

26 June 1998

Chemical Physics Letters 290 (1998) 1-8

CHEMICAL PHYSICS LETTERS

# Ultrafast electron diffraction: determination of radical structure with picosecond time resolution

J. Cao, H. Ihee, A.H. Zewail \*

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

Received 15 April 1998; in final form 24 April 1998

#### Abstract

Using ultrafast electron diffraction (UED) with the temporal diffraction-difference method recently developed in this laboratory, we report accurate determination of the radical (CF<sub>2</sub>) structure in the dissociation of diiododifluoromethane (CF<sub>2</sub>I<sub>2</sub>) with picosecond time resolution. Time-zero was clocked accurately within 2 ps and both iodine atoms were found to be liberated in less than 4 ps. The structure, absolute fraction, and electronic state of the radical were determined. The CF<sub>2</sub> radical was found to be in  $X^1A_1$  ground state with C–F and F ··· F distances of  $1.30(\pm 0.02)$  Å and  $2.06(\pm 0.06)$  Å, respectively. © 1998 Published by Elsevier Science B.V. All rights reserved.

### 1. Introduction

In our continuing effort to develop ultrafast electron diffraction [1-5], we report here new advances in accurate determination of radical structure in the dissociation reaction of  $CF_2I_2$ . Previously, we have demonstrated the approach of clocking reactions in the gas phase with UED. Diffraction changes due to C-I bond breakage in CH<sub>2</sub>I<sub>2</sub> molecules upon irradiation at 307 nm were successfully detected on the picosecond time scale [4]. UED was further applied to a more complex reaction, the dissociation of  $Fe(CO)_5$  [5]. For  $Fe(CO)_5$ , the reaction was found to be completed in less than 10 ps after excitation at 307 nm wavelength and the final major products were determined to be  $Fe(CO)_2$ , FeCO and Fe with a branching ratio of ca. 2:5:5. Furthermore, structural analysis utilizing the diffraction-difference method

provided the Fe–C and C–O bond distances of  $Fe(CO)_2$  and FeCO and suggested that their C–O bonds were weaker than those of  $Fe(CO)_5$ . As with all X-ray and electron diffraction methods [1–13], time resolution makes it possible to examine structural changes. Here we focus on an elementary reaction to study the structures of radicals produced in the course of the reaction in the gas phase.

The reaction of  $CF_2I_2$  was chosen because the products are only two channels with simple structures, the molecule  $CF_2I_2$  has a high absorption coefficient at 307 nm wavelength and its possible product radicals have higher scattering intensities than those of  $CH_2I_2$  [4]. The reaction was activated with 307 nm excitation laser pulses and snapshots of diffraction images were recorded at different delay times. The dissociation of  $CF_2I_2$  was found to be completed within 4 ps. On this picosecond time scale, the major product detected was  $CF_2$  radical and its structure was determined with an improved accuracy of one order of magnitude higher than

0009-2614/98/\$19.00 © 1998 Published by Elsevier Science B.V. All rights reserved. PII: \$0009-2614(98)00520-X

<sup>\*</sup> Corresponding author.

those in the study of  $Fe(CO)_5$ , by analyzing the diffraction-difference curves at each delay time.

## 2. Experimental

The picosecond time-resolved electron diffraction was performed in the second-generation UED apparatus developed in this laboratory [3,4]. As shown in Fig. 1, it is composed of a femtosecond laser, a picosecond electron gun, a free-jet expansion sample source, and a two-dimensional single-electron detection system. Femtosecond laser pulses from a colliding-pulse mode-locked ring dve laser were amplified in a four-stage pulsed dye amplifier pumped by a Nd:YAG laser at 30 Hz. The amplified pulses (614 nm, 3-4 mJ/pulse, 30 Hz, ~400 fs pulse width) were then split (with a beam splitter) into two beams. The clocking laser pulse (95%) was first frequencydoubled with a KDP crystal (> 500  $\mu$ J at 307 nm), then directed and focused on the scattering gas sample beneath the needle of the free-jet expansion source.

To generate the electron pulse, part of the remaining 5% was doubled and focused onto a back-illuminated photocathode in the electron gun compartment. The ultrashort photoelectron pulse was then accelerated to 18.8 keV (de Broglie wavelength is 0.088 Å), collimated and focused onto the scattering volume. The two-dimensional diffraction images at a given delay time were recorded in a charge-coupled device (CCD) at the end of a phosphor scintillator/fiber optic/image intensifier chain in the detection chamber. Time delays between the femtosecond laser pulse and the picosecond electron pulse were controlled by a computer-driven translational stage.

