

## SUPPLEMENTARY INFORMATION

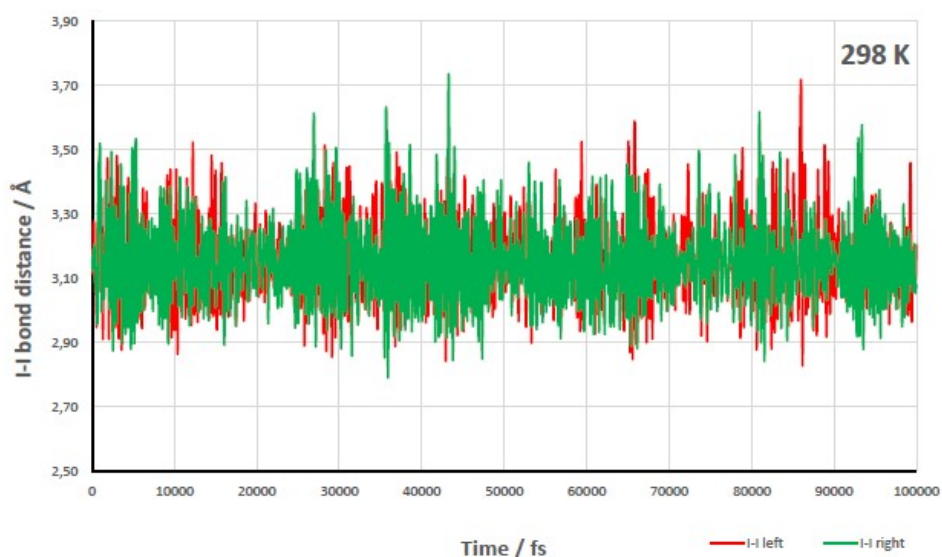
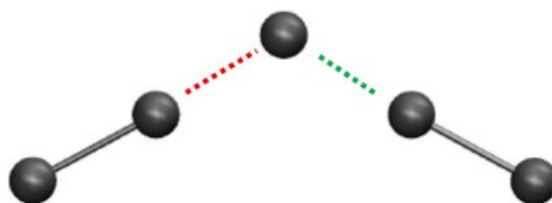
# On the Non-Existence of a Square-Planar Pentaiodide Coordination Complex $\text{I}(\text{I})_4^-$

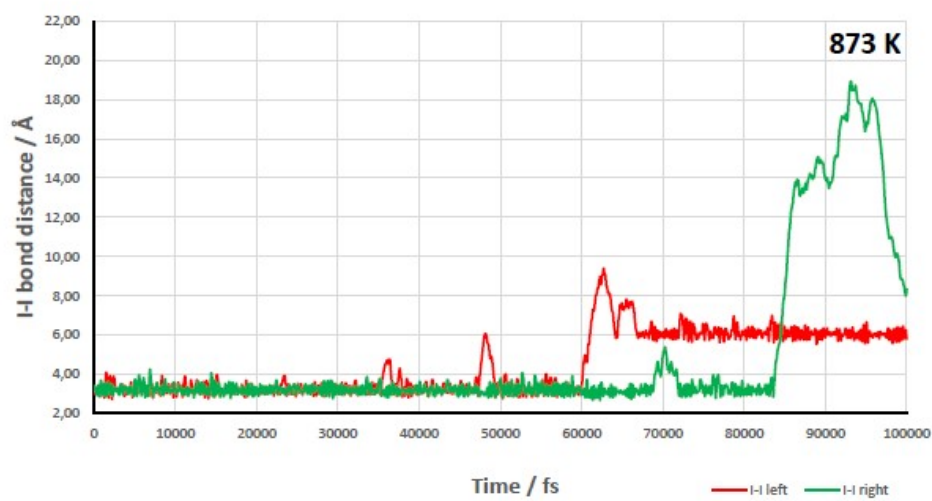
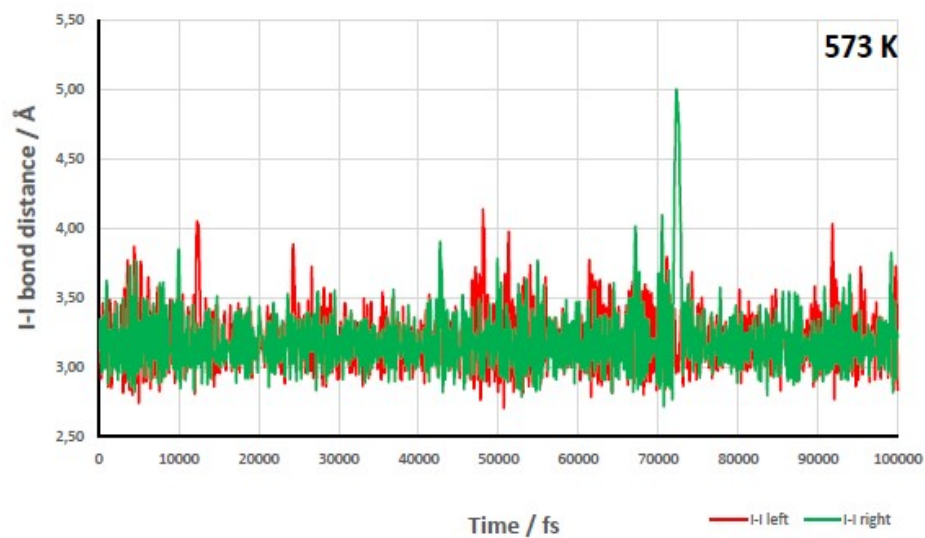
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### ADDITIONAL COMPUTATIONAL RESULTS FROM MOLECULAR DYNAMICS

