

Appendices for “Frequency-resolved ultrafast single-molecule diffraction of noisy X-ray pulses”

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Appendix A: The X-ray diffraction signal

The signal is given by the intensity of the diffracted field,

$$S(\omega_s, t_s, \mathbf{k}_s, \mathbf{r}_s) = \int d\mathbf{r} dt, \left\langle \mathbf{E}^{\dagger(trf\mathbf{k})}(\mathbf{r}, t) \mathbf{E}^{(trf\mathbf{k})}(\mathbf{r}, t) e^{-\frac{i}{\hbar} \int_{-\infty}^t d\tau \mathcal{H}_I(\tau)} \right\rangle, \quad (\text{A1})$$

where ω_s is the measured frequency, t_s is the measurement time, \mathbf{k}_s is the wvector and \mathbf{r}_s is the measurement location. The field is given by,

$$\mathbf{E}(\mathbf{r}, t) = \frac{1}{(2\pi)^4} \int d\omega \int d^3\mathbf{k} \mathbf{E}(\mathbf{k}, \omega) e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t}. \quad (\text{A2})$$

The electric field is subjected to a spectro-temporal gating using the following procedure Bennett *et al.* [1],

$$\begin{aligned} \mathbf{E}^{(t)}(\mathbf{r}, t) &= F_t(t, \bar{t}) \mathbf{E}(\mathbf{r}, t), \\ \mathbf{E}^{(tr)}(\mathbf{r}, t) &= F_r(\mathbf{r}, \bar{\mathbf{r}}) \mathbf{E}^{(t)}(\mathbf{r}, t), \\ \mathbf{E}^{(trf)}(\mathbf{r}, t) &= F_f(\omega, \bar{\omega}) \mathbf{E}^{(tr)}(\mathbf{r}, \omega), \\ \mathbf{E}^{(trf\mathbf{k})}(\mathbf{r}, t) &= F_{\mathbf{k}}(\mathbf{k}, \bar{\mathbf{k}}) \mathbf{E}^{(trf)}(\mathbf{k}, \omega), \end{aligned} \quad (\text{A3})$$

where $F_X(X, \bar{X})$ is a gating function from the physical coordinate X to the measured one \bar{X} . The signal can be recast in the form,

$$S(\omega_s, t_s, \mathbf{k}_s, \mathbf{r}_s) = \int \frac{d\omega}{2\pi} dt \int \frac{d\mathbf{k}}{(2\pi)^3} d\mathbf{r} W_B(t, \omega, \mathbf{r}, \mathbf{k}) W_D(t, \omega, \mathbf{r}, \mathbf{k}; t_s, \omega_s, \mathbf{r}_s, \mathbf{k}_s), \quad (\text{A4})$$

where,

$$W_D(t, \omega, \mathbf{r}, \mathbf{k}; t_s, \omega_s, \mathbf{r}_s, \mathbf{k}_s) = \int \frac{d\omega}{2\pi} |F_f(\omega, \omega_s)|^2 W_t(t, t_s, \omega - \omega_s) \int \frac{d^3\mathbf{k}}{(2\pi)^3} |F_{\mathbf{k}}(\mathbf{k}, \mathbf{k}_s)|^2 W_r(\mathbf{r}, \mathbf{r}_s, \mathbf{k} - \mathbf{k}_s), \quad (\text{A5})$$

is the detector spectrogram and,

$$W_B(t, \omega, \mathbf{r}, \mathbf{k}) = \int d\tau e^{-i\omega\tau} \int d\mathbf{R} e^{i\mathbf{k}\cdot\mathbf{R}} \left\langle \mathcal{T} \mathbf{E}_R^\dagger\left(\mathbf{r} + \frac{\mathbf{R}}{2}, t + \frac{\tau}{2}\right) \mathbf{E}_L\left(\mathbf{r} - \frac{\mathbf{R}}{2}, t - \frac{\tau}{2}\right) \right\rangle. \quad (\text{A6})$$

