

Chapter 4.

UED Theoretical Methodology

The goal of electron diffraction is to obtain molecular structural information from a molecule's two-dimensional scattering pattern. For UED, the goal is the same but the theoretical procedure must be adapted for the transient nature of the systems of interest. Indeed, Chapter 3 already discussed the equipment by which the detection of such signal is achieved, this chapter relates a detailed account of the steps required to determine transient molecular structure from UED data.

Data are recorded for the ground-state sample (laser off) as well as time-resolved diffraction with the laser on. Time-resolved data are taken at multiple time points before and after the arrival of the laser pulse at the interaction region. In addition, in every UED experiment, various items of data are required that do not directly provide structural information about the molecules of interest. Regardless, this data must be recorded in order to calibrate various instrument effects and experimental conditions. Images of just

the electron beam (no sample gas, no laser) are needed to calibrate the detector background. Carbon dioxide diffraction images are acquired to determine the camera length (see Section 3.2.7). In Section 3.1.4, the detection system was described to possess a neutral density filter coated on the reverse of the phosphor scintillator face plate to compensate for the exponential drop-off of scattering intensity. This filter introduces a function to the data that must be accounted for. The atomic scattering of xenon is acquired for this purpose.

4.1 Averaged patterns

In total, 100 diffraction patterns, each an exposure of the detector for four minutes (240,000 electron pulses), are acquired for each of: detector background, carbon dioxide, xenon, ground state sample, and each time point of the time-resolved diffraction. These images denoted are $F_i^N(x, y)$ where N corresponds to B (detector background), CO₂, Xe, GS, or t (for a time-resolved diffraction time point). The i in the subscript is the pattern frame number 1–100. Each pattern, F , denotes the experimental intensity at detector pixel (x, y) . In order to maximize the signal to noise, the $F_i^N(x, y)$ ($i = 1–100$) are averaged and bad pixels from each i pattern are removed. Bad data at individual pixel positions may be due to faulty pixels on the detector, cosmic rays, or other such ephemeral effects. Pixel rejection and pattern averaging is done as follows:

A binary mask pattern, $M_i^N(x, y)$, is created for each $F_i^N(x, y)$. $M_i^N(x, y)$ has a value of 1 at pixel positions that contain acceptable data in $F_i^N(x, y)$ and a value of 0 where

unacceptable. By multiplying $F_i^N(x, y)$ by $M_i^N(x, y)$ an image is obtained where only good pixels remain. The $M_i^N(x, y)$ are created initially with a value of 1 at every (x, y) .

An averaged pattern, $F^N(x, y)$, is produced by

$$F^N(x, y) = \frac{\sum_{i=1}^{100} F_i^N(x, y) \cdot M_i^N(x, y)}{\sum_{i=1}^{100} M_i^N(x, y)}, \quad (4-1)$$

and

$$S^N(x, y) = \sqrt{\frac{\sum_{i=1}^{100} \{F^N(x, y) - F_i^N(x, y)\}^2}{\sum_{i=1}^{100} M_i^N(x, y)}} \quad (4-2)$$

is the standard deviation. If any pixel in any $F_i^N(x, y)$ is saturated (>65000 ADU on the CCD) or if its value falls outside of $F^N(x, y) \pm \mu \cdot S^N(x, y)$, the value in both $F_i^N(x, y)$ and $M_i^N(x, y)$ is set to zero. μ is a user defined parameter chosen to eliminate only the most errant unsaturated pixels from a frame; a value of 2.3 is typically used. The pixel rejecting procedure is repeated twice and the final averaged $F^N(x, y)$ result is obtained and will be used henceforth. The final standard deviation values for each pixel are discarded. The reject and average procedure is illustrated by example in Fig. 4-1.

4.2 Ratio images

4.2.1 Background subtraction and removal of the filter function

As mentioned above, a spatial filter on the back side of the phosphor scintillator increases the dynamic range of detection by leveling the rapid drop-off of scattering intensity. The effect of the filter must be accounted for in order to obtain the molecular scattering function. The experimental raw averaged patterns, $F^N(x, y)$, containing the filter effect, $\eta(x, y)$, can be expressed as

$$F^N(x, y) = I_N^e(x, y) * \eta(x, y), \quad (4-3)$$

where I_N^e denotes the experimental 2D intensity for each datum N without the filter function.

