



# EFFICIENT AND QUANTITATIVE SIMULATION OF CHARGE-REARRANGEMENT-ENHANCED X-RAY IONIZATION OF MOLECULES

Natasha Feinstein, Durham University, UK — CFEL-DESY Theory Division

September 12, 2017

## Abstract

It has recently been established that charge rearrangement plays a major role in the response of molecules to ultra-intense hard x-ray pulses. Previous joint experimental-theoretical work by Rudenko et al. [Nature, **546**, 129 (2017)], using the ab initio XMOLECULE toolkit, has demonstrated that this behaviour can be captured by numerical simulation, however the computational cost of this approach is prohibitive for larger systems. XMDYN is an alternative simulation toolkit developed by Jurek et al. [Journal of Applied Crystallography, **49**, 1048 (2016)] that combines quantum and classical mechanics to reduce the computational intensity of these simulations. This investigation aimed to compare these two toolkits, specifically for a single iodo-methane molecule which will experience significant charge rearrangement, to see if this system could be modelled with sufficient accuracy at less computational expense. XMDYN was able to model this phenomena for a range of fluences, albeit with reduced accuracy for the lower fluences, with runtimes reduced by at least an order of magnitude.

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# 1 Introduction

X-ray free electron lasers are capable of producing ultra-fast, ultra-intense hard x-ray pulses. These high intensities allow for sequential single photon absorption which enables atoms to reach a high degree of ionization.

At a given photon energy the probability of photoionization, the predominant ionization channel due to photon-matter interaction, depends on the element. As a consequence, in a heterogeneous sample charge imbalance builds up during irradiation that can initiate charge rearrangement. Such conditions often arise in biological samples, where one typically finds a small number of heavy elements embedded in a light atom environment. The ability to account for charge rearrangement when simulating such a systems interaction with ultra-intense hard x-rays is therefore of high importance.

Recently a joint theoretical - experimental study on the response of iodo-methane ( $\text{CH}_3\text{I}$ ) molecules to ultra-intense hard x-rays was published aiming to shed light on this phenomena [1]. The experimental data was collected at the Linac Coherent Light source at the National Accelerator Laboratory, while for the theoretical simulations the ab initio code XMOLECULE [2] was utilized. It was found that ultrafast charge rearrangement within the molecule plays a key role in shaping the systems response to the x-ray pulse in that it enables electrons from carbon and hydrogen to be lost via iodine. This both allows the molecule to reach a higher total charge state and also introduces electrostatic repulsion between the atoms that initiates ultrafast fragmentation of the molecule [1]. The experimental and theoretical results were in good agreement.

While this implies the validity of the XMOLECULE simulations, the computational cost of this approach becomes quickly prohibitive for large systems. The purpose of this investigation was to determine whether XMDYN [3], a far less computationally expensive, classical molecular dynamics based tool, could reproduce its results for the case of a single small molecule, in particular the charge rearrangement phenomena. In this paper I analyse results obtained from a version of XMDYN that did not include charge transfer and results from a version that did. This allowed for the verification of the importance of charge transfer within the model. Results from both versions are compared to those from the XMOLECULE simulations.

## 2 Ionization dynamics due to intense x-ray radiation

Typically, an atom exposed to high intensity x rays will undergo a sequence of photoionization events which remove core electrons since, assuming the photons have enough energy to reach the inner shells, these electrons are the favourite to be ionized. The excited ion then relaxes into the ground state through fluorescence and auger decays - the latter of which leads to the emission of more electrons [4]. Depending on the decay rates, pulse duration and intensity, these processes may occur intermixed, a typical scenario at XFELs. Heavy atoms have larger photoionization cross sections than light ones. Thus, for a  $\text{CH}_3\text{I}$  molecule, which is the system I will be discussing in this report,

photoionization will occur predominantly on the iodine [1]. The developing charge imbalance is followed by charge rearrangement within the molecule: electrons move to the iodine and become available for the inner shell decay and further photoionization of the heavy element [1].

## 3 Software tools

In this section we overview the software tools used in the project.

### 3.1 XATOM

XATOM [3] is an ab initio simulation tool for atomic and x-ray physics. It calculates orbitals and orbital energies of atoms as well as the photoionization cross sections, auger rates and fluorescence rates for all electronic configurations of any element. Electronic structure is calculated using the Hartree-Fock-Slater method. Cross sections and rates are calculated using perturbation theory. In order to simulate ionization dynamics of a heavy atom, large system of coupled rate equations must be solved - this is done with a Monte Carlo approach.

