used here as an illustrative example. [http://dx.doi.org/10.1063/1.4812787]

I. INTRODUCTION

The transient axis alignment of molecules using strong adiabatic and/or non-adiabatic laser fields¹ has evolved into a technique which enables dynamical investigations in the molecular frame of reference. For ultrafast pump-probe studies, molecular alignment helps overcome one of the dominant limitations of gas phase laboratory frame observables: the angular averaging over an isotropic axis distribution. The most detailed dynamical information on molecular processes is obtained from the molecular frame of reference, which is defined by the principal axes of the inertia tensor of the molecule. Experiments in the molecular frame include the control of photodissociation branching ratios,² the determination of photoelectron angular distributions of dissociating^{3,4} and spinning⁵ molecules, the manipulation of the internal torsion in a molecule,⁶ and strong-field molecular orbital "tomography" via High Harmonic Generation (HHG),⁷ Laser-Induced Electron Diffraction (LIED),^{8–10} and (channel-resolved) Strong Field Ionization (SFI).^{11–13}

Despite the fact that state-selection of molecules has led to impressive degrees of laser-induced alignment and orientation,¹⁴ the axis alignment of molecules achieved in experiments is generally not perfect. Lab frame observations involving non-perfectly aligned samples of molecules require deconvolution of any molecular frame property: this involves detailed knowledge of the axis alignment distribution. Imaging the fragments from Coulomb explosion induced by ultrashort laser pulses or from photodissociation was used to retrieve the alignment distribution directly.¹ However, this method is only applicable in specific cases where the axial recoil approximation holds. Hence, very often it is numerical simulations of the alignment distribution which are invoked. These, in turn, depend very sensitively on critical experimental input parameters which are often not precisely known, for example the rotational temperature and the alignment laser intensity. Invoking numerical simulations is particularly useful for non-adiabatic alignment, where the form of the rotational revival structure changes strongly as a function of the input parameters. The comparison of experimentally measured with simulated revival structures may then be used to estimate the degree of alignment. Extracting the degree of alignment becomes straightforward if the molecular axis alignment dependence of the selected experimental probe is known in detail.^{3,15} Unfortunately, this is often not known *a priori*. In fact, this is, ironically, often itself the subject of the investigation involving molecular alignment.

Here we describe a quantitative self-consistent procedure which ranks the likelihood of non-adiabatic alignment simulations to reproduce the true axis alignment distribution of a molecular sample. Experimental input from an alignmentsensitive probe is required as the maximum-likelihood predictor. Importantly, the alignment dependence of the probe does not have to be known a priori, but is in fact derived as well by our method. This procedure is most useful if the simulation is expected to describe the alignment dynamics well, but key input parameters are unknown. Our procedure yields (i) the most probable angular dependence of the probe in the molecular frame, which is an intrinsic property of the molecule studied, and (ii) the most probable axis alignment distribution, which is a property of the molecular ensemble prepared in the experiment. Importantly, statistical confidence intervals are identified for both. We recently used this procedure to determine the Molecular Frame Channel-resolved Angular Ionization Probability (MF-CAIP) of 1,3-butadiene.¹³ Here we

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provide the details of this method. While we focus here on a procedure using SFI in a linearly polarized laser field as an example, we emphasize that our method is generally applicable to any probe technique that features an angular sensitivity in the molecular frame.

In our example, we employed laser-induced nonadiabatic one-dimensional axis alignment of gas-phase 1,3butadiene. Here, a symmetric top numerical alignment simulation is expected to describe the alignment dynamics.¹³ Unfortunately, two key input parameters — the rotational temperature and the exact alignment laser intensity — were not precisely known. Although there are many observables which are in principle sensitive to the molecular axis distribution, we will concentrate here on a specific SFI method. This allows us to independently confirm the accuracy of our procedure, as discussed in the following. The Channel-Resolved Above Threshold Ionization (CRATI) method recently showed that both the D_0 and the D_1 ionization continua contribute to SFI in 1,3-butadiene and that these two continuum channels can be separated:¹⁶ The parent ion $C_4H_6^+$ is associated with direct ionization to the D₀ ground state of the cation, whereas the $C_4H_5^+$ and $C_3H_3^+$ fragments derive from direct ionization to the electronically excited D₁ cation state (see Fig. 1 of Ref. 16). At the intensity of 2.0×10^{13} W/cm² employed throughout this work, the relative D₁ contribution linked to the $C_4H_5^+$ and $C_3H_3^+$ fragments is 5% on the scale of the total ionization yield. Using the fact that the axis alignment distribution is independent of the SFI channel, we were able to confirm the accuracy of our procedure. We anticipate that this method will be of use to researchers using field-free alignment methods to enhance the information content of ultrafast measurements.

