GENERAL DISCUSSION ON FEMTOCHEMISTRY: FROM ISOLATED MOLECULES TO CLUSTERS

Chairman: S. A. Rice

B. Kohler: I would like to ask two questions to Prof. Zewail. First, in your investigation of the electron transfer reaction in a benzene–I_2 complex, the sample trajectory calculations you showed appear to suggest that the charge transfer step may induce vibrationally coherent motion in I_2^-. Have you tested this possibility experimentally? My second question concerns your intriguing results on a tautomerization reaction in a model base-pair system. In many of the barrierless chemical reactions you have studied, you have been able to show that an initial coherence created in the reactant molecules is often observable in the products. In the case of the 7-azaindole dimer system your measurements indicate that reaction proceeds quite slowly on the time scale of vibrational motions (such as the N—H stretch) that are coupled to the reaction coordinate. What role do you think coherent motion might play in reactions such as this one that have a barrier?

A. H. Zewail: The observation of coherent motion in the benzene–iodine system should be related to the I_2^- motion and hopefully with better time resolution we should be able to resolve it. As for the base-pair experiment, the key motion is that of the N ·· N stretch and N—H asymmetric motions, and our time scale of observation was appropriate for the dynamics to be observed.

M. Quack: Prof. Zewail and Gerber, when you make an interpretation of your femtosecond observations (detection signal as a function of excitation), would it not be necessary to try a full quantum dynamical simulation of your experiment in order to obtain a match with your molecular, mechanistic picture of the dynamics or the detailed wavepacket evolution? Agreement between experimental observation and theoretical simulation would then support the validity of the underlying interpretation (but it would not prove it). The scheme is of the following kind:

ments flying apart. This vibrational motion during the dissociation process is subject to the so-called intramolecular vibrational energy redistribution (IVR), which plays a central role in a unimolecular dissociation reaction. The new gas electron diffraction experiments presented here by Prof. Zewail could have powerful potential to visualize IVR through the real-time probing.

2. In conventional gas electron diffraction experiments, an effusive beam is used in which vibrational levels of molecules are thermally populated and the width of a peak in a radial distribution curve is determined by thermally averaged mean amplitudes. When a molecular beam or a free jet is used, mean amplitudes could become small, since the contribution from the vibrationally excited levels is reduced significantly. As a consequence, sharper peaks are expected in the radial distribution curve, and the spatial resolution of the snapshot could be improved. However, it seems that the observed peaks in the radial distribution curve are considerably broad even though a molecular beam is used. There could be some reasons to have such broadened peaks in the radial distribution curve.

A. H. Zewail: Prof. Yamanouchi is correct in pointing out the relevance of ultrafast electron diffraction to the studies of vibrational (and rotational) motion. In fact, Chuck Williamson in our group [1] has considered precisely this point, and we expect to observe changes in the radial distribution functions as the vibrational amplitude changes and also for different initial temperatures. The broadening in our radial distribution function presented here is limited at the moment by the range of the diffraction sampled.

1. J. C. Williamson and A. H. Zewail, *J. Phys. Chem.* **98**, 2766 (1994).

P. Backhaus, J. Manz, and B. Schmidt:* Prof. A. H. Zewail has demonstrated to us some fascinating new pump–probe femtochemistry investigations of bimolecular reactions (e.g., Ref. 1; see also Ref. 2)

$$H + CO_2 \rightarrow HOCO^{\ddagger} \rightarrow OH + CO \tag{1}$$
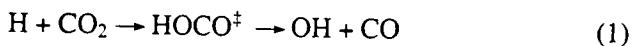
To the best of our knowledge, however, these types of "bimolecular" studies start from weakly bound precursor systems, for example,

$$IH \cdot OCO \rightarrow IH^{*} \cdot CO_2 \rightarrow I + HOCO^{\ddagger} \rightarrow I + OH + CO \tag{2}$$
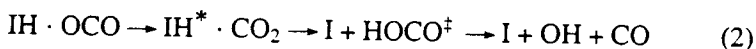
*Comment presented by J. Manz.

From the viewpoint of the van der Waals type or hydrogen-bounded reactant, these reactions may therefore be considered as "unimolecular" even though they exhibit various characteristics of bimolecular processes.