### 3.2 XMOLECULE

XMOLECULE [2] is a simulation toolkit that uses the concept applied within XATOM, but extended to the molecular case. Molecular orbitals and orbital energies are constructed using atomic orbitals calculated by XATOM as basis functions. These molecular orbitals must be continually recalculated as the system evolves, e.g. as ionic positions change. The atomic cores are treated classically and the forces acting on them are derived from the gradient of the energy of the electronic subsystem with respect to the atomic positions. Cross sections, rates and potential gradients are calculated on the fly for the given electronic structure. While XMOLECULE yields excellent results, it becomes computationally very expensive with respect to both time and memory as the system size grows and thus in practice cannot be feasibly used for systems much greater than 100 atoms.

### 3.3 XMDYN

XMDYN [3] is a modelling framework that offers a computationally cheap way of simulating x-ray irradiated matter. It is an atomistic approach which is to say that atoms within a molecule are each treated as separate objects. Each bound electron is assigned to an atomic orbital in an atom and the occupation numbers are tracked. In the current implementation only orbitals that are occupied in the ground state neutral atom are considered. Evaluation of photoionization, auger decay and fluorescence is carried out by the generation of an ionization pathway for the individual atoms and ions using a Monte Carlo scheme. Photoionization cross sections, auger rates and fluorescence rates

are calculated for the current configurations by XATOM. Molecular dynamics is carried out by treating the atoms, ions and free electrons as classical particles and using Newton's equations which are numerically integrated. Charged classical particles interact via regularized Coulomb forces.

The highest kinetic energies of the electrons can be expected to be of the order of the photon energy making it acceptable to use a non relativistic treatment. XMDYN has the option to include chemical bonds via force fields as well as the processes of secondary ionization and recombination that are important in extended systems. A new capability is the possibility to model charge transfer among ions and atoms.

## 4 Results

### 4.1 Simulation parameters and setup

The parameters for the x-ray pulse used in the XMDYN simulations were chosen according to the experimental conditions in Ref [1]. The half width full maximum of the pulse was taken to be 30 fs, the photoenergy 8.3 keV and the fluences used ranged from 0 to  $5 \times 10^{12} \mu\text{m}^{-2}$  [1]. Secondary ionization and recombination were excluded from the simulations since it was highly unlikely either would occur in a system of one small molecule. Furthermore, in the current study the bonds between atoms are not taken into account. This is a reasonable approximation for the high fluences being investigated as the bonds are broken very early on by the swift ionization of the atoms [5].

### 4.2 XMDYN simulation without charge transfer

Given the importance of charge transfer within XMOLECULE there is likely to be a fair bit of discrepancy between the results from this version of XMDYN and those from the XMOLECULE simulations. The results presented in this section will provide a reference point from which to gauge the effect of including charge transfer in the simulations.

XMDYN was run for a total of 10 fluences evenly spaced across the range  $5 \times 10^{11}$  -  $5 \times 10^{12}$  with 50 realizations used for each fluence.

#### 4.2.1 Ionic charges

The final charge states predicted by XMDYN are more consistent with the results from the independent atom model than those from XMOLECULE which is to be expected (Figure 1). Without charge transfer the molecular dynamics should have no impact on the simulation results for the final charge states meaning XMDYN should theoretically give the same results as the independent atom model for both the total molecular charge and that on the iodine fragment. In the case of the average total molecular charge the XMDYN data points lie almost directly on the curve for the independent atom model with only minor deviations however for the charge on the iodine fragment there is a greater discrepancy. The deviations seen here are likely due to statistical variation rather than a genuine difference between the charges predicted by the two models meaning that

