Ultrafast nonthermal heating of water initiated by an X-ray Free-electron Laser – Supplementary Information Appendix

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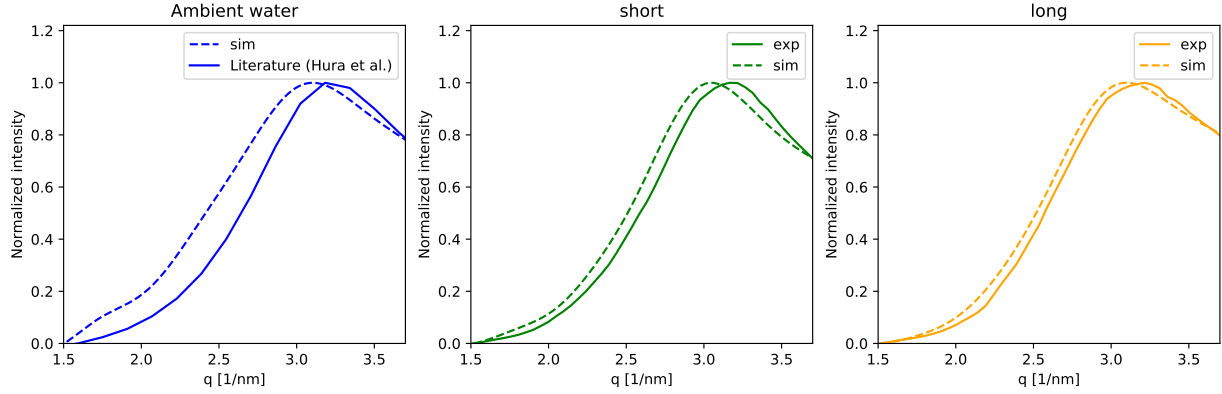
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FIG. S1. Direct comparison of scattering intensities as a function of the scattering vector, $q = 2\sin(\theta)/\lambda$, for experiments and simulations. Left: Scattering from water at ambient conditions collected with a synchrotron (Hura et al. 2001 J.Chem. Phys. 113(20)) compared to molecular dynamics simulation of 300 K water. Middle and right: XFEL pulse of 25 fs (short) duration and 75 fs (long) duration (both with a fluence of $1.35 \cdot 10^6$ J/cm^2) compared MD and NLTE simulations, calculated from the O-O radial distribution function and the electronic states of the system. The X-ray parameters in the simualtions are chosen to match the experimental ones. The curves are normalized to the maximum of the peak with the minimum subtracted.

TABLE S1. Scattered intensity as a function of the magnitude of scattering vector $q = 2\sin(\theta)/\lambda$ measured experimentally, normalized to the maximum value in the range, for 25 fs (short) and 75 fs (long) pulse durations.

