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Field-free molecular alignment for studies using x-ray pulses from a synchrotron radiation source

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A short, intense laser pulse may be employed to create a spatially aligned molecular sample that persists after the laser pulse is over. We theoretically investigate whether this impulsive molecular alignment technique may be exploited for experiments using x-ray pulses from a third-generation synchrotron radiation facility. Using a linear rigid rotor model, the alignment dynamics of model molecular systems with systematically increasing size is calculated utilizing both a quantum density matrix formalism and a classical ensemble method. For each system, the alignment dynamics obtained for a 95 ps laser is compared with that obtained for a 10 ps laser pulse. The average degree of alignment after the laser pulse, as calculated quantum mechanically, increases with the size of the molecule. This effect is quantitatively reproduced by the classical calculations. The average degree of impulsive alignment is high enough to induce a pronounced linear dichroism in resonant x-ray absorption using the intense 100 ps x-ray pulses currently available. However, for structural studies based on elastic x-ray scattering, bright x-ray pulses with a duration of 1 ps or shorter will be required in order to make full use of impulsive molecular alignment. © 2009 American Institute of Physics. [DOI: 10.1063/1.3120608]

I. INTRODUCTION

X rays are a powerful tool for probing the structure and dynamics in matter.^{1–23} Third-generation synchrotron radiation facilities such as Argonne's Advanced Photon Source (APS) deliver tunable, polarized x rays with high photon flux and a pulse duration of about 100 ps. This pulse duration imposes a restriction on the kind of dynamical processes that may be studied or exploited at a third-generation synchrotron radiation facility.

Another limitation affecting x-ray studies on gas-phase and liquid samples is the random orientations of the target molecules relative to the x-ray propagation and polarization vectors. In principle, modern laser technology allows one to overcome this obstacle: An intense laser pulse can exert control over the molecular rotational degrees of freedom, such that a molecular sample with a high degree of spatial alignment can be prepared.^{24–32} Macromolecules such as proteins may be aligned employing a continuous-wave laser.^{33–35}

The temporal development of the molecular alignment during and following the laser pulse (the transit time through the laser beam in the continuous-wave case) depends critically on the laser parameters.^{30,36–40} In the adiabatic regime,^{26,29,41,42} i.e., when the laser pulse duration τ_L is much longer than the molecular rotational period τ_{rot} , the temporal alignment profile of the molecules essentially follows the temporal intensity profile of the laser pulse. Particularly, after the laser pulse the molecules are no longer aligned. As the laser pulse duration is shortened, it becomes increasingly dif-

ficult for the rotational motion to follow the laser pulse. In the impulsive regime ($\tau_L \ll \tau_{\text{rot}}$), there is substantial alignment even *after* the laser pulse.^{29,43–46} This form of field-free alignment is characterized by a constant nonzero degree of alignment superimposed by a periodic rotational revival structure.

In practice, the x-ray pulse duration available and the laser-induced-alignment scheme that may be applied are connected. In order to exploit the high repetition rate of a storage ring, the laser has to be operated at a high repetition rate as well. This, however, limits the energy per laser pulse for a given laser system. Hence, if the laser pulse duration is too long, the laser intensity may be too low to substantially align the species of interest. On the other hand, if the laser pulse duration is too short, the induced alignment may not persist long enough to be useful for experiments with 100 ps x-ray pulses.

In an experiment at the APS, resonant absorption of polarized x rays by laser-aligned CF₃Br molecules was demonstrated.⁴⁷ The theory underlying the experiment is described in Refs. 48 and 49. The experiment was carried out using 95 ps laser pulses;⁴⁷ the thermally averaged rotational period of the CF₃Br molecules was 28 ps.⁴⁹ The alignment duration in this quasiadiabatic case was therefore defined by the 95 ps laser pulse and was well matched to the x-ray pulse duration available at the APS. However, if shorter, more intense laser pulses had been used, or if the molecules studied had been larger, the alignment dynamics would have been more impulsive. Since both cases are of practical interest, we theoretically investigate in this paper the extent to which

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impulsive alignment can be exploited at a third-generation synchrotron radiation facility. Our focus is on feasibility assuming realistic parameters.

In Sec. II, we present the computational methods employed in our investigation. We discuss the quantum (Sec. II A) and classical (Sec. II B) treatments of laser-induced alignment dynamics. The impact of nondipole effects in resonant x-ray absorption is analyzed in Sec. II C. A numerically efficient approach to calculating x-ray diffraction patterns of laser-aligned molecules is the topic of Sec. II D. We present in Sec. III numerical results on the alignment dynamics of model molecular systems. The influence of the molecular size and of the laser pulse duration is investigated in Sec. III A using quantum mechanical calculations. Specifically, we discuss Br₂ and model systems derived from Br₂ using a scaling procedure. This approach allows us to investigate, in a systematic manner, the alignment dynamics as a function of molecular size. A comparison of the quantum mechanical data with classical calculations in Sec. III B highlights those impulsive alignment effects that can be understood classically. In Sec. III C, we examine the impact of impulsive alignment on resonant x-ray absorption by laser-aligned molecules. X-ray diffraction from impulsively aligned molecules is discussed in Sec. III D. Concluding remarks are presented in Sec. IV. All equations are given in atomic units.

