Clocking transient chemical changes by ultrafast electron diffraction

J. Charles Williamson, Jianming Cao, Hyotcherl Ihee, Hans Frey & Ahmed H. Zewail

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, USA

With the advent of femtosecond (fs) time resolution in spectroscopic experiments, it is now possible to study the evolution of nuclear motions in chemical and photobiochemical reactions. In general, the reaction is clocked by an initial fs laser pulse (which establishes a zero of time) and the dynamics are probed by a second fs pulse; the detection methods include conventional and photoelectron spectroscopy and mass spectrometry¹⁻⁴. Replacing the probe laser with electron pulses offers a means for imaging ultrafast structural changes with diffraction techniques⁵⁻⁸, which should permit the study of molecular systems of greater complexity (such as biomolecules). On such timescales, observation of chemical changes using electron scattering is non-trivial, because space-charge effects broaden the electron pulse width and because temporal overlap of the (clocking) photon pulse and the (probe) electron pulse must be established. Here we report the detection of transient chemical change during molecular dissociation using ultrafast electron diffraction. We are able to detect a change in the scattered electron beam with the zero of time established unambiguously and the timing of the changes clocked in situ. This ability to clock changes in scattering is essential to studies of the dynamics of molecular structures.

Diffraction methods, generally utilizing X-rays or electrons, are direct approaches for determining complex structures at microscopic dimensions⁹⁻¹⁴. Techniques for creating ultrashort, coherent and collimated X-ray pulses are still in their infancy, and at present the X-ray flux from most sources is relatively low. For gas-phase ultrafast electron diffraction (UED) to succeed, major challenges must be surmounted. First, because the number densities of gas samples are orders of magnitude lower than solids and surfaces, gasphase diffraction intensities are very weak. Second, there is no longrange order to enhance coherent interferences, and thus the incoherent background scattering from gases is orders of magnitude greater. Last, there has not previously been a way to determine *in situ* the zero of time in UED experiments.

In gas-phase electron diffraction (GED) the scattering intensity decreases as the fourth power of the momentum transfer $s = (4\pi/\lambda)\sin(\theta/2)$, where λ is the de Broglie wavelength of the electrons and θ is the scattering angle. Conventional GED experiments require a high electron flux (of the order of microamperes) to yield internuclear separations with precision on the order of 0.001 Å (ref. 15). Over the past two decades, the speed of GED experiments has improved to the micro- and nanosecond timescale. Microsecond studies include time-of-flight investigations of molecular clusters¹⁶, and photodissociation experiments where the electron beam is electromagnetically chopped^{17,18}. A temporal resolution of 15 ns has been achieved with a pulsed laser driven electron source¹⁹.

In order to probe ps and sub-ps changes and the associated orientational anisotropy²⁰ with UED, three basic experiments must be incorporated into our apparatus: measurement of the electron pulsewidth, accurate clocking of the reaction, and detection of single electrons (necessary to reduce the electron flux and minimize space-charge broadening). To this end we have developed the new apparatus shown in Fig. 1, representative of a second generation of

diffraction experiments in our laboratories^{6,8}. The apparatus is composed of a fs laser, an ultrafast electron gun, a free-jet expansion source, and a newly designed two-dimensional single-electron detection system. Femtosecond laser pulses were created from a colliding-pulse mode-locked ring dye laser. The output from this laser was directed through a four-stage pulsed dye amplifier with no pulse compression (620 nm, 2-3 mJ, 30 Hz, 300 fs). For initiation of the reaction, 95% of this beam was doubled (310 nm, ~250 μ J). The remainder (also doubled) was focused onto a back-illuminated, negatively-biased photocathode to generate the electron pulse via the photoelectric effect.

The ejected photoelectrons were accelerated into a series of electrostatic lenses that collimate and focus the electron beam; for 19 keV, λ is 0.088 Å. The position of the electron beam was controlled with horizontal and vertical deflectors. Two closely spaced metal plates were used for streaking experiments. The vacuum system was divided into two chambers and differentially pumped (Fig. 1). The sample molecules entered the vacuum chamber in a free-jet expansion mounted on an *xyz* positioning stage. The scattering chamber background pressure with gas flow was $\sim 2 \times 10^{-4}$ torr. Both chambers were shielded with μ -metal to reduce the effects of the Earth's magnetic field.

