XFEL experiments: jitter of pump–probe time delays and pulse intensities

S. Bratos, M. Wulff, J.-Cl. Leicknam

XFEL EXPERIMENTS: JITTER OF PUMP-PROBE TIME DELAYS AND PULSE INTENSITIES

S. Bratos[1], M. Wulff [2], and J-Cl. Leicknam[1]

1 - Sorbonne Universités, UPMC Univ Paris 06, Laboratoire Physique Théorique de la Matière Condensée, 75005, Paris, France.

2 - ESRF - European Synchrotron, Complex Systems and Biomedical Sciences (CBS) CS 40220, 38043 Grenoble Cédex 9, France.

SUMMARY

Jitter of XFEL signals due to fluctuations in shot-to-shot time delays and intensities are explored in the frame of a statistical theory of X-ray diffraction from liquids. Deformed signals are calculated at different levels of pump-probe jitter. A new method is proposed to eliminate these distortions.

I. **INTRODUCTION**. Monitoring atomic motions during a chemical reaction has always been an important objective in chemical research. This sort of "filming", inaccessible in the past, can now be realized either by performing time-resolved optical or time-resolved x-ray experiments. Optical experiments, less expensive than x-ray experiments, were realized first and they proved to be highly efficient. The Nobel prize for chemistry was awarded to A. Zewail for his spectacular achievements in this field [1]. However, as the wave length of optical waves are large compared with inter-atomic distances in molecules, optical techniques can not detect atomic positions without complementary assumptions. This difficulty is absent in X-ray experiments. They can be realized, both in diffraction or absorption, either using synchrotron or free electron laser (XFEL) techniques. Pulses of the order of 100 ps can be generated by the former, and 10 fs by the latter. X-ray techniques, in particularly XFEL techniques have proven to be extremely efficient, but a number of difficulties still limit, for the time being, their intrinsic power: the shot-to shot dispersion of pump-probe time delays and of pulse intensities. An important efforts has been made to solve this problem experimentally [2][3][4][5][6][7][8][9]. The recent measure and sort technique [10] merits attention in this context. We complete this effort theoretically by calculating the signal distortions in some typical situations. We also propose a new method to eliminate these distortions..

II. **THEORY**. (a) In a time-resolved X-ray experiment, the sample is pumped by an optical pulse and probed by an X-ray pulse. The pump-probe time delay must be determined with extreme accuracy. At the present time, while XFEL sources generate pulses down to 10 fs, there is a jitter on the pump-probe time delays of several hundreds fs. The experiment must thus be repeated and the resulting signals averaged over this sequence to make the results usable. In this way, a single-pulse experiment transforms into an multi-pulse experiment. The problem is thus statistical, not only in its molecular dynamics part, but also in the electric field part. Statistical mechanics is thus omnipresent, as in ultrafast optical spectroscopy; see e.g. the text book by Mukamel [11].

(b) A statistical theory of x-ray diffraction from liquids was published some time ago [12]. Its full mathematical development is given in this reference, and will not be repeated again. Only the essential features are illustrated in what follows. The intensity of the diffracted x-rays $\Delta S(q, \tau)$ is:

$$\Delta S(\boldsymbol{q},\tau)=\int_{-\infty}^{\infty} dt\, I_X(t-\tau)\,\Delta S_{inst}(\boldsymbol{q},t)$$
$$\Delta S_{inst}(\boldsymbol{q},t)=\left(\frac{e^2}{mc^2\hbar}\right)^2 P \int_0^{\infty}\int_0^{\infty} d\tau_1 d\tau_2 \langle E_i(\boldsymbol{r},t-\tau_1)\,E_j(\boldsymbol{r},t-\tau_1-\tau_2)\rangle_O \qquad (1)$$
$$\boldsymbol{x}\langle[[f_m f_n \mathrm{e}^{-i\boldsymbol{q}\cdot\boldsymbol{r}_{mn}(\tau_1+\tau_2)}, M_i(\tau_2)], M_j(0)]\rangle_S$$