II. EXPERIMENT

For SFI, we used laser pulses at a center wavelength of $\lambda_e = 795.5$ nm from a Titanium:Sapphire (Ti:Sa) regenerative amplifier (Legend Elite, Coherent), focused to a focal spot size of around $\omega_0^e = 40 \ \mu m$. The interaction-region pulse duration was 40(5) fs (FWHM) as determined by singleshot autocorrelation.¹⁷ To create the non-adiabatic alignment field, we focused idler pulses from a white-light seeded optical parametric amplifier (TOPAS-HE, Light Conversion) at $\lambda_p = 2100$ nm to a focal spot size of around $\omega_0^p = 120 \ \mu$ m. The alignment laser pulse was temporally stretched to an interaction-region pulse duration of $\tau = 285(30)$ fs (FWHM) by two oppositely oriented 13 mm thick Fused Silica wedges (5') at an angle close to Brewster's angle (55°) . The idler pulse duration was determined via cross-correlation with a 35 fs (FWHM) duration 795.5 nm pulse from the Ti:Sa amplifier, using a thin (50 μ m) β -Barium borate (BBO) crystal for frequency mixing. The time delay between the alignment (pump) pulse and the SFI (probe) pulse was varied by a computercontrolled delay stage. The polarization of both laser pulses was linear.

The laser pulses were recombined using a 1/8'' thick 0° high reflector for 800 nm (CVI, CaF₂ window substrate) with the idler beam being transmitted. The recombined laser pulses were focused by a 50 cm focal length spherical con-

cave gold mirror and overlapped in space in the source region of a photoelectron photoion coincidence (PEPICO) spectrometer, where they crossed a tightly skimmed molecular beam. Laser propagation, spectrometer time-of-flight axes and the molecular beam direction were mutually orthogonal. Photoions and -electrons were extracted in opposite directions into the PEPICO spectrometer that features a wide-bore magnetic bottle for electron kinetic energy determination, and a coaxial mass spectrometer. Photoion mass and photoelectron kinetic energy were determined from the respective time-offlights. The start signal for the multiple-event time-to-digital converter (FAST ComTec, Model P7888) was provided by detecting the laser pulse on a fast photodiode, while the stop signals were provided by detection of individual photoions and -electrons at collection-anode triple stack micro channel plate (MCP) detectors terminating the respective timeof-flight tubes. The molecular beam was a doubly-skimmed, pulsed supersonic expansion of seeded helium originating from an Even-Lavie valve.¹⁸ We used a backing pressure of 40 bar and a low seeding ratio of 1,3-butadiene of 0.01% to ensure good rotational cooling. The repetition rate of the experiment was 1 kHz.

There are two types of intensity averaging in this experiment which require minimization. First, SFI can occur at a range of intensities within the probe laser focal volume, both spatially and temporally. This leads to averaging over different intensity dependent branching ratios in SFI to the ionic ground and excited states. Further averaging occurs over different ponderomotive potentials and Stark-shifts, with the associated reduction of contrast being a typical concern in strong field measurements. For example, in our experiments these effects reduce the modulation depth in the observed ATI photoelectron spectra. Here we minimized intensity averaging by studying SFI at threshold intensities and by implementing a constant axial intensity geometry. The latter was achieved by combining loose focusing conditions (Rayleigh range of about 1.6 mm for $\lambda_e = 795.5$ nm) with tight skimming of the molecular beam, to about 1 mm diameter at the laser axis intersection.

Second, the SFI probe will spatially average over different molecular axis alignment distributions, since these depend very sensitively on the alignment laser intensity. To minimize this type of intensity averaging in the radial direction, we chose a large mismatch in focal spot sizes for the alignment (pump) and the SFI (probe) beams as described above. To minimize this type of intensity averaging in the longitudinal direction, we chose a large mismatch in Rayleigh ranges of 5.5 mm for the alignment beam and 1.6 mm for the SFI beam.

The polarization of the ionizing field was kept parallel to the spectrometer axis in order to avoid possible systematic artefacts due to the collection efficiency of the spectrometers that might depend on the lab-frame recoil direction of the photoelectrons and -fragments. Therefore, to obtain angleresolved information, we rotated the polarization of the alignment field using an achromatic half-waveplate (New Light Photonics) in a computer-controlled rotation stage (Newport). The polarization rotation was monitored by a Glan-Taylor polarizer (Melles Griot) and a computer read-out power head

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(Ophir). Exact parallel polarization of the pump and probe pulses in the interaction region was ultimately determined from the shape of the measured angular ionization yield (see below).

A. Pump probe delay scan

In Fig. 1, we show the average $C_4H_6^+$ parent ion (upper panel) and the average cumulated C3H3+/C4H5+ fragment ion (lower panel) yield per laser shot as a function of time delay between the alignment (pump) pulse and the SFI (probe) pulse. Data are shown around the time of the rotational half-revival where the peak alignment is achieved for 1,3-butadiene. The intensity of 4.0×10^{12} W/cm² of the alignment field was optimized for maximum contrast in the pumpprobe delay scan. As described in Sec. IV, this ensured that we operated in a regime where the symmetric top approximation holds for 1,3-butadiene. The angle between the linear polarizations of the pump and the probe laser was $\alpha'_t = 7^\circ$. As discussed below, choosing a non-zero angle is useful for the maximum-likelihood classification procedure. The data shown are the sum of three consecutive scans in which the delay was increased monotonically in 100 fs increments. Overall, data from 9000 laser shots were recorded at each time delay. At each time-increment, the signal arising from both laser pulses, and from the pump and probe pulses alone, was measured. While no significant signal arose from the alignment (pump) pulse alone, the average signal from the SFI (probe) pulse amounted to 0.405 parent ions $(C_4H_6^+)$ and 0.020 frag-



