On the Theory of Time-Resolved X-ray Diffraction[†]

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We derive the basic theoretical formulation for X-ray diffraction with pulsed fields, using a fully quantized description of light and matter. Relevant time scales are discussed for coherent as well as incoherent X-ray pulses, and we provide expressions to be used for calculation of the experimental diffraction signal for both types of X-ray sources. We present a simple analysis of time-resolved X-ray scattering for direct bond breaking in diatomic molecules. This essentially analytical approach highlights the relation between the signal and the time-dependent quantum distribution of internuclear positions, including thermal effects.

I. Introduction

The real-time detection of chemical dynamics has attracted much attention in the past couple of decades. The aim is to "film" the transformation of matter, that is, map out, in real time, the interatomic distances of all atoms. This mapping leads to a series of "snapshots" which forms a "molecular movie" of the transformation.

The snapshots can be recorded using the pump–probe technique: An ultrashort pump laser pulse creates a non-stationary state, and its time evolution is subsequently monitored, at well-defined time delays, by a probe pulse. Typically, the pump pulse induces an electronic transition, and, subsequently, additional electronic states might be populated as the dynamics unfolds.

So far, the shortest probe pulses are laser pulses in the optical regime, which induce ultrafast electronic transitions in the material system. In order to interpret the signals associated with this form of probing, a detailed knowledge of the energetics of the relevant excited electronic states, as a function of the interatomic distances, is required. Alternatively, one can probe the state of dynamical nonequilibrium structures via scattering techniques (e.g., electron diffraction or X-ray diffraction). Pulsed X-rays are, for example, obtained from synchrotron radiation or plasma sources. The temporal duration of these incoherent pulses, consisting of many sub-femtosecond (atomic time scale) coherent subpulses, is currently in the range of ~100 ps to 100 fs.[1] In the near future, free-electron lasers will produce short ~100 fs to 10 fs coherent and highly intense bursts of X-rays.[1,2]

Recently, several experimental studies employing pulsed X-rays have been published with applications to dynamics in the solid state as well as photoactivated chemical reactions in solution (see, e.g., refs 3–5 and the references therein).

The theory and interpretation of experimental signals for X-ray scattering on static equilibrium structures ("classical" structures) is, of course, well-known and highly developed. Much less work has been done on time-resolved X-ray diffraction on dynamic nonequilibrium structures, where the distribution of internuclear distances, that is, the wave packet, has a non-negligible time-dependent variance which, for example, for direct bond breaking, increases with time.

There are several works that have discussed various aspects of the theory of time-resolved X-ray diffraction.[6–15] In particular, refs 12 and 13 derive expressions for the X-ray scattering signal by *explicitly* taking into account the dynamical equations for both the material system and the pulsed radiation field, where the latter is treated classically. In the present work, we treat both the material system and the pulsed radiation field quantum-mechanically, and the interpretation of the obtained expression for the X-ray scattering signal is inspired by the time-scale considerations presented in refs 8–11. Furthermore, at present, there have only been a few studies where the formalism has been implemented numerically for nonstationary states. Thus, the purpose of the present work is to (i) elucidate the theoretical framework needed in order to describe time-resolved X-ray scattering, and (ii) undertake an exploratory study for simple direct bond breaking with the aim of highlighting the relation between the time-dependent scattering signals and the dynamics of bond breaking.

In the next section, we review and elaborate on the theoretical framework for time-resolved X-ray scattering. In section III, we consider the application to direct bond breaking in diatomic molecules, highlighting the key features in the time-dependent signals, including the signatures of finite temperatures. Finally, section IV presents the conclusions.

II. Theory of Pulsed X-ray Diffraction

In the case of high-energy X-ray scattering, the Hamiltonian describing the interaction between the material system and the radiation field takes the form[6,7,16]

$$\hat{H}_{\text{int}} = \sum_j \frac{q_j^2 \hat{A}^2(\mathbf{r}_j, t)}{2m_j} \tag{1}$$

where j runs over all the charged particles, of charge q_j and mass m_j, in the material system. In this expression, $\hat{A}(\mathbf{r}, t) = \hat{A}^{(+)}(\mathbf{r}, t) + \hat{A}^{(-)}(\mathbf{r}, t)$ is the (Heisenberg) operator for the A field of the radiation with positive component ($\omega_{\mathbf{k}} = ck$),

$$\hat{A}^{(+)}(\mathbf{r}, t) = \sum_u \sum_{\mathbf{k}} \epsilon_u \sqrt{\frac{\hbar}{2\epsilon_0 V \omega_{\mathbf{k}}}} \hat{a}_{u\mathbf{k}} e^{i(\mathbf{k}\cdot\mathbf{r} - \omega_{\mathbf{k}} t)} \tag{2}$$

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and $\hat{A}^{(-)} = [\hat{A}^{(+)}]^\dagger$. Here, $\hat{a}_{u\mathbf{k}}$ is the photon annihilation operator in the second quantization description of the radiation field, and ϵ_u is the polarization vector.

Now, a single scattering event involves, in a manner of speaking, the scattering of an incident photon with wave vector $\mathbf{k}_0$ and polarization u into a photon with wave vector $\mathbf{k}_s$ with polarization v. In the traditional first-order perturbation theory treatment of X-ray scattering,[6,7,16] the scattering amplitude for this process is given as the matrix element $\langle v\mathbf{k}_s, \Psi_f | \hat{H}_{int} | u\mathbf{k}_0, \Psi_i \rangle$, where $|\Psi\rangle$ describes the material system and $|u\mathbf{k}\rangle = \hat{a}_{u\mathbf{k}}^\dagger |\text{vac}\rangle$ is a single-photon (number) state of the X-ray field. This treatment corresponds to a situation where the material system is irradiated by a coherent X-ray field with a constant, time-independent intensity. The differential scattering cross section, which is the scattering *rate* per solid angle per incident radiation flux, is obtained from Fermi's Golden rule.

In the following, we present (within the framework of time-dependent first-order perturbation theory on the material system) a derivation of the differential scattering signal in a situation where the incoming X-ray field is pulsed. We consider the material state $|\Psi(t)\rangle$ created by the pump laser pulse as described in the Introduction. The perturbation on this state due to the interaction with the X-ray pulse is given by

$$|\Psi^{(1)}(t)\rangle = \frac{1}{i\hbar} \int_0^t dt' e^{-i\hat{H}_M(t-t')/\hbar} \hat{H}_{int,M}(t') |\Psi(t')\rangle \quad (3)$$

where $\hat{H}_M$ is the Hamilton operator for the free material system, and the perturbation, $\hat{H}_{int,M}$, is the matrix element of $\hat{H}_{int}$ in the field states corresponding to the scattering event of interest.[17] We note that eq 3 is valid provided that the pump laser creates a pure state, whereas the creations of a mixed state requires a density-operator description of the material system (see, e.g., ref 18). In the following, we will point out, in several places, how the results obtained from eq 3 can be generalized to mixed states, for instance, in order to include temperature effects.

Since our goal is to calculate the differential scattering signal, we can use any representation of the scattered field as long as we, in the calculation of the differential scattering signal, add all contributions to the signal in the solid angle $d\Omega$. We therefore take the scattered field state to be $|v\mathbf{k}_s\rangle$ as in the usual treatment.