| q [1/nm]	Short	Long	q [1/nm]	Short	Long	q [1/nm]	Short	Long	q [1/nm]	Short	Long
1.5220	0.0000	0.0000	2.1594	0.1969	0.1834	2.7969	0.8485	0.8292	3.4344	0.8257	0.8980
1.5485	0.0037	0.0017	2.1860	0.2147	0.2011	2.8235	0.8767	0.8571	3.4609	0.8119	0.8880
1.5751	0.0081	0.0040	2.2125	0.2336	0.2198	2.8500	0.9028	0.8829	3.4875	0.7987	0.8780
1.6016	0.0130	0.0068	2.2391	0.2533	0.2394	2.8766	0.9263	0.9066	3.5141	0.7859	0.8682
1.6282	0.0185	0.0100	2.2657	0.2737	0.2599	2.9031	0.9468	0.9277	3.5406	0.7735	0.8585
1.6548	0.0242	0.0136	2.2922	0.2950	0.2813	2.9297	0.9642	0.9463	3.5672	0.7618	0.8489
1.6813	0.0301	0.0176	2.3188	0.3171	0.3037	2.9563	0.9788	0.9625	3.5937	0.7509	0.8398
1.7079	0.0362	0.0219	2.3454	0.3400	0.3271	2.9828	0.9896	0.9758	3.6203	0.7404	0.8310
1.7344	0.0424	0.0265	2.3719	0.3638	0.3512	3.0094	0.9967	0.9862	3.6469	0.7303	0.8224
1.7610	0.0485	0.0314	2.3985	0.3883	0.3763	3.0359	1.0000	0.9936	3.6734	0.7207	0.8139
1.7876	0.0547	0.0367	2.4250	0.4137	0.4023	3.0625	0.9996	0.9982	3.7000	0.7114	0.8056
1.8141	0.0608	0.0423	2.4516	0.4401	0.4293	3.0891	0.9960	1.0000	3.7265	0.7024	0.7975
1.8407	0.0670	0.0484	2.4782	0.4674	0.4573	3.1156	0.9903	0.9999	3.7531	0.6944	0.7899
1.8672	0.0735	0.0550	2.5047	0.4957	0.4862	3.1422	0.9821	0.9976	3.7797	0.6871	0.7827
