

**Time-resolved ultrafast x-ray scattering from an incoherent electronic mixture**Gopal Dixit<sup>1,\*</sup> and Robin Santra<sup>2,3,4,†</sup><sup>1</sup>*Department of Physics, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India*<sup>2</sup>*Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany*<sup>3</sup>*The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany*<sup>4</sup>*Department of Physics, University of Hamburg, 20355 Hamburg, Germany*

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Time-resolved ultrafast x-ray scattering from photoexcited matter is an emerging method to image ultrafast dynamics in matter with atomic-scale spatial and temporal resolutions. For a correct and rigorous understanding of current and upcoming imaging experiments, we present the theory of time-resolved x-ray scattering from an incoherent electronic mixture using quantum electrodynamical theory of light-matter interaction. We show that the total scattering signal is an incoherent sum of the individual scattering signals arising from different electronic states, and therefore heterodyning of the individual signals is not possible for an ensemble of gas-phase photoexcited molecules. We scrutinize the information encoded in the total signal for the experimentally important situation when pulse duration and coherence time of the x-ray pulse are short in comparison to the time scale of the vibrational motion and long in comparison to the time scale of the electronic motion, respectively. Finally, we show that in the case of an electronically excited crystal the total scattering signal imprints the interference of the individual scattering amplitudes associated with different electronic states and heterodyning is possible.

DOI: [10.1103/PhysRevA.96.053413](https://doi.org/10.1103/PhysRevA.96.053413)**I. INTRODUCTION**

These days, technological advancements make it possible to generate tunable, ultrafast and intense x-ray pulses from x-ray free-electron lasers (XFELs) [1–3]. Several interesting successful experiments have been performed for systems ranging from atoms to complex biomolecules since the beginning of the operation of the first XFEL in the hard-x-ray regime, the Linac Coherent Light Source (LCLS) [4]. X-ray scattering is an indispensable method for obtaining real-space structure of matter with atomic-scale spatial resolution [5]. For a complete understanding of the structural-functional relationship of matter, it is crucial to image the dynamical evolution of matter in action with their natural spatial and temporal resolutions [6]. These ultrashort x-ray pulses from XFELs (LCLS, SACLA (SPRING-8 Angstrom Compact free electron LASER), European XFEL) offer femtosecond temporal resolution for structural imaging of matter. The pump-probe approach is a common way to trace ultrafast dynamics, where the dynamics are initiated by a short pump pulse and the activated dynamics are subsequently interrogated by the probe pulse at a precise time. Time-resolved x-ray scattering (TRXS) from temporally evolving matter records molecular “movies” to map out the atomic and electronic motions on their natural time scale [7,8].

Imaging of aligned gas-phase molecules has been demonstrated experimentally at LCLS [9]. Subsequently, a ring opening electrocyclic chemical reaction in cyclohexadiene was probed using TRXS. The temporally evolving structural information was extracted by a comparison of experimental data with theoretical simulations [10]. Also, cis/trans structural dynamics in photoactive yellow protein was imaged via TRXS [11]. Recently, Glowacki and co-workers imaged ultrafast vibrational motion in photoexcited molecular iodine at LCLS

using TRXS with a spatial and temporal resolution of 0.3 Å and 30 fs, respectively. Moreover, the idea of holographic (heterodyne) detection, based on the assumption of interference between the ground-state stationary charge distribution and the nonstationary excitation, was used to analyze the data in this experiment [12]. Also, plasma-based ultrashort x-ray sources have been used to image various nonequilibrium phenomena in matter using TRXS [13]. These state-of-the-art experiments have demonstrated that TRXS is an emerging and promising approach to imaging ultrafast processes in real space and in real time with atomic-scale spatiotemporal resolutions.

When a pump pulse interacts with a molecule or a crystal, it may create a superposition of electronic states. Depending upon the parameters of the pump, the superposition is a (partially) coherent or incoherent mixture of electronic states. If the pump pulse fluctuates from shot to shot (for instance, there is typically no carrier envelope phase stabilization), an incoherent electronic superposition is created. An incoherent electronic ensemble in molecular iodine was created in the recent experiment by Glowacki and co-workers [12]. There was no coherence between the ground and excited electronic states, and only full or partial vibrational coherence in each electronic state was present. The notion of heterodyne detection used to interpret the TRXS signal [12] was recently challenged by Mukamel and co-workers in a brief comment [14]. Note that the concept of heterodyne detection has been used to interpret the TRXS signal from an electronically excited solid [13,15], but there is no consistent quantum theory of TRXS from a nonstationary solid showing that the heterodyne detection is feasible. So why does the concept of heterodyne detection come under debate in the case of photoexcited gas-phase molecules while it is assumed to work well in the case of photoexcited crystal, as has been used by Elsaesser and co-workers for a long time [13,15]? In this article, we will explore this question and show that even though in both cases the scattering signal is based on the same mathematical structure, the information encoded in the respective signals is

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completely different. Note that the possibility of heterodyne detection in TRXS from a coherent electronic wave packet in an atom has been proposed by Vrakking and Elsaesser [16]. A time-resolved version of phase-contrast imaging has been proposed to image a coherent electronic wave packet [17].

The purpose of the present paper is to provide a rigorous theoretical analysis of TRXS from an incoherent electronic mixture, explicitly taking into account molecular vibrations (lattice dynamics in the case of a solid) using the quantum theory of light-matter interaction, and to discuss under what conditions heterodyne detection is possible. Note that the theory of TRXS from a coherent electronic wave packet is well established at different levels and the information encoded in the scattering signal has been discussed in detail [18–28]. This paper is structured as follows. Section II elucidates the theoretical framework required to describe TRXS from an incoherent electronic wave packet. Section III presents results and a discussion of the theory presented in the previous section. Section III is subdivided into two subsections, where we present: (A) an analysis of the theory in the situation when the x-ray pulse duration is much shorter than the dynamical time scale of the nuclear motion in a molecule, as well as the interplay of coherence time and pulse duration of the x-ray pulse in comparison to the characteristic dynamical time scale in a molecule; and (B) TRXS from an electronically excited crystal. Conclusions are presented in Sec. IV.