Here we wish to point to a new type of femtosecond chemistry investigations of bimolecular reactions, demonstrated first by Dantus et al. [3] for the prototype system

$$2\,Hg \rightarrow Hg_2{}^* \qquad\qquad (3)$$

Essentially, an ultrashort laser pulse associates two colliding reactants to a new product. In the present case, a metastable excimer $Hg_2{}^*$ is formed from two mercury atoms. This photoassociation process may be considered as the reverse of photodissociation. From a theoretical point of view, the important difference between processes (2) and (3) is that the unimolecular photodissociation (2) starts from bound states, whereas the bimolecular photoassociation (3) starts from continuum states, as demonstrated by model simulations in Fig. 1 (supported by Deutsche Forschungsgemeinschaft).

1. N. F. Scherer, L. R. Khundkar, R. B. Bernstein, and A. H. Zewail, *J. Chem. Phys.* **87**, 1451 (1987); N. F. Scherer, C. Sipes, R. B. Bernstein, and A. H. Zewail, *J. Chem. Phys.* **92**, 5239 (1990); A. H. Zewail, in *Femtosecond Chemistry*, J. Manz and L. Wöste, Eds., Verlag Chemie, Weinheim, 1995, p. 15; A. H. Zewail, *J. Phys. Chem.* **100** (1996), in press.

2. S. I. Ionov, G. A. Brucker, C. Jaques, L. Valachovic, and C. Wittig, *J. Chem. Phys.* **99**, 6553 (1993); M. Alagia, N. Balucani, P. Casavecchia, D. Stranges, and G. G. Volpi, *J. Chem. Phys.* **98**, 8341 (1993); G. C. Schatz and M. S. Fitzcharles, in *Selectivity in Chemical Reactions*, J. C. Whitehead, Ed., Kluwer, Dordrecht, 1988, p. 353; E. M. Goldfield, S. K. Gray, and G. C. Schatz, *J. Chem. Phys.* **102**, 8807 (1995); D. C. Clary and G. C. Schatz, *J. Chem. Phys.* **99**, 4578 (1993), D. H. Zhang and J. Z. H. Zhang, *J. Chem. Phys.* **103**, 6512 (1995); see also L. Krim, P. Qiu, N. Halberstadt, B. Soep, and J. P. Visticot, in *Femtosecond Chemistry*, J. Manz and L. Wöste, Eds., Verlag Chemie, Weinheim, 1995, p. 433.