For the incident X-ray field, we use the coherent polarized one-photon, multimode wave packet[19,20]

$$|\psi_{u\mathbf{k}_0}\rangle = \sum_k c_{k-k_0} |u\mathbf{k}\rangle \quad (4)$$

where c_k defines a distribution that is peaked around zero with a width Δk. This wave packet consists of field eigenstates, each containing one photon, with wave vectors all pointing in the same direction (different from the direction of $\mathbf{k}_s$) with varying length around the average length k_0. The wave packet $|\psi_{u\mathbf{k}_0}\rangle$ is a one-photon state because it is an eigenstate of the photon number operator, $\hat{N} = \sum_u \sum_\mathbf{k} \hat{a}_{u\mathbf{k}}^\dagger \hat{a}_{u\mathbf{k}}$ with the eigenvalue 1, while the average number of photons in the kth mode equals $|c_{k-k_0}|^2 / \sum_k |c_k|^2$. To see that $|\psi_{u\mathbf{k}_0}\rangle$ represents a pulse, we consider the field intensity $I(\mathbf{r}, t) = \langle \psi_{u\mathbf{k}_0} | \hat{E}^{(-)}(\mathbf{r}, t) \hat{E}^{(+)}(\mathbf{r}, t) | \psi_{u\mathbf{k}_0} \rangle$, where $\hat{E}^{(\pm)} = -\partial \hat{A}^{(\pm)}/\partial t$ is the positive (negative) component of the electric field operator.[19-21] The field intensity is

$$I(\mathbf{r}, t) = \frac{\hbar}{2\epsilon_0 V} |\sum_k \sqrt{\omega_\mathbf{k}} c_{k-k_0} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_\mathbf{k}t)}|^2 = E_{\mathbf{k}_0}^2 |h(\mathbf{r}, t)|^2 \quad (5)$$

where $E_{\mathbf{k}_0} = \sqrt{\hbar\omega_{\mathbf{k}_0}/2\epsilon_0 V}$, and $h(\mathbf{r}, t) = \sum_k \sqrt{(k+k_0)/k_0} c_k e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_\mathbf{k}t)} \sim \sum_k c_k e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_\mathbf{k}t)}$, if we assume that the width Δk is small

compared with the average value k_0. Hence, the field intensity is proportional to the square magnitude of the Fourier transform of c_k, which means that the intensity is a pulse with duration $\Delta t \sim 1/c\Delta k$ at a given $\mathbf{r}$ or, equally, a pulse with a spatial extension in the range $\Delta r \sim 1/\Delta k$ in r at a given time. Thus, coherent X-ray pulse durations ranging from 0.02 fs,[1] which results in Δr ranging from 60 Å, originates from a Δk smaller than 0.02 Å^{-1}. This Δk is (reasonably) small compared to a k_0 on the order of 1 Å^{-1} for X-rays with energies in the tens of kiloelectronvolts regime, which justifies the above-mentioned assumption. Note that, for a monochromatic incident X-ray field, $c_{k-k_0} = \delta_{k,k_0}$, we obtain the usual result, $I(\mathbf{r}, t) = E_{\mathbf{k}_0}^2$.[21]

Using eq 4, the perturbation to be used in eq 3, $\hat{H}_{int,M} = \langle v\mathbf{k}_s | \hat{H}_{int} | \psi_{u\mathbf{k}_0} \rangle$, becomes

$$\hat{H}_{int,M} = \frac{1}{\omega_{\mathbf{k}_0}} \sqrt{\frac{\hbar}{\epsilon_0 V \omega_{\mathbf{k}_s}}} P \sum_j \frac{q_j^2}{2m_j} E_{\mathbf{k}_0}(\mathbf{r}_j, t) e^{-i(\mathbf{k}_s\cdot\mathbf{r}_j - \omega_{\mathbf{k}s}t)} \quad (6)$$

where $P = \epsilon_u \cdot \epsilon_v$ is the polarization factor between the incident and scattered photon and

$$E_{\mathbf{k}_0}(\mathbf{r}, t) = E_{\mathbf{k}_0} h(\mathbf{r}, t) e^{i(\mathbf{k}_0\cdot\mathbf{r} - \omega_{k0}t)} \quad (7)$$

The expression for $E_{\mathbf{k}_0}(\mathbf{r}, t)$ resembles the expression for a (complex) classical pulsed electric field with the carrier frequency $\omega_{\mathbf{k}_0}$. Equation 6 can therefore be viewed as a semiclassical expression for the perturbation on the material system. It should be noted, however, that $E_{\mathbf{k}_0}(\mathbf{r}, t)$ is *not* the expectation value of the corresponding operator, $\hat{E}^{(+)}(\mathbf{r}, t)$, for the state in eq 4, as one might have expected: this expectation value is zero. The present derivation of eq 6 is, in spirit, similar to the semiclassical treatment of absorption presented, for example, in ref 17. An alternative semiclassical treatment of absorption is based on a multiphoton, coherent-state representation of the electric field (see, e.g., ref 18), and in the Appendix we argue that eq 6 can also be derived from a coherent-state description of the incident X-ray pulse.

The differential scattering signal, that is, the number of scattered photons per solid angle, then becomes

$$\frac{dS}{d\Omega} = \int d\omega_{\mathbf{k}_s} \rho(\omega_{\mathbf{k}_s}) \lim_{t\to\infty} \langle \Psi^{(1)}(t) | \Psi^{(1)}(t) \rangle \quad (8)$$

where

$$\rho(\omega_{\mathbf{k}_s}) = \frac{\omega_{\mathbf{k}_s}^2 V}{(2\pi)^3 c^3} \quad (9)$$

is the frequency density of scattered states $|v\mathbf{k}_s\rangle$ that contribute to the signal per solid angle.[16] Here, and in the following, we have replaced the sum over wave vectors by an integral such that, for example, eq 4 becomes $|\psi_{u\mathbf{k}_0}\rangle = \int dk g(k - k_0) |u\mathbf{k}\rangle$. Furthermore, we assume that all particles in the material system experience the same pulse envelope centered at $t = t_p$ after the laser pump pulse, $h(\mathbf{r}_j, t) \approx h_p(t - t_p) = \int dk g(k) e^{-i\omega_\mathbf{k}(t-t_p)}$. This is a very reasonable assumption for a nanometer-sized (or smaller) system considering the extent of an ultrashort pulse, as discussed above. Hence, the differential signal per scattered frequency becomes

$$\frac{d^2S}{d\Omega d\omega_{\mathbf{k}_s}} = \frac{\omega_{\mathbf{k}_s}}{4\pi^3 c^3 \epsilon_0 \hbar \omega_{\mathbf{k}_0}^2} P^2 \int_0^\infty dt'' \int_0^\infty dt' E_{\mathbf{k}_0}^*(t'') E_{\mathbf{k}_0}(t') \times$$

$$e^{-i\omega_{\mathbf{k}s}(t''-t')} \langle \Psi(t'')|\hat{L}^\dagger e^{-i\hat{H}_M(t''-t')/\hbar} \hat{L}|\Psi(t')\rangle \quad (10)$$

where $E_{\mathbf{k}_0}(t) = E_{\mathbf{k}_0} h_p(t - t_p) \exp(-i\omega_{\mathbf{k}_0} t)$ and

$$\hat{L} = \sum_j \frac{q_j^2}{2m_j} e^{i(\mathbf{k}_0 - \mathbf{k}_s)\cdot \mathbf{r}_j} \quad (11)$$

is the scattering operator. Because of the high mass ratio between nuclei and electrons, the contributions to this operator from the nuclei are often ignored, even for highly charged nuclei, because there will be a correspondingly high number of electron contributions.

To be more specific, we now consider the Gaussian time profile, $h_p(t) = \exp(-t^2/2\gamma^2)$. Then we can write, $E_{\mathbf{k}_0}^*(t'') E_{\mathbf{k}_0}(t') = |E_{\mathbf{k}_0}(\tau)|^2 h_p^{1/2}(\delta) \exp(i\omega_{\mathbf{k}_0}\delta)$, where $\tau = (t'' + t')/2$ and $\delta = t'' - t'$. Here, $I_p(t) = |E_{\mathbf{k}_0}(t)|^2$ is the X-ray pulse intensity, and $C_p(t) = h_p^{1/2}(t) \exp(i\omega_{\mathbf{k}_0} t)$ can be viewed as the (normalized) X-ray pulse time-correlation or coherence function.[21,22] With these definitions,

$$\frac{d^2S}{d\Omega d\omega_{\mathbf{k}_s}} = \frac{\omega_{\mathbf{k}_s}}{4\pi^3 c^3 \epsilon_0 \hbar \omega_{\mathbf{k}_0}^2} P^2 \int_0^\infty d\tau I_p(\tau) \int_{-\infty}^\infty d\delta C_p(\delta) e^{-i\omega_{\mathbf{k}s}\delta} \times$$

$$\langle \Psi(\tau)|e^{i\hat{H}_M\delta/2\hbar} \hat{L}^\dagger e^{-i\hat{H}_M\delta/\hbar} \hat{L} e^{i\hat{H}_M\delta/2\hbar}|\Psi(\tau)\rangle \quad (12)$$

This is a central result of our analysis. Obviously, for the fully coherent X-ray pulse that led to this expression, the coherence time is essentially the same as the pulse duration. However, for an incoherent X-ray pulse consisting of many coherent subpulses, the coherence time is independent of (i.e., much shorter than) the pulse duration. The expression for the signal arising from an incident incoherent X-ray pulse can be obtained from eq 10 simply by averaging over the photon statistics, that is, replacing $E_{\mathbf{k}_0}^*(t'') E_{\mathbf{k}_0}(t')$ by the averaged time-correlation function of the pulse envelope, $\langle E_{\mathbf{k}_0}^*(t'') E_{\mathbf{k}_0}(t')\rangle$.[21] Hence, eq 12 remains the same for an incoherent X-ray pulse, with the pulse intensity given by $I_p(t) = \langle |E_{\mathbf{k}_0}(t)|^2\rangle$ and $C_p(\delta) = \langle E_{\mathbf{k}_0}^*(t) E_{\mathbf{k}_0}(t - \delta)\rangle/I_p(t)$, which is assumed to depend only on the relative time difference, δ.