ment ions $(C_3H_3^+ \text{ and } C_4H_5^+)$ per laser shot. This was less than the pump-probe yield at time delays away from the revival (see Fig. 1), indicating that a time-independent alignment component was achieved. The probe signal alone ---which should be time-independent — showed a slight linear increase of around 3% over the [45, 72] ps time interval of the half-revival. We attribute this to a drift in the laser conditions over the time of the measurement. In an attempt to correct it, we performed a linear fit on the probe-only signal and applied it as correction to the pump-probe data shown in Fig. 1. Error bars represent a statistical error of $\pm 1 \sigma$, where the standard deviation σ is given by the square root of the number of respective ion counts detected for each measurement point, normalized by the number of laser shots. The peak alignment for 1,3-butadiene was achieved at time $t_a = 58.0$ ps following the alignment laser pulse.

At higher alignment pulse energy, but still below the ionization threshold, we observe a change in the revival structure as compared to Fig. 1 (see the supplementary material of Ref. 13). This most likely indicates a transition from J-type revivals to C-type revivals and is typical for near symmetric top molecules such as 1,3-butadiene when higher alignment fluences are implemented^{19,20} (see also the discussion in Sec. IV).

B. Angular ionization yield

In Fig. 2, we show the relative angular ionization yield $M(\alpha', t = t_a)$ for the parent ion $C_4H_6^+$ (black) and the fragment ions $C_3H_3^+$ (red) and $C_4H_5^+$ (green). The measurement



FIG. 2. Relative angular SFI yield $M(\alpha', t = t_a)$ for the parent ion (D₀ ionic continuum) shown in black and the fragment ions $C_3H_3^+$ and $C_4H_5^+$ (D₁ ionic continuum) shown in red and green, respectively, measured at the time of maximum alignment at a pump-probe time delay of $t_a = 58.0$ ps. Statistical error bars are within the marker size and the solid lines represent fits following Eq. (2). Reprinted with permission from Mikosch *et al.*, Phys. Rev. Lett. **110**, 023004 (2013). Copyright 2013 American Physical Society.

was performed at the maximum alignment of the molecular sample, at a time delay of $t_a = 58.0$ ps between the alignment pulse and the ionization pulse at the alignment laser conditions described above. The α' is the lab-frame angle between the polarization axes of the linearly polarized SFI and alignment fields, where the latter also represents the main axis of the alignment distribution. To reduce sensitivities to possible small drifts in laser conditions, we performed many short consecutive scans, for which the relative polarization direction was rotated from 7° to 187° and back in 10° increments. The data shown in Fig. 2 incorporate a total of 1.3×10^6 laser shots at each polarization angle. Parallel relative polarization was determined from the inherent up-down symmetry axis of the measured angular ionization yield for the aligned molecular sample. Error bars representing a statistical error of $\pm 1 \sigma$ were derived from the number of respective ion counts detected: these are within the size of the markers in Fig. 2 for both the parent and the fragment ions. As can be seen, the difference in the angular ionization yield distribution is negligible for the two fragment ions $C_3H_3^+$ and $C_4H_5^+$. This is expected since they are both associated with the D₁ cation excited state SFI channel. However, the angular ionization yield distribution is significantly different for the C₄H₆⁺ parent ion associated with the D₀ cation ground state SFI channel. The difference between the two SFI channels is plotted in Fig. 3 of our previous study.¹³



FIG. 3. Laboratory frame and molecular frame. Axes and angles in the lab frame are labeled with a prime, the molecular frame axes and angles (in grey) are unprimed. In the one-dimensional alignment achieved here, the polar angle θ' was constrained whereas the azimuthal angle ϕ' (see inset) was random. The angle α' between the polarization vectors of the alignment (blue) and ionization (red) laser fields was varied in the experiment. θ' is the polar Euler angle between the lab- and the molecular-fixed z-axes and X is the azimuthal angle of rotation about the molecular-fixed z-axis (see inset).

III. LABORATORY FRAME AND MOLECULAR FRAME

The frame deconvolution problem is depicted in Fig. 3. We use primed variables for the laboratory frame and unprimed variables for the molecular frame. In the experiment, we measured, in the laboratory frame, the relative angular ionization yield $M(\alpha', t = t_a)$ of a non-perfectly aligned molecular sample at the peak alignment, as described in Sec. II. Here we only achieved one-dimensional alignment in the lab frame, i.e., the polar angle θ' was constrained whereas the azimuthal angle ϕ' was random. The polarization of the alignment pulse, by convention along the z'-axis, constitutes the main axis of the alignment distribution. The alignment distribution $A(\theta', \phi', t)$ of the sample is therefore cylindrically symmetric around this axis, i.e.,

