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Glownia et al. Reply:

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Response to Comment on “Self-Referenced Coherent Diffraction X-Ray Movie of Angstrom- and Femtosecond-Scale Atomic Motion”

(Dated: July 11, 2017)

The comment by Bennett *et al.* [1] on the experimental results reported by Glownia *et al.* [2] concerns the scattering properties that lead to interference between electronic states.

Bennett *et al.* claim that ground-to-excited state heterodyne interference effects are not present in the data in Glownia *et al.* We have re-examined the data in light of their arguments and we agree. A coordinate scaling error (not reported by Bennett *et al.*) contributed to this mis-interpretation.

Bennett *et al.* claim: “Moreover, the misinterpretation of the signal lead the authors...to incorrectly divide their dynamic data by the ground- state charge density”[1]. There are two points here, and we will now address both of them.

We agree of course that the lack of cross-terms changes the interpretation, as follows: Glownia *et al.* Fig. 1 and Fig. 2 report the data from the experiment and are not changed. The inverse Fourier transform of Fig. 2 is dominated by the autocorrelation of the excited state (see Figure 1 below). This is the main point of Bennett *et al.* This autocorrelation must be suitably deconvolved to construct an image corresponding to Fig. 3 in Glownia *et al.*, but it already displays main features of the iodine dynamics, because diatomic distributions with peaks at atomic separation R_0 have autocorrelation peaks at $R = R_0$. Therefore, the locations and velocities of the excited states have the correct values, although the autocorrelation is less sharp than the true atomic distribution.

The second point made by Bennett *et al.*, that we incorrectly divided by the ground state function, mischaracterizes the effect of the deconvolution procedure, because Fig. 3 in Glownia *et al.* differs from Fig. 1 below only by deblurring, as reported in Glownia *et al.* This is because the ground state is a compact and otherwise featureless function of R .

Bennett *et al.* further claim there can be no cross-term interference between electronic states without electronic

coherence. Again, we agree: Bennett *et al.* correctly concludes that interference cross terms between the ground and excited states are not visible. Interference cross terms between multiple excited electronic states coherently prepared by the pump laser can also occur.

Finally, Bennett *et al.* claim that gas-phase diffraction has the properties “...of an inhomogeneous gas mixture of excited- and ground-state molecules where there are no intramolecular cross terms and the intensity distributions simply add...”[1]. We disagree. Intramolecular cross terms between electronic states are present in the scattering amplitudes, and their effect on the the x-ray intensity pattern depends on the details of the measurement. This contention by Bennett *et al.* is related to their assumption that “...electronic charge densities of distinct molecules are uncorrelated”[1]; but correlated oscillating charge densities in iodine under nearly identical gas and excitation conditions can persist for many picoseconds, and have been detected tens of picoseconds later via the signals they produce in optical experiments such as photon echoes [3].

Bennett *et al.* are correct in concluding that ground-to-excited state cross-term interference was not responsible for the high fidelity in the x-ray scattering in Glownia *et al.*. These cross-terms were suppressed due to the temporal properties of the LCLS x-ray pulses and the scattering geometry.

Most important, we conclude that when we take into account the comment of Bennett *et al.* concerning the lack of ground-to-excited state cross terms in the x-ray scattering data, we find that the movie in Glownia *et al.* depicts an autocorrelation that shows the internal motion and main features of photoexcited iodine. This point will be explored in future publications.

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[1] Bennett, Physical Review Letters (2017).

[2] J. Glownia, A. Natan, J. Cryan, *et al.*, Physical Review Letters **117**, 153003 (2016).

[3] M. Comstock, V. V. Lozovoy, and M. Dantus, The Journal of Chemical Physics **119**, 65466553 (2003).

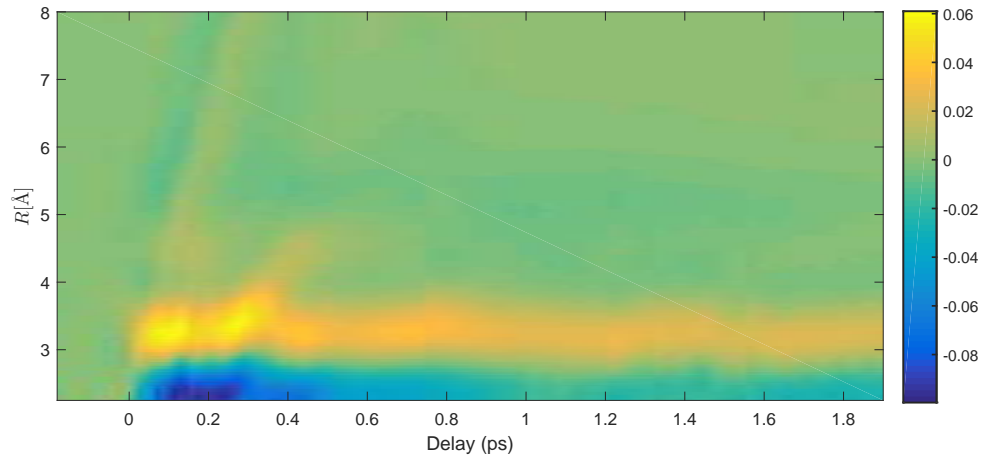


FIG. 1. Inverse Fourier transform of data in Fig. 2 of Glowina *et al.* is an autocorrelation of the charge distribution in the molecule