Below, additional information from the molecular dynamics simulations is provided in the form of selected atom-atom distances as a function of simulation time complementing the snapshot images in the main text. The main program employed for visualization was VMD 1.9.4.<sup>1</sup>





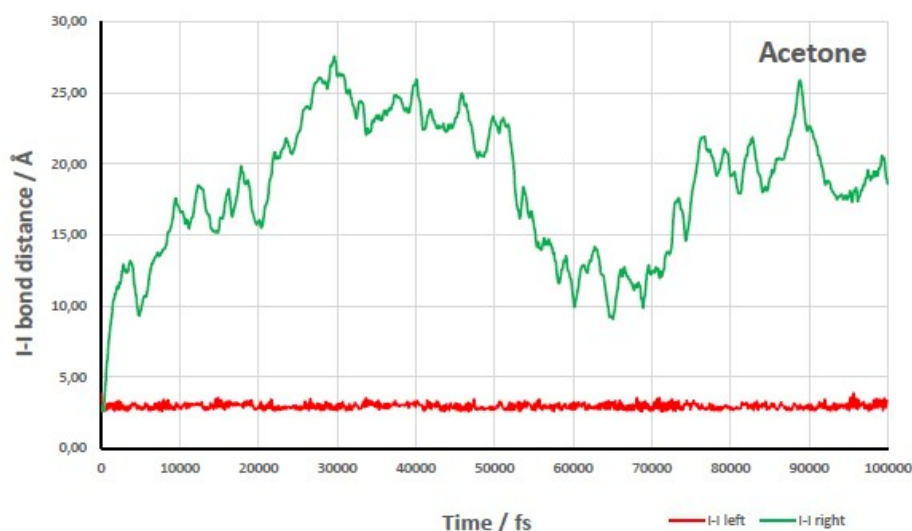
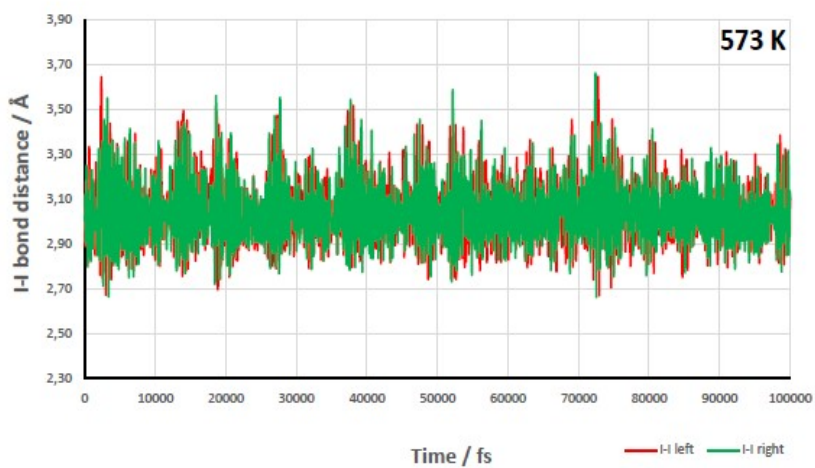
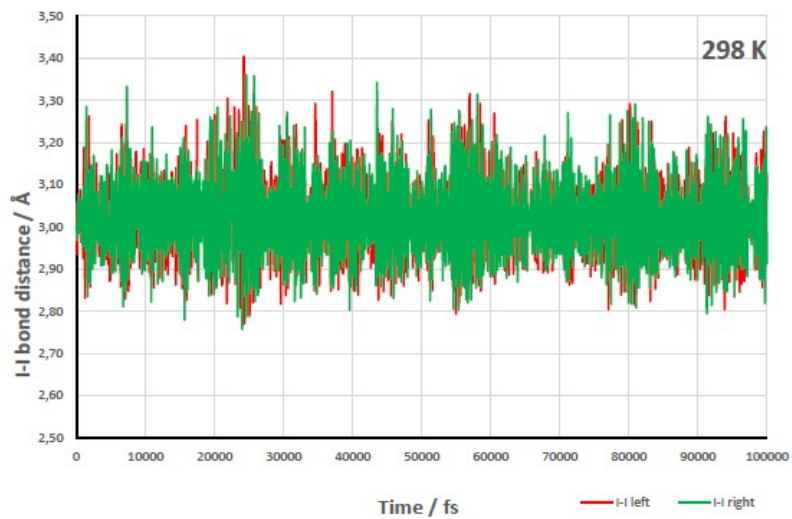
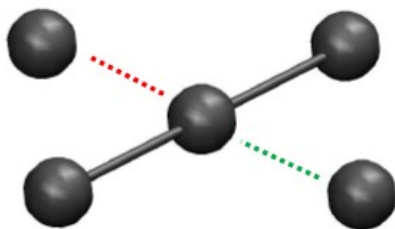