1.8938	0.0802	0.0622	2.5313	0.5252	0.5159	3.1688	0.9719	0.9932	3.8062	0.6804	0.7757
1.9204	0.0874	0.0702	2.5578	0.5560	0.5463	3.1953	0.9600	0.9870	3.8328	0.6742	0.7690
1.9469	0.0953	0.0789	2.5844	0.5876	0.5774	3.2219	0.9466	0.9793	3.8593	0.6684	0.7626
1.9735	0.1040	0.0885	2.6110	0.6202	0.6090	3.2484	0.9323	0.9704	3.8859	0.6633	0.7566
2.0001	0.1137	0.0990	2.6375	0.6536	0.6413	3.2750	0.9177	0.9610	3.9125	0.6593	0.7513
2.0266	0.1245	0.1105	2.6641	0.6874	0.6738	3.3016	0.9025	0.9509	3.9390	0.6562	0.7468
2.0532	0.1366	0.1230	2.6907	0.7212	0.7062	3.3281	0.8870	0.9405	3.9656	0.6539	0.7428
2.0797	0.1498	0.1365	2.7172	0.7544	0.7382	3.3547	0.8714	0.9298	3.9922	0.6525	0.7394
2.1063	0.1643	0.1510	2.7438	0.7868	0.7695	3.3812	0.8556	0.9190			
2.1329	0.1800	0.1667	2.7703	0.8183	0.7998	3.4078	0.8402	0.9082			
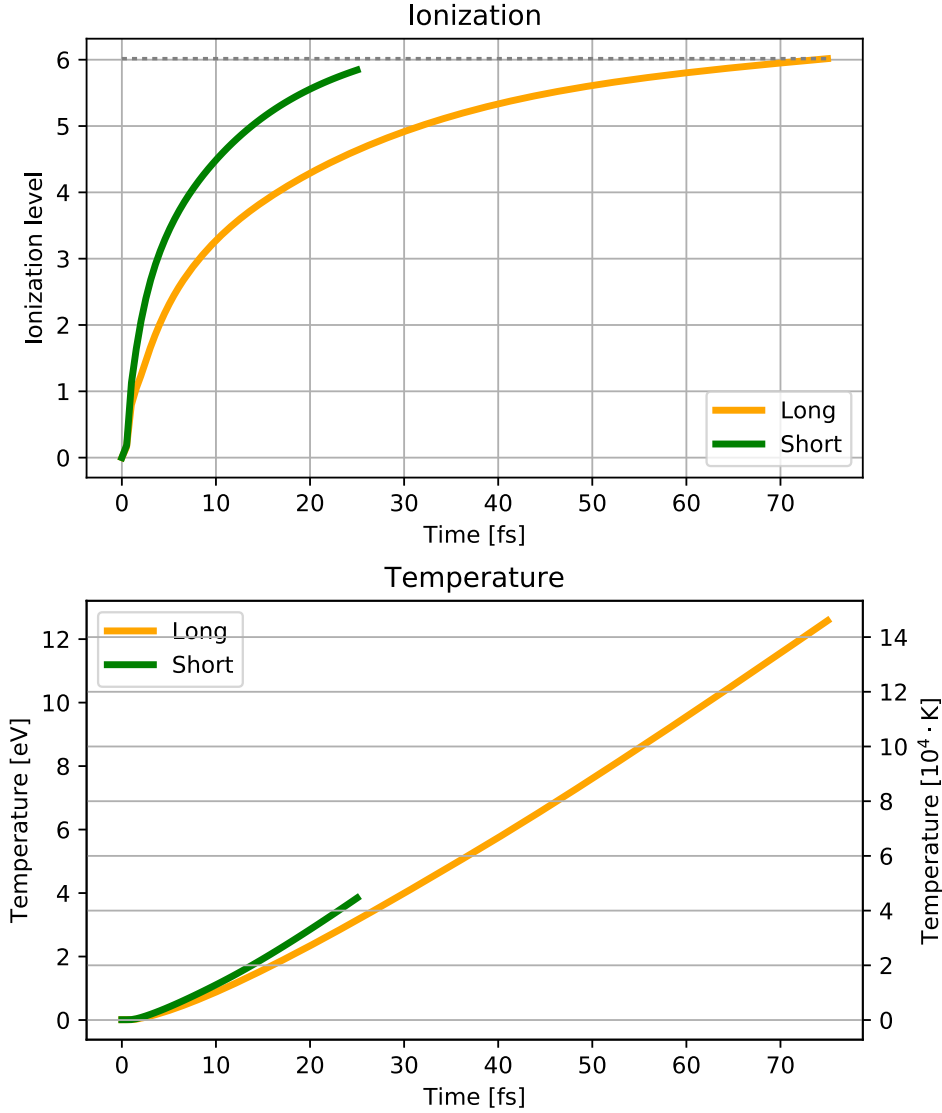
FIG. S2. Top: Average ionization levels and Bottom: Ion temperatures as calculated by NLTE simulations for pulses of 75 fs (long) duration and 25 fs (short) duration (both with a fluence of $1.35 \cdot 10^6$ J/cm^2). The average ionization levels will within the first femtoseconds correspond to a state where each atom is ionized at least once for both the