is the bare signal spectrogram is. The modes initially in the vacuum state are given by the vector potential,

$$\mathbf{A}(\mathbf{r}, t) = \sum_{\mathbf{k}, \mu} \sqrt{\frac{2\pi\hbar}{V\omega_{\mathbf{k}}}} \epsilon^{(\mu)}(\mathbf{k}) a_{\mathbf{k}, \mu} e^{i\mathbf{k}\cdot\mathbf{r} - i\omega_{\mathbf{k}}t}, \quad (\text{A7})$$

and,

$$\mathbf{A}_p(\mathbf{r}, t) = \bar{\epsilon}(\mathbf{k}_p) \int \frac{d\omega}{2\pi} A_p(\omega) e^{i\mathbf{k}_p\cdot\mathbf{r} - i\omega t}, \quad (\text{A8})$$

where $\bar{\epsilon}(\mathbf{k}_p)$ is the average polarization of the classical probe field .

The off-resonant resonant scattering of light by matter is described by the the minimal coupling,

$$\mathcal{H}_I = \int d\mathbf{r} \hat{\sigma}(\mathbf{r}, t) \hat{\mathbf{A}}^2(\mathbf{r}, t), \quad (\text{A9})$$

where $\hat{\sigma}$ is the charge density operator and \mathbf{A} is the vector potential. When the probe field is taken to classical, the first nonvanishing contribution to Eq.(A1) requires two interactions as depicted diagrammatically in Fig.(1). Solving Eq.(A4) using an ideal spatial gating,

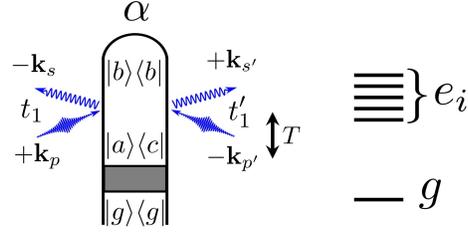


Figure 1. Diagrammatic description of off-resonant diffraction.

$$W_D(\mathbf{r}, \mathbf{r}_s, \mathbf{k}, \mathbf{k}_s) = \delta^{(3)}(\mathbf{r} - \mathbf{r}_s), \quad (\text{A10})$$

as done in Bennett *et al.* [1], we obtain Eq.(3) of the main text,

$$S^{[1]}(\bar{\omega}_s, \mathbf{Q}, T; \Lambda) = NK \int d\omega_s \omega_s^2 G(\omega_s, \bar{\omega}_s) \omega_s^2 \sum_{abc} \rho_{ac}(T) \\ \times \sigma_{ba}[\mathbf{Q}(\omega_s)] \sigma_{bc}^*[\mathbf{Q}(\omega_s)] \langle \mathbf{A}_p(\omega_s + \omega_{ba}) \mathbf{A}_p^*(\omega_s + \omega_{bc}) \rangle_{\Lambda}. \quad (\text{A11})$$

where N is the number of particles and,

$$K = \frac{|\hat{\epsilon}(\mathbf{k}_p) \cdot \epsilon_s^*|^2}{72\pi r^2 c^4}. \quad (\text{A12})$$

Appendix B: Construction of multidimensional stochastic resonance diffraction signals

1. Second order stochastic resonance: Signal-Intensity covariance

We consider a higher order post-processing calculation than mean signal by measuring the time-resolved intensity of the incident field. Once the intensity is measured Vs. time, its Fourier transform carries the phase fluctuations information of each experimental realization. The frequency domain intensity is given by,

$$\begin{aligned} I(\omega_p) &= \int dt e^{-i\omega_p t} |\mathbf{E}_p(t)|^2 \\ &= 2\pi \int d\omega' \omega' (\omega' + \omega_p) A^*(\omega') A(\omega' + \omega_p) e^{-i\lambda\{\varphi[\omega'] - \varphi[\omega' + \omega_p]\}}. \end{aligned} \quad (\text{B1})$$