## II. THEORY

In this article, atomic units are used throughout unless specified otherwise. The density matrix for an incoherent ensemble prepared by the pump pulse reads

$$\hat{\rho}_{\text{in}}^{\text{m}}(t_0) = \sum_I p_I |\phi_I(\mathbf{R})\rangle \langle \phi_I(t_0)| \langle \phi_I(\mathbf{R})| \langle \chi_I(t_0)|. \quad (1)$$

Here,  $\hat{H}_{\text{el}}(\mathbf{R})|\phi_I(\mathbf{R})\rangle = E_I(\mathbf{R})|\phi_I(\mathbf{R})\rangle$ , where  $\hat{H}_{\text{el}}(\mathbf{R})$  is the electronic Hamiltonian and  $E_I(\mathbf{R})$  is the potential energy surface of the  $I$ th electronic state within the Born-Oppenheimer approximation.  $p_I$  is the probability of finding the molecule in the electronic state  $|\phi_I(\mathbf{R})\rangle$ . Both  $|\phi_I(\mathbf{R})\rangle$  and  $E_I(\mathbf{R})$  depend on the nuclear coordinates  $\mathbf{R}$  parametrically. In Eq. (1), the vibrational wave packet in the  $I$ th electronic state is given by

$$|\chi_I(t_0)\rangle = \sum_{\xi} C_{I;\xi} e^{-iE_{I;\xi}t_0} |\chi_{I;\xi}\rangle, \quad (2)$$

where  $|\chi_{I;\xi}\rangle$  obeys the nuclear Schrödinger equation,  $[\hat{T}_N + E_I(\mathbf{R})]|\chi_{I;\xi}\rangle = E_{I;\xi}|\chi_{I;\xi}\rangle$ , with  $\hat{T}_N$  the nuclear kinetic energy operator. The form of the density matrix presented in Eq. (1) implies that there is no coherence between any electronic states, but perfect vibrational coherence in each electronic state.

Within the language of quantum field theory, a consistent quantum theory for the matter and radiation fields is applied. The light-matter interaction Hamiltonian, from the principle of minimal coupling in the Coulomb gauge, is [29]

$$\hat{H}_{\text{int}} = \alpha \int d^3x \hat{\psi}^\dagger(\mathbf{x}) \left[ \hat{\mathbf{A}}(\mathbf{x}) \cdot \frac{\nabla}{i} \right] \hat{\psi}(\mathbf{x}) + \frac{\alpha^2}{2} \int d^3x \hat{\psi}^\dagger(\mathbf{x}) \hat{\mathbf{A}}^2(\mathbf{x}) \hat{\psi}(\mathbf{x}), \quad (3)$$

where  $\hat{\psi}(\mathbf{x})[\hat{\psi}^\dagger(\mathbf{x})]$  is the annihilation [creation] field operator for an electron at position  $\mathbf{x}$ ,  $\alpha$  is the fine-structure constant,  $\hat{\mathbf{A}}$  is the vector potential operator of the radiation, and  $\frac{\nabla}{i}$  is the canonical momentum of an electron. In the present formalism, we only focus on scattering induced by the  $\hat{\mathbf{A}}^2$  operator and will not consider the contribution in the scattering process from the  $\hat{\mathbf{A}}(\mathbf{x}) \cdot \nabla$  term given in Eq. (3); i.e., we neglect the contribution from the dispersion correction. In general, the radiation field must be considered as a statistical mixture of photons occupying all possible electromagnetic modes, and  $\hat{\mathbf{A}}$  is written as [29]

$$\hat{\mathbf{A}}(\mathbf{x}) = \sum_{\mathbf{k},s} \sqrt{\frac{2\pi}{V\omega_{\mathbf{k}}\alpha^2}} \{ \hat{a}_{\mathbf{k},s} \boldsymbol{\epsilon}_{\mathbf{k},s} e^{i\mathbf{k}\cdot\mathbf{x}} + \hat{a}_{\mathbf{k},s}^\dagger \boldsymbol{\epsilon}_{\mathbf{k},s}^* e^{-i\mathbf{k}\cdot\mathbf{x}} \}. \quad (4)$$

Here,  $\omega_{\mathbf{k}}$  is the energy of a photon in the  $\mathbf{k}$ th mode and  $V$  is the quantization volume.  $\boldsymbol{\epsilon}_{\mathbf{k},s}$  is the polarization vector in the  $\mathbf{k},s$  mode and  $\hat{a}_{\mathbf{k},s}^\dagger$  ( $\hat{a}_{\mathbf{k},s}$ ) is the photon creation (annihilation) operator, with  $\mathbf{k}$  being the wave vector and  $s$  the polarization index of a given mode. The initial density operator of the radiation field is written as [30]

$$\hat{\rho}_{\text{in}}^X = \sum_{\{n\},\{\bar{n}\}} \rho_{\{n\},\{\bar{n}\}}^X |\{n\}\rangle \langle \{\bar{n}\}|, \quad (5)$$

with  $\rho_{\{n\},\{\bar{n}\}}^X$  denoting the populations and coherences of all the occupied field modes associated with the incoming beam.  $\{n\}$  denotes a complete set of numbers that specify the number of photons in all field modes. All the scattering modes are unoccupied in  $\hat{\rho}_{\text{in}}^X$ .

The differential scattering probability (DSP), a crucial quantity in x-ray scattering, is expressed as

$$\frac{dP}{d\Omega} = \frac{V\alpha^3}{(2\pi)^3} \int_0^\infty d\omega_{\mathbf{k}_s} \omega_{\mathbf{k}_s}^2 P(\mathbf{k}_s), \quad (6)$$

where  $\omega_{\mathbf{k}_s}$  refers to the scattered photon energy and  $P(\mathbf{k}_s)$  is the probability of observing a scattered photon with momentum  $\mathbf{k}_s$ , which is different from the momenta of the incoming photons. Using the expression for  $P(\mathbf{k}_s)$  given in our earlier work [23], the DSP can be written as

$$\frac{dP}{d\Omega} = \frac{V\alpha^3}{(2\pi)^3} \int_0^\infty d\omega_{\mathbf{k}_s} \omega_{\mathbf{k}_s}^2 W_{\Delta\omega}(\omega_{\mathbf{k}_s}) \sum_{J;\mu} \sum_{\{n'\}} \langle \chi_{J;\mu} | \langle \phi_J(\mathbf{R}); \{n'\} | \hat{\rho}_f | \phi_J(\mathbf{R}); \{n'\} \rangle | \chi_{J;\mu} \rangle, \quad (7)$$

where  $W_{\Delta\omega}(\omega_{\mathbf{k}_s})$  is a spectral window function used to model the range of scattered photon energies accepted by the detector;  $\hat{\rho}_f$  is the density operator of the entire system at the time of measurement,

$$\hat{\rho}_f = \lim_{t_f \rightarrow \infty} \lim_{t_0 \rightarrow -\infty} \hat{U}_{\text{total}}(t_f, t_0) \hat{\rho}_{\text{in}}^s \hat{U}_{\text{total}}^\dagger(t_f, t_0), \quad (8)$$

where  $\hat{\rho}_{\text{in}}^s = \hat{\rho}_{\text{in}}^{\text{m}} \otimes \hat{\rho}_{\text{in}}^X$ , and  $\hat{U}_{\text{total}}(t_f, t_0)$  is the time-evolution operator for the whole system, matter and x rays.