Here P is a factor characteristic of the experimental set-up such as the temporal pulse profile, polarisation, sample concentration, etc. I_X is the intensity of the incident X-ray radiation, E_i, E_j are components of the electric field generated by the optical laser, **q** is the wave vector, f_m, f_n are atomic scattering factors, r_{mn} is the distance between the atoms m and n, and M_i, M_j are components of the laser induced transition moment M between the states i and j. Einstein's convention of summing over doubled indices i, j and m,n is employed. The form of this expression can be understood comparing it with the standard expression for the diffracted x-ray intensity $S(q) \sim \Sigma_{m,n}[f_m.f_n.\exp(-iq.r_{mn})]$ [13]. The later is valid if the incident X ray wave has a constant amplitude and if fast chemical processes are absent. If the incident X-ray consists of short pulses, and if some fast chemical process is laser excited, this expression must be modified in two ways. First, the intensity and the inter-atomic distances r_{mn} are now time dependent, and I_X and r_{mn} must be replaced by $I_X(t)$ and $r_{mn}(t)$.The remaining quantities in Eq.(1) describe the laser induced electronic excitation. This can be understood noticing that, according to the Fermi golden rule, the rate of this excitation is proportional to $1/\hbar^2(\mathbf{E}.\mathbf{M})^2$, where **E** is the laser generated electric field and **M**

the transition moment. The presence in Eq. (1) of the factors $1/\hbar^2$, $E(t-\tau_1)$, $E(t-\tau_1-\tau_2)$, $M(0)$ and $M(\tau_2)$ can be understood in this way. The connection of different time points can not be explained as simply. This equation can be used as it stands when studying single pulse events.

Interpreting multi-pulse experiments is more complex, due to the scatter of pump-probe time delays and shot intensities. However, the form of Eq. (1) indicates that these problems can be studied independently from those due to molecular dynamics. Note also that Eq. (1) was conceived for a single pulse experiment. However, a slight modification makes it applicable to a multi-pulse experiment: it is sufficient to replace the single X-ray pulse intensity $I_X(t-\tau)$ by the average multi-pulse intensity $\langle I_X(t-\tau)\rangle_{MP}$, the index MP indicating multi-pulse. One can then write:

$$\Delta S(q,\tau)=\int_{-\infty}^{\infty} dt \langle I_X(t-\tau)\rangle_{MP} \Delta S_{inst}(q,t) \qquad (2)$$

where $\Delta S_{inst}(q, t)$ is the same as in Eq. (1). In the rest of this paper, the incident x-ray beam is supposed to be Gaussian:

$$I_X(t-\tau-\delta\tau)=I\exp[-\gamma_X(t-\tau-\delta\tau)^2] \qquad (3)$$

where τ is the nominal pump-probe time delay, $\delta\tau$ its ill controlled shut-to-shut time increment and $(1/\gamma_X)^{1/2}$ its temporal width.

c) To proceed further, details about the statistical distribution of $\delta\tau$ and I for subsequent shots are required. The attention of the experimentalists was centered on this question for years, and still remains an issue. According to the literature [14], the distribution of pump-probe time delays $P(\delta\tau)$ is Gaussian: $P(\delta\tau)=\sqrt{(\beta/\pi)}\exp(-\beta(\delta\tau)^2)$. The distribution of shot-to shot intensitires P(I) is less well known, but according to Eqn(2) it is needed only if the absolute intensity of the scattered radiation is explored, which is not the case here. Then, inserting Eqn(3) into Eqn(2) and integrating over $\delta\tau$, there results:

$$\Delta S(q,\tau)=I\left(\frac{\beta}{\beta+\gamma_X}\right)^{\frac{1}{2}}\int_0^{\infty} dt \exp\left(-\left(\frac{\beta\gamma_X}{\beta+\gamma_X}\right)(t-\tau)^2\right)\Delta S_{inst}(q,t) \qquad (4)$$

Jitter thus generates an effective temporal broadening of incident x-ray pulses. This is the basic equation relating the distorted and non-distorted signals $\Delta S(q,\tau)$ and $\Delta S_{inst}(q,t)$, respectively.

To proceed further, the following way can be chosen. Let the laser excitation promote the molecules from their ground electronic state 0, where the length of a given bond is r_0, to an electronic state 1, where it is r_1. According to the Franck-Condon principle, $r_1(0) = r_0$ at time t = 0. The simplest assumption to describe the bond length variation at later times consists in writing $r(t)=r_1-(r_1-r_0).\exp(-t/\tau_r)$ where τ_r is the molecular reaction (or rearrangement) time (Fig.1). The signal $\Delta S_{inst}(q,t)$, non affected by pump-probe time delay dispersion, can be written:

$$\Delta S_{inst}(q,t)=\frac{\sin(q(r_1-(r_1-r_0)\exp(-t/\tau_r)))}{q(r_1-(r_1-r_0)\exp(-t/\tau_r))} - \frac{\sin(qr_0)}{qr_0} \qquad (5)$$