The cross-correlation of the diffraction signal with a given frequency of the intensity,

$$\begin{aligned} \mathcal{S}_{SI}(\omega_s, \omega_p, \mathbf{Q}, T) &= \left\langle I[\omega_p; \Lambda] S^{[1]}(\omega_s, \mathbf{Q}, T; \Lambda) \right\rangle_{\Lambda} / 2\pi\kappa_1 \\ &= \sum_{abc} \sigma_{ba}(\mathbf{Q}) \sigma_{bc}^*(\mathbf{Q}) \mathbf{A}_{ab}^s \mathbf{A}_{cb}^{s*} e^{i\omega_{ca}T} \\ &\quad \times \int d\omega E(\omega) E^*(\omega + \omega_p) \\ &\quad \left\langle e^{i\lambda\{\varphi_{ab}^s - \varphi_{cd}^s - \varphi[\omega] + \varphi[\omega + \omega_p]\}} \right\rangle, \end{aligned} \quad (\text{B2})$$

the contribution of the last two terms comes from two separate intervals. The first when $(\omega, \omega + \omega_p)$ does not overlap with $(\omega_s + \omega_{ab}, \omega_s + \omega_{cb})$ is denoted Ω_{ind} , and second when they do will be denoted Ω_{corr} ,

$$\begin{aligned} \int d\omega E(\omega) E^*(\omega + \omega_p) \left\langle e^{i\lambda\{\varphi_{ab}^s - \varphi_{cd}^s - \varphi[\omega] + \varphi[\omega + \omega_p]\}} \right\rangle &= e^{-\lambda^2 \sigma^2 [|\omega_p| + |\omega_{ac}|]} I[\Omega_{ind}] \\ &\quad + \int_{\Omega_{corr}} d\omega E(\omega) E^*(\omega + \omega_p) e^{-\lambda^2 \sigma^2 [|\omega_s + \omega_{ab} - \omega| + |\omega_s + \omega_{cb} - \omega_p - \omega|]}, \end{aligned} \quad (\text{B3})$$

where $I[\Omega_{ind}] = \int_{\Omega_{ind}} d\omega E(\omega) E^*(\omega + \omega_p)$. The average intensity is given by,

$$\langle I[\omega_p; \Lambda] \rangle_{\Lambda} = I_p e^{-\lambda^2 \sigma^2 |\omega_p|}, \quad (\text{B4})$$

where I_p is the frequency-integrated intensity. This leads to a difference between the average intensity and the one correlated with the diffraction signal. In order to concentrate on the phase mixing terms which result in a higher temporal resolution, we assume that the interval $(\omega_s + \omega_{ab}, \omega_s + \omega_{cb})$ only contributes marginally to I_p such that the covariance \mathcal{C}_{SI} reads,

$$\begin{aligned} \mathcal{C}_{SI}(\omega_s, \omega_p, \mathbf{Q}, T) &= \left[\left\langle I[\omega_p; \Lambda] S^{[1]}(\omega_s, \mathbf{Q}, T; \Lambda) \right\rangle_{\Lambda} - \langle I[\omega_p; \Lambda] \rangle_{\Lambda} \left\langle S^{[1]}(\omega_s, \mathbf{Q}, T; \Lambda) \right\rangle_{\Lambda} \right] / 2\pi\kappa_1 \\ &= \sum_{abc} \sigma_{ba}(\mathbf{Q}) \sigma_{bc}^*(\mathbf{Q}) \mathbf{A}_{ab}^s \mathbf{A}_{cb}^{s*} e^{i\omega_{ca}T} \\ &\quad \times \left[\int_{\Omega_{corr}} d\omega E(\omega) E^*(\omega + \omega_p) \right. \\ &\quad \left. \times e^{-\lambda^2 \sigma^2 [|\omega_s + \omega_{ab} - \omega| + |\omega_s + \omega_{cb} - \omega_p - \omega|]} + \delta I_p[\Omega_{corr}] \right], \end{aligned} \quad (\text{B5})$$