The electron pulse, laser pulse and molecular beam were arranged in a cross-beam geometry, and the overlap of the three beams was controlled within 10  $\mu$ m accuracy. The camera length was measured to be 102.4 mm. For our current setup, the time resolution is mainly determined by the electron pulse width. With a flux of ~ 6000 electrons per pulse in our experiment, the corresponding temporal width is ~ 7 ps [4]. The total temporal resolution, including the contributions from the pump laser pulse width



Fig. 1. A schematic of the experimental setup used here for ultrafast electron diffraction (UED).

(~ 1.5 ps) and group velocity mismatch effect (~ 3 ps) [3], is less than 8 ps. After establishing the time zero by the lensing approach [4] within  $\pm 2$  ps accuracy in situ, the diffraction images at -150, 0, +12 and +162 ps delay times were recorded.

The sample was purchased from Shanghai Institute of Organic Chemistry [14]. Our F<sup>19</sup> NMR measurements showed that the sample purity is better than 99%. UV and infrared absorption spectra were obtained and were consistent with published results [15,16]. After connection to the diffraction chamber, the sample was further purified by four cycles of freeze-and-thaw to remove air and the residual impurities. To increase the gas density in the scattering volume, the sample cell, the gas line and the nozzle were heated to 33, 39 and 44°C, respectively. The gas pressure in the scattering chamber during the experiment was ~  $3 \times 10^{-4}$  Torr.

#### 3. Results and discussion

At each delay time, a series of over 200 two-dimensional diffraction images (85 second average exposure time for each image), including the images of scattered laser light without the electron beam, were recorded with the CCD detector. The conversion of the two-dimensional diffraction image to a one-dimensional intensity distribution,  $I(r_{\text{pixel}})$ , as a function of pixel radius  $r_{pixel}$ , was completed with home-built software by providing the center pixel coordinates (undiffracted electron beam spot) and the background offsets (CCD dark noise) of each image, and calculating the average intensity as a function of pixel radius from the center for each diffraction image [3-5]. Then, the experimental total scattering intensity curve  $I_{Tot}(r_{pixel})$  at different delay times, including that of scattered laser light  $I_{\text{Laser}}(r_{\text{pixel}})$ , was obtained by further averaging all the  $I(r_{nixel})$  at each delay time. Finally, the scattered-laser-light-free total intensity curve  $I_{Tot}(s)$  at each delay time was obtained by subtracting  $I_{\text{Laser}}(r_{\text{pixel}})$  from  $I_{\text{Tot}}(r_{\text{pixel}})$ and through the conversion of pixel number to momentum transfer s [3,4]. An experimental data file containing the one standard deviation  $(\sigma_{Tot}(r_{pixel}))$ as a function of pixel radius for each data set at different delay times was also generated for the molecular structural fitting.

To monitor the structural changes due to dissociation, we followed the diffraction-difference approach developed in our laboratory [5]. First, the modified molecular scattering intensity for the parent molecule (-150 ps data) was calculated with CF<sub>2</sub>I<sub>2</sub> structural parameters obtained in the conventional gas phase electron diffraction (GED) [17] according to:

$$sM^{\mathrm{Exp}}(s) = s\frac{I_{\mathrm{M}}(s)}{|f_a||f_b|},\qquad(1)$$

where  $f_a$  and  $f_b$  are atomic scattering amplitudes (both are iodine atoms in our case), and  $I_M$  is the molecular scattering intensity.  $I_M$ , is composed of interference terms from all atom-atom pairs and contains molecular structural information and, is given by:

$$I_{\rm M} = I_{\rm Tot}(s) - I_{\rm Back}(s) \tag{2}$$

where  $I_{\text{Back}}(s)$  is the background intensity profile. Then, the theoretical  $sM^{\text{Theo}}(s)$  was normalized to the  $sM^{\text{Exp}}(s)$  with a scaling factor  $S_{\text{C}}$  for comparison. The corresponding radial distribution curve, which provides the relative density of internuclear distances in a molecule, was also generated by Fourier transforming sM(s) curves using the standard equation in GED [18]:

$$f(r) = \int_0^{S_{\text{max}}} sM(s) \sin(sr) \exp(-ks^2) ds, \qquad (3)$$

where the constant k (k = 0.02 Å<sup>2</sup>) is a damping coefficient included for the limited *s* range.