$$A\left(\theta',\phi',t\right) = A\left(\theta',t\right)/2\pi.$$

We seek to extract $S(\theta)$, the θ (polar angle) dependent, ϕ (azimuthal angle) averaged MF-CAIP. The molecular frame angle θ is defined with respect to the molecule's axis of maximum polarizability and the principal axis with the lowest moment of inertia (the z-axis). These coincide within the symmetric top approximation of 1,3-butadiene (see Sec. IV). The fact that we retrieve azimuthal angle-averaged molecular frame information originates from the one-dimensional lab frame alignment achieved here. The time-dependent observable $M(\alpha', t)$ is the convolution of the time-independent molecular quantity $S(\theta)$ with the time-dependent lab frame alignment distribution $A(\theta', t)^{11}$

$$M(\alpha', t) = \frac{1}{8\pi^2} \int_0^{2\pi} d\phi' \int_0^{\pi} d\theta' S\left[\theta\left(\theta', \phi'; \alpha'\right)\right] \\ \times A(\theta', t) \sin(\theta'), \tag{1}$$

where the molecular frame angle θ is given by¹¹

 $\cos\theta = \cos\alpha' \cos\theta' - \sin\alpha' \sin\theta' \sin\phi'.$

IV. ALIGNMENT SIMULATIONS

Rotational constants and polarizability components for 1,3-butadiene are given in Table I, as previously derived from electronic structure calculations.¹³ The polarizabilities are given in the same frame as the inertia tensor. Since the inertia asymmetry parameter $\kappa = (2B - A - C)/(A - C)$

TABLE I. Rotational constants (in GHz) and polarizabilities (in $Å^3$) for 1,3-butadiene and the symmetric top approximation used in the numerical alignment simulations. The values are derived from electronic structure calculations.¹³

1,3-butadiene		Symmetric top approximation	
A	41.05	Ã	41.05
В	4.34	$ ilde{B}$	4.20
С	3.93		
$\alpha_{\rm XX}$	5.51		
$\alpha_{\rm YY}$	6.88	$lpha_{\perp}$	6.20
α _{ZZ}	12.20	$lpha_{\parallel}$	12.20

= -0.978 is close to the prolate limit of -1, a symmetric top approximation with rotational constants of $\tilde{A} = A$ and the intermediate *B/C* value of $\tilde{B} = 4.2$ GHz was used in the alignment simulations (see Table I). For the polarizabilities, we used $\alpha_{\parallel} = \alpha_{ZZ}$ and the arithmetic mean of α_{XX} and α_{YY} as the perpendicular polarizability α_{\perp} , since this conserves the isotropic polarizability. The symmetric top approximation implies that the orientation of the principal axes of inertia and polarizability tensors cannot be distinguished.

We used a code for the numerical simulation of impulsive alignment of symmetric-top molecules developed by Bisgaard and Stapelfeldt.²¹ It delivers the polar angle-dependent azimuthal angle-averaged axis alignment distribution $A(\theta', t)$ in the lab frame as a function of time *t* after the alignment pulse. Briefly, the time-dependent Schrödinger equation is solved numerically during the interaction of the molecules with the alignment laser pulse. The Hamiltonian is comprised of the interaction of the laser field with the molecular polarizability and the field-free rotation of the molecule. The unknown wave function is written as an expansion in the field-free eigenstates of the symmetric top. This ansatz is inserted into the timedependent Schrödinger equation. Projection onto the eigenstates results in a set of coupled, linear, and first order differential equations. The expansion coefficients in the wave function ansatz are then determined from numerical solution of this set of coupled equations. After the interaction with the laser pulse, the wave packet is subject to straightforward fieldfree evolution. The angular distribution $A(\theta', t)$ may then be expressed in terms of the expansion coefficients and Wigner's reduced rotation matrix. For further details, see Ref. 21.

The input parameters for the alignment simulation include the molecular parameters given in Table I (symmetric top approximation). Strictly, dynamic polarizabilities at the wavelength of the alignment laser are required, rather than the static values of Table I. However, since 1,3-butadiene does not exhibit any significant absorption to the red of about $\lambda = 230 \text{ nm}$,²² the dynamic polarizabilities at $\lambda_p = 2100 \text{ nm}$ are expected to be very close to the static values. We confirmed this with a polarizability calculation at $\lambda = 800$ nm.¹³ Therefore, static polarizabilities were used in the simulation. The temporal width of the alignment pulse was fixed to the experimentally measured alignment laser pulse duration τ (see Sec. II). Spatial intensity averaging was taken into account in the numerical simulations by assuming a uniform axial intensity distribution and a Gaussian radial intensity distribution for both the alignment and probe laser beams. For the alignment beam, the radial direction was uniformly discretized into 30 sections. Over each radial section, the laser intensity was assumed to be constant at the value of the intensity Gaussian at the center of the respective section. The alignment dynamics were calculated separately for each section before all radial contributions were incoherently averaged. The respective weight of each contribution in the averaging is given by the relative volume of each section, multiplied by the relative probe efficiency determined at the center of each section. Since SFI is an extremely nonlinear process, the relative probe efficiency should scale like a Gaussian having a width significantly reduced from that of the probe laser's radial intensity distribution. Since SFI is not in general a perturbative N-photon transition, one should ideally convolute the radial intensity distribution with a suitable ionization model such as the basic Molecular Ammosov-Delone-Krainov (MO-ADK) theory²³ or the advanced numerical Time-Dependent Resolution-in-Ionic-States (TD-RIS) treatment.²⁴ However, in our experiment, the focal spot size of the SFI probe pulse ω_0^e was deliberately chosen to be a factor of three smaller than that of the alignment pump pulse ω_0^p to minimize the effect of intensity averaging (see Sec. II). Therefore, for simplicity, we used a Gaussian that corresponds to the focal spot size ω_0^e to describe the relative probe efficiency. While we note that this will slightly overestimate the effects of intensity averaging in the simulation, the exact geometry is not critical due to the large mismatch of ω_0^p and ω_0^e . We have confirmed this by alignment simulations.