Then, inserting Eqn(5) into Eqn(4) and integrating provides $\Delta S(q,\tau)$. The integration can be performed either numerically or analytically if $r_1-r_0 \ll r_0$. Note that this condition is not very restrictive. When passing from a single C-C bond to a triple C-C bond, r_0 = 1.5A and r_0-r_1 = 0.3A. The experimental signal $\Delta S(q,\tau)$ can then be calculated and its distortion investigated, if the parameters r_1 and τ_r are known. The opposite problem of extracting the non perturbed signal $\Delta S_{inst}(q,t)$ from the observed signal $\Delta S(q,\tau)$ is more difficult. The best is to work with the function $\Delta S(q,\tau)$ in its analyitcal form:

$$\begin{aligned}\Delta S(q,\tau) \sim & -q(r_1-r_0).j_1(qr_0) \\ & .[erfc(-\sqrt{\frac{\beta.\gamma_X}{\beta+\gamma_X}}\tau) \\ & -erfc[(\frac{1}{2\tau_r})\sqrt{\frac{(\beta+\gamma_x)}{\beta\gamma_x}}-\sqrt{\frac{\beta.\gamma_X}{\beta+\gamma_X}}\tau]\exp((\frac{1}{4\tau_r^2})\frac{\beta+\gamma_x}{\beta\gamma_x}-\frac{\tau}{\tau_r})]\end{aligned} \qquad (6)$$

where r_0 and r_1 are bond lengths before and after reaction, τ_r is its characteristic time and $j_1(x)$ is the Bessel function of the order1 (remember that sinx/x is the Bessel function $j_0(x)$). Inserting experimental data into the left hand member of Eqn(6) then permits to calculate r_1 and τ_r using mean square optimisation techniques. As there are only two prameters r_1 and τ_r to determine, this calculation is easy.

The corresponding r space signals $\Delta S[r,\tau]$ can be calculated by Fourier inverting $\Delta S(q,\tau)$. This can be done without any special precaution if τ is large as compared with the time $\tau<1/\sqrt{\beta}$ characteristic of pump-probe dispersion. If this is not the case, $\Delta S(q,\tau)$ must be corrected carrying out the above procedure for each q,τ point such that $\tau<1/\sqrt{\beta}$, this making the Fourier transform possible. It is thus more difficult to correct the signals $\Delta S[r,\tau]$ than the signals $\Delta S(q,\tau)$.

III. **EXAMPLES** (a) Times shorter than the molecular dynamics. Those considered here are of the order of 10 fs or shorter. At these times a liquid behaves like a glass. Nevertheless, diffraction signals still vary with time, even if all inter-atomic distances r are fixed. This is due to the electric fields E_i, E_j of the optical pump pulses in Eq. (1). The noise of XFEL radiation also plays a major role. In this limit, one finds :

$$\Delta S_{XFEL}(\tau)=Const.erfc(-\sqrt{(\frac{\beta\gamma_X}{\beta+\gamma_X})}\tau)$$

One concludes that the dispersion of pump probe time delays modifies the temporal width of the average multi-pulse signals even at very short times. These effects may be large, even overwhelmingly large; compare with Fig. 2. Note also that in this short-time limit the q- and r-resolved signals exhibit the same tau dependence. In fact, in this limit $\Delta S_{inst}(q,t)$ is independent of time. A look on Eqn(6) then confirms the statement.

(b) Contracting chemical bond. In absence of distortion free experimental data in the 10 - 100 fs time domain, the following example is completely theoretical. Let us start considering a CC bond contracting from 1.5A to 1.2A; these values correspond to a single and triple CC bond respectively. This CC bond is supposed to be a part of a polyatomic molecule PolyM. Its CC diffraction peak is assumed to be sufficiently isolated from other diffraction peaks from PolyM to be explorable. The laser pump promotes PolyM from its electronic ground state A, where the CC bond is simple to a state B where it is triple. However, this transformation is not instantaneous: according to the Franck-Condon principle, light induced transitions are all vertical. At τ = 0, the CC distance remains unchanged, equal to 1.5 A. It is only at later times that it contracts gradually from 1.5A to 1.2 A. How does this contraction process manifests itself in a r resolved XFEL experiment? And how does this signal deform if the pump-probe times are dispersed? The central quantities are the pair distribution

functions g(r, t); see the textbook [Hansen,1997]. The following expressions are chosen in our model:

$$g_A = \sqrt{a_A/\pi}\ \exp[-a_A(r-r_A)^2]$$
$$g_B(r,t) = \sqrt{a_B/\pi}\ \exp\left[-a_B\left(r - r_B - \delta r_B \exp(-t/\tau_v)\right)^2\right] \qquad (7\ a,b)$$

$$n_A(t) = 1 - n_0.\exp(-t/\tau_p)$$
$$n_B(t) = n_0.\exp(-t/\tau_p) \qquad (8\ a,b)$$

