

# Comment on “Time-resolved laser induced harpoon reactions”

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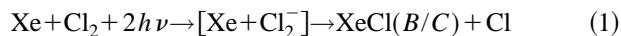
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(Received 31 May 1996; accepted 23 December 1996)

[S0021-9606(97)03112-7]

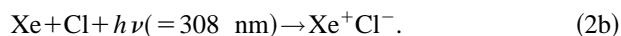
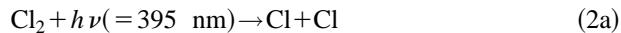
In a recent communication, Dedonder-Lardeux *et al.* reported on time resolved studies of the two-photon induced harpoon reaction between Xe and Cl<sub>2</sub> entrapped in clusters generated in a molecular beam expansion.<sup>1</sup> They also commented on the two related studies in which Xe, a molecular halogen, and femtosecond lasers were used: our liquid phase studies, in Cl<sub>2</sub>/LXe solutions;<sup>2</sup> and the gas phase studies on I<sub>2</sub>/Xe mixtures carried out in a static cell, in Zewail's group.<sup>3</sup> These systems provide a unique opportunity for the interrogation of bimolecular reactions in real-time. From this topical perspective, the published work deserves clarification.

Under the deceptively simple shorthand notation for the two-photon induced harpoon reaction at issue:



lies a wealth of photophysics that has been exploited too extensively to review here. Suffice it to note that the wealth and complications are a result of the multiplicity of entrance channels that lead to the intermolecular charge transfer intermediate, Xe<sup>+</sup>Cl<sub>2</sub><sup>-</sup>, which can loosely be regarded as the transition state of this bimolecular reaction in (1).<sup>4</sup> We will limit our focus to the three experiments, Refs. 1, 2, and 3 herein referred to as I, II, and III.

In I, two short-pulse lasers, operating at 395 nm and 308 nm, are used to interrogate Ar clusters containing Xe and Cl<sub>2</sub>. As the delay between pulses is varied, two transient contributions to the signal, consisting of the XeCl(B/C) fluorescence, is observed. The first occurs at zero-delay, and is response limited to ~0.5 ps. The second occurs when the 308 nm pulse arrives ~0.5 ps after the 395 nm pulse, and appears to be broader in time. The observation is sufficient to conclude that, at least two different entrance channels to (1) are being observed. The first is consistent with a coherent two-photon excitation, in agreement with our demonstration in II. The second implies the sequential process of photo-dissociation followed by photo-association:



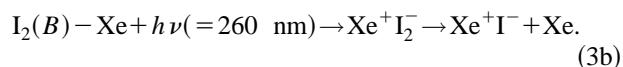
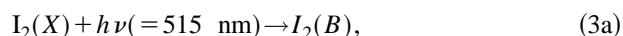
The authors contrast this observation with ours, and comment that “the reality of the sequential process has been questioned” by us, and incorrectly interpret our paper as implying that reaction (1) is limited to the “coherent two-photon absorption process.”

The sequential process (2) is the more natural mechanism, the existence of which has never been in question. In fact, recognizing the large cross sections involved in (2b), we have advanced the scheme as an analytical tool for detection

of atomic chlorine.<sup>5</sup> In the gas phase, subtleties associated with the distinction in reaction (2b) between excitation of the bound XeCl van der Waals complex vs excitation of free Xe–Cl collision pairs, do arise. Contributions from both occur, and can be sorted out experimentally.<sup>6</sup> The same issues do not arise in condensed media, such as liquid Xe, where the photogenerated atoms in reaction (2a) remain in contact with solvent Xe, available for excitation in reaction (2b). The observation of the sequential excitation signal in I is no surprise since 308 nm is resonant with the XeCl(B $\leftarrow$ X) transition. The transient nature of this signal is, however, noteworthy; since it implies that a collision pair, as opposed to bound XeCl(X), is being observed. Presumably, Xe and Cl<sub>2</sub> are initially trapped in a large Ar cluster, and the collision of a photogenerated Cl atom with Xe is being observed. The Cl atom must be cold enough to rationalize the 0.5 ps delay, and hot enough to rationalize the transient nature of its encounter with Xe. These interesting details will likely be sorted out with additional data.