$$I_N^e = I + I_B^e = I + I^a + I^l + I^d, \quad (4-4)$$

where I is the sum of all sample scattering signal, if any, I_B^e is the background scattering signal from all sources of background: electron scattering from the background gas (I^a), stray light from the laser (I^l), and the detector response (I^d). The scattering of monatomic Xe, $F^{Xe}(x, y)$, which is composed solely of atomic scattering (Section 2.2) and generates a smooth monotonic signal, is measured, as is the contribution of the detector's noise, $F^B(x, y)$, which is recorded in the absence of sample gas and laser. It is then straightforward to eliminate the filter function by defining the following ratio:

$$\begin{aligned} R^N(x, y) &= \frac{F^N(x, y) - F^B(x, y)}{F^{Xe}(x, y) - F^B(x, y)} \\ &= \frac{I_N^e(x, y) - I^d(x, y)}{I_{Xe}^e(x, y) - I^d(x, y)}. \end{aligned} \quad (4-5)$$

The process of obtaining the ratio patterns, $R^N(x, y)$, is illustrated by example in Fig. 4-2.

4.2.2 Second-round pixel rejection and normalization

Since the formation of the ratio patterns effectively levels the signal, another pass of pixel rejection is performed in order to eliminate data points that fall outside of acceptable values.

$$\overline{R^N} = \frac{\sum_{x,y}^{npix} R^N(x, y) \cdot M^N(x, y)}{\sum_{x,y}^{npix} M^N(x, y)} \quad (4-6)$$

yields the average value over all pixels in the pattern $R^N(x, y)$. Note that the sum over all pixels ($npix = 512 \times 512$ with 2×2 binning) of the mask image in the denominator simply provides the total number of viable pixels in $R^N(x, y)$. The standard deviation is given by

$$\sigma_{R^N} = \sqrt{\frac{\sum_{x,y}^{npix} \{R^N(x, y) - \overline{R^N} \cdot M^N(x, y)\}^2}{\left\{ \sum_{x,y}^{npix} M^N(x, y) \right\} - 1}}. \quad (4-7)$$

Pixels are removed from $R^N(x, y)$ if they fall outside of $8 \cdot \sigma_{R^N}$. Such pixel rejection from the ratio pattern is repeated twice, and only very errant pixels are filtered out.

The frame-referencing (diffraction-difference) method, described below in Section 4.3.3, involves the subtraction of reference point data from the other time-resolved diffraction data points in order to highlight the structural changes. Hence, it is necessary that systematic fluctuation of scattering intensity between time points is dealt

with. Patterns are normalized to the number of active pixels by

$$R^N(x, y) = \frac{R^N(x, y) \cdot M^N(x, y)}{R^N}. \quad (4-8)$$

4.2.3 Locating the diffraction pattern center

Arguably one of the most critical steps in obtaining viable data from a diffraction pattern is the correct determination of the pattern's center. A radial average of a pattern using an incorrect center is known to produce data that may appear normal but which, upon analysis, would yield a wrong structure – as described by Cardoza *et al.*¹ Since this step is of such importance, it must be done carefully and the result confirmed by two independent methods. The first, more coarse method of center-finding is graphical (see Fig. 4-3). At the center position (x_c, y_c) a radial average is performed to produce a one-dimensional curve.

$$R^N(\text{pix}) = \frac{\sum R^N(x, y)}{N_{\text{pix}}}, \quad (4-9)$$

where the sum is over all pixels in $R^N(x, y)$ at distance (in pixels from the center position) $\text{pix} = \sqrt{(x_c - x)^2 + (y_c - y)^2}$, N_{pix} is the number of pixels at pix , and x and y correspond to all pixels in the two-dimensional pattern, $R^N(x, y)$. Using an arbitrary center position, a dummy curve, $R'^N(\text{pix})$, is calculated and then used to back-construct a dummy two-dimensional pattern, $R'^N(x, y)$. The experimental ratio pattern, $R^N(x, y)$ is then divided by this dummy pattern. At the correct choice of center position the two patterns will coincide and a flat image will be produced. Incorrect values of (x_c, y_c) will

produce images with varying degrees of oscillation depending on how close the guess is to the correct position. Fig. 4-3 shows divided patterns stepped at 0.5 pixels from the correct position; the division corresponding to the correct choice of center position is located at the center of the matrix.