The remaining input parameters are the rotational temperature T and the alignment intensity I. The degree of alignment depends very sensitively on these two parameters. Unfortunately, they are hard to accurately determine in the experiment. Furthermore, the alignment intensity has traditionally been used as an adjustable parameter in the comparison of alignment simulations with experimental data.²¹ In the following, we will treat the rotational temperature T and the alignment intensity I as free input parameters.

The interaction potential V_{at} for an asymmetric top molecule with an electric field E_0 linearly polarized along the lab-frame's z-axis is given by¹

$$V_{\text{at}} = -\frac{E_0^2}{4} [\sin^2 \theta' ((\alpha_{\perp} + \beta) \cos^2 X + (\alpha_{\perp} - \beta) \sin^2 X) + \alpha_{\parallel} \cos^2 \theta']$$

where β is defined through the relations $\alpha_{XX} = \alpha_{\perp} + \beta$ and $\alpha_{YY} = \alpha_{\perp} - \beta$. As shown in the inset to Fig. 3, θ' is the polar Euler angle between the lab- and the molecular-fixed z-axes and *X* is the azimuthal angle of rotation about the molecular-fixed z-axis. Thus, the asymmetric top interaction potential V_{at} can be expressed as

where

$$V_{\rm st} = -\frac{E_0^2}{4} \left[\Delta \alpha \, \cos^2 \! \theta' + \alpha_\perp \right]$$

 $V_{\rm at} = V_{\rm st} + V_{\rm p},$

is the symmetric top interaction potential, and

$$V_{\rm p} = -\beta \frac{E_0^2}{4} \left[\sin^2 \theta' \left(\cos^2 X - \sin^2 X \right) \right]$$

is a perturbation to the symmetric top potential arising from the two different perpendicular polarizabilities. The perturbation V_p has a relative magnitude on the order of $\beta/\Delta\alpha$ compared to $V_{\rm st}$ and equals 0.11 for the case of 1,3-butadiene considered here.

The fluence in the present experiment was much lower than the critical value, for which Holmegaard *et al.* previously observed a transition from symmetric top *J*-type revivals to asymmetric top *C*-type revivals in non-adiabatic alignment experiments on the near symmetric top molecule iodobenzene²⁰ (see the supplementary material of Ref. 13). In addition, 1,3-butadiene is considerably less asymmetric in



FIG. 4. Simulated expectation values $\langle \cos^2(\theta') \rangle$ up to the first full revival (upper panel) and full axis alignment distributions around the first half-revival (lower panel) for 1,3-butadiene within the symmetric top approximation. The rotational temperature and alignment intensity are T = 1.75 K and I = 2.375×10^{12} W/cm², respectively.

both its inertia and polarizability tensor than is iodobenzene. While this gives confidence that the measured SFI yield time trace (Fig. 1) can be well described by our alignment simulation which ignores the asymmetric top perturbation V_p , it cautions that small systematic errors might be expected when comparing the simulation to the experiment (see below).

First, a couple of exploratory simulations were carried out to determine the approximate values needed to reproduce the experimental observations. Detailed simulations were then carried out to tightly sample the two-dimensional range given by T = [0.5, 5] K and I = $[1.5, 3.5] \times 10^{12}$ W/cm². In total, n = 169 sets of input parameters {T, I}_i were used. For each set $A_i(\theta', t)$, the lab-frame alignment distribution as a function of time t after the alignment laser pulse was obtained in the interval t = [44, 73] ps (step size 100 fs). An example is plotted in the lower section of Fig. 4; the parameters are $T = 1.75 \text{ K}, I = 2.375 \times 10^{12} \text{ W/cm}^2$. The maximum alignment near the half-revival is marked by a high probability for θ' values around 0 and π with a low probability for θ' values around 0.5. This appeared close to a time delay of 59 ps. The maximum alignment is followed by the anti-alignment at around 62 ps, that shows a low probability for θ' around 0 and π with a high probability for θ' values around 0.5. In the upper section of Fig. 4, the expectation value $\langle \cos^2(\theta') \rangle$ is plotted for the extended time interval of [0, 135] ps. This contains the prompt alignment (at 2.5 ps), half-revival (at 59 ps), and full-revival (at 123 ps) and confirms that the highest degree of alignment in 1,3-butadiene is achieved near the half-revival.

V. MAXIMUM-LIKELIHOOD CLASSIFICATION OF ALIGNMENT SIMULATIONS

We ranked the alignment simulations $\{A_i(\theta', t)\}_{i=1,...,n}$ (see Sec. IV) by their fitness, using the experimentally measured time-dependent probe yield $M(\alpha'_t, t)$ as the maximumlikelihood predictor. Note that for the present example of SFI in 1,3-butadiene, we separately considered the D₀ and D₁ electronic continuum SFI channels in the described procedure. The independent analysis of the two channels provides a good consistency check for our analysis.