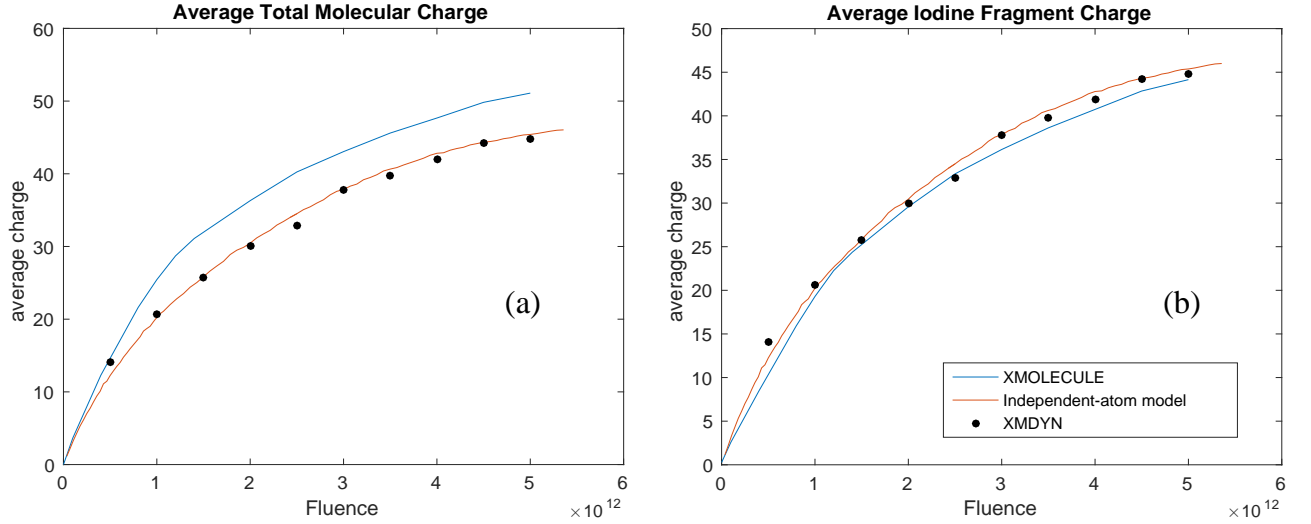


Figure 1: The average charge states for the whole molecule (a) and the iodine fragment (b) as predicted by XMOLECULE, the independent atom model and XMDYN without charge transfer.

for future simulations more than 50 realizations should be used for each fluence to ensure the results converge.

With regard to the differences between the XMDYN and the XMOLECULE results, Figure 1 shows exactly what one would expect. The total charge given by this version of XMDYN is smaller than that given by XMOLECULE since without charge transfer carbon and hydrogen can only lose their electrons if they are photoionized for which the cross section is incredibly small. The final charge states of the iodine fragment however are larger for this version of XMDYN than XMOLECULE. This is presumably due to fact that no new electrons are moving onto it from hydrogen or carbon. While the average molecular charge is increased by this mechanism, the charge on iodine is likely to be decreased since although electrons moving onto the iodine ion means there are more electrons capable of being lost it also means there are more electrons that must be lost in order for iodine to have the same charge it would without charge transfer.

#### 4.2.2 Ion Kinetic Energies

In order to investigate the kinetic energy of the iodine ion I initially plotted the mean kinetic energy for each time step for five of the fluences tested however, as can be seen from Figure 2 this yielded some very strange results. One would expect the kinetic energies to increase with the fluence since more energy is being put into the system which is not what is seen here. On top of this, the shape of the  $4 \times 10^{12}$  curve is very different to what is expected. Upon looking at the final kinetic energies of individual realizations I found that while the kinetic energies of the vast majority of realizations were below 1 eV there were a few that had final kinetic energies between 10 eV and

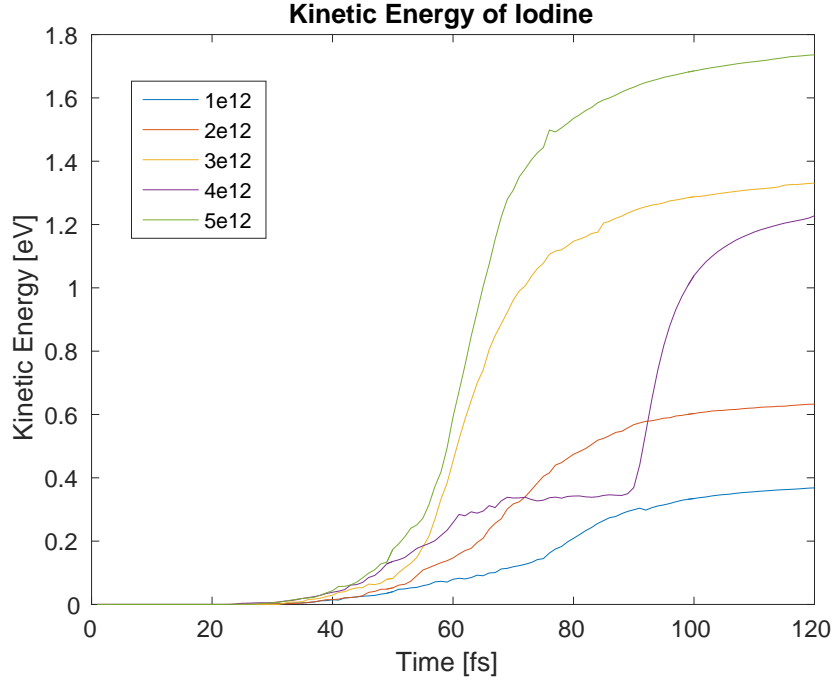


Figure 2: Mean kinetic energies of the iodine fragment with respect to time for five different fluences.