Note that $g_A(r)$ and $g_B(r,t)$ approach a delta function when a_A et a_B go to infinity. Equation (7b) states that the CC bond contracts in the state B of PolyM in times of the order of τ_v. Employing the above equations together with Eqs. (2, 4) generates the r-resolved signal $\Delta S(r, \tau)$.
The parameters of the above model are: the ground state distance r_A is 1.5A and the excited states distance r_B 1.2A; the laser induced contraction of the CC bond in the state B of PolyM is 0.3 A. The parameters a_A and a_B are both of the order of 25 A^{-2}, which corresponds to a half width of $g_A(r)$ and $g_B(r, t)$ of the order of 0.4 A. Moreover, the recombination time τ_v is assumed to be of the order of 100 fs, and the population relaxation time $\tau_p >> \tau$. These values correspond to an ultrafast chemical process.

The results are presented now. Fig. 3a illustrates $\Delta S[r, \tau]$, the r-resolved XFEL signal of a contracting CC bond in absence of pump-probe time dispersion. This signal is presented in three dimensions: the distance r and the time τ are defined on the two coordinate axes while the intensity is given by color. The red valley at 1.5A pictures the deficit of CC bonds at the initial bond length of 1.5 A, whereas the violet ridge indicates CC bonds of given length r at a given time τ. Note that the intensity of the differential signal is vanishing at $\tau = 0$: according to the Frank-Condon principle electronic transitions are vertical. At times tau~10 fs, intramolecular dynamics of PolyM intervene noticeably. It is only at times tau > 20 fs that chemistry manifests itself predominantly. The signal represents a film of a contracting CC bond. If pump-probe times are dispersed, the above picture is slightly or deeply modified; see Fig. 3b $\Delta S[r, \tau]$ is only blurred. It is only blurred if the pump-probe time dispersion is small. If the pump-probe time dispersion is not sufficiently small, the CC contraction is no longer observable and only an instantaneous jump between the initial and final

configurations is observed . This effect is widely known in other fields of physics and chemistry under the name of motional narrowing.

So much for r-resolved signals $\Delta S[r, \tau]$. Let us now pass to the q-resolved signals $\Delta S(q, \tau)$. The latter can be deduced from $\Delta S[r, \tau]$ using the well known formula $\Delta S(q,t)=4\pi/q \int_{-\infty}^{+\infty} dr\, r\, \Delta S[r,t]\sin(qr)$ which, according to the basic theory of x-ray diffraction, relates r-resolved and q-resolved signals [Warren,2005]. It is valid independently of whether pump-probe time delays are dispersed or not. This integration was accomplished numerically. The results are presented in Figs. 4. In Fig. 4a, the signal is calculated for β = infinite, i.e. in absence of pump-probe dispersion . It is presented in three dimensions: the variables q and τ are placed on the coordinate axes, whereas the value of the signal $\Delta S(q, \tau)$ is indicated by color. The violet crests indicate the increase of the signal intensity and the red valleys their decrease. The bending of the red crests toward large q's indicates progressive CC contraction from 1.5A to 1.2 A. This signal is strictly vanishing at $\tau = 0$, whatever q, which is a consequence of the Franck-Condon principle. At long times, $\Delta S (q, \tau)$ approaches the limit $Const(r_1^2\sin(qr_1)/qr_1 - r_0^2\sin(qr_0)/qr_0)$ (Fig.4b). Atomic motions during a chemical reaction can thus be monitored in this way. Nevertheless, visualizing atomic motions is much more difficult in q-resolved than in r-resolved signals. Fig. 4b pictures this signal in presence of appreciable pump-probe time dispersion. Only immutable red and violet crest are now visible, molecular dynamics can no longer be followed. Motional narrowing is dominating.

IV. CONCLUSION. Fluctuations of a multi-pulse signal due to of shot-to-shot variations in time delays and intensities are explored theoretically in the frame of a statistical theory of X-ray diffraction of liquids. A new method is also proposed to eliminate the effect of time delay jitter in XFEL experiments. Contrary to the measure and sort method which is fully experimental, the present method belongs to the ensemble of signal treatment methods. It does not require any extra experiment.

Bibliography

1: A. H. Zewail, Femtochemistry. Past, present, and future, *Pure and Applied Chemistry*, (2000) 2219-2231.

2: M. Meyer, D. Cubaynes, P. O'Keeffe, H. Luna, P. Yeates, E. T. Kennedy, J. T.Costello, P. Orr, R. Taïeb, A. Maquet, S. Düsterer, P. Radcliffe, H. Redlin, A.Azima, WB. Li5, E. Plönjes, and J. Feldhaus, Twocolor photoionization in xuv freeelectron andvisible laser fields, *Phys. Rev. A* , (2006) 011401.