Expressions similar to eq 12 have previously been reported in the literature,[11,12] where a perturbation on the form given in eq 6 was either simply postulated[11] or derived from a classical description of the incident X-ray pulse.[12] Here, eq 12 has been derived from first principles, that is, the quantum theory of light-matter interactions, with a quantum-mechanical description of the incident X-ray pulse.

A. Coherence Time Short Compared to Dynamics. We consider a situation where the coherence time, that is, the time during which $C_p(t)$ is substantially different from zero, is so short (subfemtoseconds) that we can ignore all of the dynamics in the material system during this time. This is a relevant limit for X-rays from synchrotron radiation and laser plasma sources.[1] Then

$$\frac{d^2S}{d\Omega d\omega_{\mathbf{k}_s}} =$$

$$\frac{\omega_{\mathbf{k}_s}}{2\pi^2 c^3 \epsilon_0 \hbar \omega_{\mathbf{k}_0}^2} F_p(\omega_{\mathbf{k}_s}) P^2 \int_0^\infty d\tau I_p(\tau) \langle \Psi(\tau)|\hat{L}^\dagger \hat{L}|\Psi(\tau)\rangle \quad (13)$$

where $F_p(\omega) = (2\pi)^{-1} \int_{-\infty}^\infty dt C_p(t) e^{-i\omega t}$ is the (normalized) frequency density-of-states spectrum of the incident X-ray pulse.[21] Hence, the scattered X-rays have the same frequency distribution as the incident X-ray pulse, that is, the scattering can be considered to be over-all "elastic". We note that, for an incoherent sum of coherent subpulses, both the spectral widths of each of these subpulses as well as the possible variation in their carrier frequency contribute to the width of F_p.

Now consider this expression for the typical pulses obtained from synchrotron and laser plasma sources, namely, that the total *incoherent* pulse has a duration much longer than the time scale for the electronic motion (as dictated by the inverse electronic eigenenergy spacing). As mentioned in the Introduction, the state vector for the material system, $|\Psi(t)\rangle$, is created by the pump UV-laser pulse, and it therefore contains amplitude on the electronic ground state as well as on one (or several) excited electronic state(s). We expand $|\Psi(t)\rangle$ in the adiabatic basis and sum over the relevant electronic eigenstates, $|\Psi(t)\rangle = \sum_n |\chi_n(t)\rangle|n\rangle$, where $|n\rangle$ is an electronic eigenstate, and $|\chi_n(t)\rangle$ is the associated amplitude, which is a function of the nuclear coordinates. Then

$$\frac{d^2S}{d\Omega d\omega_{\mathbf{k}_s}} = \frac{\omega_{\mathbf{k}_s}}{2\pi^2 c^3 \epsilon_0 \hbar \omega_{\mathbf{k}_0}^2} F_p(\omega_{\mathbf{k}_s}) P^2 \times$$

$$\sum_n \int_0^\infty d\tau I_p(\tau) \langle \chi_n(\tau)|(\hat{L}^\dagger \hat{L})_{nn}|\chi_n(\tau)\rangle \quad (14)$$

In this expression, $(\hat{L}^\dagger \hat{L})_{mn} = \langle m|\hat{L}^\dagger \hat{L}|n\rangle$, which still depends on the nuclear coordinates. Only the diagonal elements contribute to eq 14 because of the rapidly oscillating terms (on the time scale of the pulse duration) arising from the energy spacing between different electronic states.[8-11]

Obviously, the details in the time-profile, I_p, and the frequency spectrum, F_p, of the incident X-pulse depend on the experimental setup. However, if the duration of the pulse is either sufficiently short or sufficiently long compared to the time scale of the nuclear dynamics, I_p may be replaced by either a delta function or a constant on the nuclear time scale. Likewise, if the width of F_p can be neglected, we can obtain a simplified expression for the differential scattering signal:

$$\frac{dS}{d\Omega} =$$

$$\frac{1}{2\pi^2 \epsilon_0 c^3 \hbar \omega_{\mathbf{k}_0}} P^2 \sum_n \int_0^\infty d\tau I_p(\tau) \langle \chi_n(\tau)|(\hat{L}^\dagger \hat{L})_{nn}|\chi_n(\tau)\rangle_{\mathbf{k}_s = \mathbf{k}_0} \quad (15)$$

As pointed out earlier, the frequency widths of X-ray pulses obtained from, for example, synchrotron radiation are typically on the order of percents of the carrier frequency. Hence, in order to simulate the finer details of the experimental signal, the actual frequency distribution of the incident X-ray pulse must be taken into account.[5]

We note that the above analysis can be generalized to a material system described by the density operator $\hat{\rho}(t)$ instead of the state vector $|\Psi(t)\rangle$ by carrying out the perturbation theory in Liouville space.[18,22] Hence, we may replace the expectation values over the material system in eq 13 by $\text{Tr}[\hat{L}^\dagger \hat{L}\hat{\rho}(t)]$, and in eqs 14 and 15 by $\text{Tr}_N[(\hat{L}^\dagger \hat{L})_{nn}\hat{\rho}_n(t)]$, where the trace is over the nuclear degrees of freedom only, and $\hat{\rho}_n(t) = \langle n|\hat{\rho}(t)|n\rangle$. With this replacement, eq 15 resembles the general expression given in ref 13, which is derived from a purely classical treatment of the X-ray field and its interaction with the material system followed by quantization of the latter. This is consistent with

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the fact that the classical analysis presented in ref 13 discards the coherence of the X-ray field by considering each scattering event to be independent and instantaneous (see also ref 16), which is reasonable with the present X-ray sources.[1]

B. Coherence Time Short Compared to Only Nuclear Dynamics. Equations 13−15 are valid if the time scales (as dictated by the inverse eigenenergy spacing) of both the nuclear and the electronic motion are long compared to the coherence time of the pulse. However, for a coherence time of tens of femtoseconds, say, the time scale of the electronic motion is not long in comparison when the electronic eigenenergy spacing is in the electronvolt range, typical for small molecules. This is a relevant limit for future coherent X-ray sources.[1,2]