simulations. It can be noted that the progress of the two simulated systems is very similar relative to the their respective pulse durations. The ion temperature increase is due to thermalization with the very hot electrons in the system. The increase rate is similar for the two simulated systems, resulting in a higher end temperature for the long pulse duration system.
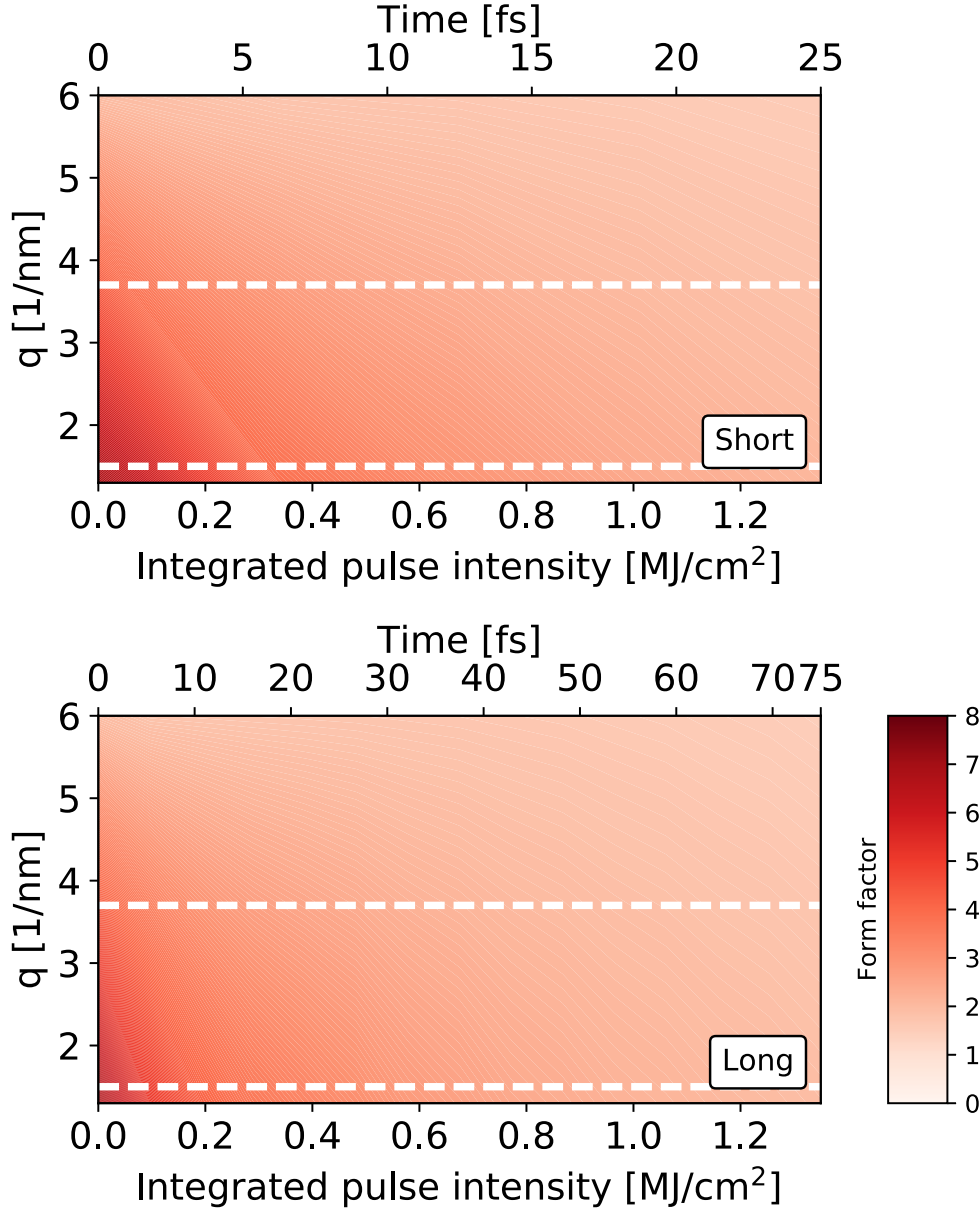
FIG. S3. Simulation of the time evolution of the oxygen form factors for pulses of 75 fs (long) duration and 25 fs (short) duration (both with a fluence of $1.35 \cdot 10^6$ J/cm^2). The experimental measurements displayed in Figure 2 in the main article were made from 1.5 to 3.7 nm^{-1}, marked here with dashed white lines. As a function of integrated pulse intensity, the ionization is very similar for the two conditions, as seen in Figure S2. This will lead to almost identical time evolutions of the atomic form factors, which are determined by the electronic configuration of the material. Note that the form factor will be low at the end of the pulse duration, resulting in that most of the signal recorded will be from earlier parts of the pulse.
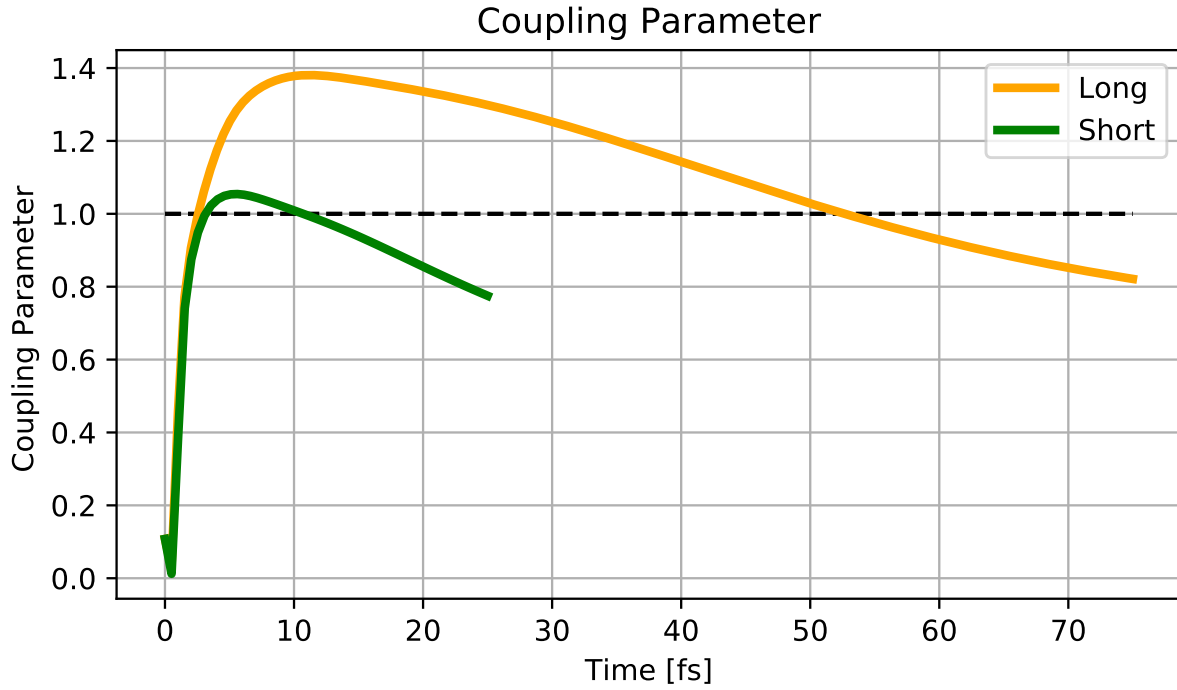