First-order time-dependent perturbation theory is used to compute  $\hat{\rho}_f$ :

$$\hat{\rho}_f = \lim_{t_f \rightarrow \infty} \lim_{t_0 \rightarrow -\infty} \int_{t_0}^{t_f} \int_{t_0}^{t_f} dt_1 dt_2 \sum_{\{n\}, \{\bar{n}\}} \rho_{\{n\}, \{\bar{n}\}}^X \sum_I p_I [\hat{U}_{m, x}(t_f, t_1) \hat{H}_{\text{int}} \hat{U}_{m, x}(t_1, t_0) |\chi_I(t_0)\rangle |\phi_I\rangle |\{n\}\rangle |\{\bar{n}\}\rangle] \\ \times \langle \phi_I | \langle \chi_I(t_0) | \hat{U}_{m, x}^\dagger(t_2, t_0) \hat{H}_{\text{int}}^\dagger \hat{U}_{m, x}^\dagger(t_f, t_2) ] . \quad (9)$$

Here,  $\hat{U}_{m, x}$  is the time-evolution operator of the noninteracting matter and x-ray fields. The position of the nuclei,  $\mathbf{R}$ , has been dropped to make the expressions more compact.

After substituting the result for  $\hat{\rho}_f$  from Eq. (9) in Eq. (7), we obtain for the DSP

$$\frac{dP}{d\Omega} = \lim_{t_f \rightarrow \infty} \sum_{s_s=1}^2 \sum_{\mathbf{k}_1 s_1 \mathbf{k}_2 s_2} \sqrt{\frac{\pi^2}{V^2 \omega_{\mathbf{k}_1}}} \sqrt{\frac{\pi^2}{V^2 \omega_{\mathbf{k}_2}}} \frac{V \alpha^3}{(2\pi)^3} (\boldsymbol{\epsilon}_{\mathbf{k}_1, s_1} \cdot \boldsymbol{\epsilon}_{\mathbf{k}_s, s_s}^*) (\boldsymbol{\epsilon}_{\mathbf{k}_2, s_2}^* \cdot \boldsymbol{\epsilon}_{\mathbf{k}_s, s_s}) \int_0^\infty d\omega_{\mathbf{k}_s} \omega_{\mathbf{k}_s} W_{\Delta\omega}(\omega_{\mathbf{k}_s}) \int_{-\infty}^{t_f} \int_{-\infty}^{t_f} dt_1 dt_2 \\ \times \sum_{J; \mu} \sum_I p_I \left[ \int d^3x \langle \chi_{J; \mu} | \langle \phi_J | \hat{U}(t_f, t_1) \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) | \phi_I \rangle | \chi_I, t_1 \rangle e^{i(\mathbf{k}_1 - \mathbf{k}_s) \cdot \mathbf{x}} \right. \\ \left. \times \int d^3x' \langle \chi_I, t_2 | \langle \phi_I | \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}') \hat{U}^\dagger(t_f, t_2) | \phi_J \rangle | \chi_{J; \mu} \rangle e^{-i(\mathbf{k}_2 - \mathbf{k}_s) \cdot \mathbf{x}'} \right] \\ \times \left[ \sum_{\{n'\}} \sum_{\{n\}, \{\bar{n}\}} \rho_{\{n'\}, \{\bar{n}\}}^X \langle \{n'\} | \hat{a}_{\mathbf{k}_1, s_1} \hat{a}_{\mathbf{k}_s, s_s}^\dagger + \hat{a}_{\mathbf{k}_s, s_s}^\dagger \hat{a}_{\mathbf{k}_1, s_1} | \{n\} \rangle e^{i(E_{\{n'\}} - E_{\{n\}})t_1} e^{i(E_{\{\bar{n}\}} - E_{\{n'\}})t_2} \langle \{\bar{n}\} | \hat{a}_{\mathbf{k}_s, s_s} \hat{a}_{\mathbf{k}_2, s_2}^\dagger + \hat{a}_{\mathbf{k}_2, s_2}^\dagger \hat{a}_{\mathbf{k}_s, s_s} | \{n'\} \rangle \right]. \quad (10)$$

Here,  $\hat{U}$  is the time-evolution operator associated with the matter Hamiltonian, and  $E_{\{n\}}$  is the energy corresponding to Fock state  $|\{n\}\rangle$ .

Let us rearrange different terms in above equation, so that we can write the expression for the DSP as

$$\frac{dP}{d\Omega} = \sum_{s_s=1}^2 \sum_{\mathbf{k}_1 s_1 \mathbf{k}_2 s_2} \frac{\alpha^3}{2\pi V \sqrt{\omega_{\mathbf{k}_1} \omega_{\mathbf{k}_2}}} (\boldsymbol{\epsilon}_{\mathbf{k}_1, s_1} \cdot \boldsymbol{\epsilon}_{\mathbf{k}_s, s_s}^*) (\boldsymbol{\epsilon}_{\mathbf{k}_2, s_2}^* \cdot \boldsymbol{\epsilon}_{\mathbf{k}_s, s_s}) \int_0^\infty d\omega_{\mathbf{k}_s} \omega_{\mathbf{k}_s} W_{\Delta\omega}(\omega_{\mathbf{k}_s}) \\ \times \int_{-\infty}^\infty \int_{-\infty}^\infty dt_1 dt_2 \sum_I p_I \int d^3x \int d^3x' \langle \chi_I, t_2 | \langle \phi_I | \hat{n}(\mathbf{x}') \hat{U}(t_2, t_1) \hat{n}(\mathbf{x}) | \phi_I \rangle | \chi_I, t_1 \rangle \\ \times e^{-i(\mathbf{k}_2 - \mathbf{k}_s) \cdot \mathbf{x}'} e^{i(\mathbf{k}_1 - \mathbf{k}_s) \cdot \mathbf{x}} \text{Tr}[\hat{\rho}_{\text{in}}^X \hat{a}_{\mathbf{k}_2, s_2}^\dagger \hat{a}_{\mathbf{k}_1, s_1}] e^{-i\omega_{\mathbf{k}_1} t_1} e^{i\omega_{\mathbf{k}_2} t_2} e^{-i\omega_{\mathbf{k}_s} (t_2 - t_1)}. \quad (11)$$

Here,  $\hat{n}(\mathbf{x}) = \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x})$  is the electron density operator. For an x-ray probe pulse with small angular spread and small bandwidth, the ranges of  $\mathbf{k}_1, s_1$  and  $\mathbf{k}_2, s_2$ , in which  $\rho_{\{n\}, \{\bar{n}\}}^X$  is not negligible, are limited. Within these ranges, the polarization vectors and the factor  $\sqrt{\omega_{\mathbf{k}_1} \omega_{\mathbf{k}_2}}$  vary slowly with  $\mathbf{k}_1, s_1$  and  $\mathbf{k}_2, s_2$ . Here we assume that the incident x-ray pulse has a mean wave vector  $\mathbf{k}_{\text{in}}$  as the incident photon momentum and a mean polarization vector  $\boldsymbol{\epsilon}_{\mathbf{k}_{\text{in}}, s_{\text{in}}}$ . Therefore, one can replace both  $\boldsymbol{\epsilon}_{\mathbf{k}_1, s_1}$  and  $\boldsymbol{\epsilon}_{\mathbf{k}_2, s_2}$  with  $\boldsymbol{\epsilon}_{\mathbf{k}_{\text{in}}, s_{\text{in}}}$ , and the factor  $\sqrt{\omega_{\mathbf{k}_1} \omega_{\mathbf{k}_2}}$  with  $\omega_{\mathbf{k}_{\text{in}}}$  as the photon energy of the incident central carrier frequency. Therefore, Eq. (11) further simplifies to