Again we write the state of the material system as $|\Psi(t)\rangle = \sum_n |\chi_n(t)\rangle |n\rangle$, where $|n\rangle$ is an electronic eigenstate and $|\chi_n(t)\rangle$ is the associated amplitude (nuclear wave packet). Employing the Born−Oppenheimer approximation, which implies an integration over the electronic states under the condition $\langle m|\hat{T}_\mathbf{R}|\chi_n(t)\rangle |n\rangle = \hat{T}_\mathbf{R}|\chi_n(t)\rangle \delta_{nm}$, we obtain

$$e^{i\hat{H}_M\delta/2\hbar}\hat{L}^\dagger e^{-i\hat{H}_M\delta/\hbar}\hat{L}e^{i\hat{H}_M\delta/2\hbar} = \sum_{mnl} e^{i\hat{H}_{N,m}\delta/2\hbar}\hat{L}^\dagger_{mn}e^{-i\hat{H}_{N,n}\delta/\hbar}\hat{L}_{nl}e^{i\hat{H}_{N,l}\delta/2\hbar} \quad (16)$$

where the right-hand side (rhs) now only acts on the nuclear wave packets. Here $\hat{H}_{N,m} = \hat{T}_\mathbf{R} + V_m(\mathbf{R})$ is the Hamiltonian for the nuclear motion in the mth electronic state, and $\hat{L}_{mn} = \langle m|\hat{L}|n\rangle$, which is still a function of the nuclear coordinates due to the parametric dependence of the electronic states on the nuclear coordinates $\mathbf{R}$. Inserting this expression into eq 12, only the diagonal elements contribute because of the rapidly oscillating terms (on the time scale of the coherence time) arising from $V_n(\mathbf{R}) - V_m(\mathbf{R})$.[8−11] Hence, if we consider an X-ray pulse with a coherence time on the order of tens of femtoseconds and assume (i) that the electronic states are energetically well separated and (ii) that the nuclear dynamics can by ignored during the coherence of the X-ray pulse, we get

$$\frac{d^2S}{d\Omega d\omega_{\mathbf{k}_s}} = \frac{\omega_{\mathbf{k}_s}}{2\pi^2 c^3 \epsilon_0 \hbar \omega^2_{\mathbf{k}_0}}F_p(\omega_{\mathbf{k}_s})P^2 \times \sum_n \int_0^\infty d\tau I_p(\tau)\langle\chi_n(\tau)||\hat{L}_{nn}|^2|\chi_n(\tau)\rangle \quad (17)$$

With a coherence time of, say, 10 fs, the width of F_p (corresponding to $\Delta k \sim 10^{-4}$ Å) is certainly very small compared to the carrier frequency. Also, $\langle\chi_n(\tau)||\hat{L}_{nn}|^2|\chi_n(\tau)\rangle$ is typically constant over $|\mathbf{k}_s - \mathbf{k}_0| < 0.01$ Å^{-1} (see section III), and the width of F_p can safely be neglected in this case. Hence,

$$\frac{dS}{d\Omega} = \frac{1}{2\pi^2 \epsilon_0 c^3 \hbar \omega_{\mathbf{k}0}}P^2 \times \sum_n \int_0^\infty d\tau I_p(\tau)\langle\chi_n(\tau)||\hat{L}_{nn}|^2|\chi_n(\tau)\rangle_{k_s=k_0} \quad (18)$$

As before, this expression can be generalized to a material system described by the density operator $\hat{\rho}(t)$, replacing the expectation value over the material system by $\text{Tr}_N[|\hat{L}_{nn}|^2\hat{\rho}_n(t)]$, where the trace is over the nuclear degrees of freedom only, and $\hat{\rho}_n(t) = \langle n|\hat{\rho}(t)|n\rangle$.

We note that omitting in eq 16 the nuclear degrees of freedom, we obtain, from eq 18 in the continuous wave limit for an incident one-photon X-ray field ($I_p(t) = E^2_{k_0}$), the usual dif-

ferential cross section[16] for a single electron in the state $|n\rangle$:

$$\frac{d\sigma}{d\Omega} = \left(\frac{c}{V}\right)^{-1}\frac{d}{dt}\frac{dS}{d\Omega} = \left(\frac{q_e^2}{4\pi\epsilon_0 mc^2}\right)^2 P^2|\langle n|e^{i(\mathbf{k}_0-\mathbf{k}_s)\cdot\mathbf{r}}|n\rangle|^2_{k_s=k_0} \quad (19)$$

where c/V is the photon flux in the incident X-ray field, and the time derivative is evaluated prior to taking the limit in eq 8.

C. The Independent Atom Model. In order to simplify the relation between the differential scattering signal and the nuclear motion, we ignore the scattering from the nuclei and adopt the independent atom model (IAM) for the electrons,[9−11,14] in which the electrons are localized around the nuclei as in a free atom. In the IAM,

$$\hat{L}_{nn} \approx f_\mathbf{R}(\mathbf{Q}) = \sum_\alpha f_\alpha e^{i\mathbf{Q}\cdot\mathbf{R}_\alpha} \quad (20)$$

where the sum runs over all the atoms (nuclei), f_α is the atomic scattering factor, $\mathbf{R}_\alpha$ is the position of the atom, and $\mathbf{Q} = \mathbf{k}_0 - \mathbf{k}_s$ is the scattering vector.

From both eqs 15 and (18), we then obtain

$$\frac{dS}{d\Omega} = \frac{1}{2\pi^2\epsilon_0 c^3\hbar\omega_{\mathbf{k}_0}}P^2 \times \sum_n \int_0^\infty d\tau I_p(\tau) \int d\mathbf{R}|f_\mathbf{R}(\mathbf{Q})|^2_{k_s=k_0}\rho_n(\mathbf{R}, \tau) \quad (21)$$

where $\rho_n(\mathbf{R}, t) = \langle\mathbf{R}|\hat{\rho}_n(t)|\mathbf{R}\rangle$ is the unnormalized nuclear density on the electronic state n (= $|\chi_n(\mathbf{R},t)|^2$ for a pure state). To obtain eq 21 from eq 15, we used the idea that $\hat{L}_{mn} \approx \hat{L}_{nn}\delta_{nm}$ in the IAM, which can be argued from a quantum-chemical point of view.[14] In this connection, we recall that eq 15 may be too crude an approximation, and one may have to perform the actual integration over eq 14, which, in the IAM, becomes identical to the rhs of eq 21 without the restriction $k_s = k_0$ and multiplied by $(\omega_{\mathbf{k}_s}/\omega_{\mathbf{k}_0})F_p(\omega_{\mathbf{k}_s})$.

Expressions similar to eq 21 have been reported previously,[9−11,13,14] but here we have derived it, for the first time, from a fully quantum-mechanical treatment of the interaction between a molecular system and a pulsed X-ray field. Our derivation reveals that, within the IAM and the restrictions mentioned above, eq 21 is valid for an incident coherent (incoherent) X-ray pulse with a duration (coherence time) that is short compared to the time scale for nuclear motion, provided that, in both cases, the pulse duration is long compared to the time scale for electronic motion.

III. Application to Direct Bond Breaking

We consider the time-resolved X-ray scattering in a very simple process: direct bond breaking in a diatomic molecule (see Figure 1). A detailed numerical implementation has been presented previously for direct bond breaking in Br$_2$;[10] our aim here is to present a simplified analysis that highlights the relation between the key features in the dynamics and the time-dependent signals. A similar approach has been used for time-resolved pump−probe spectroscopy using optical probing (see, e.g., ref 23 and the references therein). We calculate the scattering signal for a diatomic molecule in its stationary ground state and the "instantaneous" signal, $F^n_{\text{inst}}(\mathbf{Q}, t) = \int d\mathbf{R}|f_\mathbf{R}(\mathbf{Q})|^2\rho_n(\mathbf{R}, \tau)$, in an excited nonstationary state created by laser excitation. For incoherent X-ray pulses that are not ultrashort, the expression
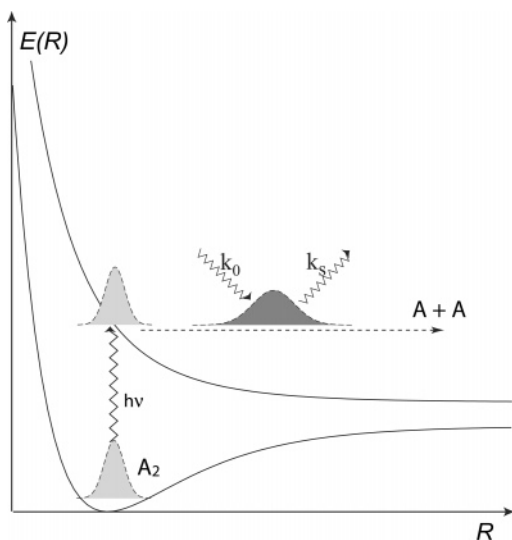
Figure 1. Schematic illustration of the laser-induced nonstationary probability density associated with the internuclear positions of a diatomic molecule. The probability density is shown in the excited (antibonding) state at two times: (a) after an instantaneous vertical excitation and (b) at a later time where the distribution is broadened as a result of the spreading of the wave packet. The scattering of an X-ray photon from this state is sketched.

for the signal must be convoluted with the temporal intensity profile of the X-ray pulse (cf. eq 21).