The maximum-likelihood classification procedure for the simulation $A_i(\theta', t)$ associated with the input parameter set *i* is illustrated in Fig. 5. From the $A_i(\theta', t)$ (top), we pick $A_i(\theta', t = t_a)$ (2nd from top), the axis alignment distribution at the time t_a of maximum alignment in the *i*th simulation, as measured by the $\cos^2(\theta')$ expectation value $\langle \cos^2(\theta') \rangle$. We parameterize the molecular angular ionization property $S(\theta)$ (right, top) with a generic functional form. For the present case, a linear combination of even Legendre polynomials which reflect the underlying symmetry is sufficient:

$$S(\theta) = \sum_{i=0}^{k_{\max}} a_{2i} P_{2i} (\cos{(\theta)}).$$
 (2)

Via analysis of fit errors, the appropriate highest order of the expansion is determined, $k_{max} = 3$ for the present case. Using ansatz (2) and $A_i(\theta', t_a)$, we fit the measured angular ionization yield $M(\alpha', t_a)$ (right, middle) via Eq. (1) with the prefactors a_{2i} as fit parameters. This yields the $S_i(\theta)$ (red, middle), the molecular frame dependence of the probe for the *i*th simulation $A_i(\theta', t_a)$. Note that since the expansion of $S(\theta)$ into a basis of even Legendre polynomials directly translates into an expansion of $M(\alpha', t_a)$ into the same basis, the quality of the fit of $M(\alpha', t_a)$ will not depend on the input parameter set *i*. From the deconvoluted $S_i(\theta)$ and the simulation $A_i(\theta', t)$, we then construct the relative time-dependent probe yield $M_i(\alpha'_t, t)$ for the *i*th simulation (2nd from bottom) via Eq. (1).

Note that despite the fact that the probe yield time trace is for the fixed polarization geometry $\alpha' = \alpha'_t$, its reconstruction involves and, hence, tests the dependence of $S_i(\theta)$ on all angles θ . This stems from the limited degree of alignment and the integration over the lab-frame angles. We demonstrate this for the present case ($\alpha'_t = 7^\circ$) in Fig. 6, which plots the contributions to integral (1) as a function of θ for the trace reconstruction $M_i(\alpha'_t, t = [44, 73]$ ps). Data are shown for the parameter set (T = 1.75 K, I = 2.375×10^{12} W/cm²) for the D₀ ionic ground state SFI channel and are characteristic for the trace reconstructions considered here. The shape of this histogram results from integral (1), i.e., the convolution of $S_i(\theta)$ with the time-dependent alignment distribution (which commonly peaks at $\theta' = 0, \pi$) and the Jacobian (which is zero for $\theta' = 0, \pi$ and largest for $\theta' = \pi/2$, where the alignment distribution commonly reaches its minimum).

In order to gauge the fitness of the alignment simulations $\{A_i(\theta', t)\}$, we rank the constructed traces $\{M_i(\alpha'_t, t)\}$ by their agreement with the measured experimental benchmark $M(\alpha'_t, t)$ (Fig. 5, right, bottom). Note that as we only compare relative probe yields and, to account for possible small errors in the rotational constants used in the simulation, we treat the amplitude of the probe yield and its offset in yield and time as free parameters. By variation, we find the minimum χ^2_{red} value²⁵ for $M_i(\alpha'_t, t)$ and $M(\alpha'_t, t)$ as a function of these



FIG. 5. Maximum-likelihood classification procedure for numerical alignment simulations with free parameters using measured angular and time-dependent experimental data $M(\alpha', t = t_a)$ and $M(\alpha' = \alpha'_t, t)$. For details, see text.

parameters (see Fig. 5), which for simplicity we will call χ^2_{red} from here on.

VI. RESULTS AND DISCUSSION

The χ^2_{red} values derived for each simulation *i* as described in Sec. V span a hypersurface over the free simulation input parameters. For the present case, the interpolated twodimensional χ^2_{red} surface is plotted in Fig. 7 for the parameter ranges T = [0.5, 5] K and I = [1.5, 3.5] × 10¹² W/cm² considered here. The upper panel represents $\chi^2_{red}(T, I)$ derived from a maximum-likelihood classification procedure performed using the measured data from the strong (90% of the total ionization yield) D₀ ground state SFI channel as experimental input. The lower panel displays the same for a classification performed on the much weaker (5% of the total ionization yield) D₁ excited state SFI channel (see the discussion below). For the analysis based on the D₀ channel, we present the underlying data from the classification of the alignment simulations for the 169 input parameter sets in Fig. 8. χ^2_{red} is plotted as a function of the rotational temperature T for the different intensities I in the upper panel. In the lower panel, χ^2_{red} is plotted as a function of intensity I for the different rotational temperatures T. The solid lines in Fig. 8 are polynomial fits of fourth order. The most likely values of the parameters T and I are marked by the global minima of the χ^2_{red} fits. As can be seen from Fig. 7, the most likely parameters are a rotational temperature of T = 1.72 K and an alignment intensity of I = 2.36 × 10¹² W/cm³. The blue solid line in the upper panel of Fig. 1 depicts the constructed ionization



FIG. 6. Histogram of the contributions to integral (1) as a function of θ derived for the parameter set (T = 1.75 K, I = 2.375 × 10¹² W/cm²). Integral (1) results in the reconstructed ionization yield time traces { $M_i(\alpha'_t, t)$ }, which are analyzed for their agreement with the experiment in the maximum likelihood classification procedure. The figure shows that the maximum-likelihood measure involves and, hence, tests the dependence of S(θ) at all angles θ , despite the fact that the time trace is for the fixed polarization geometry $\alpha' = \alpha'_t$.