FIG. S4. The plasma coupling parameter as calculated by NLTE simulations for pulses of 75 fs (long) duration and 25 fs (short) duration (both with a fluence of $1.35 \cdot 10^6$ J/cm^2). The coupling parameter $\Gamma = \frac{\langle E_{\text{potential}} \rangle}{\langle E_{\text{kinetic}} \rangle}$ describes the relation between the potential energy and the kinetic energy in the system, and is traditionally used to describe what physical regime the system is in. When $\Gamma << 1$ the system is in the weakly coupled regime associated with room temperature conditions. Within 1–2 fs the system will leave the regime that allows liquids and enter the warm dense matter regime.
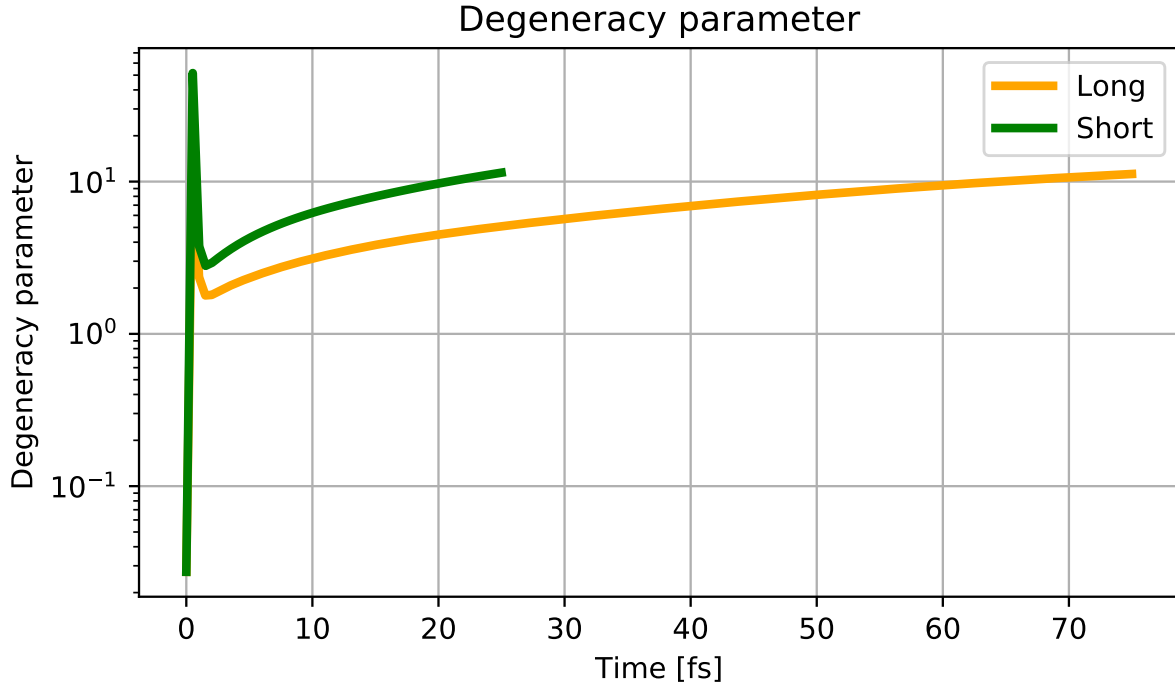
FIG. S5. The degeneracy parameter for pulses of 75 fs (long) duration and 25 fs (short) duration (both with a fluence of $1.35 \cdot 10^6$ J/cm^2). The degeneracy parameter $\Theta = \frac{T_e}{E_F}$ describes the relation between the electron temperature T_e and the Fermi energy E_F and describes how degenerate the system is. When the system is very degenerate ($\Theta \ll 1$) the system must be modelled using quantum treatment; for non-degenerate systems ($\Theta > 1$) statistical methods, such as those used here, are a good approximation.