Fine center determination and independent confirmation of the graphical method described above is accomplished by comparing one-dimensional data from the left and right sides of the detector similar to the method employed by the authors in Ref. 1. Two-dimensional ratio patterns $R^N(x, y)$ are split in half such that each new pattern is either from the left or right side of the detector only. Then, following Eq. (4-9), each half is converted to its own one-dimensional curve, $R_{left}^N(pix)$ and $R_{right}^N(pix)$. If the center is correct then the difference between the left and right curves will be without oscillatory component (note that data intensity on the left and right portions of the detector is often different so some offset is expected). Fig. 4-4(a) shows the curve from a correctly determined center for CO₂ data. Fig. 4-4(b) shows the resulting curve from a center offset from its correct position by 1 pixel. The center for time-resolved data is further checked by subtracting the $R_{left}^N(pix)$ and $R_{right}^N(pix)$ of a reference time point from those of another time point. If the difference data from the left, right, and full detectors match, then a satisfactory center position is confirmed. This method is adequate in locating the center to within 0.2 pixels.

4.3 One-dimensional intensity curves

4.3.1 Radial average and final round pixel rejection

Once the center position is determined correctly, the radial average of $R^N(x, y)$ is performed as in Eq. (4-9), to yield the one-dimensional data, $R^N(\text{pix})$, as a function of pixel from the pattern center. The radial average also permits a final round of errant pixel rejection. At each value of pix from the center ($\text{pix} = \sqrt{(x_c - x)^2 + (y_c - y)^2}$; $0 < \text{pix} < 256$ when binning is 2×2), an average intensity and a standard deviation are calculated, $\bar{R}^N(\text{pix})$ and $\sigma_{R^N}(\text{pix})$, respectively. If any value of $R^N(\text{pix})$ falls outside of $\bar{R}^N(\text{pix}) \pm 5 \cdot \sigma_{R^N}(\text{pix})$ it is removed from the data. Again, the parameter 5 is empirically selected to remove only the most excessive spikes. This is cycled three times removing 0 to 5 pixels from each pix value per cycle. The result is the one-dimensional intensity ratio curve, $R^N(\text{pix})$. Furthermore, a curve of the standard deviations ($\sigma_{R^N}(\text{pix})$, actually, 3σ) is produced and utilized in the structural refinement as discussed below in Section 4.4. $\sigma_{R^N}(\text{pix})$ is evaluated by “the standard deviation of the mean” as follows:²

$$\sigma_{R^N}(\text{pix}) = \frac{3 \cdot \sqrt{\sum_{\text{pix}} \{R^N(x, y) - \bar{R}^N(\text{pix})\}^2}}{N_{\text{pix}}}, \quad (4-10)$$

where N_{pix} is the number of pixels in the 2D pattern at a given distance in pixels, pix , from the center [as seen in Eq. (4-9)]. The radial average and calculation of the standard deviations is illustrated in Fig. 4-5.

4.3.2 The experimental $I(s)$

Intensity ratio curves, $R^N(pix)$, are converted to the reciprocal space used by diffractionists by the relation of the scattering angle (in this case, in terms of pix) to the momentum transfer parameter, s , as shown in Eq. (2-1). With consideration of Eqs. (4-4) and (4-5), it follows that

$$I_N^e(s) = I(s) + I_B^e(s) \cong R^N(s) \cdot I_{Xe}^T(s), \quad (4-11)$$

where $I_B^e(s)$ is now the sum of background contributions from the background gas (I^a) and the laser (I^l) [recall that I^d was removed in Eq. (4-5)]. $I_{Xe}^T(s)$ is the simulated atomic scattering of xenon. Several assumptions are made in Eq. (4-11). First, the background contribution to the data (which is recorded in two-dimensions, $I_B^e(x, y)$) can be approximated by $I_B^e(s)$ in one dimension. Second is that any background contribution to $I_{Xe}^e(x, y)$ in Eq. (4-5) is small enough compared to the xenon sample scattering itself that it can be effectively cancelled out of $R^N(s)$ with multiplication by $I_{Xe}^T(s)$ (which is further assumed to be a reasonable match to the experimental xenon scattering). $I_N^e(s)$ are obtained for $N = \text{CO}_2$, ground-state sample, and each time-resolved diffraction data point.

4.3.3 The frame-referencing method and $\Delta I(s)$

During time-resolved diffraction data acquisition, upon irradiation of the molecular beam by the excitation laser, a fraction of the molecules will absorb and undergo photophysical and/or photochemical processes, while most do not interact with

the photons and will remain in their initial state throughout the experiment. Molecules absorbing a photon will undergo an electronic transition and possibly structural changes. With this in mind, the scattering intensity, $I(s)$, at a given time point, t , can be expressed as a sum of scattering intensities for each of the possible configurations, α .

$$I(s;t) = \sum_{\alpha} I_{\alpha}(s;t) = \sum_{\alpha} f_{\alpha}(t) I_{\alpha}(s), \quad (4-12)$$

where $f_{\alpha}(t)$ is the fractional contribution of $I_{\alpha}(s)$ at time t . This total intensity has a significant component of unreacted, unperturbed molecules in their initial states.