To extract the transient radical structures, the difference total intensity data,  $\Delta I_{\text{Tot}}$ , was obtained by subtracting  $I_{\text{Tot}}$  at -150 ps from  $I_{\text{Tot}}$  at each positive delay time.  $\Delta I_{\text{Tot}}$  was used instead of  $I_{\text{Tot}}$  for the analysis of transient structural changes, because of the enhanced product contribution to diffraction intensity, reduced background scattering intensity and cancellation of systematic error in the diffraction-difference curve. The determination of the fractions and structural parameters of each fragment, for a given difference total intensity curve,  $\Delta I_{\text{Tot}}$ , was made using home-developed software in an iterative manner, similar to that used in conventional GED [18–20], by minimizing the chi-square:

$$\chi^{2} = \sum_{\text{pixel}} \frac{\left(S_{c} \cdot \Delta s M^{\text{Theo}}(s) - \Delta s M^{\text{Exp}}(s)\right)^{2}}{\sigma_{i}^{2}} \quad (4)$$

where the  $\Delta sM(s)$  is the difference modified molecular scattering intensity,  $\sigma_i$  is the one standard deviation of  $\Delta sM^{\text{Exp}}(s)$  at each pixel position (or *s* position), and the summation is over all pixels (17– 225).  $\Delta s^{\text{Exp}}M(s)$  is obtained from  $\Delta I_{\text{Tot}}$  through Eq. (1).  $\sigma_i$  was calculated with experimental  $\sigma_{\text{Tot}}(r_{\text{pixel}})$ for each data set obtained in the radial sum and the error propagation rules [21]. First, the  $\sigma_{sM(s)}$  for the experimental sM(s) curve was generated by:

$$\sigma_{sM(s)} = \sqrt{2} \cdot \sigma_{\text{Tot}}(r_{\text{pixel}}) \cdot \frac{s}{|f_a||f_b|}, \qquad (5)$$

where the factor  $\sqrt{2}$  accounts for the subtraction of  $I_{\text{Back}}$  (Eq. (2)). Then, the standard deviation for the difference curve  $(\Delta sM^{\text{Exp}}(s) = sM^{\text{Exp}}(s) - sM^{\text{Exp}}_{-150 \text{ ps}}(s))$  was finally calculated as:

$$\sigma_i = \sqrt{\sigma^2 + \sigma_{-150\,\mathrm{ps}}^2} \,. \tag{6}$$

By starting from an assumed product distribution and the structural parameters for each species, the software first fits the residual background with the experimental  $\Delta I_{\text{Tot}}$  values at the zero points of the theoretical  $\Delta I_{\text{M}}(s)$ . Then the experimental  $\Delta sM(s)$ is obtained with the background-free  $\Delta I_{\text{Tot}}$  through Eq. (1), and the  $\chi^2$  is calculated to evaluate the goodness of the fit. This whole procedure is repeated until the best least-square fit between theoretical and experimental  $\Delta sM(s)$  curves is reached (minimum of  $\chi^2$ ) [19,20]. During fitting, the scaling factor was fixed at the value of the data set for the parent molecules (data at -150 ps).

With one-photon absorption at 307 nm, a  $CF_2I_2$ molecule can dissociate in two different pathways:  $CF_2I + I$  and  $CF_2 + 2I$ . In the fitting, we first floated the structural parameters and population for both radicals. The contribution of CF<sub>2</sub>I radical to the diffraction intensity was found negligibly small, less than 1%. For the further refinement, only  $CF_2I_2$ molecule and CF<sub>2</sub> radical were included. The CF<sub>2</sub>I<sub>2</sub> structural parameters were kept fixed at the value obtained in conventional GED [17]. The fraction of  $CF_2$ , the internuclear distances r(C-F) and  $r(\mathbf{F}\cdots\mathbf{F})$ , and the mean amplitudes of vibration l(C-F) and  $l(F \cdots F)$  were fitted. The fitting results for structural parameters and populations are summarized in Table 1. The errors are three standard deviations of the fitting. The  $\chi^2$  and R value, which is frequently used as a measure of goodness of fit in electron diffraction, are also listed in the Table 1. The R is calculated as:

$$R^{2} = \frac{\sum \frac{1}{\sigma_{i}^{2}} \cdot \left(S_{c} \cdot \Delta sM^{\text{Theo}}(s) - \Delta sM^{\text{Exp}}(s)\right)^{2}}{\sum \frac{1}{\sigma_{i}^{2}} \cdot \left(\Delta sM^{\text{Exp}}(s)\right)^{2}}.$$
(7)