FIG. 7. Interpolated maximum-likelihood parameter χ^2_{red} surfaces as a function of the free parameters in the simulation, i.e., the rotational temperature T and the alignment intensity I. The classification procedure is performed independently for the D₀ channel (upper panel) and the lower statistics D₁ channel (lower panel). The two-dimensional 1 σ confidence intervals characterized by $(\chi^2_{red})_{min} + 1$ are marked by red contour lines; the confidence interval for the analysis based on the high-statistics D₀ channel is nested within the respective interval for the D₁ channel-based analysis, indicating consistency.



FIG. 8. χ^2_{red} values from the alignment classification procedure based on D_0 SFI data as a function of rotational temperature T for different intensities I (upper panel) and as a function of intensity I for different temperatures T (lower panel). The most probable alignment simulation (lowest χ^2_{red}) features T = 1.75 K and I = 2.375 × 10¹² W/cm³. While the dashed lines mark (χ^2_{red})_{min} + 1 and give the maximum extent of the 1 σ confidence interval for the respective input parameter (T = [0.95, 3.4] K, I = [1.9, 2.6] × 10¹²W/cm²), the confidence interval is in fact a much more constrained two dimensional surface marked by the red contour lines in Fig. 7.

yield time trace $M(\alpha'_t, t)$ for the D₀ channel for the simulation with the set of input parameters closest to these values (T = 1.75 K, I = 2.375 × 10¹² W/cm³). Similarly, the red solid line in the lower panel of Fig. 1 shows the constructed D₁ ionization yield time trace for the best-fitting simulation in an independent classification procedure performed for the D₁ SFI data (see below). While the agreement with the respective measured D₀ and D₁ SFI yield time trace M(α'_t , t) is not perfect, quantified by χ^2_{red} values of 12.2 (D₀) and 1.6 (D₁), i.e., significantly above unity, it can be seen from the figure that the constructed traces describe the measured data reasonably well. Based on the discussion in Sec. IV, we suspect that

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FIG. 9. Deconvoluted MF-CAIPs $S(\theta)$ for the D_0 ionic ground state SFI channel in 1,3-butadiene as derived from the procedure described in this paper. While the red line depicts the most likely MF-CAIP, all the blue distributions are within the 1σ confidence interval. The distributions are normalized to the same area.

the less pronounced off-peak modulation of the reconstructed trace as compared to the measured trace, observed especially for the D_0 ionization channel (Fig. 1, upper panel), represents a small systematic error associated with the approximation of 1,3-butadiene as a symmetric top rotor. The fact that the χ^2_{red} value is lower for the time-trace associated with D_1 ionization stems from the larger statistical error bars for the fragment yield, which mask this suspected systematic error (Fig. 1, lower panel).

The 1σ confidence interval of a free parameter is bounded by the points where the minimum χ^2 value has increased by one.²⁵ For multiple free parameters, the maximumlikelihood confidence interval will be a hypersurface. For the present case of Fig. 7, the 1σ confidence surface over T and I for the classification performed on the D₀ SFI channel is bounded by the red contour line "13.2," which marks $(\chi^2_{red})_{min}$ + 1. In Fig. 9, we show all MF-CAIPs $S_i(\theta)$ affiliated with simulations $A_i(\theta', t)$ within this confidence surface. The distributions are normalized to the same area, with the most likely MF-CAIP shown in red. The extrema of all shown MF-CAIPs bound what is plotted in Fig. 2(b) of Ref. 13 as absolute 1σ confidence interval of the deconvoluted molecular frame data. Note that the relative confidence intervals of the MF-CAIPs associated with different SFI channels will be significantly smaller, since they were measured simultaneously on the same molecular sample (see Fig. 3 of Ref. 13). In Fig. 10, we display all lab frame axis alignment distributions of the molecular sample at the time of maximum alignment, $A_i(\theta', t_a)$, which fall within the 1σ confidence interval. The most likely distribution is plotted in red and shows that a significant degree of alignment ($\langle \cos^2(\theta') \rangle = 0.69$, see below) is achieved in the present experiment.

The common measure of the degree of axis alignment of a molecular sample is the expectation value of $\cos^2(\theta')$ of its alignment distribution $A(\theta')$.¹ For reference, we plot in



FIG. 10. Lab-frame axis alignment distributions $A(\theta', t_a)$ of the molecular sample at the time t_a of maximum alignment, normalized to the same area. The most probable distribution is shown in red, while all distributions within the 1σ confidence interval are shown in blue.