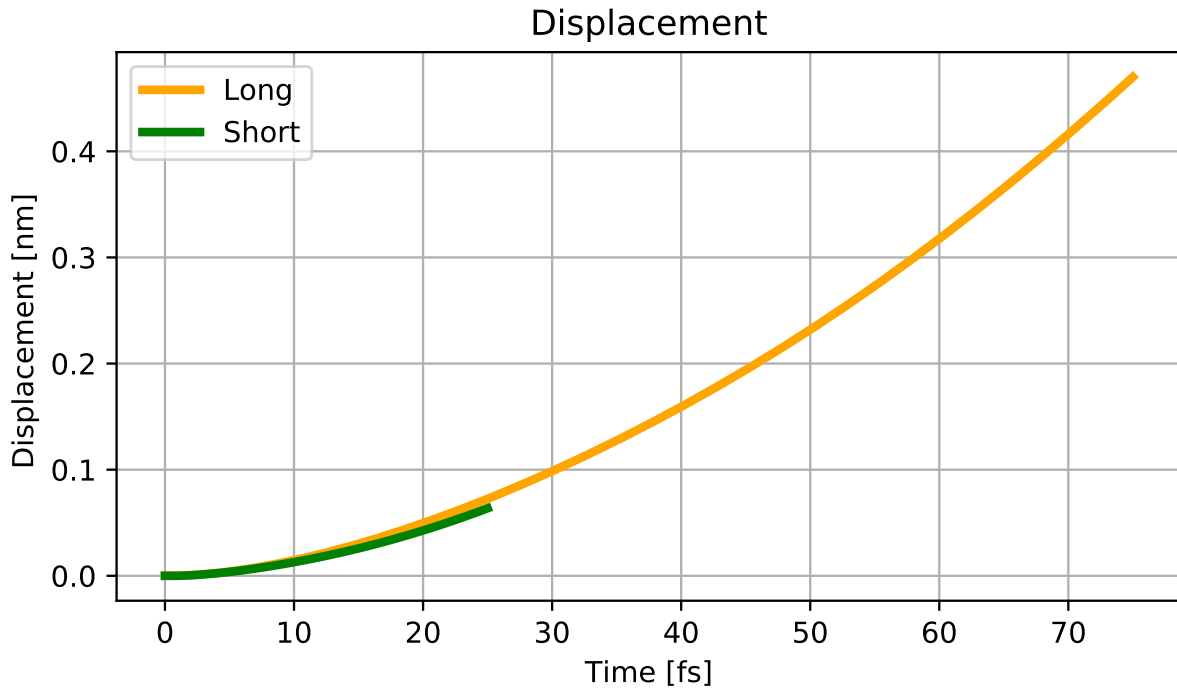
FIG. S6. Displacement calculation using temperature and collision rates as calculated by NLTE simulations for pulses of 75 fs (long) duration and 25 fs (short) duration (both with a fluence of $1.35 \cdot 10^6$ J/cm^2). The displacement rate is very similar for the two systems, resulting in a higher end displacement for the longer pulse duration system. Calculated as in H. O. Jönsson et al., Journal of Synchrotron Radiation 22 (2015) 256. All the NLTE simulations presented here take into account: screened hydrogenic models for the atoms and ions which also allow for double core states; photoionization, Auger ionization and collisional ionizations; continuum lowering using Stewart-Pyatt degeneracy lowering. The model also considers instant electron-electron thermalization and uses an electron-ion coupling coefficient using Spitzer's formula. An example of an input file listing relevant parameters is available below.