3: D. M. Fritz, D. A. Reis, B. Adams, R. A. Akre, J. Arthur, C. Blome, P. H. Bucksbaum, A. L. Cavalieri, S. Engemann, S. Fahy, R. W. Falcone, P. H. Fuoss, K. J. Gaffney, M. J. George, J. Hajdu, M. P. Hertlein, P. B. Hillyard, M. Horn-von Hoegen, M. Kammler, J. Kaspar, R. Kienberger, P. Krejcik, S. H. Lee, A. M. Lindenberg, B. McFarland, D. Meyer, T. Montagne, É. D. Murray, A. J. Nelson, M. Nicoul. Pahl, J. Rudati, H. Schlarb, D. P. Siddons, K. Sokolowski-Tinten, Th. Tschentscher, D. von der Linde, J. B. Hastings, Ultrafast Bond Softening in Bismuth: Mapping a Solid's Interatomic Potential with X-rays, *Science*, (2007) 633-636.

4: T. Maltezopoulos, S. Cunovic, M. Wieland, M. Beye, A. Azima, H. Redlin, M. Krikunova, R. Kalms, U. Frühling, F. Budzyn, Single-shot timing measurement of extreme-ultraviolet free-electron laser pulses, *New Journal of Physics*, (2008) 033026.

5: A. Azima, S. Düsterer, P. Radcliffe, H. Redlin, N. Stojanovic, W. Li, H. Schlarb, J. Feldhaus, D. Cubaynes, M. Meyer, J. Dardis, P. Hayden, P. Hough, V Richardson, E. T. Kennedy, and J. T. Costello, Time-resolved pump-probe experiments beyond the jitter limitations at FLASH, *Applied Physics Letters*, (2009) 144102.

6: J. M. Glownia, J. Cryan, J. Andreasson, A. Belkacem, N. Berrah, C. I. Blaga, C. Bostedt, J. Bozek, L. F. DiMauro, L. Fang, J. Frisch, O. Gessner, M. Gühr, J. Hajdu, M. P. Hertlein, M. Hoener, G. Huang, O. Kornilov, J. P. Marangos, A. M. March, B. K. McFarland, H. Merdji, V. S. Petrovic, C. Raman, D. Ray, D. A. Reis, M. Trigo, J. L. White, W. White, R. Wilcox, L. Young, R. N. Coffee, and P. H. Bucksbaum, Time-resolved pump-probe experiments at the LCLS, *Optics Express*, (2010) 17620-17630.

7: F. Löhl, V. Arsov, M. Felber, K. Hacker, W. Jalmuzna, B. Lorbeer, F. Ludwig, K.-H. Matthiesen, H. Schlarb, B. Schmidt, P. Schmüser, S. Schulz, J. Szewinski, A. Winter, and J. Zemella, Electron Bunch Timing with Femtosecond Precision in a Superconducting Free-Electron Laser, *Phys. Rev. Lett.*, (2010) 144801.

8: Bionta, Mina R.; Lemke, H. T.; Cryan, J. P.; Glownia, J. M.; Bostedt, C.; Cammarata, M.; Castagna, J.-C.; Ding, Y.; Fritz, D. M.; Fry, A. R.; Krzywinski, J.; Messerschmidt, M.; Schorb, S.; Swiggers, M. L.; Coffee, R. N., Spectral encoding of x-ray/optical relative delay, *Optics Express 10*, (2011) 21855-21865.

9: F. Tavella, N. Stojanovic, G. Geloni & M. Gensch, Few-femtosecond timing at fourth-generation X-ray light sources, *Nature Photonics* , (2011) 162–165.

10: M. Harmand, R. Coffee, M. R. Bionta, M. Chollet, D. French, D. Zhu, D. M. Fritz, H.T. Lemke,N. Medvedev, B. Ziaja, S. Toleikis, M. Cammarata, Achieving few-femtosecond time-sorting at hard X-ray free-electron lasers, *Nature Photonics*, (2013) 215–218.

11: S. Mukamel, Principles of Nonlinear Optics and Spectroscopy, 1995

12: S. Bratos, F. Mirloup, R. Vuilleumier and M. Wulff, Time-resolved x-ray diffraction: Statistical theory and its application to the photo-physics of molecular iodine, *J. Chem. Phys.*, (2002) 10615.