A theoretical simulation was also carried out to further test the robustness of this method. A theoretical diffraction-difference curve,  $\Delta I^{\text{Sim}}(r_{\text{nivel}})$  was generated by summing  $\Delta I_{\text{Back}}(r_{\text{pixel}})$ ,  $\Delta I_{\text{M}}(r_{\text{pixel}})$  and  $\Delta I_{\text{Noise}}(r_{\text{pixel}})$ .  $\Delta I_{\text{Back}}(r_{\text{pixel}})$  was the experimental background determined in the diffraction-difference analysis and  $\Delta I_{\rm M}(r_{\rm nixel})$  is the theoretical difference curve calculated with fitting results for the difference curve at given delay time.  $\Delta I_{\text{Noise}}(r_{\text{nixel}})$  was generated with a Gaussian random number generator by feeding in the  $\sigma_i$  obtained from Eq. (6) with experimental  $\sigma_{\text{Tot}}(r_{\text{pixel}})$  [22]. Then, the  $\Delta sM^{\text{Sim}}(s)$  and  $\Delta f^{\text{Sim}}(r)$  were generated from  $\Delta I^{\text{Sim}}(r_{\text{pixel}})$  with the same procedure as in the above data analysis. The agreement between the theoretical simulation and the experimental data was found to be very good. As shown in Table 1, the  $\chi^2$  of the fitting for each diffraction-difference curve is comparable to the number of data points, 208. Both  $\chi^2$  values and simulation results indicate that the diffraction-difference curves contain mostly random noise, and the contribution of systematic errors is negligibly small [21,22]. This confirms the advantages of the diffrac-

Table 1 Summary of results for the experimental diffraction-difference curves

Delay time	0 ps	12 ps	162 ps			
$r(C-F)\pm 3\sigma$	$1.27\pm0.03$	$1.29\pm0.02$	$1.30\pm0.02$			
$r(\mathbf{F}\cdots\mathbf{F})\pm 3\sigma$	$2.07 \pm 0.09$	$2.07 \pm 0.06$	$2.06 \pm 0.06$			
$l(F-F) \pm \sigma$	$0.03 \pm 0.06$	$0.04 \pm 0.03$	$0.04 \pm 0.05$			
$l(\mathbf{F}\cdots\mathbf{F})\pm\sigma$	$0.06 \pm 0.08$	$0.06 \pm 0.05$	$0.06 \pm 0.06$			
$CF_2$ fraction (%) $\pm 3\sigma^a$	$18.0 \pm 1.0$	$26.3 \pm 1.0$	$26.6 \pm 1.0$			
$\chi^2$	274	205	301			
R	0.102	0.061	0.073			

<sup>a</sup> The scattering intensity fluctuations in  $I_{\text{Tot}}$  were also estimated and included.

tion-difference method in extracting transient structures with UED compared to fitting the  $I_{\text{Tot}}$  directly [5].

The experimental sM(s) and f(r) curves at -150ps and the difference  $\Delta sM(s)$  and  $\Delta f(r)$  curves at different delay times, relative to the data of  $CF_2I_2$  at -150 ps, are shown in Fig. 2. The theoretical sM(s)and f(r), calculated with the structural parameters from conventional GED studies [17], and the fitting results for  $\Delta sM(s)$  and  $\Delta f(r)$  are also imposed on each data set for comparison. The absence of temporal evolution after +12 ps indicates that the whole fragmentation process takes place on the ultrafast time scale. Since no CF<sub>2</sub>I radical was detected even at the time zero, as shown in Table 1, the estimated bond breakage time for both iodine atoms of a  $CF_2I_2$ molecule is less than 4 ps at 307 nm. Note that the fraction of CF<sub>2</sub> product detected at 0 ps is 18%, higher than half of the total final fraction ( $\sim 26\%$ ). This indicates that the actual time zero determined in this experiment is at about +1.4 ps.