50 eV. These outliers, it turned out from viewing the event logs, were caused by the rare cases in which carbon was ionized allowing for electrostatic repulsion. The strange patterns seen in this first plot are due to the fact that the 50 realizations run for each fluence were not enough for this effect to average out. The  $3 \times 10^{12}$  fluence ended up with a higher average kinetic energy than the  $4 \times 10^{12}$  fluence because there happened to be more realizations in which carbon was photoionized. The shape of the  $4 \times 10^{12}$  curve is explained by the time at which the photoionization of carbon took place. For the other fluences all such events took place between 40 and 70 fs so that the iodine ion began gaining kinetic energy from electrostatic repulsion around the same time as it began gaining it from momentum conservation - thus there is no sudden change in the gradient. In the  $4 \times 10^{12}$  realization for which carbon was photoionized, the event occurred at around 88 fs causing a dramatic change in the rate the kinetic energy was increasing.

Recreating the same plot but with 500 realizations per fluence (Figure 3) the effect of photoionization of the carbon atom averaged out so that there were no peculiar patterns. However, while this plot looks more sensible, it is not in fact terribly informative since it merges two phenomena, obfuscating the effect of both.

Finally, I replotted the mean kinetic energies for each time step but removing the realizations in which carbon was ionized thus giving me a plot for how the kinetic energy changed for each fluence with respect to time due to momentum conservation alone (Figure 4). As one would expect, the curves are now much more jagged - not because

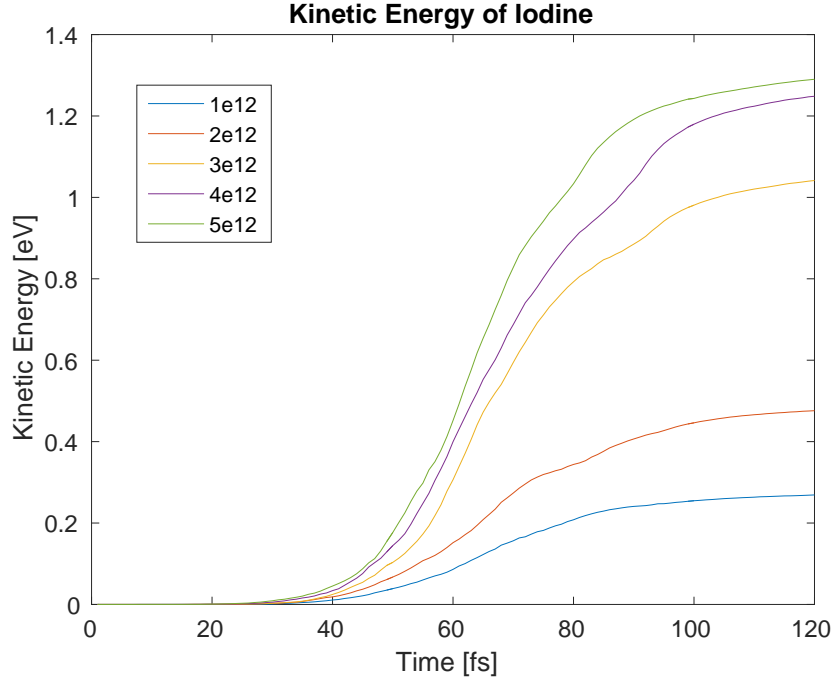


Figure 3: Mean kinetic energies (taken over 500 realizations) of the iodine fragment with respect to time for five different fluences.

of the decrease in number of realizations used but because while the electrostatic repulsion between the two ions causes a smooth change in velocity, the emission of electrons from the iodine ion will not give boosts to the velocity in the same direction and can be temporally irregular. The maximum kinetic energies are of course much smaller in this plot showing that the gain in kinetic energy caused by the emission of electrons is negligible compared to that caused by electrostatic repulsion. With the introduction of charge transfer we can expect far greater average kinetic energies since electrostatic repulsion will no longer just be an outlier effect.

### 4.2.3 Summary

As expected there is a fair amount of discrepancy between the results from this version of XMDYN and those from XMOLECULE. With no way for charge to move between atoms the final charge states are governed purely by photoionization events and auger decays such that the results are the same as for the independent atom model. The kinetic energies predicted are far smaller than those predicted by XMOLECULE due to the absence of electrostatic repulsion in the majority of realizations. If the introduction of charge transfer brings XMDYN's results closer to those produced by XMOLECULE it will confirm its importance.