The component most critical to the success of UED is the detection system. The electron flux must be very low in order to keep the temporal resolution ultrafast. Early on we recognized that all of the scattered electrons must be detected for the experiment to succeed⁶, and we introduced the two-dimensional charge-coupled



Figure 1 Top, second-generation ultrafast electron diffraction apparatus, consisting of an electron gun chamber, a diffraction chamber and a detector chamber. Two is laser pulses are used; the first initiates the chemical change and the second generates the electron pulse. Bottom, detection scheme. Incident electrons either directly bombard a small CCD or strike a phosphor-coated fused fibre-optic window. Light emitted from the phosphor is amplified by an image intensifier and brought to a scientific-grade CCD. Both CCDs are thermoelectrically cooled.

device (CCD) as a detector in a direct electron bombardment mode⁸. To increase the longevity and flexibility of the singleelectron detection system, our second-generation apparatus now employs two CCDs: one is a small, direct-bombardment device installed in the scattering chamber, and the other is a large, scientific-grade device mounted in a separate chamber at the end of a phosphor scintillator/fibre optic/image intensifier chain. Details will be published elsewhere.

To confirm the time resolution of the apparatus, we have measured the electron pulse duration *in situ* as a function of the number of electrons per pulse using the high-speed deflection technique in a streak camera arrangement. Streak velocities (which measure the conversion from temporal to spatial resolution, as shown in Fig. 2) attained with this setup are on the order of 1.6×10^8 m s⁻¹, or ~2 pixels per ps on the detector. The resolution of the streak experiment is therefore ± 0.5 ps. Steak images spanning three orders of magnitude of electron number are shown in Fig. 2.



Figure 2 a, Surface contour plots of low- and high-intensity streaked electron pulse pairs. Each pair comes from two incident light pulses, one of which is delayed by 66.7 ps. The horizontal coordinate is the steaking axis. The temporal durations of pulses with high electron numbers (top trace: $7,400e^-$, 6.6 ps; $3,790e^-$, 4.3 ps) are broadened by space-charge effects. For low electron numbers (bottom trace: $295e^-$, 0.5 ps; $150e^-$, 0.5 ps), measurement of the pulse width is limited by the resolution of the streak experiment. The electron pulse width was obtained by subtracting the width of the unstreaked electron beam (4 pixels) from the width of the streaked pulses (lorentzian profiles). **b**, Measured electron pulse widths as a function of the number of electrons. The streak velocity was 2.1 pixels per ps, or $1.6 \times 10^8 \text{ m s}^{-1}$. The sweep voltage is $\sim 1 \text{ kV ns}^{-1}$. **c**, Experimental photoionization-induced lensing transient. The ordinate reflects the relative difference between the average profile of the electron beam spot in the presence of the excitation laser and a reference profile (no laser).

For electron intensities on the order of 10^4 electrons per pulse, the width is typically ~10 ps. The laser and electron beam waists at overlap was measured to be $450 \pm 50 \,\mu\text{m}$, so the velocity mismatch contribution⁷ to the total experimental temporal resolution is ~4 ps.

To clock chemical changes, we must establish the zero of time (t_0) . A streak camera⁹ or photo-triggered deflection plates²¹ can give t_0 to within 10–20 ps, but these methods require some extrapolation and do not duplicate the design of crossed-beam experiments. Another approach is to rely on changes in the diffraction pattern of the



Figure 3 Experimental modified molecular scattering curves for two sets of data taken with 15-ps (left panel) and 30-ps (right panel) electron pulses. The delay times between the fs laser pulse and the ps electron pulse are shown. Theoretical calculations of sM(s) at -20 ps are presented (see text).

system under investigation, but this is not an independent means of finding t_0 . More importantly, this method is simply not practical for gas-phase work because of the long integration times required to obtain a single data point.

In the clocking technique developed here for UED, we use the crossed-beam geometry of the actual diffraction experiment, rather than relying on scattered electrons. The idea is to let the initiation laser pulse create a coulombic field (by ionization), which deflects the unscattered electron beam only during and after the laser pulse passes through. The phenomenon, termed lensing, occurs because the field focuses the charged electron beam. Fig. 2 shows the degree of lensing versus time; the lensing is a maximum when the laser and electron pulses are temporally overlapped. The results accurately show the precise t = 0 (to ~ 2 ps) and hence allow a direct clocking of changes in the diffraction experiment with ps resolution. We recorded lensing transients as a function of the position, polarization and diameter of the pump laser, and conducted control experiments where no gas was flowing and where the sample source tip was far removed from or close to the interaction region.

After successfully establishing t_0 , we conducted the first timeresolved gas-phase electron diffraction experiment with picosecond resolution. Diiodomethane (CH₂I₂) was selected as our prototype system because the loss of an iodine atom after dissociation at 310 nm is a major structural change which occurs in less time than the rotational period (~10 ps)^{22,23}. To clock the change, diffraction images were recorded on the CCD at delays of -20 ps, 0 ps, and up to +70 ps (Figs 3 and 4).