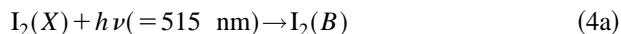
One of our achievements in II was the definitive establishment of the four-body scattering event, the coherent two-photon two-electron transition of reaction (1), by isolating it from all other channels. In our one-color experiment, the choice of 320 nm radiation, which is to the red of the XeCl(B–X) transition, was sufficient to avoid sequential excitation. We demonstrated that two photons were absorbed in  $t \leq 100$  fs in promoting reaction (1), and qualified it as coherent. The qualification is to be made with care. The resonant two-photon transition has the Cl<sub>2</sub>(<sup>1</sup>P<sub>u</sub>) surface as a real intermediate, and within 100 fs the Cl–Cl bond can stretch a long distance on this repulsive surface. Accordingly, simulations of the “time-for-first-collision” were made to establish that the observed signal was only consistent with a transition limited to the Franck–Condon region of the pair in reaction (1), rather than secondary collisions between Cl and solvent Xe as implicated in reaction (2).

The focus of paper III is the “Femtosecond laser control of a chemical reaction.” It proposes the preparation of a vibrational superposition in the B(<sup>3</sup>P<sub>0u</sub>) electronic state of I<sub>2</sub>, and the subsequent interception of the I<sub>2</sub>(B)–Xe collision complex with a second laser, to initiate the harpoon reaction:



The process could in principle be followed by monitoring the B $\rightarrow$ X fluorescence of XeI at 253 nm. Note, only collision complexes that fall within the probe window may be excited

in (3b). This resonance condition is determined by the difference potential between  $\text{Xe}-\text{I}_2(B)$  and  $\text{Xe}^+\text{I}_2^-$  which although dominated by its  $1/r$  dependence on intermolecular separation, may also be modulated by the coherent vibrations of  $\text{I}_2(B)$ . Indeed, if this could be demonstrated, if the process described in reaction (3) could be singled out for observation, then it would constitute coherent control of a bimolecular reaction. However, as the authors recognize in their penultimate paragraph in III, an alternate channel for the production of  $\text{Xe}^+\text{I}^-$  exists in their experiments, namely: the sequential two-photon preparation of the molecular ion-pair,  $\text{I}^+\text{I}^-$ , and its subsequent reaction with Xe:



followed by



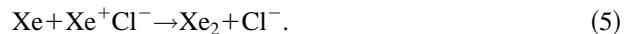
This last reaction, (4c), is known to have a large collisional cross section, and known to proceed without activation.<sup>7</sup> In contrast with reaction (3), the bimolecular reaction now occurs on collisional time scales, long after the termination of the laser pulses. It is not too difficult to estimate that the XeI fluorescence from this channel would completely overwhelm the signal, precluding the possibility of observing process (3).<sup>8</sup> This fact is borne out by the experiment.

In III, first,  $\text{I}_2$  alone is introduced in the gas cell and interrogated by the standard pump-probe experiment, i.e., reaction (4a) followed by reaction (4b) in which a vibrational wave packet is prepared by the pump laser and excited to the molecular ion-pair states when it reaches the probe window. The process is monitored through the ion-pair emission, the  $D' \rightarrow A'$  transition of  $\text{I}_2$  near 340 nm. The fluorescence intensity oscillates as a function of delay between pump and probe pulses, reflecting the  $\sim 500$  fs period of the wave packet oscillating on the  $B$  potential curve of  $\text{I}_2$ . Upon addition of Xe to the cell, the ion-pair emission subsides and the  $\text{XeI}(B \rightarrow X)$  fluorescence is observed. The time dependence of the  $\text{Xe}^+\text{I}^-$  emission faithfully tracks that of  $\text{I}^+\text{I}^-$  observed in the absence of Xe. This is consistent with reaction (4), where the probe resonance is not effected by Xe and inconsistent with reaction (3), where it must be. More to the point, since the time dependence of fluorescence from  $\text{I}^+\text{I}^-$  and  $\text{Xe}^+\text{I}^-$  are identical, we may conclude that the information content of the two observables is the same. They both measure the coherent oscillation of the vibrational superposition in bare  $\text{I}_2(B)$ ; neither contains information about the timing of the bimolecular reaction between Xe and  $\text{I}_2$ .