II. METHODS

A. Quantum-mechanical treatment of laser-induced alignment dynamics

The degree of spatial alignment of a molecular ensemble may be characterized by the dynamical ensemble-averaged quantity $\langle \cos^2(\theta_{ml}) \rangle(t)$, θ_{ml} being the angle between the most polarizable molecular axis and the laser polarization axis. Using the quantum density matrix formalism, this quantity is defined as

$$\langle \cos^2(\theta_{ml}) \rangle(t) = \text{Tr}[\hat{\rho}_L(t) \cos^2(\theta_{ml})], \quad (1)$$

where $\hat{\rho}_L(t)$ is the density operator describing the laser-driven rotational wave packet dynamics. The computational task thus involves determining the time-dependent matrix elements,

$$[\hat{\rho}_L(t)]_{J'KM}^{J'KM} = \langle J'KM | \hat{\rho}_L(t) | JKM \rangle, \quad (2)$$

between two symmetric rotor states $|JKM\rangle$ and $|J'KM\rangle$ (see, for instance, Refs. 48 and 50). For linear molecules, we set $K=0$.⁴⁸ Since in this paper we study molecular systems in which a large number of rotational states are excited, stable, and efficient schemes are needed for calculating the Clebsch–Gordan coefficients with large quantum numbers and for time propagation. The Clebsch–Gordan coefficients are numerically calculated with a stable three-term recurrence algorithm^{51,52} that is implemented in the SLATEC numerical package.⁵³

Because the rotational revival period increases with the size of the molecule, the computational effort for the time propagation of the molecular density operator can be very demanding, particularly when the revival period is orders of

magnitude longer than the laser pulse duration τ_L . To reduce the computational time, we partition the total Hamiltonian in time as follows:

$$\hat{H}(t) = \begin{cases} \hat{H}_{\text{mol}}, & \text{for } |t| > t_{\text{off}} \\ \hat{H}_{\text{mol}} + \hat{H}_L(t), & \text{for } |t| \leq t_{\text{off}}, \end{cases} \quad (3)$$

where $\hat{H}_{\text{mol}}$ is the time-independent rotational Hamiltonian of the molecules and $\hat{H}_L(t)$ is the cycle-averaged laser-molecule interaction. For symmetric-top molecules,

$$\hat{H}_L(t) = -2\pi\alpha I_L(t) \Delta\alpha(\omega_L) \left[\cos^2(\theta_{ml}) - \frac{1}{3} \right], \quad (4)$$

where α is the fine-structure constant, $I_L(t)$ is the temporal intensity profile of the laser pulse with angular frequency ω_L , and $\Delta\alpha(\omega_L)$ is the polarizability anisotropy of the molecule. We assume throughout that the polarizability along the molecular symmetry axis is greater than the polarizability perpendicular to the symmetry axis; $\Delta\alpha(\omega_L)$ is therefore positive. The temporal intensity profile is assumed to be a Gaussian peaked at $t=0$. The value of t_{off} is chosen to be at least $4\tau_L$. Hence, for $|t| > t_{\text{off}}$, the laser-molecule interaction is negligible, and the field-free propagation may be carried out analytically, which is most conveniently done by adopting the interaction picture.⁴⁸ The numerical propagation scheme we use for $|t| \leq t_{\text{off}}$ is described in Ref. 48.

B. Classical treatment of laser-induced alignment dynamics

Each linear classical rotor is subjected to the Hamiltonian in Eqs. (3) and (4), which is also used in the quantum calculations. The corresponding classical equations of motion read

$$\frac{d\theta_{ml}(t)}{dt} = \dot{\theta}_{ml}(t), \quad (5)$$

$$\begin{aligned} \frac{d\dot{\theta}_{ml}(t)}{dt} &= \frac{(2BJ_z)^2 \cos[\theta_{ml}(t)]}{\sin^3[\theta_{ml}(t)]} \\ &\quad - 4\pi B\alpha I_L(t) \Delta\alpha(\omega_L) \sin[2\theta_{ml}(t)]. \end{aligned} \quad (6)$$

In the presence of the laser pulse, the classical equations of motion are propagated in time with the Runge–Kutta fourth-order integrator. We exploit that J_z , the component of the angular momentum with respect to the laser polarization axis, is a constant of the motion. Equation (6) is valid when $J_z \neq 0$. The relation

$$J_z = \frac{\dot{\phi}_{ml}(t) \sin^2[\theta_{ml}(t)]}{2B} \quad (7)$$

ensures that in this case, $\sin[\theta_{ml}(t)] \neq 0$ (ϕ_{ml} is the azimuthal angle). When $J_z=0$, the first term on the right-hand side of Eq. (6) is not present.