$$\frac{dP}{d\Omega} = \frac{d\sigma_{\text{th}}}{d\Omega} \int_{-\infty}^\infty d\gamma \int_{-\infty}^\infty d\delta \int_0^\infty d\omega_{\mathbf{k}_s} W_{\Delta\omega}(\omega_{\mathbf{k}_s}) \frac{\omega_{\mathbf{k}_s}}{(2\pi \omega_{\mathbf{k}_{\text{in}}})^2} \alpha e^{-i\omega_{\mathbf{k}_s} \delta} \sum_I p_I \int d^3x \int d^3x' \\ \times \left\langle \chi_I, \gamma + \frac{\delta}{2} \right| \langle \phi_I | \hat{n}(\mathbf{x}') \hat{U} \left( \gamma + \frac{\delta}{2}, \gamma - \frac{\delta}{2} \right) \hat{n}(\mathbf{x}) | \phi_I \rangle \left| \chi_I, \gamma - \frac{\delta}{2} \right\rangle e^{-i\mathbf{k}_s \cdot (\mathbf{x} - \mathbf{x}')} G^{(1)} \left( \mathbf{x}', \gamma + \frac{\delta}{2}; \mathbf{x}, \gamma - \frac{\delta}{2} \right). \quad (12)$$

Here,

$$\frac{d\sigma_{\text{th}}}{d\Omega} = \alpha^4 \left( \sum_{s_s=1}^2 |\boldsymbol{\epsilon}_{\mathbf{k}_{\text{in}}, s_{\text{in}}}^* \cdot \boldsymbol{\epsilon}_{\mathbf{k}_s, s_s}|^2 \right) \quad (13)$$

is the Thomson scattering cross section of a free electron and  $G^{(1)}(\mathbf{x}', \gamma + \frac{\delta}{2}; \mathbf{x}, \gamma - \frac{\delta}{2})$  is the first-order correlation function of the x-ray field. We assume that the x-ray field is a chaotic ensemble of single x-ray pulses, such that

$$G^{(1)} \left( \mathbf{x}', \gamma + \frac{\delta}{2}; \mathbf{x}, \gamma - \frac{\delta}{2} \right) = e^{-\frac{\pi \delta^2}{2\delta_c^2}} e^{i\omega_{\mathbf{k}_{\text{in}}} \delta} 2\pi \alpha I(\gamma) e^{i\mathbf{k}_{\text{in}} \cdot (\mathbf{x} - \mathbf{x}')}, \quad (14)$$

where the coherence time  $\delta_c$  is much shorter than the pulse duration and  $I(\gamma)$  is the intensity of the x-ray pulse. For simplicity, the object is assumed to be much smaller than the transverse coherence length. Note that new time variables,  $\gamma = \frac{t_1 + t_2}{2}$  and  $\delta = t_2 - t_1$ , have been introduced in Eq. (12).

After substituting the first-order correlation function for chaotic x-ray pulses, the expression of the DSP can be written as

$$\frac{dP}{d\Omega} = \frac{d\sigma_{\text{th}}}{d\Omega} \int_0^\infty d\omega_{\mathbf{k}_s} W_{\Delta\omega}(\omega_{\mathbf{k}_s}) \frac{\omega_{\mathbf{k}_s}}{\omega_{\mathbf{k}_{\text{in}}}} \int_{-\infty}^\infty d\gamma \frac{I(\gamma)}{\omega_{\mathbf{k}_{\text{in}}}} \int_{-\infty}^\infty \frac{d\delta}{2\pi} C(\delta) e^{i\omega\delta} \times \sum_I p_I \int d^3x \int d^3x' \left\langle \chi_I, \gamma + \frac{\delta}{2} \left| \langle \phi_I | \hat{n}(\mathbf{x}') \hat{U} \left( \gamma + \frac{\delta}{2}, \gamma - \frac{\delta}{2} \right) \hat{n}(\mathbf{x}) | \phi_I \rangle \right| \chi_I, \gamma - \frac{\delta}{2} \right\rangle e^{i\mathbf{Q} \cdot (\mathbf{x} - \mathbf{x}')}, \quad (15)$$

where  $\omega = \omega_{\mathbf{k}_{\text{in}}} - \omega_{\mathbf{k}_s}$  is the photon energy transferred,  $\mathbf{Q} = \mathbf{k}_{\text{in}} - \mathbf{k}_s$  is the photon momentum transfer, and  $C(\delta) = e^{-\frac{\pi\delta^2}{2\delta_c^2}}$  defines the coherence function of the incident x-ray pulse. It is important to emphasize that the expression given in Eq. (15) for the DSP is a key result for TRXS from an incoherent electronic mixture in which no restrictions regarding the pulse duration or coherence time of the x-ray pulse in comparison to the characteristic dynamical time scales of the photoexcited target system are employed. Moreover, an intuitive and straightforward interpretation of Eq. (15) is not feasible as it is intertwined with  $\omega_{\mathbf{k}_s}$ ,  $\gamma$ , and  $\delta$  variables. In the following, we will simplify Eq. (15) considering practically relevant situations.

### III. RESULTS AND DISCUSSION

#### A. X-ray pulse short in comparison to the nuclear motion

Let us consider the situation where the probe x-ray pulse is sufficiently short to freeze the vibrational dynamics, i.e., the nuclear motion is assumed to be much slower than the x-ray pulse duration. Within this assumption, after collecting all the  $\gamma$ -dependent phases of the vibrational wave packets together with the  $I(\gamma)$ , the  $\gamma$ -dependent integral in Eq. (15) can be performed such that

$$\frac{dP}{d\Omega} = \mathcal{F} \frac{d\sigma_{\text{th}}}{d\Omega} \int_0^\infty d\omega_{\mathbf{k}_s} W_{\Delta\omega}(\omega_{\mathbf{k}_s}) \frac{\omega_{\mathbf{k}_s}}{\omega_{\mathbf{k}_{\text{in}}}} \int_{-\infty}^\infty \frac{d\delta}{2\pi} C(\delta) e^{i\omega\delta} \sum_I \sum_{J;\mu} p_I \int d^3x \int d^3x' \times \left\langle \chi_I, \tau_d + \frac{\delta}{2} \left| \langle \phi_I | \hat{n}(\mathbf{x}') | \phi_J \rangle | \chi_{J;\mu} \right\rangle e^{-iE_{J;\mu}\delta} \langle \chi_{J;\mu} | \langle \phi_J | \hat{n}(\mathbf{x}) | \phi_I \rangle | \chi_I, \tau_d - \frac{\delta}{2} \right\rangle e^{i\mathbf{Q} \cdot (\mathbf{x} - \mathbf{x}')}. \quad (16)$$

Here,  $\mathcal{F}$  is the fluence of the probe pulse (in units of number of photons per area) and  $\tau_d$  is the pump-probe delay time. Note that if one had allowed for any electronic coherences in the superposition of electronic states, then the  $\gamma$ -dependent integration would have eliminated any contributions from pairs of different electronic states, because an x-ray probe pulse duration of femtoseconds is long in comparison to the typical sub-femtosecond electronic time scales of interest here.