The scattering factor $f_\mathbf{R}(\mathbf{Q})$ for a diatomic molecule with bond vector $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$, takes, within the IAM, the form

$$|f_\mathbf{R}(\mathbf{Q})|^2 = \sum_{\alpha,\beta}^{2} f_\alpha(\mathbf{Q})^* f_\beta(\mathbf{Q}) e^{i\mathbf{Q}\cdot(\mathbf{R}_\alpha - \mathbf{R}_\beta)}$$

$$= |f_1(\mathbf{Q})|^2 + |f_2(\mathbf{Q})|^2 + f_1(\mathbf{Q})^* f_2(\mathbf{Q}) e^{-i\mathbf{Q}\cdot\mathbf{R}} +$$
$$f_1(\mathbf{Q}) f_2(\mathbf{Q})^* e^{i\mathbf{Q}\cdot\mathbf{R}}$$

$$= |f_1(\mathbf{Q})|^2 (2 + e^{-i\mathbf{Q}\cdot\mathbf{R}} + e^{i\mathbf{Q}\cdot\mathbf{R}}) \quad (22)$$

where, in the last line, we have specialized to a homonuclear diatomic, where the atomic scattering factors are identical (i.e., $f_1(\mathbf{Q}) = f_2(\mathbf{Q})$). The signal is then proportional to the expression

$$F_{\text{inst}}^n(\mathbf{Q}, t) = \int d\mathbf{R} |f_\mathbf{R}(\mathbf{Q})|^2 |\chi_n(\mathbf{R}, t)|^2$$

$$= 2|f_1(Q)|^2 \left(\int d\mathbf{R} |\chi_n(\mathbf{R}, t)|^2 + \right.$$
$$\left. \text{Re}\{ \int d\mathbf{R} e^{i\mathbf{Q}\cdot\mathbf{R}} |\chi_n(\mathbf{R}, t)|^2 \} \right)$$

$$(23)$$

where $Q = |\mathbf{Q}|$.

Since the interaction potential of the diatomic molecule is spherical symmetric, it is natural to consider the Hamiltonian in polar coordinates. Thus, the nuclear Hamiltonian for the relative motion takes the well-known form

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R} - \frac{\hat{L}^2}{\hbar^2 R^2}\right) + V(R) \quad (24)$$

where μ is the reduced mass, R is the internuclear distance, $\hat{L}$ is the angular momentum operator of the relative motion, and $V(R)$ is the electronic energy. Rotational invariance implies $[\hat{H},\hat{L}] = 0$, and the angular momentum associated with the relative motion is a constant of motion. We consider the dynamics of a state with a definite angular momentum, and write the radial part of the wave function in the form $u_l(R,t)/R$. We note that

$$\hat{H}\left(\frac{u_l(R,t)}{R}Y_{lm}(\theta,\phi)\right) = \frac{Y_{lm}(\theta,\phi)}{R}\hat{H}(l)u_l(R,t) \quad (25)$$

where Y_{lm} are the spherical harmonics eigenstates associated with the angular momentum, and $\hat{H}(l)$ is equivalent to a one-dimensional Hamiltonian given by

$$\hat{H}(l) = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + V_l(R) \quad (26)$$

with the effective potential

$$V_l(R) = V(R) + \frac{\hbar^2 l(l+1)}{2\mu R^2} \quad (27)$$

where the angular momentum quantum number $l = 0,1, \cdots$. Using eq 25, the time evolution of a state that is in a stationary rotational state can then be written in the form

$$e^{-i\hat{H}t/\hbar}\left(\frac{u_l(R)}{R}Y_{lm}(\theta,\phi)\right) = \frac{Y_{lm}(\theta,\phi)}{R}e^{-i\hat{H}(l)t/\hbar}u_l(R) \quad (28)$$

Thus, the radial motion takes place in the effective one-dimensional potential, $V_l(R)$. For a strongly repulsive potential, the motion is, to a good approximation, independent of l.

The complex exponential in eq 23 can be expanded in the form[24]

$$e^{i\mathbf{Q}\cdot\mathbf{R}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} i^l \frac{\hat{j}_l(QR)}{QR} Y_{lm}^*(\alpha,\delta) Y_{lm}(\theta,\phi) \quad (29)$$

where $\hat{j}_l(QR)$ is a Riccati−Bessel function (eigenfunction of the Hamiltonian in eq 26 for $V(R) = 0$), and (Q, α, δ) specifies the magnitude and direction of the $\mathbf{Q}$ vector. The Riccati−Bessel function is related to the spherical Bessel function $j_l(QR) = \hat{j}_l(QR)/(QR)$.

A. Signal, Ground State. First, we consider the scattering signal when the molecule is in the stationary vibrational−rotational ground state. Within a harmonic approximation to the vibrational ground state, $u_0(R)$ is given by a Gaussian

$$|G(R,t=0)|^2 = [2\pi(\Delta R)_0^2]^{-1/2} \exp\left[-\frac{(R - R_0)^2}{2(\Delta R)_0^2}\right] \quad (30)$$

where $(\Delta R)_0^2 = \hbar/(2m\omega)$. The scattering signal in eq 23 becomes

$$F_{\text{inst}}(\mathbf{Q}) = 2|f_1(Q)|^2(1 + \text{Re}\{\int d\mathbf{R} e^{i\mathbf{Q}\cdot\mathbf{R}} |\chi_{\text{gr}}(\mathbf{R}, t)|^2\})$$

$$= 2|f_1(Q)|^2\left(1 + [2\pi(\Delta R)_0^2]^{-1/2}\int_0^\infty dR \frac{\sin(QR)}{QR} \times \right.$$
$$\left. \exp\left[-\frac{(R - R_0^2)}{2(\Delta R)_0^2}\right]\right) \quad (31)$$

In this case, where the initial state is spherical symmetric, only the $l = m = 0$ term in eq 29 contributes to the integral because of the orthonormality of the spherical harmonics:

$$\langle Y_{l'm'}|Y_{lm}\rangle =$$
$$\int_0^\pi \int_0^{2\pi} Y_{l'm'}^*(\theta,\phi)Y_{lm}(\theta,\phi)\sin\theta d\theta d\phi = \delta_{ll'}\delta_{mm'} \quad (32)$$

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Typically $(\Delta R)_0/R_0$ corresponds to a few percent, and $(\Delta R)_0$ is largest for molecules with small masses and small force constants. In the classical limit $(\Delta R)_0^2 \to 0$, the integrand is nonzero only for $R = R_0$,

$$[2\pi(\Delta R)_0^2]^{-1/2} \exp\left[-\frac{(R - R_0)^2}{2(\Delta R)_0^2}\right] \to \delta(R - R_0) \text{ for } (\Delta R)_0^2 \to 0 \tag{33}$$

and

$$F_{\text{inst}}(\mathbf{Q}, t) = 2|f_1(Q)|^2\left(1 + \frac{\sin(QR_0)}{QR_0}\right) \tag{34}$$

which is just the classical standard result for a spherical symmetric molecule.

B. Signal, Excited Nonstationary State. Next, we consider the scattering signal when the molecule is in a nonstationary excited-state obtained by excitation out of the initial stationary vibrational–rotational ground state.

We consider an electronic transition in a molecule, from the electronic ground state "gr" to an excited state "ex". Within the electric-dipole approximation and first-order perturbation theory for the interaction with an electromagnetic field (see eq 3), the state vector associated with the nuclear motion in the excited electronic state "ex" is given by (at times, t, when the laser pulse has vanished)[25,26]

$$\chi_{\text{ex}}(x, t) = \frac{1}{i\hbar}\int_{-\infty}^{\infty} dt' e^{-i\epsilon_0 t'/\hbar} E_L(t')\phi(x, t - t') \tag{35}$$

where $\phi(x, t - t') = \langle x|\exp[-i\hat{H}_{\text{ex}}(t - t')/\hbar]|\phi\rangle$, $E_L(t)$ is the (pump) laser field, and

$$|\phi\rangle = \mu_{12} |\chi_{\text{gr}}\rangle, \tag{36}$$

is the Franck–Condon wave packet. In this expression, $|\chi_{\text{gr}}\rangle$ is the initial stationary nuclear state in the electronic ground state with energy ϵ_0, and μ_{12} is the projection of the electronic transition-dipole moment on the polarization vector of the electric field, which we define as the z-axis. Thus, the excited-state wave function can be thought of as a coherent superposition of Franck–Condon wave packets promoted to the upper state at times t' with different weighting factors (given by $E_L(t')$) and phases. At time t, each of these wave packets in the superposition has evolved for a time $t - t'$.