The reacting molecules can be highlighted using the *frame-referencing* method. Diffraction data from before excitation (reference data) are subtracted from diffraction data at time t (excitation occurs at $t = 0$). The frame-referenced data are without most of the unreacted species as well as all the atomic scattering and systematic background, thereby emphasizing the structural changes (and the temporal evolution of those changes) during the reaction. For example, if $t_{ref} < 0$,

$$\begin{aligned} \Delta I(s;t) &= I(s;t) - I(s;t_{ref}) \\ &= \sum_{\alpha} f_{\alpha}(t) I_{\alpha}(s) - 1 \times I_r(s) \\ &= \left[f_r(t) I_r(s) + \sum_{\alpha \neq r} \{ f_{\alpha}(t) I_{\alpha}(s) \} \right] - \left\{ f_r(t) + \sum_{\alpha \neq r} f_{\alpha}(t) \right\} I_r(s) \\ &= \sum_{\alpha \neq r} \{ f_{\alpha}(t) I_{\alpha}(s) \} - \left\{ \sum_{\alpha \neq r} f_{\alpha}(t) \right\} I_r(s) \\ &= \sum_{\alpha \neq r} f_{\alpha}(t) \{ I_{\alpha}(s) - I_r(s) \}, \end{aligned} \quad (4-13)$$

where the r subscript refers to the reference. See Fig. 4-6 for a graphic demonstration. In this case, because the structure of the reference (ground state) has already been

determined, Eq. (4-12) provides the structures of the intermediates/products and their fractions. A positive time point could also be used as the reference frame in order to enhance the signal of a particular transient structure, as shown elsewhere.³

4.4 Refining diffraction data

4.4.1 The experimental $sM(s)$

The experimentally obtained scattering intensity, $I_N^e(s)$, contains the molecular and atomic scatterings as well as any background, I_B^e , that results from background gas (smoothly varying and as large as 30% of the signal) and laser scattering (minor), as shown above [Eq. (4-11)]. Accordingly, and using the independent atomic model (see Section 2.2),

$$I_N^e(s) \cong I_M^e(s) + I_A^e(s) + I_B^e(s) \quad (4-14)$$

for which the molecular scattering which contains the structural information may be isolated by

$$I_M^e(s) \cong \lambda \cdot I_N^e(s) - I_A^T(s) - I_B^T(s), \quad (4-15)$$

where $I_A^T(s)$ is the atomic scattering of molecule N calculated [Eq. (2-6)] using scattering factors available in the literature.⁴ λ is the scale factor needed to match the amplitudes of theoretical and experimental curves. $I_B^T(s)$ is a fifth-order polynomial of the form

$$I_B^T(s) = \sum_{i=0}^{order} c_i \cdot s^i \cdot I_{Xe}^T(s), \quad (4-16)$$

where c_i are the coefficients for each polynomial term, the calculation of which will be

described below. $I_B^T(s)$ accounts for the background contributions without adding significant oscillations to alter the sinusoidal components of the molecular scattering.

The experimental modified molecular scattering function, $sM^e(s)$ or $\Delta sM^e(s;t)$ as defined by Eq. (2-12) in Section 2.3, is actually dependent upon the theoretical model $I_M^T(s)$ that is chosen. As shown in Eq. (4-15), $I_M^e(s)$, and consequently $sM^e(s)$, may only be defined once the coefficients of $I_B^T(s)$, and the scale factor λ are assigned values. To obtain these values, a statistical measure of difference between experiment and theory, χ^2 , is required.

$$\chi^2 = \sum_s \left\{ \frac{I_M^e(s) - I_M^T(s)}{\sigma_{I^e}(s)} \right\}^2, \quad (4-17)$$

which, substituting Eqs. (4-10), (4-11), and (4-14), may be expanded to

$$\chi^2 = \sum_s \left\{ \frac{R^N(s) \cdot \lambda \cdot I_{Xe}^T(s) - I_A^T(s) - \sum_{i=0}^{order} c_i \cdot s^i \cdot I_{Xe}^T(s) - \sum_{\alpha}^{N_{\alpha}} f_{\alpha}(t) \cdot I_{M_{\alpha}}^T(s)}{\sigma^{R_N}(s) \cdot I_{Xe}^T(s)} \right\}^2, \quad (4-18)$$