Fig. 11 for each conducted simulation its associated maximum-likelihood parameter χ^2_{red} versus its $\langle \cos^2(\theta') \rangle$ value at the time of maximum alignment (top panel). The data are shown for the maximum-likelihood classification performed on the strong D₀ ground ionic state SFI channel. For the middle panel of Fig. 11, the data points marking the lower contour have been selected, i.e., the most likely simulation for each $(\cos^2(\theta'))_{\text{max}}$ interval. The black solid line represents a fourth order polynomial fit. Note that, strictly speaking, the definition of a confidence interval in this way is ambiguous since $\langle \cos^2(\theta') \rangle_{\text{max}}$ is not a free parameter in the alignment model. Nevertheless, the middle panel of Fig. 11 provides a useful measure of the degree of alignment, together with a confidence interval. As determined from the fit, we achieved $\langle \cos^2(\theta') \rangle_{\rm max} = 0.69^{+0.06}_{-0.09}$ in this experiment. The performed simulation of maximum likelihood yields $\langle \cos^2(\theta') \rangle_{max}$ = 0.70 (minimum χ^2_{red} data point slightly to the right of the fit minimum and corresponding red alignment distribution in Fig. 10). As a consistency check, we plot a histogram of the $\langle \cos^2(\theta') \rangle_{\text{max}}$ values for all alignment simulations within the 1σ confidence interval (see Fig. 10), i.e., all $\langle \cos^2(\theta') \rangle_{max}$ values with $\chi^2_{red} < (\chi^2_{red})_{min} + 1$ in the upper panel of Fig. 11. This is displayed in the lower panel of Fig. 11 and shows good agreement with the fit in the middle panel.

Since the underlying true alignment distribution of the molecular sample is independent of the chosen SFI channel, performing the described maximum-likelihood classification procedure for the weaker D₁ excited state SFI channel offers a consistency check on our analysis. This is particularly relevant since the D₀ and the D₁ continuum channels were measured simultaneously in a single experiment on the aligned molecules. The interpolated surface $\chi^2_{red}(T, I)$ derived from the experimental input data associated with the D₁ SFI channel (lower panel of Fig. 1 and red/green data points in Fig. 2) is shown in the lower panel of Fig. 7. The same 169 alignment



FIG. 11. Upper panel: Maximum-likelihood parameter χ^2_{red} as a function of $\langle \cos^2(\theta') \rangle_{max}$ for each conducted simulation. Middle panel: The minimum χ^2_{red} for each $\langle \cos^2(\theta') \rangle_{max}$ interval together with a polynomial fit. The dashed line marks the 1σ confidence interval. We achieve $\langle \cos^2(\theta') \rangle_{max} = 0.69^{+0.06}_{-0.09}$ in this experiment. Lower panel: Histogram of the $\langle \cos^2(\theta') \rangle_{max}$ values for all alignment distributions within the 1σ confidence interval. All data shown are derived from an analysis based on the D₀ ground ionic state SFI channel.

simulations, $\{A_i(\theta', t)\}$, were used as in the classification procedure based on the D₀ SFI channel data (upper panel). A similar χ^2_{red} surface was obtained but with the minimum shifted to slightly higher rotational temperatures and lower alignment intensities. The simulation yielding the minimum χ^2_{red} value incorporates a rotational temperature of T = 2.5 K and an alignment intensity of I = 2.0×10^{12} W/cm². Importantly, this input parameter set is within the two-dimensional confidence interval for the D₀ channel-based analysis, as seen from the upper panel of Fig. 7. Moreover, the two-dimensional confidence interval for the D_0 surface (red contour line "13.2") is entirely contained within the two-dimensional confidence interval for the D₁ surface (red contour line "2.6"). This indicates consistency and is expected since the number of events for the parent ion was much higher, translating into tighter confidence limits in the parameter space for the D₀ channelbased analysis. As described above, the lower χ^2_{red} values for the D₁ channel-based analysis stem from the masking of a suspected small systematic error, due to the limits of the symmetric top approximation, by the larger statistical error bars for the fragment yield (see Fig. 1, lower panel).

While there are two free input parameters for the molecular alignment simulation discussed here, our classification procedure is suited to handle an arbitrary number of free input parameters. For the case of a larger number of free parameters, the procedure might be extended to include the prompt and the full revival in the time-dependent measurements and simulations of Figs. 1 and 4. This is expected to reduce the magnitude of the confidence intervals. To impose even more experimental constraints on the procedure, it is possible to measure the channel-resolved ionization yield time trace for a range of relative polarizations between the pump and probe pulses and incorporate all of these traces in the χ^2 analysis.

VII. CONCLUSION

We have described a quantitative procedure for ranking the likelihood of alignment simulations to reproduce the true axis alignment of a molecular sample. The procedure requires experimental input from an alignment-sensitive probe as the maximum-likelihood predictor. It allows simultaneous determination of (i) the molecular alignment-dependence of the probe and (ii) the alignment distribution of the sample, together with their respective confidence intervals. We believe that these general methods will be useful to researchers studying the angular dependence of laser-induced processes in molecules, including photodissociation, photoelectron spectroscopy, and strong field processes.

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