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Response to Comment on “Coherent Control of Retinal Isomerization in Bacteriorhodopsin”

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Joffre attempts to show that the linear response of any quantum system to an external perturbation is phase insensitive, but he uses incorrect mathematical assumptions, misinterprets the time invariance principle, and ignores causality. We argue that the opposite case—an explicit phase dependence for a signal measured in the linear excitation regime—can equally be shown using Joffre’s approach and assumptions.

The comment by Joffre (*I*) claims to make a general statement covering all possible cases of the field-matter interaction in which the measured signal is governed by a two-field interaction. The photoisomerization of retinal in bacteriorhodopsin under question (2), is an example of a strongly coupled system (retinal) to a bath (protein). The system response with respect to photoinduced isomerization necessarily involves at least four modes: a coupling mode, the primary torsional or reactive mode, and dissipation to two accepting modes of the system-bath interaction (3). Joffre attempts to illustrate the general properties of an inherently multilevel problem with a simple two-level system. By definition, this model system cannot properly capture the photoisomerization process. Effectively, Joffre has attempted to treat a multilevel quantum problem without involving quantum mechanics. The derivation and strong assertions of complete generality for a “global system response” function (*I*) raise many questions that require a more detailed analysis than given to establish their validity.

As we show, the outcome for a stationary signal given by equation 3 in (*I*) is not a unique solution to the problem as formulated (Eq. 1). The method proposed by Joffre allows one to derive an alternative result showing explicitly a phase sensitivity for the measured response. Let us start from equation 1 in (*I*) for the stationary value of the signal S . In accordance with Joffre, and making use of the hypothesis of time invariance, we replace $E(t)$ by $E(t + T)$, where T is an arbitrary time delay.

$$S = \iint R(t_1, t_2) E(t_1 + T) E(t_2 + T) dt_1 dt_2 \quad (1)$$

According to (*I*), “this relation holds for any values of t_1 , t_2 , and T , and can thus be applied to the particular case” where $T = -t_2$ (4) that results in

$$S = E(0) \iint R(t_1, t_2) E(t_1 - t_2) dt_1 dt_2 \quad (2)$$

Expressing $R(t_1, t_2)$, $E(t)$ as functions of their Fourier transforms $R(\omega_1, \omega_2)$, $E(\omega) \equiv A(\omega)e^{i\phi(\omega)}$, we obtain a final expression showing explicitly the dependence of the signal S on the phase modulation $\phi(\omega)$ in applied electric field.

$$S = E(0) \int R(\omega, -\omega) A(\omega) e^{i\phi(\omega)} d\omega \quad (3)$$

Thus, the approach proposed by Joffre in (*I*) leads to two mutually exclusive results, given by Eq. 3 above and equation 4 in (*I*). The claims of generality and associated conclusions based on this approach are therefore unfounded.

Unlike a “global system response” function introduced by Joffre in an arbitrary manner, the response of a quantum system is governed by a quantum response function, based on a particular response theory. Such a function satisfies the causality principle, which tells us that the signal must vanish if the observation time is chosen to be before the excitation event. This situation is illustrated in figure 5A in (2), where the signal, measured at 625 nm in a 20- to 600-ps delay window, is nonzero and indeed has a stationary character (within the accuracy of the measurement), but for negative delays, it has a magnitude that is clearly zero. The extrapolation of this feature of the signal, measured in a restricted delay window of a 20- to 600-ps delay, to the entire time axis stretching from $-\infty$ to $+\infty$ as done by Joffre (*I*), is invalid. Therefore, the signal S introduced in (*I*) by equation 1 is not independent of the observation delay time T , and an arbitrary change of the observation time T cannot give the same magnitude for the observed signal S . The causality principle can be ignored in the case of a perturbation of a system by a sta-

tionary field (e.g., a monochromatic electric field or a thermal field) that begins at $-\infty$ and ends at $+\infty$ and is characterized by time-independent parameters. However, it is well known that such fields do not carry any phase information, and thus any further consideration of the phase sensitivity in the material response is unnecessary. This is exactly the case presented by Joffre: Equation 1 in (*I*) is set up such that the observable is mathematically stated to be a constant, and thus there are no equations needed after this point.

The excitation conditions we reported in (2) were strictly nonstationary; the excitation energy was localized, depending on the pulse profile, in a time window of 20 to 500 fs. The duration of the optimized pulses corresponds to the characteristic time for nuclear passage through a conical intersection or other transition point connecting the reactant and product surfaces for retinal photoisomerization (5–7) that determines the chemical branching ratio between cis and trans, that is, the observable. The system response during this interaction time is clearly in the nonstationary regime. In this regard, the work of Flores and Batista (7) dealt with essentially the identical problem and found that the chemical branching ratio (reaction probability) is extremely sensitive to the phase of the excitation pulses [see figure 2 in (7)], in contradiction to Joffre’s key starting assumption.