After substituting the expression for the vibrational wave packet, Eq. (2), the expression for the DSP becomes

$$\frac{dP}{d\Omega} = \mathcal{F} \frac{d\sigma_{\text{th}}}{d\Omega} \int_0^\infty d\omega_{\mathbf{k}_s} W_{\Delta\omega}(\omega_{\mathbf{k}_s}) \frac{\omega_{\mathbf{k}_s}}{\omega_{\mathbf{k}_{\text{in}}}} \int_{-\infty}^\infty \frac{d\delta}{2\pi} C(\delta) e^{i\omega\delta} \sum_{I;v,\xi} \sum_{J;\mu} p_I C_{I;v}^* C_{I;\xi} \times \int d^3x \int d^3x' \langle \chi_{I;v} | \langle \phi_I | \hat{n}(\mathbf{x}') | \phi_J \rangle | \chi_{J;\mu} \rangle \langle \chi_{J;\mu} | \langle \phi_J | \hat{n}(\mathbf{x}) | \phi_I \rangle | \chi_{I;\xi} \rangle e^{i(E_{I;v} - E_{I;\xi})\tau_d} e^{-i(2E_{J;\mu} - E_{I;v} - E_{I;\xi})\frac{\delta}{2}} e^{i\mathbf{Q} \cdot (\mathbf{x} - \mathbf{x}')}. \quad (17)$$

Now the  $\delta$  integral can be performed straight away, yielding another Gaussian as a function of the coherence time,

$$\int_{-\infty}^\infty \frac{d\delta}{2\pi} e^{-\frac{\pi\delta^2}{2\delta_c^2}} e^{-i(\omega_{\mathbf{k}_s} - \omega_{\mathbf{k}_{\text{in}}})\delta} e^{-i(2E_{J;\mu} - E_{I;v} - E_{I;\xi})\frac{\delta}{2}} = \frac{\delta_c}{\pi\sqrt{2}} e^{-\frac{\delta_c^2}{2\pi}(\omega_{\mathbf{k}_{\text{in}}} - \omega_{\mathbf{k}_s} + \tilde{E}_I - E_{J;\mu})^2}, \quad (18)$$

where  $(E_{I;v} + E_{I;\xi})/2$  has been replaced with the mean energy  $\tilde{E}_I$  of the vibrational wave packet in the  $I$ th electronic state. As the x-ray pulse duration is short enough to freeze the nuclear motion,  $|\tilde{E}_I - E_{J;\mu}| \ll 1/\delta_c$  holds and  $\exp[i(E_{I;v} - \tilde{E}_I)\delta_c/2]$  may be approximated by unity.

The typical situation is that the TRXS experiment does not use an energy-resolving scattering detector; i.e.,  $W_{\Delta\omega}(\omega_{\mathbf{k}_s}) = 1$ . Then the energy integral can also be performed:

$$\int_0^\infty d\omega_{\mathbf{k}_s} \omega_{\mathbf{k}_s} \frac{\delta_c}{\pi\sqrt{2}} e^{-\frac{\delta_c^2}{2\pi}(\omega_{\mathbf{k}_{\text{in}}} - \omega_{\mathbf{k}_s} + \tilde{E}_I - E_{J;\mu})^2} \simeq \omega_{\mathbf{k}_{\text{in}}}. \quad (19)$$

To obtain this result, two assumptions are made: (i) Only electronic and vibrational states contribute to the total scattering signal such that  $|\tilde{E}_I - E_{J;\mu}| \ll \omega_{\mathbf{k}_{\text{in}}}$  (i.e., the scattering process does not lead to an energy transfer anywhere close to the incoming photon energy [31,32]), and (ii) the width of the Gaussian in Eq. (19) must be small in comparison to  $\omega_{\mathbf{k}_{\text{in}}}$ ; i.e., the incoming x-ray pulse must be sufficiently monochromatic such that  $\delta_c \omega_{\mathbf{k}_{\text{in}}} \gg 1$ . Note that the Waller-Hartree approximation is used in performing the  $\omega_{\mathbf{k}_s}$  integral [32,33].

After combining the results obtained after performing the  $\delta$  and  $\omega_{\mathbf{k}_s}$  integrals in Eqs. (18) and (19), respectively, the expression for the DSP reduces to

$$\frac{dP}{d\Omega} = \frac{dP_e}{d\Omega} \sum_I \sum_{J;\mu} p_I \int d^3x \int d^3x' \langle \chi_I, \tau_d | \langle \phi_I | \hat{n}(\mathbf{x}') | \phi_J \rangle | \chi_{J;\mu} \rangle \langle \chi_{J;\mu} | \langle \phi_J | \hat{n}(\mathbf{x}) | \phi_I \rangle | \chi_I, \tau_d \rangle e^{i\mathbf{Q} \cdot (\mathbf{x} - \mathbf{x}')} , \quad (20)$$

where  $\frac{dP_e}{d\Omega} = \mathcal{F} \frac{d\sigma_{\text{th}}}{d\Omega}$  is the DSP from a free electron. Note that first quantization for the nuclear degrees of freedom is employed here; i.e.,  $\langle \chi_I | \langle \phi_I | \hat{n} | \phi_J \rangle | \chi_J \rangle$  implies an integration over  $\mathbf{R}$  [i.e.,  $\int d\mathbf{R} \chi_I^*(\mathbf{R}) \langle \phi_I | \hat{n} | \phi_J \rangle (\mathbf{R}) \chi_J(\mathbf{R})$ , where  $\langle \phi_I | \hat{n} | \phi_J \rangle (\mathbf{R})$  acts as an operator in  $\mathbf{R}$  space].

Now let us consider TRXS from a molecule consisting of a heavy element like iodine. This corresponds to the situation of the recent TRXS experiment [12] on the iodine molecule. As there are many electrons in iodine, one gets a large cross section if the electrons do not change their state in the x-ray scattering process. So it is appropriate to assume that the dominating contribution comes from electronic terms where  $I = J$ , i.e., electronically elastic scattering. Thus, under this assumption the DSP is given by

$$\frac{dP}{d\Omega} = \frac{dP_e}{d\Omega} \sum_I p_I \langle \chi_I, \tau_d | |f_I(\mathbf{Q})|^2 | \chi_I, \tau_d \rangle. \quad (21)$$

Here,  $f_I(\mathbf{Q}) = \int d^3x \langle \phi_I | \hat{n}(\mathbf{x}) | \phi_I \rangle e^{i\mathbf{Q} \cdot \mathbf{x}} = \int d^3x \rho_I(\mathbf{x}) e^{i\mathbf{Q} \cdot \mathbf{x}}$  is the electronic form factor. The completeness relation in  $\mathbf{R}$  space,

$$\sum_{\mu} | \chi_{J;\mu} \rangle \langle \chi_{J;\mu} | = \mathbb{1}_{\mathbf{R}}, \quad (22)$$

was used to obtain Eq. (21) from Eq. (20).