13: B.E. Warren, X-Ray Diffraction, 1990

14: Cavalieri, A. L., Fritz, D. M., Lee, S. H., Bucksbaum, P. H., Reis, D. A., Rudati, J., Mills, D. M., Fuoss, P. H., Stephenson, G. B., Kao, C. C., Siddons, D. P., Lowney, D. P., MacPhee, A. G., Weinstein, D., Falcone, R. W., Pahl, R., Als-Nielsen, J., Blome, C., D\"usterer, S., Ischebeck, R., Schlarb, H., Schulte-Schrepping, H., Tschentscher, Th., Schneider, J., Hignette, O., Sette, F., Sokolowski-Tinten, K., Chapman, H. N., Lee, R. W., Hansen, T. N., Synnergren, O., Larsson, J., Techert, S., Sheppard, J., Wark, J. S., Bergh, M., Caleman, C., Huldt, G., van der Spoel, D., Timneanu, N., Hajdu, J., Akre, R. A., Bong, E., Emma, P., Krejcik, P., Arthur, J., Brennan, S., Gaffney, K. J., Lindenberg, A. M., Luening, K., Hastings, J. B., Clocking Femtosecond X Rays, *Phys. Rev. Lett.* , (2005) 114801.

15: P.A. Janson, Deconvolution of Images and Spectra, 1997

16: J.P. Hansen and I.R.M Mac Donald , Theory of Simple Liquids, 2006

211

212

213

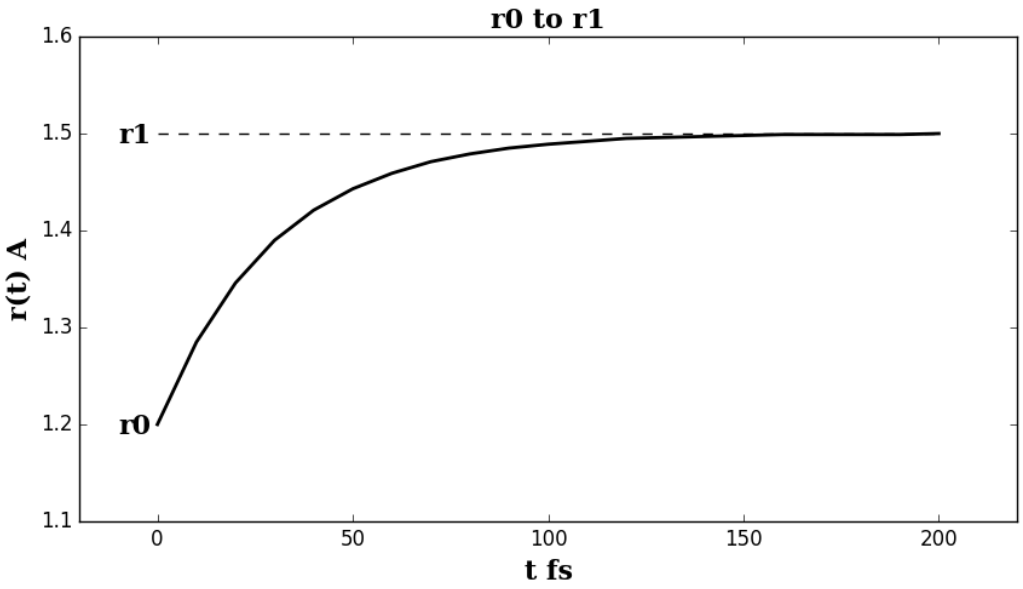

Fig. 1: Variation of the bond length r(t) from r0 to the laser excited state r1.