The structure of the parent molecule was also fitted with the non-linear least-square method, and results are summarized in Table 2. Other error sources, such as the uncertainties of camera length

Radial distribution, *f(r)* 



	UED		Gas phase diffraction		
	$r \pm 3\sigma$	$l\pm\sigma$	$r \pm 3\sigma$	$l\pm 3\sigma$	
C–F	$1.34\pm0.08$	$0.04\pm0.09$	$1.336\pm0.005$	$0.036 \pm 0.012$	
C–I	$2.07\pm0.07$	$0.04\pm0.25$	$2.148 \pm 0.004$	$0.060\pm0.010$	
$F \cdots F$	$2.18 \pm 0.63$	$0.08 \pm 0.22$	$2.182 \pm 0.014$	0.060	
$F \cdots I$	$2.84 \pm 0.31$	$0.11 \pm 0.02$	$2.870 \pm 0.006$	$0.083 \pm 0.004$	
Ι···Ι	$3.54\pm0.03$	$0.11\pm0.02$	$3.572\pm0.008$	$0.090 \pm 0.003$	

<sup>a</sup>For the detailed discussion of error analysis in UED, see text.

and electron wavelength, were estimated and included in the final error analysis. Agreement between UED results and those of conventional GED [17] is very good considering the extremely low flux of our picosecond electron pulse. Note that our *k* value is 0.02 Å<sup>2</sup> and the peaks in f(r), which reflect relative density of internuclear distances, is less resolved than those reported in the literature with smaller values of *k* ranging from 0.01 to 0.0025 Å<sup>2</sup> [18]. The fitting for the parent molecule is not as good as those of difference curves because of the

#### Molecular scattering, sM(s)



Fig. 2. The experimental sM(s) and f(r) curves at -150 ps and the difference  $\Delta sM(s)$  and  $\Delta f(r)$  curves at different delay times, relative to the data of CF<sub>2</sub>I<sub>2</sub> at -150 ps (solid lines). Shaded lines represent the theoretical sM(s) and f(r), derived with the structural parameters from conventional gas-phase electron diffraction [17], and the fitting results for  $\Delta sM(s)$  and  $\Delta f(r)$ . The delay time between the initiation laser pulse and the picosecond electron pulse are also shown.

much larger background scattering intensity and the presence of the systematic error in the detector.

To visualize the contribution of product  $CF_2$  to the scattering intensity,  $\Delta s M^{CF_2}(s)$  and  $\Delta f^{CF_2}(r)$ curves containing only the CF<sub>2</sub> signal were also generated at each delay time, as shown in Fig. 3. The curves were obtained through the diffraction-difference curves by adding a fraction of scattering intensity from parent molecules, e.g.  $\Delta s M^{CF_2}(s)$  at 162 ps was obtained by adding 26.6% of the experimental sM(s) at -150 ps to  $\Delta sM(s)$  at 162 ps delay time, to compensate its negative contribution to the difference curves. The molecular structures of CF<sub>2</sub>I<sub>2</sub> and CF<sub>2</sub> with internuclear distances determined by GED and UED are plotted in the Fig. 4. and their radial distribution functions are also shown for comparison. Even though the parent  $CF_2I_2$  is a much stronger scatter than the CF<sub>2</sub> radical for electrons, the CF<sub>2</sub> signal is clearly seen at each delay time, as shown in Fig. 3. The errors in the  $\Delta sM^{CF_2}(s)$ and  $\Delta f^{CF_2}(r)$  are larger than those in diffraction-difference curves  $\Delta sM(s)$  and  $\Delta f(r)$ , because the error in sM(s) at -150 ps is propagated in through the addition.

Fragmentation of  $CF_2I_2$  following UV excitation has been studied by photofragment translational spectroscopy [16,23]. After absorbing one UV photon, several dissociation channels are energetically possible, which include radical channels and a three-body dissociation channel:

$$\begin{array}{rcl} \mathrm{CF}_2\mathrm{I}_2 & \to \mathrm{CF}_2\mathrm{I} + \mathrm{I} & (\text{channel 1}) \\ & \to \mathrm{CF}_2\mathrm{I} + \mathrm{I}^* & (\text{channel 2}) \\ & \to \mathrm{CF}_2 + \mathrm{I} + \mathrm{I} & (\text{channel 3}) \end{array}$$

depending upon the photon energy [16,23]. For 308 nm wavelength, the reported branching ratio was 5:10:2 (39/59/12%). The available energy for the CF<sub>2</sub>I radical in channel 2 was measured to be 8.6 kcal/mol and less than the dissociation energy of second iodine atom,  $D_{02} = 12.0$  kcal/mol [16,23]. Therefore, having 26% dissociation of parent molecules, about 16% final products should be CF<sub>2</sub>I radicals, if only one photon absorption takes place.