Now if the vibrational distribution  $| \chi_I(\mathbf{R}, \tau_d) |^2$  is sufficiently narrow, i.e., the electronic form factor squared must be approximately constant in the vicinity of the first moment of the vibrational distribution where the extension of that vicinity is given by the width of the vibrational distribution, then the main quantity of Eq. (21) may be simplified as  $\langle \chi_I, \tau_d | |f_I(\mathbf{Q})|^2 | \chi_I, \tau_d \rangle \approx \langle \chi_I, \tau_d | \chi_I, \tau_d \rangle |f_I(\mathbf{Q}, \mathbf{R}_{\tau_d}^{(I)})|^2 = |f_I(\mathbf{Q}, \mathbf{R}_{\tau_d}^{(I)})|^2$  with  $\mathbf{R}_{\tau_d}^{(I)} = \langle \chi_I, \tau_d | \mathbf{R} | \chi_I, \tau_d \rangle$ . Using this approximation, Eq. (21) may be written as

$$\frac{dP}{d\Omega} = \frac{dP_e}{d\Omega} \sum_I p_I |f_I(\mathbf{Q}, \mathbf{R}_{\tau_d}^{(I)})|^2. \quad (23)$$

Let us compare this result to the expression employed in Ref. [12]. To this end, we restrict the summation over  $I$  in Eq. (23) to only two electronic states: the ground electronic state ( $g$  in the notation of Ref. [12]) and the first excited electronic state ( $e$ ). Thus,

$$\frac{dP}{d\Omega} = \frac{dP_e}{d\Omega} [a |f^{(e)}(\mathbf{Q}, \mathbf{R}_{\tau_d}^{(e)})|^2 + (1-a) |f^{(g)}(\mathbf{Q}, \mathbf{R}_{\tau_d}^{(g)})|^2], \quad (24)$$

where  $a$  represents the population in the excited electronic state. Expressed in words, the scattering signal in the situation considered is obtained by incoherently averaging the differential scattering probabilities associated with the two electronic states  $g$  and  $e$ . By contrast, Eq. (4) in Ref. [12]) suggests that the x-ray scattering intensity at the detector is proportional

to  $|af^{(e)} + (1-a)f^{(g)}|^2$ , which represents a coherent average of the scattering amplitudes and, as demonstrated here, is not applicable to an incoherent electronic mixture. Interestingly, as shown in Ref. [23], such a coherent average is generally not even applicable when the electronic superposition is perfectly coherent. [Note that the electronic form factors  $f_I$  in Eq. (23) refer to the entire system considered. In the case of a gas-phase system, such as that considered in Ref. [12], one must average Eq. (23) over all molecular positions. As a consequence, molecule-molecule interference terms drop out. For that reason, the electronic form factors in Eq. (24) refer to individual molecules. We present more on this in Sec. III B.]

Our present finding does not support the idea of heterodyne detection of the scattering signal obtained from an incoherent electronic mixture in gas-phase photoexcited molecules, which was the key idea to analyze the recent experimental work in Ref. [12]; our present result is thus consistent with the brief remark made by Mukamel and co-workers [14] (see also Refs. [18,19]). As reflected in Eq. (21), the total scattering signal from an incoherent electronic mixture consists of an incoherent sum of individual scattering patterns obtained from each electronic state and weighted by an appropriate nuclear wave-packet density. The signal obtained from each electronic state is sensitive to vibrational coherence in each electronic state as a function of the pump-probe delay time.

The fractional contribution to the scattering signal from an excited electronic state is precisely of the order of the associated excitation probability, as one would expect. Ignoring higher-order terms of the excitation probability is not required in the present case, which is in contrast to the analysis used in Ref. [12], where the square of the excitation probability was ignored to explain an enhancement of the excited electronic-state scattering signal using the heterodyne detection concept.

It is very important to stress that assigning an additional degree of freedom corresponding to the pump-probe delay time to the total static electron density when transitioning from static x-ray scattering to TRXS and writing the total time-dependent electron density as a sum of electron densities, one for each electronic state, is not a correct approach and leads to a wrong interpretation of TRXS. However, this brings us to another important question: If heterodyne detection is not feasible in the case of an incoherent electronic mixture in gas-phase photoexcited molecules, then what justifies the extensively applied heterodyne detection for analyzing the total scattering signal from an electronically excited crystal [13,15]? We will answer this question in the next section.

## B. Time-resolved x-ray scattering from an electronically excited crystal

In order to develop a consistent quantum theory-based formalism for ultrafast x-ray scattering from an electronically excited crystal, we employ the following assumptions.



- (1) There is no electronic coherence.
  - (2) The unit cells may be assumed to be independent of one another (independent-unit-cell model).
  - (3) Each unit cell is either in its electronic ground state or in a well-defined excited state. In other words, only two eigenstates are considered.
  - (4) In the ground electronic state, the vibrational probability distribution is assumed to be stationary. In the excited state, the vibrational distribution is nonstationary.
- In order to obtain the TRXS signal from an electronically excited crystal, the key quantity from Eq. (21) is

$$S = \sum_I p_I \langle \chi_I, \tau_d | f_I(\mathbf{Q}) | \chi_I, \tau_d \rangle$$

$$= \sum_I p_I \int d\mathbf{R} |\chi_I(\mathbf{R}, \tau_d)|^2 \left| \int d^3x \rho_I(\mathbf{x}, \mathbf{R}) e^{i\mathbf{Q}\cdot\mathbf{x}} \right|^2. \quad (25)$$

We now use the index  $i$  to refer to the  $i$ th unit cell. Following the procedure described in Refs. [34,35], the global electronic configuration index  $I$  is given by  $I = (I_1, I_2, \dots, I_i, \dots)$ , where each  $I_i$  takes on only two values [0 and 1, or ground state (GS) and excited state (ES)]. By assumption of the independent-unit-cell model,

$$\underbrace{p_I |\chi_I(\mathbf{R}, \tau_d)|^2}_{\text{entire crystal}} = \prod_i \underbrace{p_{I_i} |\chi_{I_i}(\mathbf{R}_i, \tau_d)|^2}_{\text{ith unit cell}}. \quad (26)$$