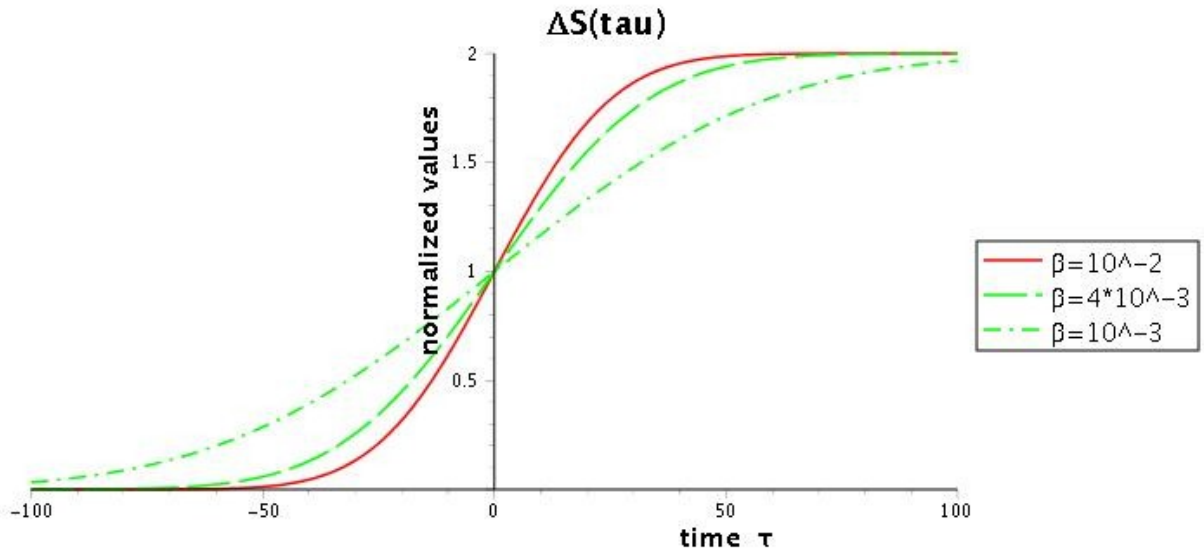

Fig. 2: Variation of ΔS at shortest pump-probe times delays.

:

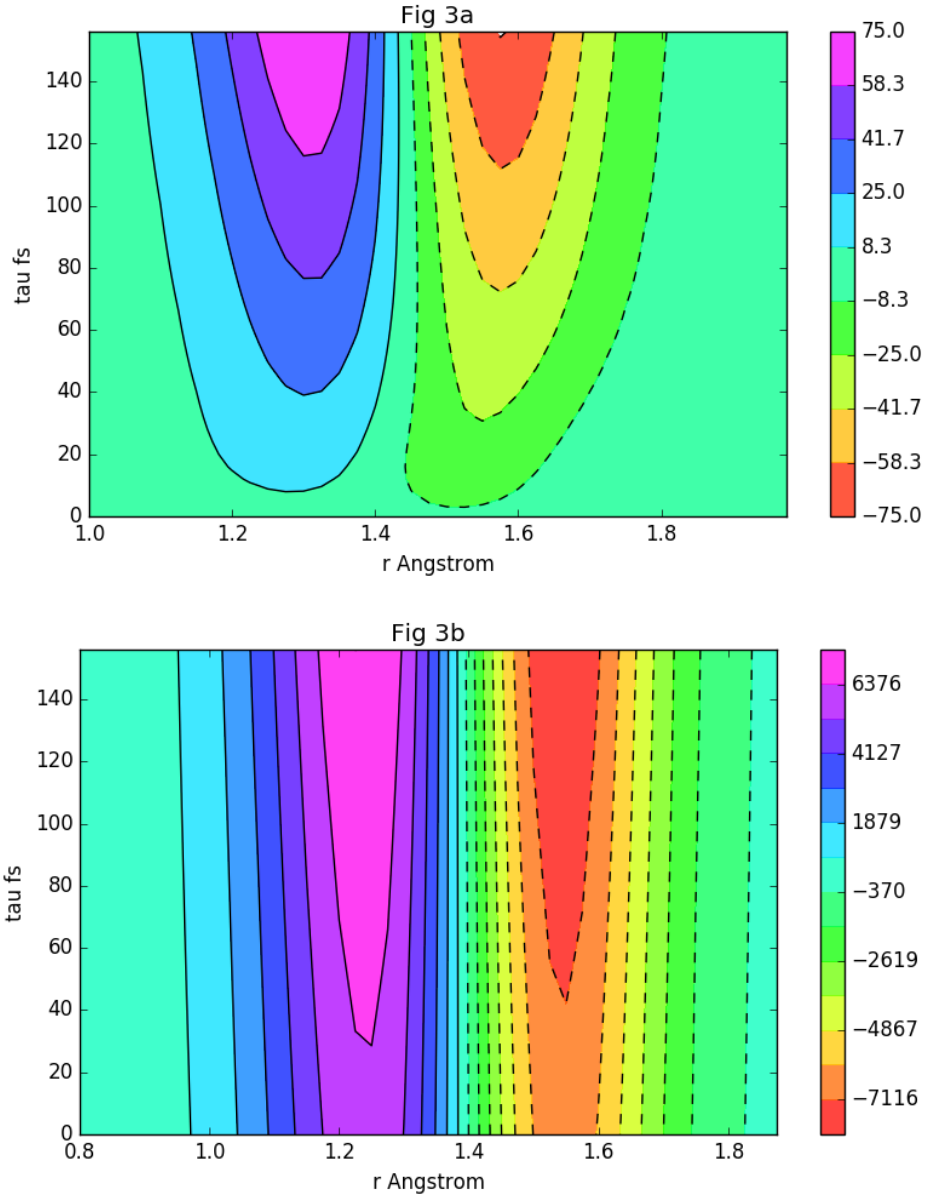

Fig. 3: Contraction of the CC bond after laser excitation: multi-pulse signal in r space. The CC bond contracts from the single bond length (1.5 A) to the triple bond length (1.2 A). The process is supposed to be accomplished in 100 fs. (a) The signal $\Delta S(r, \tau)$ in absence of pump-probe time delay dispersion, (b) in its presence (1000 fs). The contraction of the CC bond is clearly visible in Fig. (a), but is not in Fig. (b).