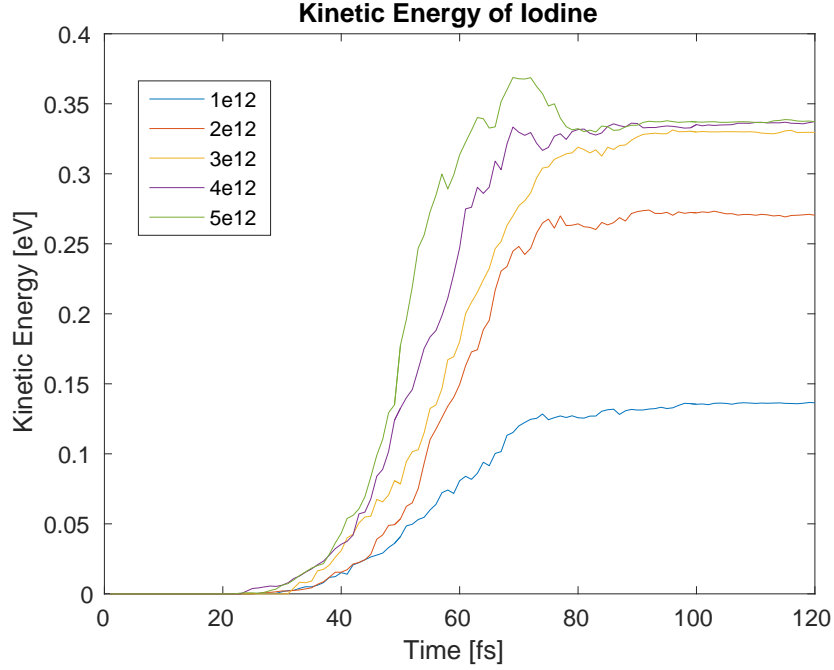


Figure 4: Mean kinetic energies (excluding realizations in which carbon was ionized) of the iodine fragment with respect to time for five different fluences.

### 4.3 XMDYN simulations including charge transfer

In XMOLECULE charge migration is a natural consequence of the model and happens smoothly. In XMDYN, where the atoms are treated as separate objects with atomic orbitals this is not the case. In order to allow for charge transfer we use an over-the-barrier model, taking the ionic potentials to equal to the Coulomb potential of a point charge. Within this approximation the potential barrier between atoms is tracked with the equation:

$$E_B > -\frac{1}{R} \left\{ (Q_0 + 1) + 2\sqrt{Q_0 + 1}\sqrt{Q_1} \right\} \quad (1)$$

such that when this equation is satisfied for a given electron it is allowed to move between atoms. In this equation  $E_B$  represents the binding energy of the electron,  $Q_0$  is the charge on ion with the smaller charge,  $Q_1$  is the charge on the ion with the larger charge and  $R$  is the distance between the two ions. An electron is always moved from the highest occupied orbital of one atom to another. That electron will always be added to the highest energy level available.

When the electron moves from one atom to another there will be a change in energy determined by the initial and final binding energy of the electron as well as the Coulomb potential between the two atoms. In order for the total energy of the system to be conserved this energy is shared between the atoms as kinetic energy. This sudden change

in the kinetic energy (the 'kick') is distributed between the atoms such that momentum is conserved.

This version of XMDYN was run for seven fluences in total - five evenly spaced between  $1 \times 10^{12}$  and  $5 \times 10^{12}$  and a further two low fluences,  $1 \times 10^{11}$  and  $4 \times 10^{11}$ . 500 realizations were run for each fluence.