The initial conditions for the individual rotors before the laser pulse are picked from the Boltzmann distribution for the rotor energies as follows. The field-free Hamiltonian, i.e., the energy of the rotor, is given by

$$H_{\text{mol}} = \Xi_1^2 + \Xi_2^2, \quad (8)$$

where

$$\Xi_1 = \frac{\sqrt{B}J_z}{\sin[\theta_{ml}]} \quad (9)$$

and

$$\Xi_2 = \frac{\dot{\theta}_{ml}}{2\sqrt{B}}. \quad (10)$$

Therefore, assuming a Boltzmann distribution for the rotor energies, Ξ_1 and Ξ_2 may be picked using a random number generator for two-dimensional Gaussian samples. The width of the Gaussian distribution depends on the rotational temperature, which was assumed here to be 1 K. The initial value for $\dot{\theta}_{ml}$ follows immediately from Ξ_2 . In order to determine J_z from Ξ_1 , we pick the initial θ_{ml} from a uniform distribution for $\cos[\theta_{ml}]$.

The rotational dynamics after the laser pulse ($t > t_{\text{off}}$) may be determined analytically. Specifically, we obtain from Eqs. (5) and (6)

$$\cos[\theta_{ml}(t)] = C_1(t_{\text{off}})\cos(\omega t) + C_2(t_{\text{off}})\sin(\omega t), \quad (11)$$

with

$$C_1(t_{\text{off}}) = \cos[\theta_{ml}(t_{\text{off}})]\cos(\omega t_{\text{off}}) + \frac{\dot{\theta}_{ml}(t_{\text{off}})}{\omega}\sin[\theta_{ml}(t_{\text{off}})]\sin(\omega t_{\text{off}}), \quad (12)$$

$$C_2(t_{\text{off}}) = \cos[\theta_{ml}(t_{\text{off}})]\sin(\omega t_{\text{off}}) - \frac{\dot{\theta}_{ml}(t_{\text{off}})}{\omega}\sin[\theta_{ml}(t_{\text{off}})]\cos(\omega t_{\text{off}}). \quad (13)$$

In these expressions,

$$\omega = \sqrt{\left(\frac{2BJ_z}{\sin[\theta_{ml}(t)]}\right)^2 + (\dot{\theta}_{ml}(t))^2}, \quad (14)$$

which is valid when J_z differs from zero (so that $\sin[\theta_{ml}(t)] \neq 0$). When $J_z = 0$, then $\omega = \dot{\theta}_{ml}$.

C. Resonant x-ray absorption

Our calculations in Sec. III C are based on the theory developed in Ref. 48. An assumption made in Ref. 48 is that the x-ray absorption process may be described within the electric dipole approximation. Numerical data were presented in Ref. 48 for resonant x-ray absorption by adiabatically aligned Br_2 . There is a strong pre-edge resonance at an x-ray photon energy of 13.474 keV,⁵⁴ which is associated with the transition of a 1s electron to the lowest unoccupied molecular orbital (LUMO). The LUMO is denoted here as $|\sigma_{4p}^\mu\rangle$, indicating that the LUMO is a σ orbital of ungerade symmetry and is associated with the atomic 4p orbitals. Because the two delocalized molecular orbitals $|\sigma_{1s}^g\rangle$ and $|\sigma_{1s}^\mu\rangle$ have a spatial extension that is comparable to the wavelength of the incoming x-ray photon, the electric dipole approximation is, strictly speaking, not valid. Since the systems studied

in Sec. III comprise Br_2 and model molecular systems derived from Br_2 , we briefly discuss the impact of nondipole corrections. We note that the decay width of a Br 1s vacancy is 2.5 eV,⁵⁵ whereas the energy splitting between the $|\sigma_{1s}^g\rangle$ and $|\sigma_{1s}^\mu\rangle$ orbitals of Br_2 is less than 3 meV.⁵⁶ Hence, the σ_{1s}^g and σ_{1s}^μ binding energies may be regarded as indistinguishable.

The absorption cross section for a one-photon-induced transition from the occupied molecular orbital $|\varphi_i\rangle$ to the unoccupied molecular orbital $|\varphi_f\rangle$ is proportional to²³

$$M_{fi} = |\langle\varphi_f|e^{ik\cdot x}\boldsymbol{\varepsilon}\cdot\mathbf{p}|\varphi_i\rangle|^2, \quad (15)$$

where $\mathbf{k}$ is the x-ray momentum, $\mathbf{x}$ is the electron position operator, $\boldsymbol{\varepsilon}$ is the x-ray polarization vector, and $\mathbf{p}$ is the electron momentum operator. We evaluate M_{fi} in the molecular frame. The vectors $\mathbf{k}$ and $\boldsymbol{\varepsilon}$ thus depend on the Euler angles that connect the molecular frame with the laboratory frame. To an excellent approximation, the 1s-type molecular orbitals of Br_2 may be written as linear combinations of the atomic 1s orbitals, $|\psi_{1s}\rangle$, of the two Br atoms,

$$\sigma_{1s}^g(\mathbf{x}) = \frac{1}{\sqrt{2}}[\psi_{1s}(\mathbf{x} + \mathbf{R}_e) + \psi_{1s}(\mathbf{x} - \mathbf{R}_e)], \quad (16)$$

$$\sigma_{1s}^\mu(\mathbf{x}) = \frac{1}{\sqrt{2}}[\psi_{1s}(\mathbf{x} - \mathbf{R}_e) - \psi_{1s}(\mathbf{x} + \mathbf{R}_e)]. \quad (17)$$

Here, $\mathbf{R}_e$ and $-\mathbf{R}_e$ are the locations of the two Br nuclei in the molecular frame.