Fig. 3. Contribution of CF<sub>2</sub> radical to the diffraction intensity at each delay time. The radial distribution functions (f(r)) are shown in the left panel, and the modified molecular scattering intensity (sM(s)) curves are shown in the right panel. The experimental (solid line) and theoretical (shaded line) sM(s) and f(r) curves for parent CF<sub>2</sub>I<sub>2</sub> at -150 ps are also shown. The heavy shaded line represents the difference between the experimental and theoretical radial distribution curves at -150 ps.



Fig. 4. The molecular structures of  $CF_2I_2$  and  $CF_2$ . The internuclear distances for  $CF_2I_2$  were determined by conventional GED [17] and  $CF_2$  were determined by the reported UED. The internuclear distances and the radial distribution curves for  $CF_2I_2$  and  $CF_2$  are also shown.

However, for comparison with our experimental results, we must consider the different fluence of the laser pulses used. For translational spectroscopy experiments, the fluence was ~ 0.01 J/cm<sup>2</sup> (~  $10^7$  $W/cm^2$ ) from an nanosecond laser, whereas in our experiments, a much higher laser power  $\sim 5 \times 10^{11}$  $W/cm^2$  was used. It is highly probable that the product CF<sub>2</sub>I radical subsequently absorbs another photon (ladder switching) [24,25] and further dissociates rapidly into  $CF_2 + I$ . If enough energy is partitioned into the translational energies of the photofragments, the final CF<sub>2</sub> radical will be in the ground electronic state. A femtosecond transitionstate spectroscopy experiment will establish the nature of these channels, as was done in the case of the reaction of  $C_2F_4I_2$  [26,27].

The structure of  $CF_2$  radical has been studied both theoretically and experimentally [28–34]. The equilibrium geometry of both ground state ( $X^IA_1$ ) and the first excited state ( ${}^{3}B_1$ ) of  $CF_2$ , which lies about 2.42 eV above the ground state, were measured with

microwave spectrum [29], UV absorption spectroscopy [28] and laser-induced fluorescence spectroscopy [30]. The internuclear distances r(C-F) and  $r(F \cdots F)$  for these two states were determined to be 1.30 and 2.06 Å ( $\angle$ FCF = 104.9°) for ground state [28], and 1.325 and 2.29 Å ( $\angle$  FCF = 119.4°) for the first excited state [30], respectively. These values are also supported by ab initio calculations [30–34]. The internuclear distances of the CF<sub>2</sub> radical (1.30 and 2.06 Å) determined here by UED in the reaction suggest that the radicals formed after dissociation at 307 nm are in the ground state. The mean amplitudes of vibration determined by UED (0.04 and 0.06 Å) are also consistent with the values (0.045 and 0.053 Å) we calculated using the force field [30] for  $CF_2$  in the ground state.

In conclusion, with the achievement of direct monitoring of the transient radical structure with high accuracy on the picosecond time scale by using the temporal diffraction-difference method, UED has now the potential for wider applications. In this

#### Acknowledgements

This research was supported by a grant from Airforce Office of Scientific Research and the Office of Naval Research.