We specialize now to a delta pulse $E_L(t') = E_L\delta(t')$ on the nuclear time scale and a parallel transition where the transition-dipole moment is parallel to the bond vector $\mathbf{R}$. Then

$$\chi_{\text{ex}}(\mathbf{R}, t) = \frac{1}{i\hbar}\phi(\mathbf{R}, t) =$$
$$\frac{1}{i\hbar}e^{-i\hat{H}_{\text{ext}}/\hbar}\left(E_L|\mu_{12}|\frac{u_l(R)}{R}\cos\theta Y_{lm}(\theta, \phi)\right) \tag{37}$$

Assume $l = 0$, then $\cos\theta Y_{00} = \sqrt{1/3}Y_{10}$, and, according to eq 28,

$$\chi_{\text{ex}}(\mathbf{R}, t) = \frac{E_L|\mu_{12}|}{i\hbar R}\sqrt{1/3}Y_{10}e^{-i\hat{H}_{\text{ex}(l=1)t}/\hbar}u_0(R) \tag{38}$$

where we have assumed that the transition-dipole moment μ_{21} is constant, that is, independent of the internuclear distance (the Condon approximation), and where the spherical harmonic $Y_{10} = \sqrt{3/(4\pi)}\cos\theta$. The time evolution of the initial Gaussian is

now described within a time-dependent local harmonic approximation (LHA) to the center of the wave packet. The dynamics is then described by a Gaussian wave packet of the form[27,28]

$$G(x,t) = \exp[i\alpha_t(x - x_t)^2/\hbar + ip_t(x - x_t)/\hbar + i\gamma_t/\hbar] \tag{39}$$

where x_t and p_t are the expectation values of position and momentum, respectively, α_t and γ_t are complex numbers, $(\Delta x)_t^2 = \hbar/(4\text{Im}\alpha_t)$, the imaginary part of γ_t accounts for the normalization, and the real part of γ_t implies that the wave packet acquires a phase (the classical action). The probability density of the Gaussian is

$$|G(R,t)|^2 = [2\pi(\Delta R)_t^2]^{-1/2} \exp\left[-\frac{(R - R_t)^2}{2(\Delta R)_t^2}\right] \tag{40}$$

Then using eq 23, assuming the same atomic scattering factors as in the electronic ground state,

$$(\cos\theta)^2 = 2\sqrt{\pi}(2Y_{20}/\sqrt{5} + Y_{00})/3 \tag{41}$$

and eqs 29 and 32, we obtain

$$F_{\text{inst}}(\mathbf{Q},t) = A|f_1(Q)|^2\left(1 + N(t)\int_0^{\infty} dR\frac{\sin(QR)}{QR} \times\right.$$
$$\exp\left[-\frac{(R - R_t)^2}{2(\Delta R)_t^2}\right] - (3\cos^2\alpha - 1)N(t) \times$$
$$\left.\int_0^{\infty} dR\frac{\hat{j}_2(QR)}{QR} \exp\left[-\frac{(R - R_t)^2}{2(\Delta R)_t^2}\right]\right) \tag{42}$$

where $A = 2E_L^2|\mu_{12}|^2/3\hbar^2$, $N(t) = [2\pi(\Delta R)_t^2]^{-1/2}$ is the time-dependent normalization factor of the wave packet, and $\hat{j}_2(x) = (3/x^2 - 1)\sin x - (3/x)\cos x$ is a Bessel function. Because of the nonisotropic distribution of the molecules prior to X-ray scattering, the signal depends on Q as well as on the angle α between the polarization vector of the laser pulse and the $\mathbf{Q}$ vector.

The change in signal as a function of time is due to the change in the average internuclear distance R_t as well as the spreading of the wave packet $(\Delta R)_t$. $(\Delta R)_t/R_t$ for direct bond breaking corresponding to a purely repulsive potential can be much bigger than that for stationary structures. In the limit of an ultrashort δ pump, the Franck–Condon wave packet is localized at early times; however, the momentum uncertainty of the initial state gives rise to fast spreading of the wave packet. Longer pulses produce broader wave packets with slower spreading. Thus, at any given time, the signal is due to scattering from a distribution of structures. The magnitudes of the time-dependent terms in eq 42, at a fixed value of Q, decrease as the internuclear distance R_t increases (since the magnitudes of the spherical Bessel functions decrease at large internuclear distances).

In the classical limit $(\Delta R)_t^2 \to 0$, the integrands are nonzero only for $R = R_t$, and

$$F_{\text{inst}}(\mathbf{Q},t) =$$
$$A|f_1(Q)|^2\left(1 + \frac{\sin(QR_t)}{QR_t} - (3\cos^2\alpha - 1)\frac{\hat{j}_2(QR_t)}{QR_t}\right) \tag{43}$$
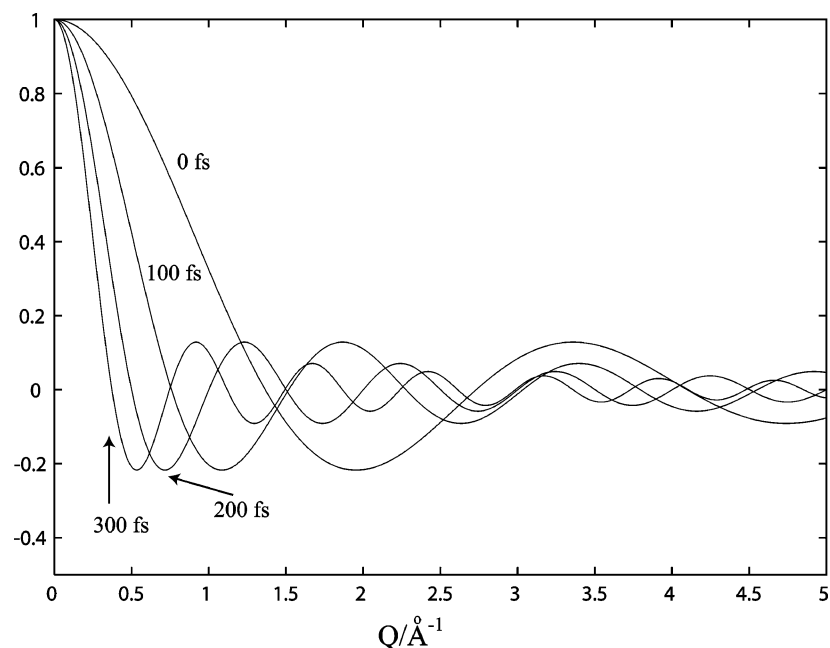
however, as we will see in a moment, the accuracy of this