Making use of the fact that the atomic 1s orbitals are small in comparison to the x-ray wavelength and exploiting the ungerade symmetry of the LUMO and the spherical symmetry of the atomic 1s orbitals, the x-ray absorption cross section for the $\sigma_{1s}^g \rightarrow \sigma_{4p}^\mu$ transition (for fixed $\mathbf{k}$ and $\boldsymbol{\varepsilon}$) may then be written as

$$\sigma_{\sigma_{1s}^g \rightarrow \sigma_{4p}^\mu} = \sigma_{\text{dip}} \cos^2(\mathbf{k} \cdot \mathbf{R}_e). \quad (18)$$

In this expression, σ_{dip} is the cross section for the $\sigma_{1s}^g \rightarrow \sigma_{4p}^\mu$ transition obtained in the electric dipole approximation, i.e., the cross section employed in Ref. 48.

The cross section for the $\sigma_{1s}^\mu \rightarrow \sigma_{4p}^\mu$ transition disappears in the electric dipole approximation. Taking into consideration the nondipole corrections that follow from Eq. (15) and taking into account that the σ_{1s}^g and σ_{1s}^μ binding energies are indistinguishable within the decay width of a Br 1s core hole, the cross section for the $\sigma_{1s}^\mu \rightarrow \sigma_{4p}^\mu$ transition reads

$$\sigma_{\sigma_{1s}^\mu \rightarrow \sigma_{4p}^\mu} = \sigma_{\text{dip}} \sin^2(\mathbf{k} \cdot \mathbf{R}_e). \quad (19)$$

In view of the energetic indistinguishability of the σ_{1s}^g and σ_{1s}^μ channels, the resonant cross section observed in an x-ray absorption spectroscopy experiment,

$$\sigma_{\sigma_{1s}^g \rightarrow \sigma_{4p}^\mu} + \sigma_{\sigma_{1s}^\mu \rightarrow \sigma_{4p}^\mu} = \sigma_{\text{dip}} \quad (20)$$

is insensitive to the nondipole corrections. This is exploited in Sec. III C. Nondipole effects as suggested by Eqs. (18) and (19) have been experimentally observed in resonant x-ray Raman spectroscopy by detecting the polarization of inelastically scattered x rays.⁵⁷ See also Refs. 58–60.

D. X-ray diffraction

We introduce three different reference frames: the detector reference frame, the laser reference frame, and the molecular reference frame. The set of Euler angles Ω_{dl} connects the detector and laser reference frames; Ω_{ml} connects the molecule and laser reference frames. The laser-driven rotational dynamics of the molecule is most conveniently calculated in the laser reference frame; the diffraction pattern is defined in the detector reference frame and the molecular structure is most easily expressed in the molecule reference frame.

The differential probability (in the detector reference frame) of electronically elastic x-ray scattering by laser-aligned molecules is given by⁵⁰

$$\frac{dP}{d\Omega} = \int d\Omega_{ml} f(\Omega_{ml}) \frac{d\sigma_{th}}{d\Omega} |F_{mol}(\mathbf{Q}, \Omega_{dl}, \Omega_{ml})|^2. \quad (21)$$

The product of the Thomson scattering cross section $d\sigma_{th}/d\Omega$ and the molecular form factor, $|F_{mol}(\mathbf{Q}, \Omega_{dl}, \Omega_{ml})|^2$, gives the differential scattering cross section in the detector reference frame at fixed Ω_{dl} and Ω_{ml} . The vector $\mathbf{Q}$ in Eq. (21) is the x-ray momentum transfer^{2,23} defined in the detector reference frame. For symmetric-top molecules,

$$f(\Omega_{ml}) = \int_{-\infty}^{+\infty} dt j_X(t) \rho_L(\theta_{ml}, t), \quad (22)$$

where $j_X(t)$ is the temporal pulse profile of the incoming x-ray flux,

$$\rho_L(\theta_{ml}, t) = \sum_{J_1 J_2 K M} \frac{\sqrt{(2J_1 + 1)(2J_2 + 1)}}{8\pi^2} d_{MK}^{J_1}(\theta_{ml}) d_{MK}^{J_2}(\theta_{ml}) \times [\hat{\rho}_L(t)]_{J_2 K M}^{J_1 K M} \quad (23)$$

is the probability at the time t that the angle between the laser polarization axis (the z axis in the laser reference frame), and the molecular symmetry axis (the z axis in the molecule reference frame) is θ_{ml} . Note that $\rho_L(\theta_{ml}, t)$ and thus $f(\Omega_{ml})$ is independent of the other two Euler angles that are needed to connect the laser and molecule reference frames. The function $d_{MK}^J(\theta_{ml})$ in Eq. (23) is related to the matrix elements of the Wigner rotation matrix⁶¹ via

$$D_{MK}^J(\phi_{ml}, \theta_{ml}, \chi_{ml}) = e^{-i\phi_{ml}M} d_{MK}^J(\theta_{ml}) e^{-i\chi_{ml}K}. \quad (24)$$