The experimental modified molecular scattering intensity, sM(s), was obtained at each time point

$$sM(s) = s \frac{I_{\text{tot}}(s) - I_{\text{back}}(s)}{|f_a| |f_b|}$$
(1)

where I_{tot} is the total scattering intensity, I_{back} is the background (including atomic) scattering intensity, and f_a and f_b are atomic scattering amplitudes^{15,19}. Typical sM(s) raw data taken at -20 ps



e- beam pulse width = 30 ps



Figure 4 Radial distribution functions f(r) and $\Delta f(r)$ obtained from the sM(s) and $\Delta sM(s)$ curves of Fig. 3, also for two sets of data (15-ps and 30-ps electron pulse width, left and right panel, respectively). The corresponding theoretical f(r) curve for the -20 ps data is shown. The changes obtained are in the region of the C-I and I---I internuclear separations (see text). Note that in f(r) the peak corresponding to the I---I distance should have about twice the area of the first peak (C-I and H---I); the peak area scales approximately as $n_{ij}Z_i/r_{ij}$ (where Z is the atomic

number and *n* is the multiplicity for nuclear pairs). However, because of damping in equation (2), the peaks appear to be of equal areas, and this is evident in our simulations for different values of *k*. The theoretical simulations shown in the figure are based on the structural data of ref. 24. We have also used more recent data from K. Hedberg's and co-workers (personal communication) and obtained very similar *f(r)* curves (data not shown), within the reported resolution.

are shown in Fig. 3. The theoretical fits, calculated from structural parameters²⁴ (see also Fig. 4 legend) of CH_2I_2 , are superimposed on the experimental data. To unambiguously establish the magnitude of the change with time, we also recorded the sM(s) in the absence of the fs initiation laser and obtained the residual of that sM(s) minus the sM(s) taken at -20 ps. This residual is essentially flat (Fig. 3), indicating that the two are identical. Thus, the sM(s) at -20 ps is a calibration point in time, independent of any theoretical fit. The change in the diffraction pattern as a function of time is shown in two sets of data having differing temporal resolutions (15 ps and 30 ps); the $\Delta sM(s)$ curves are relative to the -20 ps data.

Radial distribution curves were obtained from the sM(s) curves according to the standard GED equation:

$$f(r) = \int_{-\infty}^{s_{\text{max}}} sM(s)\sin(sr)\exp(-ks^2) ds$$
 (2)

where the constant k is a damping coefficient included for the limited s range. Figure 4 shows the experimental and theoretical f(r) obtained from the -20 ps sM(s) curves of Fig. 3. The timeevolution of $\Delta f(r)$ is also presented for the two sets of data. At positive time the amplitudes of the dominating C-I and I...I peaks decrease, corresponding to the loss of an iodine atom. Both the sM(s) and f(r) representations of our diffraction data clearly show a chemical change occurring as the delay between the fs laser pulse and the ps electron pulse sweeps from negative, to zero, and to positive times. From the f(r) data, we obtained the standard deviation for more than 100 diffraction images for each data set, and established that the signal-to-noise ratio is better than 60. Thus, we could detect a change as small as 3%, which is a factor of 5 less than the changes reported here.

Breakage of one C–I bond reduces the I···I peak twice as quickly as the C–I peak because CH_2I_2 has two C–I bonds and one I···I internuclear separation. This is observed in our data, corroborated by theoretical simulations of f(r) (not shown) which account for the percentage change of CH_2I_2 to CH_2I and I. Similar time-resolved studies were made for $C_2F_4I_2$ and CHI_3 . Quantitative analysis in the future should yield the changes due to the second C–I bond breakage, and elucidate the structure of the intermediate. Last, ground-state diffraction patterns of three other molecules (CF_3I , CCI_4 and SF₆) were recorded with our new UED apparatus (data not shown). As mentioned earlier, the diffraction patterns were converted to experimental sM(s) curves and radial distribution functions. The experimental and theoretical agreement is very good.

From the results presented here, it is now evident that ultrafast electron diffraction has achieved the temporal resolution and detection sensitivity necessary for picosecond and subpicosecond studies of complex molecular systems. In future work, utilizing modulation and difference detection techniques, efforts will be directed toward the suppression of background scattering from unreactive species so that molecular structural changes can be analysed with precision.

Received 8 October 1996; accepted 21 January 1997.