Here,  $\mathbf{R}_i$  represents the nuclear positions in the  $i$ th unit cell;  $p_{I_i}$  is the associated electronic population and  $\chi_{I_i}(\mathbf{R}_i, \tau_d)$  is the associated vibrational wave function. Now let us express the total electron density in terms of the electron density of individual unit cells,

$$\int d^3x \rho_I(\mathbf{x}, \mathbf{R}) e^{i\mathbf{Q}\cdot\mathbf{x}} = \sum_i \int d^3x \rho_{I_i}(\mathbf{x}, \mathbf{R}_i) e^{i\mathbf{Q}\cdot\mathbf{x}}, \quad (27)$$

where  $\rho_{I_i}(\mathbf{x}, \mathbf{R}_i)$  is the electron density in the  $i$ th unit cell, which depends on the electronic state of the  $i$ th unit cell and on the nuclear positions in that unit cell. Let  $\mathbf{r}_i$  be the real-space lattice vector for the position of the  $i$ th unit cell. Using this, we write the electron position for the  $i$ th unit cell as  $\mathbf{x}_i = \mathbf{x} - \mathbf{r}_i$ . Hence, the above equation becomes

$$\int d^3x \rho_I(\mathbf{x}, \mathbf{R}) e^{i\mathbf{Q}\cdot\mathbf{x}} = \sum_i \left[ \int d^3x_i \rho_{I_i}(\mathbf{x}_i + \mathbf{r}_i, \mathbf{R}_i) e^{i\mathbf{Q}\cdot\mathbf{x}_i} \right] e^{i\mathbf{Q}\cdot\mathbf{r}_i}. \quad (28)$$

Let  $F_i(\mathbf{Q}) = \int d\mathbf{x}_i \rho_{I_i}(\mathbf{x}_i + \mathbf{r}_i, \mathbf{R}_i) e^{i\mathbf{Q}\cdot\mathbf{x}_i}$  be the structure factor of the  $i$ th unit cell in the electronic state  $I_i$  for a given  $\mathbf{R}_i$ . The dependence of  $F_i(\mathbf{Q})$  on  $I_i$  and  $\mathbf{R}_i$  must not be forgotten. So, Eq. (28) reduces to

$$\int d^3x \rho_I(\mathbf{x}, \mathbf{R}) e^{i\mathbf{Q}\cdot\mathbf{x}} = \sum_i F_i(\mathbf{Q}) e^{i\mathbf{Q}\cdot\mathbf{r}_i}. \quad (29)$$

Thus, after collecting results from Eqs. (26)–(29), Eq. (25) is written as

$$S = \sum_{I_1, I_2, \dots} \prod_i p_{I_i} \int d\mathbf{R}_i |\chi_{I_i}(\mathbf{R}_i, \tau_d)|^2 \sum_{i', j'} F_{i'}(\mathbf{Q}) \times F_{j'}^*(\mathbf{Q}) e^{i\mathbf{Q}\cdot(\mathbf{r}_{i'} - \mathbf{r}_{j'})}. \quad (30)$$

We must distinguish between terms where  $i' = j'$  and terms where  $i' \neq j'$ , i.e.,

$$S = \sum_{i'} S_{i'i'} + \sum_{\substack{i', j' \\ i' \neq j'}} S_{i'j'} e^{i\mathbf{Q}\cdot(\mathbf{r}_{i'} - \mathbf{r}_{j'})}, \quad (31)$$

where

$$S_{i'i'} = \sum_{I_1, I_2, \dots} \prod_i p_{I_i} \int d\mathbf{R}_i |\chi_{I_i}(\mathbf{R}_i, \tau_d)|^2 |F_{i'}(\mathbf{Q})|^2 = \prod_{i \neq i'} \sum_{I_i} p_{I_i} \int d\mathbf{R}_i |\chi_{I_i}(\mathbf{R}_i, \tau_d)|^2 \left[ \sum_{I_{i'}} p_{I_{i'}} \int d\mathbf{R}_{i'} |\chi_{I_{i'}}(\mathbf{R}_{i'}, \tau_d)|^2 |F_{i'}(\mathbf{Q})|^2 \right]. \quad (32)$$

We assume that  $\langle \chi_I | \chi_I \rangle_{\mathbf{R}} = 1$ ; i.e., the vibrational wave function for all nuclei is normalized. Since we further assume that each  $\chi_I$  factorizes into factors  $\chi_{I_i}(\mathbf{R}_i, \tau_d)$ , one for each unit cell, this is consistent with assuming that each  $\chi_{I_i}(\mathbf{R}_i, \tau_d)$  is normalized. This means

$$\prod_{i \neq i'} \sum_{I_i} p_{I_i} \underbrace{\int d\mathbf{R}_i |\chi_{I_i}(\mathbf{R}_i, \tau_d)|^2}_{=1} = \prod_{i \neq i'} \sum_{I_i} p_{I_i} = 1. \quad (33)$$

Here we exploited that irrespective of whether one allows only two or more electronic states,  $\sum_{I_i} p_{I_i} = 1$ . Hence,

$$S_{i'i'} = \sum_{I_{i'}} p_{I_{i'}} \int d\mathbf{R}_{i'} |\chi_{I_{i'}}(\mathbf{R}_{i'}, \tau_d)|^2 |F_{i'}(\mathbf{Q})|^2 = (1 - \eta) \int d\tilde{\mathbf{R}} |\chi_{GS}(\tilde{\mathbf{R}})|^2 |F^{GS}(\mathbf{Q}, \tilde{\mathbf{R}})|^2 + \eta \int d\tilde{\mathbf{R}} |\chi_{ES}(\tilde{\mathbf{R}}, \tau_d)|^2 |F^{ES}(\mathbf{Q}, \tilde{\mathbf{R}})|^2. \quad (34)$$

In this expression,  $\tilde{\mathbf{R}}$  denotes the nuclear coordinates in the unit cell. Because the scattering contributions  $S_{i'i'}$  depend on the electronic state of unit cell  $i'$  (and on the vibrational state associated with the electronic state), but not on the actual position of the unit cell, we may employ a generic  $\tilde{\mathbf{R}}$  rather than  $\mathbf{R}_{i'}$ . Here, the connection of  $p_{I_i}$  in the above equation with the notation used by Elsaesser and co-workers [13,15] has been made via

$$p_{I_i} = \begin{cases} \eta, & \text{if } I_i = 1 \text{ (ES),} \\ (1 - \eta), & \text{if } I_i = 0 \text{ (GS).} \end{cases} \quad (35)$$