SIMULATION INPUT EXAMPLE FILE

```
c    1D Kinetics for water in XFEL


c    --------------------------------------------------------------

c    Aliases
```

9

```
c ---------------------------------------------------------------

alias N         11
c number of zones used
alias TE        0.01
c start electron temp
alias RHO       0.998
c water at 20 degrees


alias E1         6900
c laser energy in eV, 91.84eV=13.5nm. 38.75eV=32nm
alias E2 E1 * 1.0104
c wavelenght bandwidth


c REGIONS IN 1D
alias n1 N


c CHEMICAL STOICHIOMETRY
c water
alias N_o  1.  * RHO * AVGD / 18
alias N_h  2.  * RHO * AVGD / 18


alias ILASER  1e+26
alias ILASER1 4 * ILASER
alias ILASER2 0 * ILASER


c ---------------------------------------------------------------
c   Materials
c ---------------------------------------------------------------


c DECLARE THAT THE INTRINSIC HYDROGENIC MODEL
c SHOULD BE USED FOR ALL ELEMENTS
```

```
c DEFINING THE MATERIAL REGIONS
atoms hydrogenic o
atoms hydrogenic h


region  n0 n1  TE
 element 1 N_o
 element 2 N_h



c ------------------------------------------------------------
c   Geometry
c ------------------------------------------------------------


geometry plane


rlin n0 n1 0. 7e-5



c ------------------------------------------------------------
c   Radiation
c ------------------------------------------------------------


angles 1

ebins 120 0.01 30.0
ebins 120 30.0 600.0
ebins 60  600.0 6.e3
ebins 60 6.e3 8.e3
ebins 20 8.e3 2.e4



c ------------------------------------------------------------
c   Sources
c ------------------------------------------------------------
```

```
alias MULT HPEV / ( E2 - E1)


c pulse part 1, on


source jbndry 1 E1 E2 value history 1 MULT
   xfilebc 1  -1. 0. 1. 0                    ! normal incidence


history 1 ILASER1 1e-15
tv 0.0 1.
tv 24.9999 1.


c pulse part 2, off

 source jbndry 2 E1 E2 value history 2 MULT
   xfilebc 2  -1. 0. 1. 0


history 2 ILASER2 1e-15
tv 25. 1.
tv 100. 1.



c ---------------------------------------------------------------
c   Controls
c ---------------------------------------------------------------


tstart 0.
tquit  1.000e-13


c ---------------------------------------------------------------
c   Switches and Parameters
c ---------------------------------------------------------------
```

```
switch 11 2 ! make only .plt file


c NLTE on and calculated using rate matrices. Continuum transfer used for rad intensity
switch 20 1


switch 25 1 ! time-dependent



switch 28 0 ! LTE initialization


c using time dependent temperature calculation, use electronic heating rates,
c only consider atomic process directly affecting the free electron distribution
switch 31 1



switch 44 0 ! maximum # of iterations


switch 72  1 ! timesteps between spectral calculations


switch 127 24 ! max 2 inner shells with holes as normal states


switch 126 10 ! maximum principal quantum number for states with inner shell holes.


switch 29 2 ! initial populations will be LTE for given ion density



switch 125 1 ! average spectral emission over bins


c Stewart-Pyatt or Ecker-Kroll continuum lowering used, degeneracy lowering
switch 55  1
```

```
c change collisional ionization for continuum lowering. Collision strength
c and rate coefficients use the original threshold values.
switch 170 -1


c photoexcitation contribution to opacities and emissivities for continuum transfer.
c Simulation includes contributions from all transitions not identified as lines,
c and a given transition will be averaged over each
c continuum bin failing with the transition profile.
switch 17  1


switch 36 1                        ! Turn on continuum transfer, use integral formalism


c controls for generating screened hydrogenic data.