Figure 2. The "classical result" in eq 43, i.e., $F_{inst}(Q,t)/(A|f_1(Q)|^2) - 1$, for direct bond breaking of Br_2. The classical trajectory corresponding to the interatomic potential specified in the text is given by $R_t/\text{Å} = 2.3 - (2.0/4.64) \ln(2.0/[\exp(0.0496t) + \exp(-0.0496t)])$, where time is measured in femtoseconds.
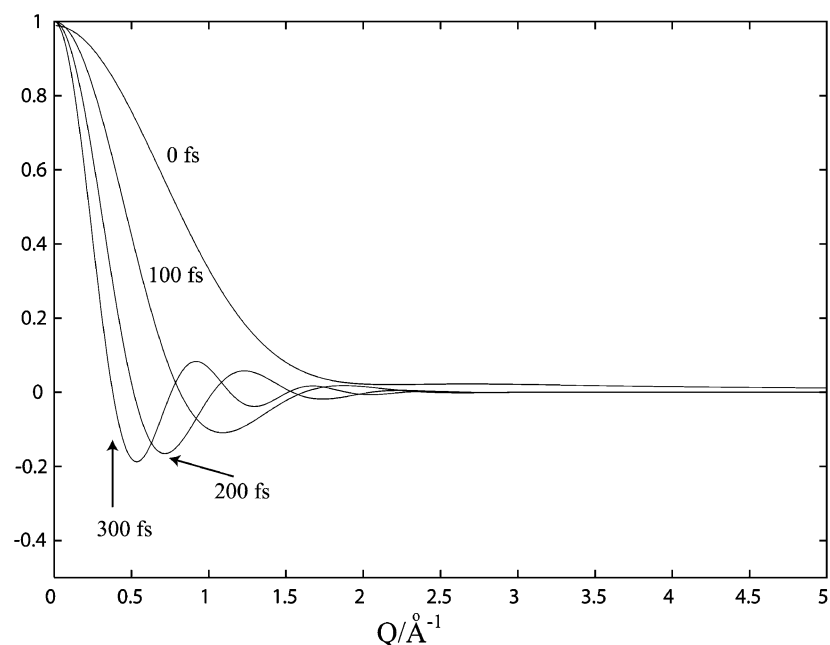

Figure 3. The exact result in eq 42, i.e., $F_{inst}(Q,t)/(A|f_1(Q)|^2) - 1$, based on a wave packet description of the interatomic motion for the same potential as in Figure 2. The width of the wave packet is $(\Delta R)_t = 1.0$ Å.

expression, as a result of the non-negligible width of the wave packet, is poor.

We consider now a numerical illustration, focusing on the signatures in the signal of the bond breaking, including the wave packet spreading. As an example, we consider the dynamics in a purely repulsive exponential potential corresponding to direct bond breaking. The potential $V(R) = V_0 \exp[-a(R - R_0)]$, with $V_0 = 0.949$ eV, $a = 4.64$ Å^{-1}, and $R_0 = 2.3$ Å, gives a good description of the $^1\Pi_u$ state of the Br_2 molecule (with the reduced mass 39.95 amu), and, with laser excitation at ~25 000 cm^{-1}, this state is the only one being populated.[29] This potential leads to essentially free relative motion after about 60 fs (i.e., the dissociation time of the bond), corresponding to an interatomic distance of about 3 Å.

When $\cos \alpha = 1/\sqrt{3}$, the last term in eq 42 disappears, and the signal is isotropic. We consider, in the following, the time dependence of the second term, that is, $F_{inst}(Q,t)/(A|f_1(Q)|^2) - 1$. Figure 2 shows the "classical result" in eq 43 for various times as a function of Q. Note that the signal at $t = 0$ (with the exception of a constant factor) is equivalent to the signal from the electronic ground state, and the signal continues to evolve in time also when the bond is broken. Figure 3 shows the exact result based on eq 42, including the finite width of the wave packet. If the wave packet was created with a δ pulse, as described above, the initial width would be equal to that of the ground state, and, already after about 100 fs, it will be on the order of $(\Delta R) = 1.0$ Å. If we use $(\Delta R)_t = 0.1$ Å, a result very close to the classical result is obtained, but, for $(\Delta R)_t = 1.0$ Å,

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which is shown in Figure 3, the signal is clearly modified, and a pronounced signal and time dependence is visible only for small values of Q. Clearly, when these "instantaneous" results are convoluted with the temporal intensity profile of the X-ray pulse, according to eq 21, the time dependence of the signal will tend to get washed out as the temporal duration of the X-ray pulse increases.

C. Thermal Effects. Above, we have considered the time-resolved X-ray scattering signal assuming that the initial state is the vibrational−rotational ground state. At any given time, the signal (eq 23) is due to scattering from a distribution of structures. This distribution is temperature dependent, and the signal is obtained as a thermal average over the initial states. The signal depends, in particular, on the probability density of interatomic distances.

We will here consider a mixed initial state which can be handled analytically for the vibrational part of the probability density. We consider a harmonic oscillator with a statistical mixture of states corresponding to thermal equilibrium.

The population of the nth quantum state is given by $p_n = e^{-E_n/(kT)}/Z$, where $E_n = \hbar\omega(n + 1/2)$, and $Z^{-1} = 2 \sinh[\hbar\omega/(2kT)]$. The probability density in position space (the diagonal density matrix element) is obtained from the stationary states of the harmonic oscillator $\phi_n(R,0)$, and takes the well-known Gaussian form[30]

$$\rho_{\mathrm{T}}(R, t = 0) = \sum_{n=0}^{\infty} |\phi_n(R,0)|^2 p_n$$

$$= \sqrt{\frac{m\omega}{\pi\hbar} \tanh\left(\frac{\hbar\omega}{2kT}\right)} \exp\left[-\frac{m\omega}{\hbar} \tanh\left(\frac{\hbar\omega}{2kT}\right)(R - R_0)^2\right] \quad (44)$$

which is a broadened version of eq 30.

We consider now laser excitation out of any of the pure vibrational quantum states (assuming again $l = 0$). The laser pulse is again a δ pulse, which, according to eq 38, creates Franck−Condon wave packets given by

$$\chi_{\mathrm{ex}}^n(\mathbf{R}, t) = \frac{E_{\mathrm{L}}|\mu_{12}|}{i\hbar R} \sqrt{1/3}\, Y_{10} \phi_n(R,t) \quad (45)$$

where $\phi_n(R,t) = \exp(-i\hat{H}_{\mathrm{ex}}t/\hbar)\phi_n(R,0)$, and $\phi_n(R,0)$ are the stationary vibrational states associated with the electronic ground state. Now, for UV-excitation out of a statistical mixture of pure states corresponding to thermal equilibrium, the probability density in position space becomes

$$\rho_{\mathrm{T}}(\mathbf{R}, t) = \sum_{n=0}^{\infty} |\chi_{\mathrm{ex}}^n(\mathbf{R}, t)|^2 p_n$$

$$= \frac{E_{\mathrm{L}}^2|\mu_{21}|^2}{3\hbar^2} Y_{10}^2/R^2 \sum_{n=0}^{\infty} |\phi_n(R,t)|^2 p_n \quad (46)$$

The summation can again be evaluated when $\phi_n(R,0)$ are stationary states of a harmonic oscillator.

We consider the (laser-induced) dynamics within the framework of the time-dependent LHA. That is, for $t > 0$, the stationary states evolve into generalized harmonic oscillator states, given by[28]

$$\phi_n(R,t) = (2^n n!)^{-1/2} G(R,t) H_n[\kappa_t(R - R_t)] e^{-in\beta_t} \quad (47)$$

where the time evolution of the expectation values of position R_t and momentum p_t is given by Hamilton's equations (with

initial conditions R_0 and $p_0 = 0$), $G(R,t)$ is the Gaussian wave packet of eq 39, H_n is the nth Hermite polynomial, $\kappa_t = \sqrt{2\mathrm{Im}\alpha_t/\hbar}$, and $\beta_t = (2/m)\int_0^t dt' \mathrm{Im}\alpha_{t'}$. That is,

$$|\phi_n(R,t)|^2 = (2^n n!)^{-1} |G(R,t)|^2 |H_n[\kappa_t(R - R_t)]|^2 \quad (48)$$

where

$$|G(R,t)|^2 = [2\pi(\Delta R)_t^2]^{-1/2} \exp\left[-\frac{(R - R_t)^2}{2(\Delta R)_t^2}\right] \quad (49)$$

with $(\Delta R)_t^2 = \hbar/(4\mathrm{Im}\alpha_t)$ being the time-dependent variance associated with the Gaussian, that is, $\phi_0(R,t)$. Using a well-known summation formula,[31] the density matrix at time t becomes

$$\sum_{n=0}^{\infty} |\phi_n(R,t)|^2 p_n = [2\pi(\Delta R)_t^2]^{-1/2} \exp\left[-\frac{(R - R_t)^2}{2(\Delta R)_t^2}\right] Z^{-1} \times$$

$$\sum_{n=0}^{\infty} |H_n[\kappa_t(R - R_t)]|^2 \frac{e^{-E_n/(kT)}}{2^n n!}$$

$$= \sqrt{\frac{1}{2\pi(\Delta R)_t^2} \tanh\left(\frac{\hbar\omega}{2kT}\right)} \exp\left[-\frac{(R - R_t)^2}{2(\Delta R)_t^2} \tanh\left(\frac{\hbar\omega}{2kT}\right)\right] \quad (50)$$

This result is a generalization of the density matrix associated with a time-dependent "thermal coherent state" of a harmonic oscillator[32] to the corresponding density matrix for a locally harmonic potential with a varying curvature. Thus, at any temperature, we have a Gaussian distribution centered around the time-dependent expectation value R_t and with a time-dependent width. In the low-temperature limit, $\hbar\omega \gg 2kT$, eq 50 reduces to eq 49.