- 1. Chergui, M. (ed.) Femtochemistry: Ultrafast Chemical and Physical Processes in Molecular Systems (World \$cientific, Singapore, 1996).
- 2. Manz, J. & Wöste, L. (eds) Femtosecond Chemistry (VCH, New York, 1995).
- Zewail, A. H. Femtochemistry: Ultrafast Dynamics of the Chemical Bond (World Scientific, Singapore, 1994).
- Manz, J. & Castleman, A. W. Femtochemistry. J. Phys. Chem. (spec. iss.) 97(48), 12423-12649 (1993).
 Williamson, J. C. & Zewail, A. H. Structural femtochemistry: experimental methodology. Proc. Natl Acad. Sci. USA 88, 5021-5025 (1991).
- Williamson, J. C., Dantus, M., Kim, S. B. & Zewail, A. H. Ultrafast diffraction and molecular structure. Chem. Phys. Lett. 196, 529–534 (1992).
- Williamson, J. C. & Zewail, A. H. Ultrafast electron diffraction. Velocity mismatch and temporal resolution in crossed-beam experiments. *Chem. Phys. Lett.* 209, 10–16 (1993).
- Dantus, M., Kim, S. B., Williamson, J. C. & Zewail, A. H. Ultrafast electron diffraction. 5. Experimental time resolution and applications. J. Phys. Chem. 98, 2782-2796 (1994).
- Råksi, F. *et al.* Ultrafast x-ray absorption probing of a chemical reaction. *J. Chem. Phys.* 104, 6066– 6069 (1996).
- Tomov, I. V., Chen, P. & Rentzepis, P. M. Picosecond time-resolved x-ray diffraction during laser-pulse heating of an Au(111) crystal. J. Appl. Crystallogr. 28, 358–362 (1995).

- Kim, K.-J., Chattopadhyay, S. & Shank, C. V. Generation of femtosecond X-rays by 90-degrees Thomson scattering. Nucl. Instr. Meth. Phys. Res. A 341, 351-354 (1994).
- 12. Williamson, S., Mourou, G. & Li, J. C. M. Time-resolved laser-induced phase transformation in aluminum. Phys. Rev. Lett. 52, 2364–2367 (1984).
- Elsayed-Ali, H. E. Time-resolved reflection high-energy electron diffraction of metal surfaces. Proc. SPIE 2521, 92-102 (1995).
- Aeschlimann, M. et al. A picosecond electron gun for surface analysis. Rev. Sci. Instrum. 66, 1000– 1009 (1995).
- Hargittai, I. & Hargittai, M. (eds) Stereochemical Applications Of Gas-Phase Electron Diffraction (VCH, New York, 1988).
- Dibble, T. S. & Bartell, L. S. Electron diffraction studies of the kinetics of phase changes in molecular clusters. 3. Solid-state phase transformations in SeF₆ and (CH₃)₃CCl. J. Phys. Chem. 96, 8603–8610 (1992).
- Ischenko, A. A. et al. A stroboscopical gas-electron diffraction method for the investigation of shortlived molecular species. Appl. Phys. B 32, 161–163 (1983).
- Rood, A. P. & Milledge, J. Combined flash-photolysis and gas-phase electron diffraction studies of small molecules. J. Chem. Soc. Faraday Trans. 2 80, 1145–1153 (1984).
- Ischenko, A. A., Schäfer, L., Luo, J. Y. & Ewbank, J. D. Structural and vibrational kinetics by stroboscopic gas electron diffraction: the 193 nm photodissociation of CS₂. J. Phys. Chem. 98, 8673– 8678 (1994).
- Williamson, J. C. & Zewail, A. H. Ultrafast electron diffraction. 4. Molecular structures and coherent dynamics. J. Phys. Chem. 98, 2766-2781 (1994).
- Williamson, S., Mourou, G. & Letzring, S. Picosecond electron diffraction. Proc. SPIE 348, 313–317 (1983).
- Kawasaki, M., Lee, S. J. & Bersohn, R. Photodissociation of molecular beams of methylene iodide and iodoform. J. Chem. Phys. 63, 809–814 (1975).
- Baughcum, S. L. & Leone, S. R. Photofragmentation infrared emission studies of vibrationally excited free radicals CH₃ and CH₂I₂. J. Chem. Phys. 72, 6531–6545 (1980).
- Hassel, O. & Viervoll, H. Electron diffraction investigation of molecular structure II, results obtained by the rotating sector method. Acta Chem. Scand. 1, 149–168 (1947).

Acknowledgements. We thank S. Preuss for his help in the construction and testing of the experimental apparatus, and H. Elsayed-Ali for providing us with part of the design of the electron gun.

Correspondence should be addressed to A.H.Z