#### References

- [1] J.C. Williamson, A.H. Zewail, Proc. Natl. Acad. Sci. USA 88 (1991) 5021.
- [2] J.C. Williamson, M. Dantus, S.B. Kim, A.H. Zewail, Chem. Phys. Lett. 196 (1992) 529.
- [3] M. Dantus, S.B. Kim, J.C. Williamson, A.H. Zewail, J. Phys. Chem. 98 (1994) 2782.
- [4] J.C. Williamson, J. Cao, H. Ihee, H. Frey, A.H. Zewail, Nature 386 (1997) 159, and references therein.
- [5] H. Ihee, J. Cao, A.H. Zewail, Chem. Phys. Lett. 281 (1997) 10.
- [6] A.A. Ischenko, L. Schäfer, J.Y. Luo, J.D. Ewbank, J. Phys. Chem. 98 (1994) 8673.
- [7] H.E. Elsayed-Ali, Proc. SPIE 2521 (1995) 92.
- [8] F. Ráksi, K.R. Wilson, Z. Jiang, A. Ikhlef, C.Y. Côté, J.-C. Kieffer, J. Chem. Phys. 104 (1996) 6066.
- [9] R.W. Schoenlein, W.P. Leemans, A.H. Chin, P. Volfbeyn, T.E. Glover, P. Balling, M. Zolotorev, K.-J. Kim, S. Chattopadhyay, C.V. Shank, Science 274 (1996) 236.
- [10] B. Perman, V. Šrajer, Z. Ren, T. Teng, C. Pradervand, T. Ursby, D. Bourgeois, F. Schotte, M. Wulff, R. Kort, K. Hellingwerf, K. Moffat, Science 279 (1998) 1946.
- [11] V. Šrajer, T. Teng, T. Ursby, C. Pradervand, Z. Ren, S. Adachi, W. Schildkamp, D. Bourgeois, M. Wulff, K. Moffat, Science 274 (1996) 1726.
- [12] I.V. Tomov, P. Chen, P.M. Rentzepis, J. Appl. Cryst. 28 (1995) 358.

- [13] C. Rischel, A. Rousse, I. Uschmann, P.-A. Albouy, J.-P. Geindre, P. Audebert, J.-C. Gauthier, E. Förster, J.-L. Martin, A. Antonetti, Nature 390 (1997) 490.
- [14] D.-B. Su, J.-X. Duan, Q.-Y. Chen, J. Chem. Soc. Chem. Commun. (1992) 807.
- [15] I. McAlpine, H. Sutcliffe, Spect. Acta 25A (1969) 1723.
- [16] E.A.J. Wannenmacher, P. Felder, J.R. Huber, J. Chem. Phys. 95 (1991) 986.
- [17] H.-G. Mack, H. Oberhammer, E.O. John, R.L. Kirchmeier, J.M. Shreeve, J. Mol. Struct. 250 (1991) 103.
- [18] I. Hargittai, M. Hargittai (Eds.), Stereochemical Applications of Gas-Phase Electron Diffraction (VCH, New York, 1988) and references therein.
- [19] K. Hedberg, M. Iwasaki, Acta Cryst. 17 (1964) 529.
- [20] L.S. Bartell, in: A. Weissbergre, B.W. Rossiter (Eds.), Physical Methods of Chemistry (Wiley, New York, 1972).
- [21] J.R. Taylor, An Introduction to Error Analysis: the Study of Uncertainties in Physical Measurements (The University Science Book, Mill Valley, CA, 1982).
- [22] W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery, Numerical Recipes in C: the Art of Scientific Computing (Cambridge University Press, 1992).
- [23] G. Baum, P. Felder, J.R. Huber, J. Chem. Phys. 98 (1993) 1999.
- [24] U. Boesl, H.J. Husser, E.W. Schlag, Chem. Phys. Lett. 87 (1982) 1.
- [25] L. Bañares, T. Baumert, M. Bergt, B. Kiefer, G. Gerber, J. Chem. Phys. 108 (1998) 5799.
- [26] L.R. Khundkar, A.H. Zewail, J. Chem. Phys. 92 (1990) 231.
- [27] D. Zhong, S. Ahmad, A.H. Zewail, J. Am. Chem. Soc. 119 (1997) 5978.
- [28] C.W. Mathews, Can. J. Phys. 45 (1967) 2355.
- [29] W.H. Kirchhoff, D.R. Lide Jr., F.X. Powell, J. Mol. Spect. 47 (1973) 491.
- [30] M.R. Cameron, S.H. Kable, G.B. Bacskay, J. Chem. Phys. 103 (1995) 4476.
- [31] B.-S. Cheong, H.-G. Cho, J. Phys. Chem. A 101 (1997) 7901.
- [32] Z.-L. Cai, J. Phys. Chem. 97 (1993) 8399.
- [33] N. Russo, E. Sicilia, M. Toscano, J. Chem. Phys. 97 (1992) 5031.
- [34] C.W. Bauschlicher Jr., H.F. Schaefer III, P.S. Bagus, J. Am. Chem. Soc. 99 (1977) 7106.