where,

$$\delta I_p = I[\Omega_{ind}] e^{-\lambda^2 \sigma^2 [|\omega_p| + |\omega_{ac}|]} - I_p e^{-\lambda^2 \sigma^2 |\omega_p|}. \quad (\text{B6})$$

when the interval $(\omega_s + \omega_{ab} \pm \omega_p, \omega_s + \omega_{cb} \pm \omega_p)$ does not include the central frequency and $\lambda\sigma$ is large, δI_p becomes negligible which results in the phase-mixing terms only. When the phase fluctuations are strong and σ is larger than the pulse bandwidth such that the exponent in Eq.(B5) is rapidly decreasing and the field envelope can be considered to be constant throughout the integration interval of Ω_{corr} , we can estimate the integral,

$$\begin{aligned} & \int d\omega E(\omega + \omega_s + \omega_{ab}) \\ & \times E^*(\omega + \omega_p + \omega_s + \omega_{ab}) e^{-\lambda^2 \sigma^2 |\omega - \Delta|} \\ & \approx I_p [\Omega_{corr}] \frac{2}{\lambda^2 \sigma^2}, \end{aligned} \quad (B7)$$

where $\Delta = \omega_{ca} - \omega_p$. This constant sum in contrast to \mathcal{S}_{SI} , where averaging over many realizations with fluctuating phase results in a trade-off between frequency and temporal resolution. The signal in this case reads,

$$\begin{aligned} \mathcal{C}_{SI}(\omega_s, \omega_p, \mathbf{Q}, T) &= \kappa_2^{-1} \text{Cov}_\Lambda \left\{ I[\omega_p; \Lambda] S^{[1]}(\omega_s, \mathbf{Q}, T; \Lambda) \right\} \\ &= \sum_{abc} \sigma_{ba}(\mathbf{Q}) \sigma_{bc}^*(\mathbf{Q}) \overline{A_{ab}^s A_{cb}^{s*}} e^{i\omega_{ca} T}, \end{aligned} \quad (B8)$$

and $\kappa_2^{-1} = \frac{\pi \kappa_1}{\sigma^2 \lambda^2} I_p [\Omega_{corr}]$. This signal recovers the single molecule diffraction studied in [2] and contains the full temporal dynamics.

2. Diffraction-Field covariance

We now imagine a scenario in which the frequency dispersed expression for the electric field (including the phase) can be stored for each realization of the stochastic field. This is possible by heterodyne measurement of the incident field with a known reference, and then shifting the reference by $\pi/2$. This will reveal the symmetric contribution to the phase (cosine) and the antisymmetric (sine) and reconstruct the field, including the phase. Using this technique, we can avoid the additional integration that emerges naturally in Eq.(B1). The first nonvanishing contribution is given by,

$$\mathcal{S}_{S;EE}(\omega_s, \omega_1, \omega_2, \mathbf{Q}, T) = \kappa_2^{-1} \left\langle E[\omega_1; \Lambda] S^{[1]}(\omega_s, \mathbf{Q}, T; \Lambda) E^*[\omega_2; \Lambda] \right\rangle_\Lambda, \quad (B9)$$

This signal results in a the phase exponent,

$$\left\langle e^{i\lambda(\varphi_{ab}^s - \varphi_{cb}^s + \varphi[\omega_1] - \varphi[\omega_2])} \right\rangle_\Lambda.$$

When the interval (ω_1, ω_2) does not overlap $(\omega_s + \omega_{ab}, \omega_s + \omega_{cb})$, this can be factorized as,

$$\left\langle e^{i\lambda(\varphi_{ab}^s - \varphi_{cb}^s)} \right\rangle \left\langle e^{i\lambda\{\varphi[\omega_1] - \varphi[\omega_2]\}} \right\rangle = e^{-\lambda^2 \sigma^2 |\omega_{ca}|} e^{-\lambda^2 \sigma^2 |\omega_1 - \omega_2|}, \quad (B10)$$