Now, let us consider the other part of Eq. (31):

$$\begin{aligned}
 S_{i'j'} &= \sum_{I_1, I_2, \dots} \prod_i p_{I_i} \int d\mathbf{R}_i |\chi_{I_i}(\mathbf{R}_i, \tau_d)|^2 F_{i'}(\mathbf{Q}) F_{j'}^*(\mathbf{Q}) \\
 &= \left[ \sum_{I_{i'}} p_{I_{i'}} \int d\mathbf{R}_{i'} |\chi_{I_{i'}}(\mathbf{R}_{i'}, \tau_d)|^2 F_{i'}(\mathbf{Q}) \right] \left[ \sum_{I_{j'}} p_{I_{j'}} \int d\mathbf{R}_{j'} |\chi_{I_{j'}}(\mathbf{R}_{j'}, \tau_d)|^2 F_{j'}^*(\mathbf{Q}) \right] \\
 &= \left[ (1 - \eta) \int d\tilde{\mathbf{R}} |\chi_{GS}(\tilde{\mathbf{R}})|^2 F^{GS}(\mathbf{Q}, \tilde{\mathbf{R}}) + \eta \int d\tilde{\mathbf{R}} |\chi_{ES}(\tilde{\mathbf{R}}, \tau_d)|^2 F^{ES}(\mathbf{Q}, \tilde{\mathbf{R}}) \right] \\
 &\quad \times \left\{ (1 - \eta) \int d\tilde{\mathbf{R}} |\chi_{GS}(\tilde{\mathbf{R}})|^2 [F^{GS}(\mathbf{Q}, \tilde{\mathbf{R}})]^* + \eta \int d\tilde{\mathbf{R}} |\chi_{ES}(\tilde{\mathbf{R}}, \tau_d)|^2 [F^{ES}(\mathbf{Q}, \tilde{\mathbf{R}})]^* \right\}. \tag{36}
 \end{aligned}$$

This motivates introducing effective structure factors that are averaged over nuclear coordinates:  $F_{\text{eff}}^{GS}(\mathbf{Q}) = \int d\tilde{\mathbf{R}} |\chi_{GS}(\tilde{\mathbf{R}})|^2 F^{GS}(\mathbf{Q}, \tilde{\mathbf{R}})$ , and  $F_{\text{eff}}^{ES}(\mathbf{Q}, \tau_d) = \int d\tilde{\mathbf{R}} |\chi_{ES}(\tilde{\mathbf{R}}, \tau_d)|^2 F^{ES}(\mathbf{Q}, \tilde{\mathbf{R}})$ . Using these two effective structure factors, we arrive at

$$S_{i'j'} = |(1 - \eta) F_{\text{eff}}^{GS}(\mathbf{Q}) + \eta F_{\text{eff}}^{ES}(\mathbf{Q}, \tau_d)|^2. \tag{37}$$

Using the results from Eqs. (31), (34), and (37), it follows that

$$\begin{aligned}
 S &= \sum_i [(1 - \eta) \langle (F^{GS})^2 \rangle + \eta \langle (F^{ES})^2 \rangle] + \sum_{i \neq j} |(1 - \eta) F_{\text{eff}}^{GS}(\mathbf{Q}) + \eta F_{\text{eff}}^{ES}(\mathbf{Q}, \tau_d)|^2 e^{i\mathbf{Q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \\
 &= |(1 - \eta) F_{\text{eff}}^{GS}(\mathbf{Q}) + \eta F_{\text{eff}}^{ES}(\mathbf{Q}, \tau_d)|^2 \left| \sum_i e^{i\mathbf{Q} \cdot \mathbf{r}_i} \right|^2 + \sum_i [(1 - \eta) \langle (F^{GS})^2 \rangle + \eta \langle (F^{ES})^2 \rangle - |(1 - \eta) F_{\text{eff}}^{GS}(\mathbf{Q}) + \eta F_{\text{eff}}^{ES}(\mathbf{Q}, \tau_d)|^2], \tag{38}
 \end{aligned}$$

where the short-hand notations  $\langle (F^{GS})^2 \rangle = \int d\tilde{\mathbf{R}} |\chi_{GS}(\tilde{\mathbf{R}})|^2 |F^{GS}(\mathbf{Q}, \tilde{\mathbf{R}})|^2$  and  $\langle (F^{ES})^2 \rangle = \int d\tilde{\mathbf{R}} |\chi_{ES}(\tilde{\mathbf{R}}, \tau_d)|^2 |F^{ES}(\mathbf{Q}, \tilde{\mathbf{R}})|^2$  are used. The second term on the right-hand side of the second equality sign in Eq. (38) gives rise to diffuse scattering, whereas the first term contains the lattice sum  $\sum_i e^{i\mathbf{Q} \cdot \mathbf{r}_i}$ , which gives rise to Bragg scattering at reciprocal lattice vectors  $\mathbf{Q} = \mathbf{G}_{hkl}$ . Hence, the quantum theory developed here gives Bragg peak strengths proportional to  $|(1 - \eta) F_{\text{eff}}^{GS}(\mathbf{G}_{hkl}) + \eta F_{\text{eff}}^{ES}(\mathbf{G}_{hkl}, \tau_d)|^2$ , which is consistent with the expression used by Elsaesser and co-workers for the heterodyne detection in TRXS from an electronically excited crystal [13,15]. Finally, note that Eq. (31) applies also to the situation of TRXS from a photoexcited gas-phase sample. In that case,  $\mathbf{r}_{i'}$  and  $\mathbf{r}_{j'}$  refer to the positions of the individual gas-phase molecules. After averaging over those positions, all contributions from  $i \neq j$  disappear. As a consequence, the scattering signal is simply proportional to Eq. (34): The expression required to describe the recent TRXS experiment on photoexcited molecular iodine [12] is an incoherent sum of two scattering patterns, one corresponding to the ground electronic state and the other to the excited electronic state.

#### IV. CONCLUSION

The present work is focused on a rigorous, formal understanding of TRXS from an incoherent electronic mixture in gas-phase photoexcited molecules and electronically excited crystals. The considered electronic mixture has no coherence between electronic states, but has perfect vibrational coherence. In the case of gas-phase photoexcited molecules, the total scattering signal consists of an incoherent sum of the

signal associated with each electronic state weighted by the corresponding nuclear wave-packet densities. We find that there is no possibility of heterodyning of the signal related to different electronic states. Our finding remains unchanged even if we consider that the coherence time and pulse duration of the x-ray pulse are long in comparison to the time scale of the electronic motion but short in comparison to time scale of the vibrational motion. This conclusion is in contrast with recent experimental work where heterodyne detection was used to analyze the total scattering signal [12]. Also, a gas-phase sample of aligned molecules does not give rise to any molecule-molecule interferences, as the center-of-mass position vectors of the molecules remain completely random relative to each other. Therefore, alignment does not change this conclusion and rules out the feasibility of heterodyne detection. In the case of an electronically excited crystal, the total signal contains interference between signals arising from different electronic states, as a consequence of interfering contributions from different unit cells, even when vibrations are systematically taken into consideration, and shows the feasibility of the heterodyne detection. Note that we can derive the expression used by Elsaesser and co-workers under the assumption of the independent-unit-cell approximation; that approximation cannot in general be expected to be accurate for a real solid. The conceptual feasibility of heterodyne detection in a photoexcited crystal is due to the periodic nature of the crystal. In a gas-phase sample, the interferences required for heterodyning disappear. We believe that our present findings for TRXS from photoexcited gas-phase molecules and crystals will help to develop a better understanding of current and future TRXS experiments.

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