where $\sigma^{R_N}(s)$ is the error calculated in the radial average [Eq. (4-10)], N_{α} is the total number of molecules in the model, the $f_{\alpha}(t)$ are the fractions of each molecule α at the time t , and $I_{M_{\alpha}}^T(s)$ is the theoretical molecular scattering intensity of molecule α (see Section 4.3.3). The parameters λ , c_i , and f_{α} are linear in the first derivative of χ^2 and thus may be solved for exactly using the normal equations method⁵ by which $I_M^e(s)$ is then determined. Utilizing Eq. (2-11), the experimental modified molecular scattering

function becomes

$$sM^e(s) = s \frac{I_M^e(s)}{f_I f_J}, \quad (4-19)$$

while the theoretical modified molecular scattering function is defined as

$$sM^t(s) = s \frac{I_M^t(s)}{f_I f_J}. \quad (4-20)$$

$\Delta sM^e(s;t)$ and $\Delta sM^t(s;t)$ can be calculated in the same fashion. A graphical example of the steps leading from $R^N(\text{pix})$ to $sM^e(s)$ is shown in Fig. 4-7 for the example of $N =$ ground-state benzaldehyde.

4.4.2 Statistical measures: χ^2 and R

Structural refinement is carried out in the molecular scattering space by minimizing χ^2 as defined in Eq. (4-17). Since the conversion of $I_M(s)$ to $sM(s)$ involves only the multiplication of a constant, χ^2 remains the same regardless of whether $I_M(s)$ or $sM(s)$ is used for refinement.

$$\chi^2 = \sum_s \left\{ \frac{(sM^e(s) - sM^t(s))}{\sigma_{sM^e}(s)} \right\}^2 = \sum_s \left\{ \frac{I_M^e(s) - I_M^t(s)}{\sigma_{I^e}(s)} \right\}^2, \quad (4-21)$$

where $\sigma_{sM^e} = s \frac{\sigma_{I^e}}{f_I f_J}$. Although χ^2 is primarily used to quantify the fit, although R , a standard goodness-of-fit parameter in electron diffraction, may also be checked throughout the refinement.

$$R = \sqrt{\frac{\sum_s \{(sM^e(s) - sM^T(s))/\sigma_{sM^e}(s)\}^2}{\sum_s (sM^T(s)/\sigma_{sM^e}(s))^2}} \quad (4-22)$$

The difference between χ^2 [Eq. (4-21)] and R [Eq. (4-22)] is in the division by the theoretical term of $\sum_s (sM^T(s)/\sigma_{sM^e}(s))^2$ making R a unitless quality-of-fit parameter.

Typically in the analyses, χ^2 is minimized while R is simultaneously monitored. The smaller the values of these statistical measures, the better is the agreement between theory and experiment. For ground-state structural analyses R is typically < 0.1 , similar to conventional GED, while for transient structures R is usually between 0.3 and 0.8, a consequence of the much reduced signal to noise ratio in the difference data.

4.4.3 Structural refinement and assessment of errors

Unlike the parameters mentioned above that can be solved for exactly by a system of normal equations linear with respect to the derivative of χ^2 , the structural and vibrational parameters of a molecule have a non-linear relationship to the derivative of χ^2 and must be fit in an iterative manner. Regardless, the derivative of χ^2 with respect to each parameter φ is utilized to find a minimum position.

$$\beta \equiv -\frac{1}{2} \frac{\partial \chi^2}{\partial \varphi} = 0 \quad (4-23)$$

Section 2.3 showed how the non-linear (structural and vibrational) parameters are related to the molecular scattering function. The Levenberg-Marquardt algorithm is invoked for obtaining these parameters by locating the χ^2 minimum for the entire set of fitted

parameters, $\{\varphi_i\}$. In the non-linear fitting procedure, minima on the χ^2 surface are approximated by parabolas. If the approximation holds well, given a position on the surface (the initial set of parameters), it is possible to calculate the parameter change needed to reach the minimum set of values. When the approximation is poor, and the step does not improve the fit, it is satisfactory simply to move down the gradient somewhat before attempting the move again (inverse-Hessian versus steepest-descent methods). The Levenberg-Marquardt algorithm permits switching between the two methods using the steepest descent when far from the minimum (and the parabolic approximation is poorest) and the inverse-Hessian step when the minimum is at hand. The details of the algorithm can be found in Ref. 5 and seen in the analysis code reproduced in Appendix VI.