### 4.3.1 Ion Kinetic Energies

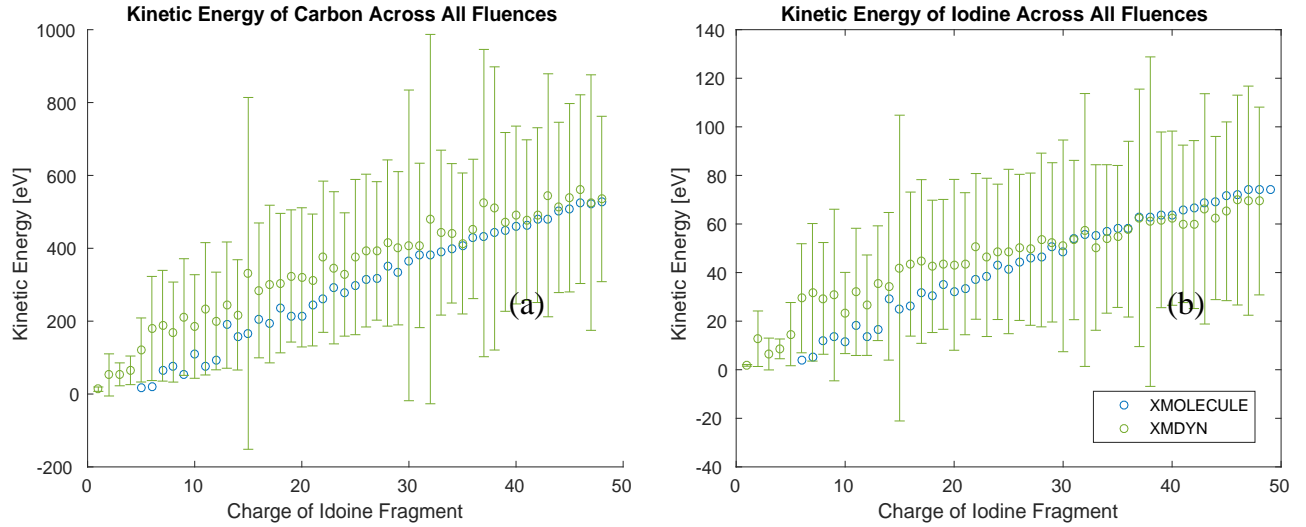


Figure 5: Mean kinetic energies of the carbon (a) and iodine (b) fragments with respect to charge on the iodine fragment for both XMOLECULE and XMDYN with charge transfer. Mean taken across all fluences and error bars on XMDYN data points give the standard deviation of the spread.

There was a concern that for this version of XMDYN the kinetic energies of the ions would be much too high since on top of the electrostatic repulsion the atoms would be given additional kinetic energy associated with the transfer of electrons. However, as can be seen from Figure 5 the mean kinetic energies of both iodine and carbon given by XMDYN lie close to those predicted by XMOLECULE with the majority of the XMOLECULE data points lying comfortably within the standard deviation of the XMDYN results. In general XMDYN did give slightly higher mean kinetic energies for a given charge with this difference being more pronounced for lower charge states of iodine.

Another difference to be noted is that XMDYN gives a far greater spread in the kinetic energies for each charge with standard deviations averaging around 40 eV, with some reaching 70 eV, for iodine compared to XMOLECULE whose standard deviations for iodine do not even reach 10 keV. Interestingly, though a little large, this spread is much closer the experimental spread of kinetic energies which had standard deviations reaching approximately 40 keV. The large variation in the XMDYN kinetic energies for each

charge can be accounted for by looking at the spread of the energies imparted to the system from the 'kicks' given by charge transfer. By viewing the event logs one sees that before approximately 60 fs there is a constant exchange of electrons within the system suggesting that the rapid ongoing movement of electrons between the atoms, indicative of a continuous barrier suppression, is a key feature of the XMDYN simulations. In XMOLECULE electron migration is captured in the shifting of the molecular orbitals and so does not allow for the dynamic movement of electrons that XMDYN does. Perhaps XMDYN, in allowing this rapid cyclic charge exchange between all the atoms in the system, is capturing some physics that XMOLECULE in its current state does not and thus accounts for the larger kinetic energy spread.

### 4.3.2 Ionic Charges

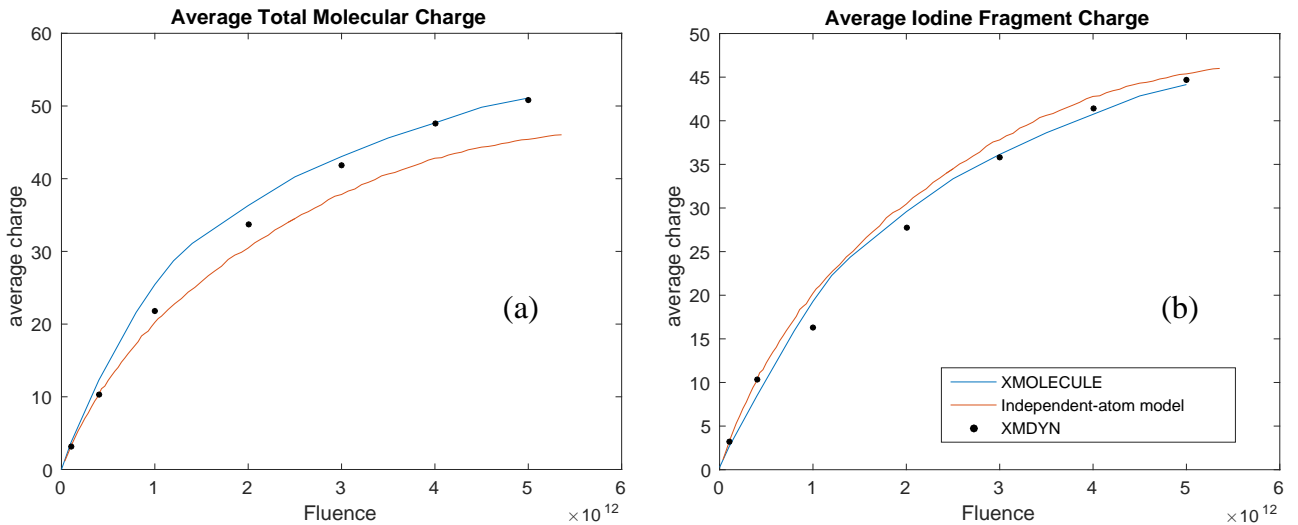


Figure 6: The average charge states for the whole molecule (a) and the iodine fragment (b) as predicted by XMOLECULE, the independent atom model and XMDYN with charge transfer.