c 1: include neutral-neutral ionozation rates for Ar,Kr and Xe,
c 0: collisional ionization rates use fits to Sampson and Golden results,
c 0: collisional excitation rates use van Regemorter formula, smooth energy
c levels to approach ionization limit starting at level 2 above ground.
switch 133 10002


c  Free-free opacities and emissivities (bremsstrahlung) used in continuum transfer
c and laser absorption use a coulomb logarithm
switch 35 -1


c ground state degeneracies is not changed when applying continuum lowering.
switch 155 1


c doubly excited states will be included for all isosequences with iso >= 2
switch 165 2


switch 166 2 ! use first inner shell for double excited state
```

```
param 40 0.5e-15 ! time between edits
param 41 1.e-17 ! initial timestep
param 44 5.e-17 ! min timestep
param 45 5.e-17 ! maximum timestep
param 61 1.e-3 ! iso-sequence population threshold
param 95 0.01 ! minimum zbar for kinetics
param 102 0.01 ! minimum temperature


c -----------------------------------------------------------
c   Edits
c -----------------------------------------------------------

plot "r vs zbar"
xvar r
yvar zbar  0:7


plot "r vs tev"
xvar r
yvar tev


plot "r vs tiv"
xvar r
yvar tiv


plot "r vs tauii"
xvar r
yvar tauii


plot "r vs tauee"
xvar r
yvar tauee
```

```
plot "r vs oxygene"
xvar r
yvar yisofrac 1 0 0:8


plot "r vs carbon"
xvar r
yvar yisofrac 3 0 0:8


plot "r vs nitrogen"
xvar r
yvar yisofrac 4 0 0:8


plot "r vs sulphur1"
xvar r
yvar yisofrac 5 0 0:8


plot "r vs sulphur2"
xvar r
yvar yisofrac 5 0 9:17


plot "r vs 2KO"
xvar r
yvar yn_0 1 0 0:8


plot "r vs 2KN"
xvar r
yvar yn_0 4 0 0:8


plot "r vs 2KC"
xvar r
yvar yn_0 3 0 0:8
```

```
plot "r vs 2KS1"
xvar r
yvar yn_0 5 0 0:8


plot "r vs 2KS2"
xvar r
yvar yn_0 5 0 9:17


plot "r vs 1KO"
xvar r
yvar yn_1 1 0 0:8


plot "r vs 1KN"
xvar r
yvar yn_1 4 0 0:8


plot "r vs 1KC"
xvar r
yvar yn_1 3 0 0:8


plot "r vs 1KS1"
xvar r
yvar yn_1 5 0 0:8


plot "r vs 1KS2"
xvar r
yvar yn_1 5 0 9:17


plot "r vs 0KO"
xvar r
yvar yn_2 1 0 0:8
```

```
plot "r vs OKN"
xvar r
yvar yn_2 4 0 0:8


plot "r vs OKC"
xvar r
yvar yn_2 3 0 0:8


plot "r vs OKS1"
xvar r
yvar yn_2 5 0 0:8


plot "r vs OKS2"
xvar r
yvar yn_2 5 0 9:17


plot "r vs Oxygen0holes"
xvar r
yvar ynf_2 1 0 0:8


plot "r vs Oxygen1holes"
xvar r
yvar ynf_1 1 0 0:8


plot "r vs Oxygen2holes"
xvar r
yvar ynf_0 1 0 0:8


plot "r vs material_pressure"
xvar r
yvar pmat
```

```
plot "r vs ion_pressure"
xvar r
yvar pmat_i


plot "r vs electron_pressure"
xvar r
yvar pmat_e


plot "r vs radiation_pressure"
xvar r
yvar prad


plot "r vs total_pressure"
xvar r
yvar ptot


plot "r vs number_of_e"
xvar r
yvar ne


plot "r vs number_of_i"
xvar r
yvar ni


plot "r vs gplasma"
xvar r
yvar gplasma
```