The calculation of $[\hat{\rho}_L(t)]_{J_2 K M}^{J_1 K M}$ appearing in Eq. (23) has been described in Sec. II A. We now outline the approach used in calculating the molecular form factor and $d_{MK}^J(\theta_{ml})$. To evaluate the molecular form factor, we use the independent-atom approximation,^{2,23,62}

$$F_{mol}(\mathbf{Q}, \Omega_{dl}, \Omega_{ml}) = \sum_{j=1}^N f_j(\mathbf{Q}) e^{i\phi_j(\Omega_{dl}, \Omega_{ml})}, \quad (25)$$

where N is the number of atoms in the molecule and $Q = |\mathbf{Q}|$. The form factor of the j th atom,

$$f_j(Q) = \frac{4\pi}{Q} \int_0^\infty dr r \rho_j(r) \sin(Qr), \quad (26)$$

is expressed here in terms of the spherically averaged ground-state electron density $\rho_j(r)$ of the j th atom obtained using the Hartree–Slater method implemented by Herman and Skillman.⁶³ The phase

$$\phi_j = \sum_{m, m', m''} (-1)^m D_{m', m}^1(\Omega_{dl}) D_{m'', -m}^1(\Omega_{ml}) (\mathbf{Q}')_{m'} (\mathbf{R}_j')_{m''} \quad (27)$$

in Eq. (25) is the dot product of $\mathbf{Q}$ and the position vector of the j th atom, $\mathbf{R}_j$, evaluated in the laser reference frame. We used prime accents in Eq. (27) to indicate vectors represented in the spherical basis.

An algebraic expression for $d_{MK}^J(\theta_{ml})$ in terms of a polynomial of finite order is available.^{61,64} However, this expression is numerically unstable for high J values. We therefore proceed as follows.⁶⁴ Using a similarity transformation, the Wigner rotation matrix $D(0, \theta_{ml}, 0)$ can be factorized as

$$D(0, \theta_{ml}, 0) = D\left(-\frac{\pi}{2}, 0, 0\right) D\left(0, -\frac{\pi}{2}, 0\right) D(\theta_{ml}, 0, 0) \times D\left(0, \frac{\pi}{2}, 0\right) D\left(\frac{\pi}{2}, 0, 0\right). \quad (28)$$

This transformation allows us to express $d_{MK}^J(\theta_{ml})$ as a Fourier decomposition,

$$d_{MK}^J(\theta_{ml}) = \sum_{K'=-J}^J (i)^{M-K} d_{K'M}^J\left(\frac{\pi}{2}\right) d_{K'K}^J\left(\frac{\pi}{2}\right) e^{-iK'\theta_{ml}}. \quad (29)$$

Thus, for arbitrary θ_{ml} , $d_{MK}^J(\theta_{ml})$ can be obtained from the matrix elements associated with the matrix $d^J(\pi/2)$. The computation of $d^J(\pi/2)$ can be carried out efficiently using recursion and symmetry relations.^{65–67}

III. RESULTS

A high-repetition-rate table-top laser system recently acquired at Argonne National Laboratory provides laser pulses with a pulse energy of 0.2 mJ at a repetition rate of 50 kHz. Two pulse durations, 10 and ~ 100 ps, may be selected. In the calculations presented in this paper, we focus mostly on the parameters of this laser system. We assume that the laser is focused to a width of 30 μm (full width at half maximum). In practice, the x-ray beam is focused inside the laser volume to a width of 10 μm ,^{47,68–71} thereby allowing one to probe a spatial region characterized by a relatively uniform laser intensity distribution. In the following calculations, spatial intensity-averaging effects are therefore neglected. We examine the effects of pulse duration and molecular size on the laser-induced alignment dynamics assuming an initial rotational temperature of 1 K.

A. Quantum-mechanical treatment of laser-induced alignment dynamics

In order to explore the impact of the molecular size on the alignment dynamics, we assume that the polarizability

FIG. 1. (Color) $\langle \cos^2(\theta_{ml}) \rangle(t)$ obtained using quantum calculations for molecules with (a) $R_m = R_e$, (b) $R_m = \sqrt[3]{2}R_e$, and (c) $R_m = 2R_e$. In each panel, the rotational response to a 10 ps laser pulse is compared to the rotational response to a 95 ps laser pulse. $R_m = R_e$ corresponds to Br_2 .

anisotropy of the molecule, $\Delta\alpha(\omega_L)$, is proportional to R_m^3 , where R_m is the linear dimension of the molecule, since $\Delta\alpha(\omega_L)$ tends to scale linearly with the volume of the molecule.^{33–35} Also, we assume that the mass density of the molecule is uniform, such that the rotational constant B is inversely proportional to R_m^5 . We choose the bromine molecule $^{79}\text{Br}-^{81}\text{Br}$ as the reference molecule. In this case, $B = 0.080\,530\text{ cm}^{-1}$, $\Delta\alpha = 27.45\text{ a.u.}$, and $R_m = R_e$, where $R_e = 2.16\text{ a.u.}$ is half the Br–Br distance.⁴⁸ Because the two nuclei are distinguishable, nuclear spin statistics is irrelevant.