It would seem that the explanation given here, that the origin of the observed signal in III is strictly due to reaction (4), is accepted while maintaining that the mechanism constitutes active control of a bimolecular reaction.<sup>9</sup> To see the

difficulty in such a reconciliation, consider in Eq. (4c) the substitution of a photomultiplier for Xe and photocurrent for  $\text{Xe}^+\text{I}^-$ . The photocurrent tracks the  $\text{I}^+\text{I}^-$  fluorescence, just as the XeI chemiluminescence does, yet we would not think of this standard pump-probe experiment as an active control of electric current.

The timing of a bimolecular reaction, through control of final products, was achieved in our work, in II. We used the direct two-photon excitation in reaction (1) for the sudden preparation of  $\text{Xe}^+\text{Cl}^-$  in liquid Xe, and followed the bond formation in the bimolecular reaction between solute and solvent:



The bond was shown to form in  $\sim 320$  fs, in good agreement with an analytical estimate for ballistic motion over the ionic transition state. The method relied on optical control. Left to its own reaction (5) will proceed to completion in the liquid phase. However, the progress of the reaction could be interrupted by diverting the reactive flux from the ionic surface to the covalent ground surface by stimulating the radiative dissociation:



This redirection of the reaction is manifested as depletion of the normal reaction product, as depletion of fluorescence from  $\text{Xe}_2^+\text{Cl}^-$ , as a function of laser intensity. Nearly 60% of the reaction flux was diverted. Moreover, the mechanism was verified by quantitative reproduction of the observed signal through kinetics, using previously measured cross sections and without adjustment of parameters. Despite the simplicity of its design, the real-time tracking of a bimolecular reaction through control of its final product was achieved in II.

<sup>1</sup>C. Dedonder-Lardeux *et al.*, J. Chem. Phys. **104**, 2740 (1996).

<sup>2</sup>R. Zadoyan and V. A. Apkarian, Chem. Phys. Lett. **205**, 475 (1993).

<sup>3</sup>E. D. Potter *et al.*, Nature, **355**, 66 (1992).

<sup>4</sup>For a systematic discussion of the various entrance channels, see, M. Hill and V. A. Apkarian, J. Chem. Phys. **105**, 4023 (1996).

<sup>5</sup>W. G. Lawrence and V. A. Apkarian, APC Atmospheres **95**, 591 (1990).

<sup>6</sup>G. Inoue, J. K. Ku, and D. W. Setser, J. Chem. Phys. **80**, 6006, (1984); A. W. McCown and J. G. Eden, *ibid.* **81**, 2933 (1984); W. G. Lawrence and V. A. Apkarian, Israel. J. Chem. **30**, 135 (1990); E. B. Gordon *et al.*, Chem. Phys. Lett. **242**, 75 (1995).

<sup>7</sup>B. V. O'Grady and R. J. Donovan, Chem. Phys. Lett. **122**, 503 (1985); R. J. Donovan, *et al.*, J. Chem. Soc. Far. Trans. **85**, 541 (1988).

<sup>8</sup>At the experimental partial pressure of Xe of = 50 Torr, the collision frequency between  $\text{I}_2$  and Xe is  $\sim 10^8 \text{ s}^{-1}$ . Within the reported laser pulse-width of 150 fs, the probability of capturing a  $\text{Xe}-\text{I}_2$  collision pair is less than  $10^{-5}$ . The cross section for the intermolecular charge transfer transition in (3b) may at best be comparable to that of the intramolecular charge transfer transition in (4b), since the latter has an oscillator strength near unity. Allowing only 10% reaction efficiency of  $\text{I}^+\text{I}^-$  in Eq. (4c), the contribution to the XeI fluorescence from Eq. (3) cannot exceed  $10^{-4}$  of that via Eq. (4).

<sup>9</sup>J. L. Herek, A. Materny, A. H. Zewail, Chem. Phys. Lett. **228**, 15 (1994).