Convergence is reached when the difference between χ^2 values of consecutive steps is less than 0.000001. The error bars associated with each parameter, φ , are computed as follows. The estimated covariance matrix of the standard errors in the fitted parameters becomes

$$[C] \equiv [\alpha]^{-1} = \left[\frac{1}{2} \frac{\partial^2(\chi^2)}{\partial \varphi_i \partial \varphi_j} \right]^{-1} \quad (4-24)$$

from which the variance associated with the estimated parameter, φ_i , is calculated

$$\sigma^2(\varphi_i) = C_{ii}. \quad (4-25)$$

The error associated with the estimated parameter is

$$\delta(\varphi_i) = \sqrt{\Delta\chi^2_\nu} \sqrt{\sigma^2(\varphi_i)}, \quad (4-26)$$

where $\Delta\chi^2_\nu$ is a coefficient determined from the confidence level and the number of

degrees of freedom of the fit, ν .⁵

Table 4-1. $\Delta\chi_\nu^2$ as a Function of Confidence Level and Degrees of Freedom

Level	ν					
	1	2	3	4	5	6
68.3%	1.00	2.30	3.53	4.72	5.89	7.04
90%	2.71	4.61	6.25	7.78	9.24	10.6
95.4%	4.00	6.17	8.02	9.70	11.3	12.8
99%	6.63	9.21	11.3	13.3	15.1	16.8
99.73%	9.00	11.8	14.2	16.3	18.2	20.1
99.99%	15.1	18.4	21.1	23.5	25.7	27.8

In practice, UED structural refinement error bars are reported without the multiplication by $\sqrt{\Delta\chi_\nu^2}$ in Eq. (4-26) and, instead often multiplied by a weight factor, $\sqrt{\chi^2/\Delta range}$, where $\Delta range$ is the number of pixels in the one-dimensional data $R^N(pix)$ that are used in the structural refinement (e.g., if the range 34–210 pixels of $R^N(pix)$ is used, then $\Delta range = 176$). This error weight is only used in the reported errors when refinement is conducted using the old UED refinement program “Uedana” (see below, Section 4.8).

4.5 Structure and vibrations

4.5.1 Quantum chemical calculations

Structural refinement in UED requires an initial-guess geometry in order to calculate the theoretical molecular scattering intensity, $I_M^T(s)$. Although one could, in principle, use a chemically intuitive guess, UED data analysis is always begun with the structural results of *ab initio* or density functional theory (DFT) calculations. Ideally, regardless of the choice of initial guess, structural refinement should converge to one

single true structure. In practice, however, this is not always true, especially when there is a large number of structural parameters involved and the fitting surface contains many local minima. Therefore, it is good practice to have an initial guess as close to the true structure as possible. For this, a high-level theoretical calculation is desired, such as DFT, coupled cluster (CC), quadratic configuration interaction with single and double excitations (QCISD), or multi-configuration self-consistent field (MCSCF). In UED studies, all calculations have been carried out using either Gaussian98⁶ or GAMESS⁷ packages.

For the structures of molecules in the singlet (S_0) or triplet (T_1) ground state, highly accurate results are available at fairly low computational costs. The B3LYP level⁸ with the 6-311G(d,p) basis set has been found useful in determining structure, energy, and vibrational frequencies.⁹

Several methods are available for calculating the properties of excited states. Among them, multi-configuration self-consistent field (MCSCF) uses a minimum set of orbitals (active space) for a configuration interaction (CI) calculation; just enough to determine the relevant excited-state characteristics.¹⁰ The CAS (complete active space method) of MCSCF allows the user to choose which molecular orbitals make up the set of active orbitals that best describe the electronic transition. For example, if one were interested in the first excited singlet state of ethylene (S_1 , a $\pi\pi^*$ state), one would choose the occupied π orbital and the lowest unoccupied π^* orbital as the active space and the two π electrons as the active electrons. The procedure is carried out graphically by

viewing the calculated molecular orbitals and choosing which ones closest resemble the orbitals needed to define the space.

4.5.2 Temperature and mean amplitudes of vibration

Structural refinement is conducted using internal coordinates of each molecule in the form of a geometrically consistent z-matrix. The z-matrix is converted into a set of Cartesian coordinates for each atom, which is then used to form the array of internuclear distances (r_e). r_e are converted to r_a using the formula described in Section 2.3, which then serve as input for $I_M^T(s)$ and $sM^T(s)$ (see source code in Appendix IV). Mean amplitudes of vibration, l_h values (or u values in some older sources), are calculated using empirical formulas fit to electron diffraction determined values for a set of molecules. For C–C distances $1.217 \text{ \AA} \leq r_e \leq 5.618 \text{ \AA}$,¹¹