Figure 1(a) shows $\langle \cos^2(\theta_{ml}) \rangle(t)$ for Br_2 . For both 10 ps and 95 ps laser pulses, the highest degree of alignment is achieved at the peak of the laser pulse. At 1 K, the ensemble-averaged rotational period of Br_2 is about 100 ps (Table I). Therefore, even for the 95 ps laser pulse, the rotational response is not quite adiabatic: after the laser pulse, $\langle \cos^2(\theta_{ml}) \rangle(t)$ displays weak oscillations about the thermal average of 1/3. In the case of the 10 ps laser pulse, the rotational response approaches the impulsive limit, and the alignment dynamics after the laser pulse is quite pronounced.

TABLE I. Ensemble-averaged rotational period T_{rot} at a temperature of 1 K as a function of R_m .

R_m	T_{rot} (ps)
R_e	99.6
$\sqrt[3]{2}R_e$	204.4
$2R_e$	696.2

Using our scaling model, we calculated the rotational response also for $R_m = \sqrt[3]{2}R_e$ [Fig. 1(b)] and $R_m = 2R_e$ [Fig. 1(c)]. For molecules exposed to the 95 ps laser pulse, the degree of alignment at the peak of the laser pulse increases with the molecular size. This merely reflects the fact that the strength of the laser-molecule interaction increases with the polarizability anisotropy, which increases with the size of the molecule. However, this correlation between the molecular size and the maximum degree of laser-induced alignment does not hold in the case of the 10 ps laser pulse. The reason for this is that the 10 ps pulse duration is too short for the heavier molecules to achieve an optimal spatial alignment. As may be seen in Table I, the rotational period for all three model systems is much longer than 10 ps.

It further follows from Table I that even for the 95 ps laser pulse, the rotational response, especially for $R_m = 2R_e$, should be expected to deviate substantially from adiabatic behavior. This is confirmed by Fig. 1(c), where clear rotational revivals after the laser pulse appear for both 10 and 95 ps laser pulses. The degree of alignment after the laser pulse, averaged over time, is higher using the 10 ps laser pulse. This is true for all three model systems. It may also be concluded from Fig. 1 that the average degree of alignment after the laser pulse increases with the size of the molecule.

Among the six scenarios presented in Fig. 1, the highest degree of field-free alignment is obtained during the rotational revivals of the system with size $R_m = 2R_e$ using the 10 ps laser pulse [Fig. 1(c)]. This molecule, however, has a revival period of the order of nanoseconds. Thus, the field-free alignment associated with the rotational revivals can be experimentally observed or exploited only if dephasing affecting the rotational wave packet is sufficiently slow.

At a gas density of 10^{15} cm^{-3} and a temperature of 1 K, we estimate that the molecule-molecule collision times are of the order of microseconds or longer. A potentially more important dephasing mechanism is coupling between the rotational and vibrational degrees of freedom, i.e., when the rigid-rotor model fails to be an adequate approximation. Consider, for instance, the effect of centrifugal distortion.⁷² For a semirigid diatomic molecule, the energy of each rotational eigenstate is approximately given by

$$E_{\text{rot}} = BJ(J+1) - DJ^2(J+1)^2, \quad (30)$$

where D is the centrifugal distortion constant. In order to converge our calculations for $R_m = 2R_e$, the range of J values included had to extend from 0 up to about 600. For $J=600$, the first and second terms on the right-hand side of Eq. (30) are comparable if $D/B \approx 3 \times 10^{-6}$. Since in real molecules D/B can be as high as 10^{-4} ,⁷³ the centrifugal correction is generally not negligible. Therefore, the rotational eigenenergies are not exactly integer multiples of $2B$, so that in practice the phase relations giving rise to the rotational revivals can be satisfied only approximately.

B. Classical treatment of laser-induced alignment dynamics

As a consequence of rotational-vibrational coupling, the amplitude of the rotational revivals will be smaller in an

FIG. 2. (Color) Comparison between classical and quantum-mechanical alignment dynamics for (a) $\tau_L=10$ ps, $R_m=R_e$, (b) $\tau_L=95$ ps, $R_m=R_e$, (c) $\tau_L=10$ ps, $R_m=\sqrt[3]{2}R_e$, (d) $\tau_L=95$ ps, $R_m=\sqrt[3]{2}R_e$, (e) $\tau_L=10$ ps, $R_m=2R_e$, and (f) $\tau_L=95$ ps, $R_m=2R_e$. $R_m=R_e$ corresponds to Br_2 .

experiment than suggested by Fig. 1. However, the *average* degree of alignment following an impulsive kick is a much more stable feature. To demonstrate this, we use a classical ensemble method (Sec. II B) that employs a large number of classical rigid rotors to obtain the classical rotational response. From a computational point of view, the advantage of the classical approach is that the computational effort grows only linearly with the number of classical rotors employed. To a first approximation, the number of rotors required for convergence does not increase with the molecular size (for the sizes considered in this paper). See Refs. 74–77 for other studies of the quantum-classical correspondence in laser-induced rotational dynamics.

In Fig. 2, we provide computational evidence that the results obtained from the classical calculations reproduce the quantum-mechanically calculated $\langle \cos^2(\theta_{ml}) \rangle(t)$ relatively well. The agreement is particularly good during the laser pulse. Even after the laser pulse, at least in the time intervals shown, the classical approach is capable of capturing complex dynamical features [see, for instance, Fig. 2(e)].