3. U. Marvet and M. Dantus, *Chem. Phys. Lett.* **245**, 393 (1995).

4. P. Backhaus, M. Dantus, J. Manz, and B. Schmidt, in preparation.

5. J. Koperski, J. B. Atkinson, and L. Krause, *Can. J. Phys.* **72**, 1070 (1994).

6. F. H. Mies, W. J. Stevens, and M. Krauss, *J. Molec. Spectrosc.* **72**, 303 (1978).

7. E. W. Smith, R. E. Drullinger, M. M. Hessel, and J. Cooper, *J. Chem. Phys.* **66**, 15 (1977).

J. Manz: Moreover, I have another comment on the contributions by A. H. Zewail and G. Gerber and a question to all my colleagues and, in particular, to the Chairman, Prof. S. A. Rice:
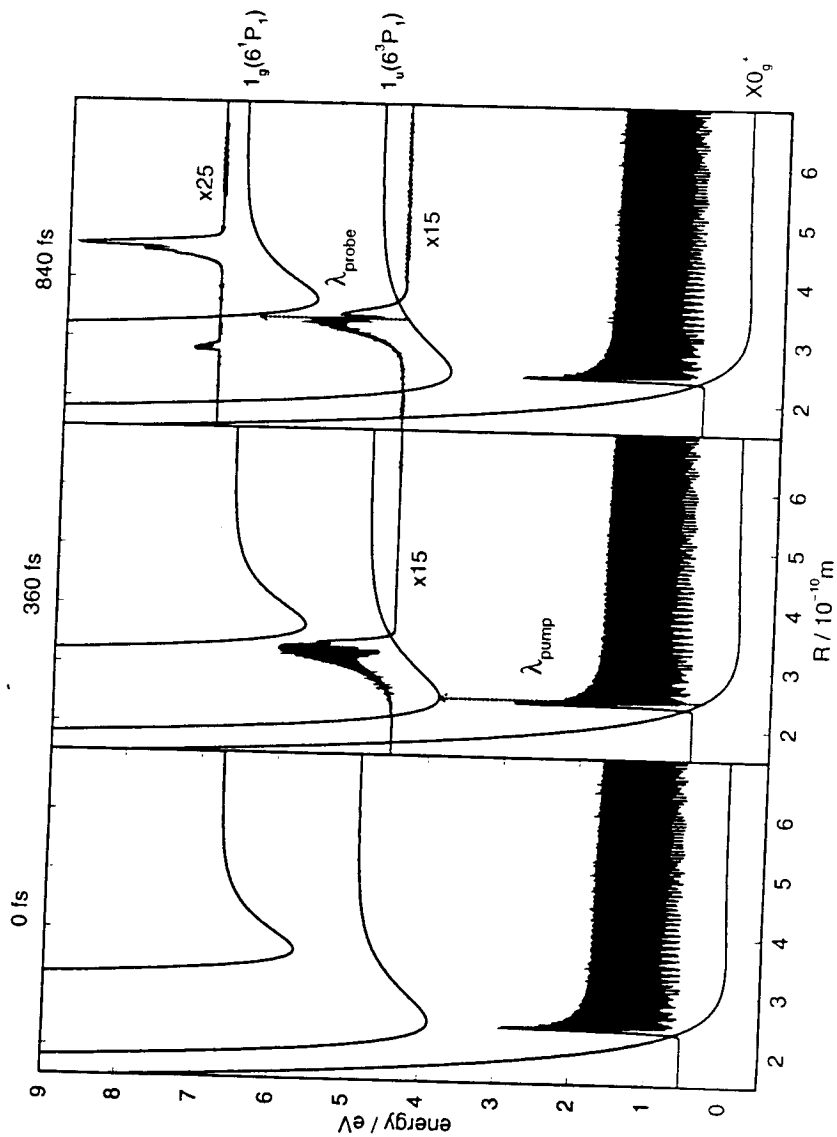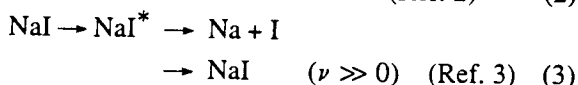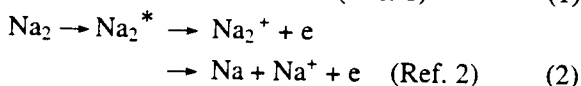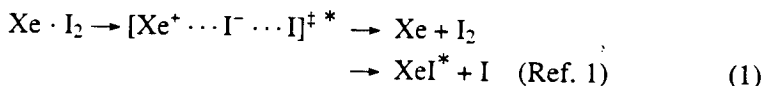
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Figure 1. Photoassociation $2Hg \rightarrow Hg_2^*$ by ultrashort femtosecond laser pulses. The figure shows a sequence of three snapshots of the wavepacket dynamics tailored to the experiment of Marvet and Dantus [3]. At $t = 0$ fs, the reactants $Hg(XO_g^+)$ are in a continuum state with energy E and rotational quantum numbers J, M. The pump laser pulse ($\lambda_{pump} = 312$ nm, $I_{max} = 2 \times 10^{11}$ W/cm^2, $\tau = 65$ fs) creates a small fraction of dimers Hg_2^* ($1_u(6^3P_1)$), and the probe pulse ($\lambda_{pump} = 624$ nm, $I_{max} = 2 \times 10^{13}$ W/cm^2, $\tau = 65$ fs) monitors the coherent vibration of these Hg_2^* (1_u) excimers by depopulation due to the $1_u \rightarrow 1_g(6^1P_1)$ transition. The remaining population of $Hg_2^*(1_u)$ depends on the delay time of the pump and probe laser pulses (in the present case $t_d = 480$ fs) and is measured by fluorescence. All laser parameters are adapted to the experimental situation [3]. The present simulation is exemplary for $E = 0.529$ eV, $J = 0, M = 0$, and Boltzmann averaging over equivalent calculations for other values of E, J, M accounts for the thermal ($T = 433.15$ K) situation of the experiment; see Ref. 4. The potential energies and transition dipoles are adapted from Refs. 5, 6, and 7, respectively; for the $1_g \rightarrow 1_u$ transition, we assume $\mu = 1ea_0$; This does not affect the relative pump and probe signal (in arbitrary units).

Prof. G. Gerber and A. H. Zewail have presented to us three fascinating experiments on femtosecond laser control of the branching ratio of competing product channels:

$$Xe \cdot I_2 \rightarrow [Xe^+ \cdots I^- \cdots I]^{\ddagger *} \rightarrow Xe + I_2$$
$$\rightarrow XeI^* + I \quad (\text{Ref. 1}) \quad\quad (1)$$
$$Na_2 \rightarrow Na_2{}^* \rightarrow Na_2{}^+ + e$$
$$\rightarrow Na + Na^+ + e \quad (\text{Ref. 2}) \quad\quad (2)$$
$$NaI \rightarrow NaI^* \rightarrow Na + I$$
$$\rightarrow NaI \quad (\nu \gg 0) \quad (\text{Ref. 3}) \quad (3)$$