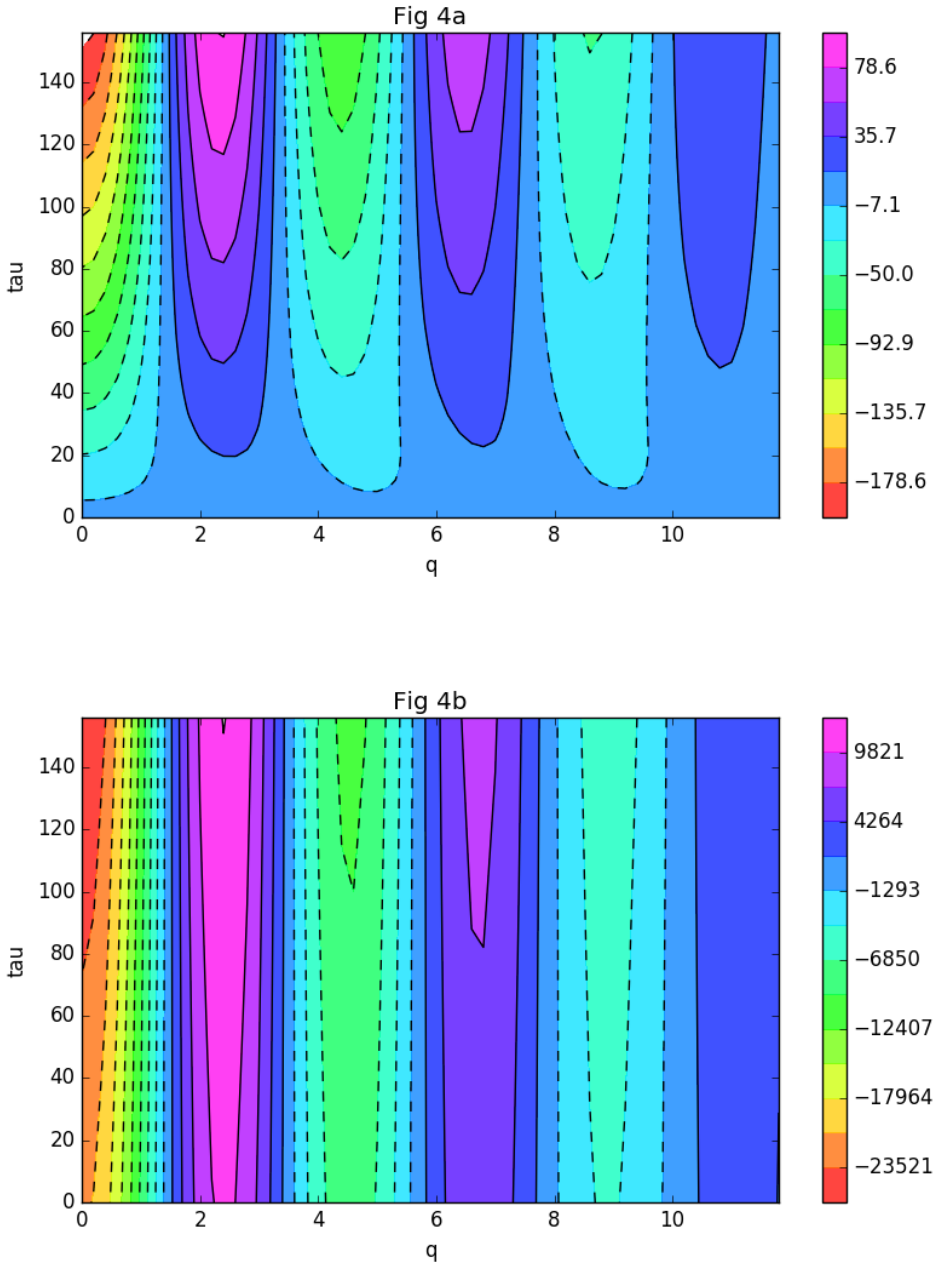

Fig. 4: Contraction of a CC bond after laser excitation: the multi-pulse signal in q space. This signal is defined as the difference of multi-pulse signals S(q, τ) in presence or absence of pump-probe time delay dispersion. Time-delay dispersion is supposed to be of the order of 1000 fs. The contraction is no longer perceptible at this level of jitter.