The most substantial exception is the nonadiabatic alignment dynamics after the laser pulse in the case that $\tau_L=10$ ps and $R_m=R_e$ [Fig. 2(a)]. This exception illustrates that rotational revivals cannot be described classically. However, as shown in Fig. 3 for the largest system we studied, the average degree of alignment after the 10 ps laser pulse is accurately reproduced by the classical method. For this reason, the noticeable average degree of alignment seen in Fig. 3 is likely to persist even in the presence of rotational dephasing.

Using the classical picture, it is straightforward to determine the highest possible average degree of alignment after

the laser pulse. A sufficiently strong kick by an intense, short laser pulse forces classical rotors to rotate in a plane that includes the laser polarization axis. The azimuthal molecular motion becomes negligible. For each classical rotor, the azimuthal angle is therefore fixed (but arbitrary). This corresponds to $\langle \cos^2(\theta_{ml}) \rangle = 1/2$. This upper limit is almost reached for $\tau_L=10$ ps and $R_m=2R_e$, as may be seen in Fig. 3.

C. Resonant x-ray absorption

X-ray absorption spectroscopy is a powerful tool for studying the properties of molecules in an element-specific way. The x-ray absorption near-edge structure (XANES)^{6,8} allows one to study the valence electronic structure of the atom of interest. In addition, XANES provides information about the local coordination chemistry. The extended x-ray absorption fine structure^{9,10} is highly sensitive to changes in bond lengths. The interpretation of x-ray absorption experiments in the gas phase, for example, the assignment of the symmetries of near-edge resonances, might be facilitated if at least partially aligned molecular samples can be prepared.

FIG. 3. (Color) Comparison between classical and quantum-mechanical alignment dynamics for $\tau_L=10$ ps, $R_m=2R_e$.

FIG. 4. (Color online) Laser/x-ray cross correlation, detected via resonant absorption of linearly polarized x rays, as a function of the time delay between the laser and x-ray pulses. See the text for details. (a) $\tau_L=10$ ps, $R_m=R_e$, (b) $\tau_L=95$ ps, $R_m=R_e$, (c) $\tau_L=10$ ps, $R_m=\sqrt[3]{2}R_e$, (d) $\tau_L=95$ ps, $R_m=\sqrt[3]{2}R_e$, (e) $\tau_L=10$ ps, $R_m=2R_e$, and (f) $\tau_L=95$ ps, $R_m=2R_e$. $R_m=R_e$ corresponds to Br_2 .

Figure 4 presents the results of calculations on resonant x-ray absorption by the three model molecular systems introduced earlier. The rotational dynamics was calculated quantum mechanically, as in Fig. 1. Linearly polarized x-ray pulses with a Gaussian temporal profile were assumed. The x-ray pulse duration (full width at half maximum) was taken to be 120 ps.⁴⁷ In order to characterize the laser-induced x-ray linear dichroism, we calculated the resonant x-ray absorption signal as a function of the laser/x-ray time delay for two different laser/x-ray configurations: parallel laser and x-ray polarization vectors, and perpendicular laser and x-ray polarization vectors. The cross correlation $R_{\parallel\perp}$ shown in Fig. 4 is the ratio between the two signals. A positive time delay means that the x-ray pulse comes after the laser pulse. An experimental procedure to measure $R_{\parallel\perp}$ is described in Ref. 47.

As may be seen in Fig. 4, the laser/x-ray cross correlation using the 120 ps x-ray pulses is fairly insensitive to any rotational revival structure. Nevertheless, by kicking the molecules using the 10 ps laser pulse, a substantial x-ray linear dichroism is induced (see Fig. 4). It follows from the analysis presented in Ref. 49 that for x-ray pulses that are much longer than the rapid oscillations visible in Fig. 1, the laser/x-ray cross correlation is given by

$$R_{\parallel\perp} = \frac{2\langle\cos^2(\theta_{ml})\rangle}{1 - \langle\cos^2(\theta_{ml})\rangle}, \quad (31)$$

where $\langle\cos^2(\theta_{ml})\rangle$ is a temporal average. Since the maximum average degree of alignment after the laser pulse corresponds to $\langle\cos^2(\theta_{ml})\rangle=1/2$ (cf. Sec. III B), we may conclude from Eq. (31) that the maximum average $R_{\parallel\perp}$ after the laser pulse

is two. The trend seen in the left column of Fig. 4 is consistent with this expectation.

The right column of Fig. 4 shows laser/x-ray cross correlations calculated assuming a laser pulse duration of 95 ps. When the laser and x-ray pulses overlap, the cross correlation is greater than two for all three model molecular systems; in the case that $R_m=2R_e$, the cross correlation is greater than six [Fig. 4(f)]. However, the cross correlation obtained when the x-ray pulse comes after the laser pulse is consistently smaller for 95 ps laser pulses in comparison to the 10 ps laser pulses.