where NaI $(\nu \gg 0)$ denotes the vibrationally excited NaI molecule in the electronic ground state. Essentially, they employ two femtosecond laser pulses with proper time delay t_d. The first pump pulse initiates $(t = 0)$ a coherent nuclear motion in the electronic excited state. This is represented by a nuclear wavepacket that is driven from the molecular equilibrium configuration of the reactant at time $t = 0$ toward new configurations close to those of the products at time $t = t_d$. The second control pulse $(t = t_d)$ then induces an electronic transition that serves to stabilize the desired product. Historically, it is amazing and certainly encouraging and gratifying that this type of femtosecond laser control by two femtosecond pump and control laser pulses had been predicted by Tannor et al. already in 1985 [4] (see also Ref. 5), that is, one or two years before the first femtosecond laser chemistry investigation of a chemical reaction, carried out by Zewail et al. in 1987 [6]. I should like to ask whether the experimental (see Refs. 1–3) or theoretical pioneers (see Ref. 4) or any other colleagues could point to any other experimental verifications of the Tannor–Rice–Kosloff strategy [4] beyond processes (1–3).

1. E. P. Potter, J. L. Herek, S. Pedersen, Q. Liu, and A. H. Zewail, *Nature* **355**, 66 (1992).

2. T. Baumert, R. Thalweiser, V. Weiss, and G. Gerber, in *Femtosecond Chemistry*, Vol. 2. J. Manz and L. Wöste, Eds., Verlag Chemie, Weinheim, 1995, p. 397.

3. J. L. Herek, A. Materny, and A. H. Zewail, *Chem. Phys. Lett.* **228**, 15 (1994).

4. D. J. Tannor and S. A. Rice, *J. Chem. Phys.* **83**, 5013 (1985); D. J. Tannor, R. Kosloff, and S. A. Rice, *J. Chem. Phys.* **85**, 5805 (1986).

5. S. A. Rice, *J. Chem. Phys.* **90**, 3063 (1986); S. A. Rice, Perspectives on the control of quantum many body dynamics: Application to chemical reactions, *Adv. Chem. Phys.*, **101**, (1997).

6. M. Dantus, M. J. Rosker, and A. H. Zewail, *J. Chem. Phys.* **87**, 2395 (1987).

S. A. Rice: My answer to Prof. Manz is that, as I indicated in my presentation, both the Brumer–Shapiro and the Tannor–Rice control schemes have been verified experimentally. To date, control of the branching ratio in a chemical reaction, or of any other process, by use of temporally and spectrally shaped laser fields has not been experimentally demonstrated. However, since all of the control schemes are based on the fundamental principles of quantum mechanics, it would be very strange (and disturbing) if they were not to be verified. This statement is not intended either to demean the experimental difficulties that must be overcome before any verification can be achieved or to imply that verification is unnecessary. Even though the principles of the several proposed control schemes are not in question, the implementation of the analysis of any particular case involves approximations, for example, the neglect of the influence of some states of the molecule on the reaction. Moreover, for lack of sufficient information, our understanding of the robustness of the proposed control schemes to the inevitable uncertainties introduced by, for example, fluctuations in the laser field, is very limited. Certainly, experimental verification of the various control schemes in a variety of cases will be very valuable.

S. Mukamel: In relation to the report by Prof. Gerber, I would like to comment that chemical bonding can also be viewed as *electronic coherence*. By looking at the relevant single-electron density matrix in the atomic orbital representation, we note that the diagonal elements give the local charges whereas the off-diagonal elements (coherences) represent bond order. Our studies of nonlinear optical spectroscopy of conjugated polyenes have shown that, using this view, one can define electronic normal modes and view the electronic system as a collection of coupled harmonic oscillators representing collective electronic motion [1]. This is a very different picture than using the global electronic eigenstates. Using this picture, it is possible to treat electronic and nuclear degrees of freedom along similar lines. It also furnishes a very powerful means in computing optical response functions, which are size consistent [2].

1. S. Mukamel, A. Takahashi, H. X. Wang, and G. Chen, *Science* **266**, 250 (1994).

2. V. Chernyak and S. Mukamel, *J. Chem. Phys.* **104**, 444 (1996).

G. Gerber: In response to Prof. Mukamel, I should remark that the coherence between molecular electronic states induced by our intense ultrashort laser pulse is not restricted to bound states but also includes repulsive electronic surfaces. In that sense chemical bonding is related to electronic coherence.