$$l_h = 0.013837 + 0.023398r_e - 0.000147r_e^2. \quad (4-27)$$

And for C–H distances $1.080 \text{ \AA} \leq r_e \leq 4.677 \text{ \AA}$,¹²

$$l_h = 0.050134 + 0.027368r_e - 0.001805r_e^2. \quad (4-28)$$

It was found that these formulae would also hold for C–X and H–X distances where X = N, O, Si, S, Cl, and Br.¹³ In UED Eq. (4-27) is used for all C–X distances and Eq. (4-28) is used to calculate the l_h values for all H–X distances. However, since these formula are intended for molecules at approximately 298 K, and vibrational amplitudes are temperature dependent, and UED operating conditions (and product temperatures) are often well above room temperature, it is necessary to re-evaluate l_h for the elevated temperatures needed. The following relation based on a harmonic system is needed.¹⁴

$$l_h^2 = \frac{h}{8\pi^2 \mu \nu} \coth\left(\frac{h\nu}{2kT}\right), \quad (4-29)$$

where h is Planck's constant, k is the Boltzmann constant, μ is the reduced mass of the internuclear pair, ν is the harmonic vibrational frequency, and T is the temperature of the system. Eq. (4-29) is used to solve for ν at room temperature, then assuming that ν is independent of temperature the l_h at the desired T can be trivially calculated. The solution for ν is contained in the source code in Appendix V.

In principle, it may be the case that each distance in a molecule (or at least distances contained within specific moieties) has its own temperature, however in UED it is assumed that all l_h of a molecule are of the same T . As mentioned in Section 3.1.3, the temperatures of ground-state samples are taken to be the same as the temperature of the heated nozzle. However, temperatures of product species are much more ambiguous. In these cases an estimate is made using the available energy after excitation and a statistical distribution of that energy throughout the calculated vibrational normal modes. In a photochemical reaction the internal energy of the product, $E_{\text{int}}^{\text{product}}$ (not including zero-point energy), is determined by

$$E_{\text{int}}^{\text{product}} = E_{\text{elec}}^{\text{parent}} + E_{\text{zp}}^{\text{parent}} + E_{\text{int}}^{\text{parent}} + h\nu - E_{\text{elec}}^{\text{product}} - E_{\text{zp}}^{\text{product}}, \quad (4-30)$$

where the electronic and zero-point energies are provided by quantum chemical calculations and $h\nu$ is the excitation photon energy. By neglecting translational and rotational energies ($E_{\text{int}} = E_{\text{vib}}$), the temperature may be solved for from the vibrational partition function.

$$E_{vib} = \sum_i \frac{h\nu_i \cdot e^{-\left(\frac{h\nu_i}{kT}\right)}}{1 - e^{-\left(\frac{h\nu_i}{kT}\right)}}, \quad (4-31)$$

where ν is the frequency of the i th normal mode given by quantum chemical calculations. The assumptions above regarding the translational and rotational energies make T extracted from Eq. (4-31) the upper bound of the statistical vibrational temperature.

The difference in appearance of $sM(s)$ and $f(r)$ data calculated considering a C–C distance at various temperatures is shown in Fig. 4-8. One obvious consequence is the large difference between cold and hot internuclear pairs. This manifests itself in diffraction difference (frame referenced, where the reference is the cold parent) data by dispersive elements illustrated especially clearly in the $\Delta f(r)$ curve.

4.6 Temporal evolution kinetics

UED time-resolved data show an exponential rise of a product structure with time. Using the fractions of component structures at each time point a single exponential rise is fit to the data. The fitting function is that derived for femtosecond transition-state spectroscopy of the population of a decaying state convoluted with a Gaussian probe pulse.¹⁵

$$y(t) = A + B \cdot \left(e^{-k_1(t-t_0)} e^{\frac{(k_1 \cdot z)^2}{2}} - e^{-k_2(t-t_0)} e^{\frac{(k_2 \cdot z)^2}{2}} \right) \cdot \frac{1}{2} \cdot \left[1 + \operatorname{erf} \left(\frac{t-t_0}{z} - k_1 \cdot z \right) \right] \quad (4-32)$$

where A is the total product fraction before time-zero, B is the total product fraction at the conclusion of the reaction, t_0 is the time when the excitation laser pulse crosses the sample, k_1 is the rate of decay of the product structure, k_2 is the rate of formation of the

product structure, and $z = \sigma_i = \frac{w}{2\sqrt{2 \cdot \ln(2)}}$ where w is the full width at half max (FWHM) of the normalized temporal Gaussian profile of the probe electron pulse described by

$$f_i(t) = \frac{1}{\sigma_i \sqrt{2\pi}} e^{-\frac{t^2}{2\sigma_i^2}} \quad (4-33)$$

and σ_i is the pulse temporal standard deviation. The error function is

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-s^2} \cdot ds \quad (4-34)$$