D. X-ray diffraction

X-ray diffraction techniques are used to determine the atomic positions in a molecule.^{12–16,23} This is most successfully done using crystals. Due to rotational averaging, the information content of x-ray scattering patterns obtained for molecules in the gas phase or in a liquid environment is generally too limited for a complete determination of the molecular structure. Unfortunately, as will become clear below, the maximum average degree of alignment discussed in the previous subsections [$\langle\cos^2(\theta_{ml})\rangle=1/2$] is too small to have a sufficiently pronounced impact on an x-ray scattering pattern. Therefore, if field-free alignment is required, one has to exploit rotational revivals. On the other hand, this means that 120 ps x-ray pulses are too long.

It is anticipated that tunable, polarized x-ray pulses with a duration of 1 ps will become available at the APS.⁷⁸ One of the opportunities offered by such a development is illustrated in Fig. 5, where calculations are shown for bromine mol-

FIG. 5. (Color) Ultrafast x-ray diffraction imaging of rotational wave-packet dynamics of bromine molecules at 1 K kicked by a horizontally polarized 50 fs laser pulse, centered at $t=0$, with a peak intensity of 3×10^{13} W/cm². The top panel shows the time evolution of $\langle \cos^2(\theta_m) \rangle$. The probability $\rho_L(\theta_m, t)$ to observe a given θ_m is shown in the middle panel as a polar plot for three different time delays. The corresponding x-ray diffraction patterns (20 keV photon energy, 1 ps pulse duration) are shown in the bottom panel. The coordinates x and y lie in the x-ray detector plane; z is the distance between the detector plane and the target.

ecules at 1 K exposed to a linearly polarized 50 fs laser pulse with a peak intensity of 3×10^{13} W/cm². For the diffraction patterns appearing in the bottom panel of Fig. 5, we assumed an x-ray photon energy of 20 keV. The x-ray polarization axis was assumed to be horizontal, parallel to the laser polarization axis. The propagation axis of the incoming x-ray pulses is perpendicular to the image plane in Fig. 5.

The top panel of Fig. 5 shows $\langle \cos^2(\theta_m) \rangle(t)$, which displays a revival pattern with a period of about 200 ps. The molecules are maximally aligned at the time delay A. This is about 100 ps after the laser pulse, i.e., the molecules are no longer perturbed by the laser field. Using 1 ps x-ray pulses, one can capture the structure of the bromine molecules in the extremely short time interval during which the strong alignment persists. The corresponding x-ray diffraction pattern, shown on the left in the bottom panel of Fig. 5, clearly reflects the nodal structure expected for two horizontally aligned scattering centers.

At the time delay B, $\langle \cos^2(\theta_m) \rangle \approx 0.45$. The associated x-ray diffraction pattern is almost completely azimuthally symmetric. This is the reason why we consider it unlikely that the maximum average degree of alignment discussed earlier can be exploited for x-ray scattering studies. Maximum antialignment occurs at the time delay C. In this case, the x-ray diffraction pattern has a nodal structure that is similar to, but rotated by 90° about the x-ray propagation axis relative to the x-ray diffraction pattern obtained at the time delay A.

A spatial resolution of 1 Å corresponds to a scattering angle of 36° at an x-ray photon energy of 20 keV. The differential scattering cross section at 36° is of the order of 10 barns. The pixel size at 36° is 0.04 sr.⁷⁹ To estimate the number of incoming x-ray photons required to measure the

patterns shown in Fig. 5 to a resolution of 1 Å, we make the following assumptions: the x-ray beam crosses the molecular beam at right angles, the gas density is 10^{15} cm⁻³, the x-ray focal width is 10 μm, and the width of the molecular beam is 1 mm. Hence, requiring that at least one photon be scattered into the pixel, about 10^{10} incident x-ray photons are needed.

IV. CONCLUSION

The technique of adiabatic alignment allows one to prepare strongly aligned molecular samples during the laser pulse. This effect can be understood classically, is insensitive to dephasing, and may thus be applied to molecules in the liquid phase. However, the aligning laser field acts as a perturber and is necessarily present at the instance of maximum alignment. Moreover, for fixed laser parameters, the rotational response becomes increasingly nonadiabatic as the molecular size increases. Very large molecules can, in principle, be aligned using a continuous-wave laser field. However, unless the molecules are trapped in the continuous-wave laser field, the transit time through the laser beam may be comparable to, or even shorter than, the rotational time scale.

The alternative is to focus on the impulsive regime. Exploiting impulsive alignment using existing third-generation synchrotron radiation facilities is a challenge. The duration of an alignment maximum during a rotational revival does not increase with the system size. Another concern, particularly for large, floppy molecules, is that substantial dephasing may occur before the first rotational (half-) revival is reached.

For this reason, we emphasized the average degree of alignment following an impulsive kick. In this case, $\langle \cos^2(\theta_m) \rangle$ cannot exceed 1/2. Nevertheless, this essentially classical alignment effect leads to a pronounced x-ray linear dichroism, where the experimentally accessible parameter $R_{\parallel\perp}$ can reach a value of up to two. This effect may be practically useful for resonant x-ray absorption experiments. For x-ray scattering experiments, on the other hand, a higher degree of alignment is required. Sufficiently strong, field-free alignment is obtained only during rotational revivals. In order to be able to exploit rotational revivals for structural studies of molecules, a bright source of 1 ps hard-x-ray pulses is required. It is expected that such a source will become available at Argonne's APS.

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