which suppresses the temporal evolution even further. This can be eliminated by calculating the covariance, which recovers the phase mixing terms. We define the covariance signal as,

$$\begin{aligned} \mathcal{C}_{S;EE}(\omega_s, \omega_1, \omega_2, \mathbf{Q}, T) &= \kappa_2^{-1} \left\langle E[\omega_1; \Lambda] S^{[1]}(\omega_s, \mathbf{Q}, T; \Lambda) E^*[\omega_2; \Lambda] \right\rangle_\Lambda \\ &\quad - \kappa_2^{-1} \left\langle E[\omega_1; \Lambda] E^*[\omega_2; \Lambda] \right\rangle_\Lambda \left\langle S^{[1]}(\omega_s, \mathbf{Q}, T; \Lambda) \right\rangle_\Lambda. \end{aligned} \quad (B11)$$

The ensemble average over the stochastic degrees of freedom yields,

$$\left\langle e^{i\lambda\{\varphi_{ab}^s - \varphi_{cb}^s - \varphi[\omega_1] + \varphi[\omega_2]\}} \right\rangle_\Lambda - \left\langle e^{i\lambda\{\varphi_{ab}^s - \varphi_{cb}^s\}} \right\rangle_\Lambda \left\langle e^{-i\lambda\{\varphi[\omega_1] - \varphi[\omega_2]\}} \right\rangle_\Lambda, \quad (B12)$$

this factor does not vanish when the integration interval (ω_1, ω_2) overlaps with $(\omega_s + \omega_{ab}, \omega_s + \omega_{cb})$, which results in the phase mixing contributions. Assuming $\omega_2 > \omega_1$ and $\omega_{ca} > 0$ (without loss of generality) we have,

$$\varphi_{ab}^s - \varphi_{cd}^s - \varphi[\omega_1] + \varphi[\omega_2] = \int_{\omega_s + \omega_{ab}}^{\omega_1} d\omega\phi - \int_{\omega_s + \omega_{cb}}^{\omega_2} d\omega\phi, \quad (\text{B13})$$

where the sign flips when boundary frequencies cross. This will not change the correlation function that only depends on the the interval length. The overall correlation function then reads,

$$\mu_{abc}(\sigma) = \begin{cases} e^{-\lambda^2\sigma^2|\omega_1 - \omega_s - \omega_{ab}|} e^{-\lambda^2\sigma^2|\omega_2 - \omega_s - \omega_{cb}|}; & \omega_{ca} > 0 \\ e^{-\lambda^2\sigma^2|\omega_2 - \omega_s - \omega_{ab}|} e^{-\lambda^2\sigma^2|\omega_1 - \omega_s - \omega_{cb}|}; & \omega_{ca} < 0 \end{cases}. \quad (\text{B14})$$

By tuning $\omega_1 = \omega_s + \omega_{ab}$ and $\omega_2 = \omega_s + \omega_{cb}$, one can probe the temporal dynamics around these two frequency windows of width $\propto 1/\lambda^2\sigma^2$. This demonstrates the frequency-time resolution tradeoff for noisy pulses. The overall signal reads,