We note that the time invariance principle equally applies to nonstationary conditions; it simply means that “the dynamical properties of the system are assumed to be unchanged by a translation of the time origin” [referring to the same textbook (8) as Joffre]. In other words, if the excitation event is shifted by an arbitrary time interval T , the signal, measured after the same shift T with respect to the original measuring time, will not be changed. This general principle agrees with our experimental observations. However, it does not mean that the observation time T , which can be arbitrarily chosen for stationary conditions but is fixed (a constant) can be substituted as a time variable in an integral. Such incorrect mathematical manipulations lead to erroneous results, as shown in (9).

In this context, Joffre’s argument hinges on a single reference in which the material response function was properly handled (10). This work showed that it is not possible to coherently control the chemical branching ratio of a closed quantum system, using a single occupied ground state, under linear excitation conditions. This detail was not missed in our earlier work but was specifically cited. The approximately linear intensity dependence we observed (11) was previously discussed in terms of the fundamental difference between closed and open quantum systems (12). It should be noted that Joffre’s treatment is unable to account for the analytical results from the same authors (10) for a multilevel closed system in which there is more than one pathway available to the excitation process (13).

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The important lesson from this so-called bi-chromatic control study is that coherent control within the linear intensity regime requires multiple levels that are coupled through an interaction induced by the applied field (14). Joffre's treatment is also not able to account for the 1-photon coherent control scenarios through polarization- and phase-shaped pulses (15). In addition, it cannot account for impulsive Raman effects on reactions that are both linear and phase sensitive (16). Moreover, other experiments have demonstrated coherent control at intensity conditions that are nominally within the linear intensity regime (16–18), further illustrating that the comment (1) is invalid as a generalization.

We recognize that the relations provided by Joffre are intended to focus attention toward fundamental issues with respect to weak field coherent control. However, the comment does not provide further insight into the problem but rather confuses the issue with an incorrect treatment of the observable and omission of key references that do not support Joffre's case. High-level theoretical treatments, in which the molecular details of the reaction coordinate are convolved to the field interaction, are needed to

fully understand the excitation process. On the experimental front, it remains to further exploit the new tools for selective excitation of vibrational coherences to probe reaction branching ratios; important information on mode-specific coupling to reaction coordinates directing primary events in chemical processes and biological functions should be forthcoming.

References and Notes

1. M. Joffre, *Science* **317**, 453 (2007); www.sciencemag.org/cgi/content/full/317/5837/453b.
2. V. I. Prokhorenko *et al.*, *Science* **313**, 1257 (2006).
3. L. Seidner, W. Domcke, *Chem. Phys.* **186**, 27 (1994).
4. Joffre applies this relation after changing the time variables $t_1 \rightarrow t_1 - T$ and $t_2 \rightarrow t_2 - T$; however, the "particular case" where the delay time T is set to the time variable can be done at any moment and for any function under the integral.
5. T. Kobayashi, T. Saito, H. Ohtani, *Nature* **414**, 531 (2001).
6. M. Abe, Y. Ohtsuki, Y. Fujimura, W. Domcke, *J. Chem. Phys.* **123**, 144508 (2005).
7. S. C. Flores, V. S. Batista, *J. Phys. Chem. B* **108**, 6745 (2004).
8. P. N. Butcher, D. Cotter, *The Elements of Nonlinear Optics* (Cambridge Univ. Press, Cambridge, 1990).
9. See supporting material on *Science Online*.
10. P. Brumer, M. Shapiro, *Chem. Phys.* **139**, 221 (1989).
11. We noted in (2) that it is necessary to reduce the intensity by at least a factor of 10 to completely rule out possible nonlinear field contributions.
12. In open quantum systems, the states are dynamically coupled. The coupling of one state with another creates cross terms between the phase and amplitude components in the field interaction that imparts time or phase sensitivity to the state preparation.
13. M. Shapiro, P. Brumer, *J. Chem. Phys.* **84**, 4103 (1986).
14. This is exactly the case for the photoisomerization of retinal. Excitation to the upper electronic states of retinal would produce well-defined phase relationships between upper electronic states through the Franck-Condon factors; these states would then be available with variable phase relationships to interfere at the conical intersection.
15. D. Voronine, D. Abramavicius, S. Mukamel, *J. Chem. Phys.* **124**, 034104 (2006).
16. W. Wohlleben, T. Buckup, J. L. Herek, M. Motzkus, *Chem. Phys. Chem.* **6**, 850 (2005).
17. J. L. Herek, W. Wohlleben, R. J. Cogdell, D. Zeidler, M. Motzkus, *Nature* **417**, 533 (2002).
18. J. Hauer, T. Buckup, M. Motzkus, *J. Chem. Phys.* **125**, 061101 (2006).

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References

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