Thus, the result at temperature T is identical to the situation where the initial state is the vibrational ground state, except for a broadening of the Gaussian with a (time-dependent) standard deviation in position given by

$$\sigma_{\mathrm{T}}(t) = (\Delta R)_t / \sqrt{\tanh\left(\frac{\hbar\omega}{2kT}\right)} \quad (51)$$

Typically $\hbar\omega/k$ (the vibrational "temperature") is on the order of 1000 K. For Br_2, $\hbar\omega/k = 463$ K, which implies that, for $T \leq 463$ K, one obtains $\sigma_{\mathrm{T}} \leq 1.47\sigma_0$, where $\sigma_0 = (\Delta R)_t$.

We can conclude that, at finite temperatures, the distribution of internuclear distances, i.e., the width of the dynamical nonequilibrium structure, is broadened by a time-independent (temperature-dependent) factor.

IV. Conclusions

The final result for the differential scattering cross section presented in eq 21 takes a simple intuitive form that is closely related to the standard result where the material system is in a stationary state. Thus, with the material system in a nonstationary state, one must simply add the results from a series of instantaneous structures with weights given by the temporal profile of the X-ray pulse. In this paper, we have investigated the basic formalism for X-ray scattering with pulsed fields, where we have paid attention to the identification of the proper form of the perturbation on the material system based on a fully quantized description of the radiation field, and to the various approximations that must be introduced in order to arrive at eq

21. Among other things, our investigations reveals that eq 21 is only valid provided that the frequency spread (or non-monochromaticity) of the incident X-ray pulse can be ignored. Otherwise, an average over the different frequency components must be performed, which is explicitly included in our analysis.

There are a number of questions that require further work; for example, questions concerning the signal for coherent X-ray pulses in the time domain where the pulses cannot be considered to be ultrashort on the time scale of nuclear motion, the signal when the electronic states of the material system are closely spaced, the validity of the IAM, and the inversion of experimental signals.

We have derived analytical expressions that capture the main features of the time-resolved X-ray signal for laser-induced direct bond breaking in a diatomic molecule. The expressions (valid for ultrashort coherent or incoherent X-ray pulses) display, in particular, the relation between the time-resolved signal, the average interatomic distance, and the uncertainty of the distance. The time-dependent uncertainty for non-stationary states plays an important role. Thus, because of this uncertainty, a pronounced time dependence of the signal will show up only for small values of Q. We have derived an analytical expression for the width of the dynamical nonequilibrium structure that is also valid at finite temperatures. This expression shows that the width is broadened by a time-independent, but temperature-dependent, factor.

In order to create a "molecular movie" of direct bond breaking, ultrashort (and intense) X-ray pulses are required. Such pulses will become available in the near future.

Appendix

In this appendix we argue that the analysis presented in section II remains essentially unaltered when using a more "classical-like" description of the incident X-ray pulse as a highly excited multimode coherent state.[33] We represent the incident X-ray pulse as a polarized, multimode coherent state

$$|\psi_{u\mathbf{k}_0}\rangle = \prod_k |\alpha_{k-k_0}u\mathbf{k}\rangle \qquad (A.52)$$

where a single-mode coherent state is a wave packet given by[21,33,34]

$$|\alpha_{\mathbf{k}}u\mathbf{k}\rangle = e^{-|\alpha_{\mathbf{k}}|^2/2} \sum_n \frac{(\alpha_k \hat{a}_{u\mathbf{k}}^\dagger)^n}{n!}|\text{vac}\rangle \qquad (A.53)$$

Hence, $|\psi_{u\mathbf{k}_0}\rangle$ consists of single-mode coherent states with wave vectors all pointing in the same direction (different from the direction of $\mathbf{k}_s$) but of varying length around the average length k_0. This state is not an eigenstate of the photon number operator $\hat{N} = \sum_u\sum_{\mathbf{k}} \hat{a}_{u\mathbf{k}}^\dagger \hat{a}_{u\mathbf{k}}$, but rather an eigenstate of the annihilation operator, $\hat{a}_{u\mathbf{k}}|\psi_{u\mathbf{k}_0}\rangle = \alpha_{k-k_0}|\psi_{u\mathbf{k}_0}\rangle$. Hence, the kth mode in eq A.52 contains an *average* of $|\alpha_{k-k_0}|^2$ photons, and, by analogy with the treatment in section II, α_k in eq A.52, defines a distribution that is peaked around zero with the width Δk, where $\Delta k \ll \mathbf{k}_0$. The state $|\psi_{u\mathbf{k}_0}\rangle$ is an eigenstate of the operator $\hat{E}^{(+)}(\mathbf{r}, t)$ with the eigenvalue $E(\mathbf{r}, t)$. Hence, the expectation value of the incident electric field is $2\text{Re}[E(\mathbf{r}, t)]$:

$$E(\mathbf{r}, t) = i\sum_k E_{\mathbf{k}}\alpha_k e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)} = iE_{\mathbf{k}_0}h(\mathbf{r}, t)e^{i(\mathbf{k}_0\cdot\mathbf{r}-\omega_{k0}t)} \qquad (A.54)$$

where $E_{\mathbf{k}} = \sqrt{\hbar\omega_{\mathbf{k}}/2\epsilon_0 V}$, and $h(\mathbf{r}, t) = \sum_k \sqrt{(k+k_0)/k_0}\alpha_k e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)}$ $\sim \sum_k \alpha_k e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)}$. By a similar analysis, $I(\mathbf{r}, t) = E_{\mathbf{k}_0}^2 |h(\mathbf{r}, t)|^2$. The relative uncertainty in the electric field amplitude diminishes with increasing mean photon number, and the average field variation resembles that of a pulsed classical field with the carrier wave defined by $\mathbf{k}_0$. For an, in this sense "classical-like", incident X-ray wave packet of highly excited coherent states, the field undergoes no noticeable change in the average photon number in the direction of $\mathbf{k}_0$ by scattering one photon into the direction $\mathbf{k}_s$ (different from the direction of $\mathbf{k}_0$). Hence, we use the final state $|\psi_{u\mathbf{k}_0}\rangle|v\mathbf{k}_s\rangle$. The perturbation to be used in eq 3 is therefore determined as $\hat{H}_{\text{int,M}} = \langle v\mathbf{k}_s|\langle\psi_{u\mathbf{k}_0}|\hat{H}_{\text{int}}|\psi_{u\mathbf{k}_0}\rangle$, which becomes

$$\hat{H}_{\text{int,M}} = \frac{-i}{\omega_{\mathbf{k}_0}}\sqrt{\frac{\hbar}{\epsilon_0 V\omega_{\mathbf{k}_s}}}P\sum_j \frac{q_j^2}{2m_j}E(\mathbf{r}_j, t)e^{-i(\mathbf{k}_s\cdot\mathbf{r}_j-\omega_{\mathbf{k}_s}t)} \qquad (A.55)$$

where P is the polarization factor between the incident beam and the scattered photon. It should be noted that, in the derivation of this expression, we have ignored contributions arising from the terms in $\hat{H}_{\text{int}}$ containing operator products $\hat{a}_{v\mathbf{k}_s}^\dagger$ $\hat{a}_{u\mathbf{k}}^\dagger$, although they are not strictly zero in this case, simply because these contributions do not represent the scattering process in question. Accepting these considerations, the results in section II remain unaltered by changing the representation of the incident X-ray pulse to a highly excited multi-mode coherent state.

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