In both Figure 6.a and 6.b the first two XMDYN points can be seen to be sitting directly on the independent atom model curve before there is a distinct jump. Looking at Figure 6.b specifically, one sees that at this point the charge on the iodine ion drops below the independent-atom model curve (and in fact the XMOLECULE curve but I will discuss this later) suggesting that electrons have moved onto it. Thus it seems sensible to assume then that it is between the fluences  $4 \times 10^{11}$  and  $1 \times 10^{12}$  that charge transfer starts to occur. I validated this by plotting the mean final charge states of carbon and hydrogen on a separate graph for the same seven fluences. What can also be seen from this plot is that when charge migration begins to occur the charges on both carbon and hydrogen jump immediately up to almost their maximum values. The charge on hydrogen is of course capped at one and, as with XMOLECULE, carbon never loses its

two core electrons [1]. Looking at Figure 6.a one sees that as the fluence is increased the XMDYN points climb up towards the XMOLECULE curve, meeting it at  $4 \times 10^{12}$ . Given that there is no great change to the final charge states of carbon and hydrogen between the fluences of  $1 \times 10^{12}$  and  $4 \times 10^{12}$  this climb towards an agreement with XMOLECULE is possibly due to the ease with which iodine is able to lose these extra electrons. If, within the XMDYN simulations, the electrons that move on to iodine are less easily lost than in the XMOLECULE simulations for the lower fluences this would explain why the XMDYN points initially drop below the XMOLECULE curve in figure 6.b once charge transfer begins to occur.