$$\begin{aligned} C_{S;EE}(\omega_s, \omega_1, \omega_2, \mathbf{Q}, T) &= \kappa_2^{-1} \left\{ \left\langle E[\omega_1; \Lambda] S^{[1]}(\omega_s, \mathbf{Q}, T; \Lambda) E^*[\omega_2; \Lambda] \right\rangle_{\Lambda} - \left\langle E[\omega_1; \Lambda] E^*[\omega_2; \Lambda] \right\rangle_{\Lambda} \left\langle S^{[1]}(\omega_s, \mathbf{Q}, T; \Lambda) \right\rangle_{\Lambda} \right\} \quad (\text{B15}) \\ &= |A^s|^2 \underbrace{\mu_{ggg} |\sigma_{gg}(\mathbf{Q})|^2}_{(a)} + \sum_e \mu_{geg} |A_{ge}^s|^2 \underbrace{|\sigma_{eg}(\mathbf{Q})|^2}_{(b)} + \sum_{e_1 e_2} \mu_{e_1 g e_2} A_{e_1 g}^s A_{e_2 g}^{s*} \underbrace{\sigma_{e_1 g}(\mathbf{Q}) \sigma_{e_2 g}^*(\mathbf{Q})}_{(d)} e^{i\omega_{e_1 e_2} T} \\ &+ \sum_{e_1 e_2 e_3} \mu_{e_1 e_2 e_3} A_{e_1 e_2}^s A_{e_3 e_2}^{s*} \underbrace{\sigma_{e_1 e_2}(\mathbf{Q}) \sigma_{e_3 e_2}^*(\mathbf{Q})}_{(c)} e^{i\omega_{e_1 e_3} T} \\ &+ 2\Re \left\{ \sum_{e_1} e^{i\omega_{e_1 g} T} \left[\underbrace{\mu_{e_1 g g} A_{e_1 g}^s A_{g g}^{s*} \sigma_{e_1 g}(\mathbf{Q}) \sigma_{g g}^*(\mathbf{Q})}_{(e \ \& \ h)} + \sum_{e_2} \mu_{e_1 e_2 g} A_{e_1 e_2}^s A_{g e_2}^{s*} \underbrace{\sigma_{e_1 e_2}(\mathbf{Q}) \sigma_{g e_2}^*(\mathbf{Q})}_{(f \ \& \ g)} \right] \right\}. \end{aligned}$$

We verify in this case that each contribution to the signal can be controlled by $\mu_{abc}(\sigma)$. Generally ω_1 and ω_2 can be chosen from different bands (or scales) such that the contribution by diagram can be explicitly written (mostly $\omega_{ca} > 0$ excluding the last two term),

$$\begin{cases} \mu_{ggg} = e^{-\lambda^2\sigma^2|\omega_1 - \omega_s|} e^{-\lambda^2\sigma^2|\omega_2 - \omega_s|}; & \text{a} \\ \mu_{geg} = e^{-\lambda^2\sigma^2|\omega_1 - \omega_s - \omega_{ge}|} e^{-\lambda^2\sigma^2|\omega_2 - \omega_s - \omega_{ge}|}; & \text{b} \\ \mu_{e_1 e_2 e_3} = e^{-\lambda^2\sigma^2|\omega_1 - \omega_s - \omega_{e_1 e_2}|} e^{-\lambda^2\sigma^2|\omega_2 - \omega_s - \omega_{e_3 e_2}|}; & \text{c, } e_1 < e_3 \\ \mu_{e_1 g e_2} = e^{-\lambda^2\sigma^2|\omega_1 - \omega_s - \omega_{e_1 g}|} e^{-\lambda^2\sigma^2|\omega_2 - \omega_s - \omega_{e_2 g}|}; & \text{d, } e_1 < e_2 \\ \mu_{e_1 g g} = e^{-\lambda^2\sigma^2|\omega_2 - \omega_s - \omega_{e_1 g}|} e^{-\lambda^2\sigma^2|\omega_1 - \omega_s|}; & \text{(e \& h)} \\ \mu_{e_1 e_2 g} = e^{-\lambda^2\sigma^2|\omega_2 - \omega_s - \omega_{e_1 e_2}|} e^{-\lambda^2\sigma^2|\omega_1 - \omega_s - \omega_{g e_2}|}; & \text{(f \& g)} \end{cases}. \quad (\text{B16})$$

This is a demonstration of a possible combination for the correlation function used in Eq.(8) of the main text, one has to determine the contributions for $\omega_{ca} < 0$ as well.

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- [1] K. Bennett, J. D. Biggs, Y. Zhang, K. E. Dorfman, and S. Mukamel, *Journal of Chemical Physics* **140** (2014), 10.1063/1.4878377.
[2] K. Bennett, M. Kowalewski, J. R. Rouxel, and S. Mukamel, *Proceedings of the National Academy of Sciences* **115**, 6538 (2018).