In the usual case where the product structure shows no decay during the course of the reaction, k_1 is set to 0 and Eq. (4-32) reduces to

$$y(t) = A + B \cdot \left(1 - e^{-k_2(t-t_0)} e^{\frac{(k_2 \cdot z)^2}{2}} \right) \cdot \frac{1}{2} \cdot \left[1 + \text{erf}\left(\frac{t-t_0}{z}\right) \right] \quad (4-35)$$

A , B , and t_0 , although known from the refinement and the experimental conditions, are fit along with k_2 using Microcal Origin. Reaction time constants reported henceforth correspond to $\tau = 1/k_2$ unless otherwise noted.

It should be noted that although other structures (e.g., those of initially excited states) are, in principle, present and therefore contributing to the electron scattering signal, their similarity to the ground-state structure renders them essentially invisible. This represents a handicapping feature of diffraction in general where uniqueness of a state is not necessarily reflected in uniqueness of structure. The frame-referenced image is flat if the resulting state and the ground state possess the same structure.

4.7 The refinement procedure

The above sections provide the theoretical framework for how a molecular structure is extracted from a set of diffraction patterns and how the dynamics are evaluated. However, the actual practice of solving a time-resolved diffraction pattern performed by the UED diffractionist is yet to be described. Although it will be shown by example in the subsequent chapters dealing with specific molecular systems, a brief account will be given here.

First, using the structures obtained by quantum chemical calculations and the thermal temperature calculated using the excess energy, the theoretical $sM^T(s)$ curves are constructed for the parent molecule and a variety of products. Using the $\Delta sM^T(s)$ corresponding to a possible reaction channel, the $\Delta sM^e(s)$ is formed and the two are compared by finding the optimized fractional contributions and polynomial background (the scale factor is taken from the result of the ground state or by fitting the ground-state structure to the data at a negative time point). Typically, there will be many possible pathways corresponding to various literature-predicted products, relevant excited states, and hypothetical products that are unlikely but still lie within the range of available energy. From these possibilities, the pathways with the lowest R and χ^2 values are selected for the structural refinement. Structural refinement is begun by fitting each structural parameter individually, then in further combinations, and so on until all parameters can be refined simultaneously. A stationary point in the refinement is reached when 1) two subsequent refinements of all structural parameters does not lower the χ^2 or change the structure and 2) when the β values [see Eq. (4-23)] are below a threshold

(about 0.001). Once the stationary point is reached, it is evaluated by the user's chemical and physical intuition to determine its worth. Since diffraction patterns have multiple solutions it is possible to start with a wrong model and successfully refine it to a stationary position. It is likely though that the geometry of the stationary point is something that is not physically reasonable (e.g., a 0.8 Å C–C bond distance or an 80° bond angle). If this is the case, and it is reproducible, then that model is discarded and the procedure is repeated for another. Sometimes, though, all single product channels produce unphysical refined structures. When this is the case, it becomes necessary to test pathways using combinations of several products. Again each molecule in the combination is structurally refined and compared with the quantum chemically derived structure to determine its physical viability. In principle, the whole procedure is repeated with growing numbers of product combinations until something reasonable is reached.

4.8 Note on data analysis programs

Two generations of data analysis programs have been used in the application of UED to the molecular systems described in the following chapters. The old program “Uedana,” and the new program “UED_2004” are both coded in-house and in most ways are largely the same. The account of data analysis given above is that used by UED_2004. Uedana treats a few items differently, the most notable being the treatment of component fractions, scale factor, and the polynomial background. In Uedana these parameters are refined using the same non-linear procedure utilized for refining the structure and camera distance. The architecture of this program also prevents the scale

factor and background from being refined simultaneous to other parameters or each other. The scale factor, in fact, is not used to scale the data as λ in Eq. (4-15), but instead scales $I_M^T(s)$ in Eq. (4-17) as $1/\lambda$. It should be recalled that those parameters are linear and solved for exactly with UED_2004 (though with the same end results). The error bars are also calculated differently with Uedana having an added weight factor (see Section 4.4.3) that reduces the reported error. The distinction between programs is made when necessary in the following chapters, but analysis should be regarded as having been conducted using UED_2004 unless otherwise noted. The Appendices contain source code of UED_2004 for the most critical aspects of the structural refinement process.

4.9 References

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