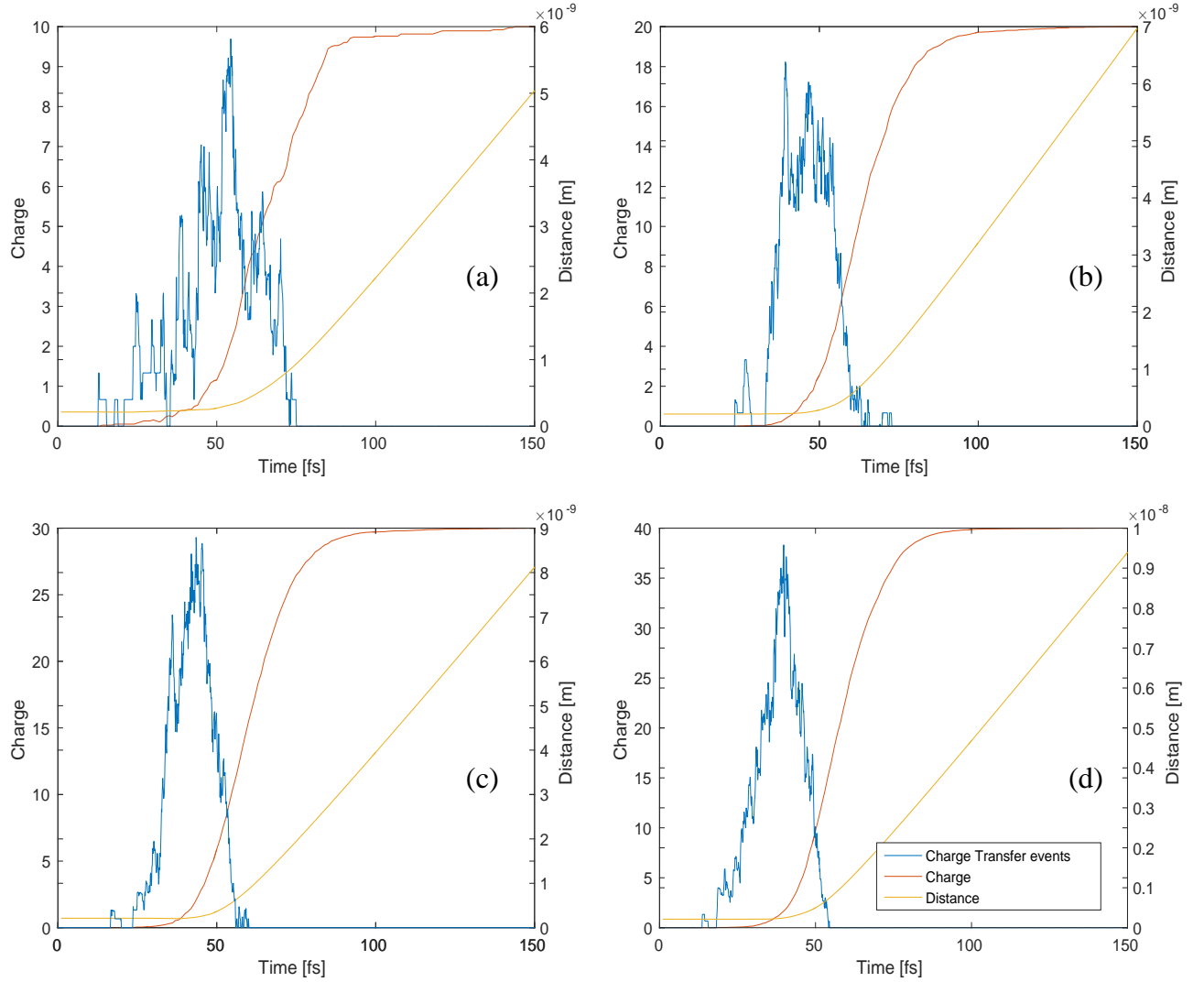


Figure 7: The average charge on the iodine fragment, distance between the iodine and the carbon ions and number of charge transfer events with respect to time for four different final charge states.

As discussed in the previous section, rather than the electrons moving onto iodine and

staying there, there is, when charge transfer is allowed, a constant transfer of electrons between all the atoms in the molecule. The electrons that move onto iodine will initially be in the highest orbital and since only the electrons in the inner shells of iodine have a non negligible cross section for photoionization, the electron will need to move into a lower orbital to be lost this way. The other way they could be lost is through auger decay. It is possible that for the lower fluences the electrons move around too quickly for either of these processes to have a particularly high chance of happening and that by the time charge transfer stops the ionization dynamics have, for the most part, too. To discern whether or not this could be the case I investigated the average distribution of charge transfer events for four different final charge states - 10, 20, 30 and 40. (Figure 7) While I did indeed find that charge transfer stopped earlier for the higher final charge states, and thus on average for higher fluences, this is far from conclusive and more work would need to be done to establish whether or not this could explain the disagreement between XMOLECULE and XMDYN and why for higher fluences this disagreement vanishes.

Another small difference that can be noted is that while the final two XMDYN points for the total molecular charge lie on the XMOLECULE curve, the corresponding points for the iodine charge fragment sit just above it. It is possible that the reason for this difference in the mean distribution of the charge is also due to the constant movement of electrons in that sometimes the electrons might happen to be on the carbon or one of the hydrogens when the potential barrier comes up even if on average they spend more time on the iodine. Again, further investigations would need to be carried out to determine whether or not this is the case.

### 4.3.3 Summary

By including a mechanism for charge transfer in the XMDYN simulations, one sees a much stronger agreement with the XMOLECULE results. Despite initial concern that the kinetic energies would be much too high due to the kick associated with charge transfer one finds that this is in fact not the case and that the kinetic energies for both carbon and iodine are, though a little higher, in fairly close agreement with those predicted by XMOLECULE. For further investigation it would be worth producing a plot of the kinetic energies of the hydrogen fragments with respect to the charge on the iodine. Given that the hydrogens would have taken the majority of the kick (due to conservation of momentum) it is possible that their kinetic energies would be much higher than those predicted by XMOLECULE. With respect to the final charge states predicted by this version of XMDYN, one finds a good agreement between the two models for the higher fluences however below  $4 \times 10^{12}$  the final charge states are lower than those predicted by XMOLECULE suggesting that the iodine in the XMDYN simulations does not lose the new electrons that move onto it as a result of charge transfer as easily as in the XMOLECULE simulations.

## 5 Conclusion

By comparing the results from the two versions of XMDYN one finds that the addition of charge transfer to the simulations has a significant impact on the predicted response of the system - both on the final charge states and the dynamics. Furthermore, we find that with the addition of charge transfer, the XMDYN software produces results similar to those obtained from XMOLECULE simulations with excellent agreement between the two models for fluences above  $4 \times 10^{12} \mu\text{m}^{-2}$ . Not only this but the XMDYN simulations actually yielded a spread of kinetic energies for iodine and carbon with standard deviations closer to those found experimentally.

The XMDYM simulations were far less computationally expensive with each realization taking only around 8 minutes to run compared to the XMOLECULE simulations which took hours. This means that XMDYN can potentially be used for much larger systems. While promising, the version of XMDYN used here did produce results that deviated from those produced by XMOLECULE for the lower fluences, particularly with respect to the final charge states which, for fluences below  $2 \times 10^{12} \mu\text{m}^{-2}$ , were closer to those predicted by the independent atom model. Further investigations are required into the causes of the discrepancies between the two simulation tools.

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