Figure S1. The initial, V-shaped  $I_5^-$  ion as obtained from geometry optimization at DFT level, and its time evolution during 100 ps simulation at 25, 300 and 600 °C. At the bottom also results from the V-shaped  $I_5^-$  ion in an acetone droplet are included

In Fig. S1, it is clear that no dramatic changes take place at the lower temperatures, although some higher degree of mobility can be noted in the atom-atom distance traces at 300 °. However, at 600 °C splitting of the V-shaped pentaiodide ion is triggered into  $I_3^-$  and  $I_2$  units. The dynamics are a bit complex, in which the left-hand  $I_2$  unit partly splits off, rotates and becomes re-attached after about 60 ps. Eventually the right-hand  $I_2$  unit becomes separated from the remaining  $I_3^-$  ion after about 85 ps of simulation. The corresponding simulation in an acetone droplet at 25 °C shows that the decomposition into the two polyiodide fragments essentially starts immediately and proceeds until the droplet model sets the outer limit for distance separation between the  $I_2$  and  $I_3^-$  fragments. In general, the solvent causes a significantly larger fluctuation of the internal polyiodide atom-atom distances.



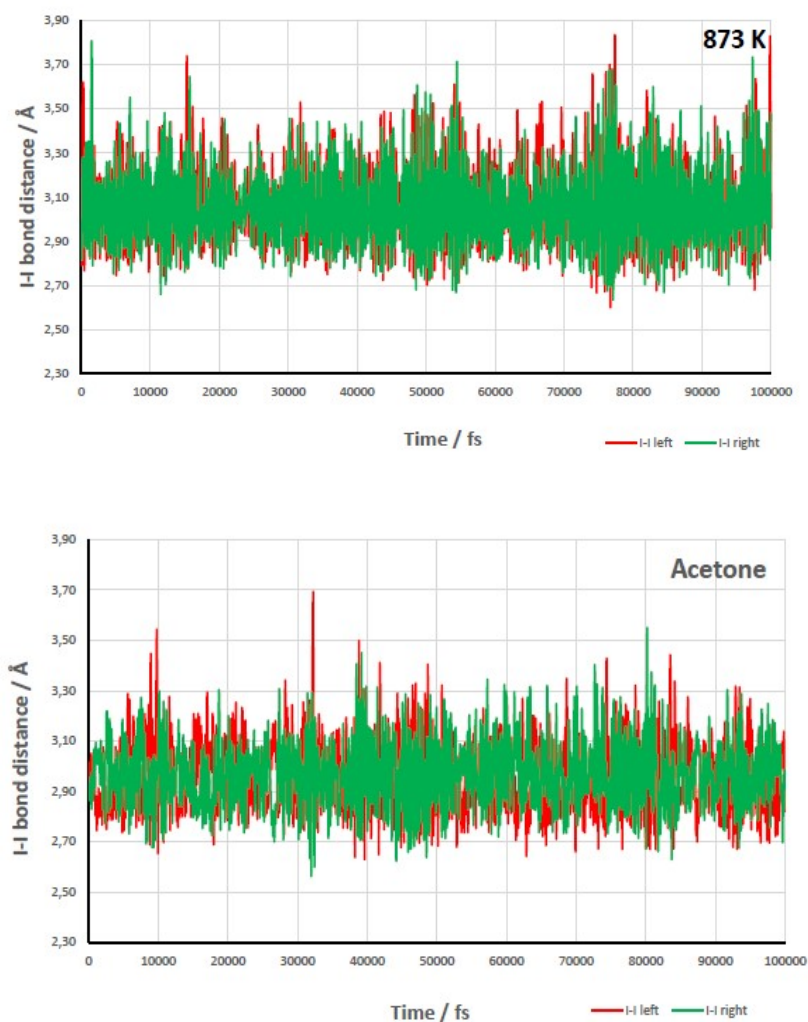


Figure S2. The initial square-planar  $I_4^-$  coordination complex as obtained from geometry optimization at DFT level, and its time evolution during 100 ps simulation at 25, 300 and 600 °C. At the bottom also results from the square-planar  $I_4^-$  ion in an acetone droplet are included

The results from the simulation results in Fig. S2 are quite event-less illustrating the integrity of the square-planar  $I_4^-$  form of the pentaiodide ion in the absence of interacting cations, albeit increasing temperature and acetone as solvent clearly increases the amplitude of variation of the atom-atom distances. The two non-selected atom-atom contacts show highly similar time evolution traces as the two selected ones.

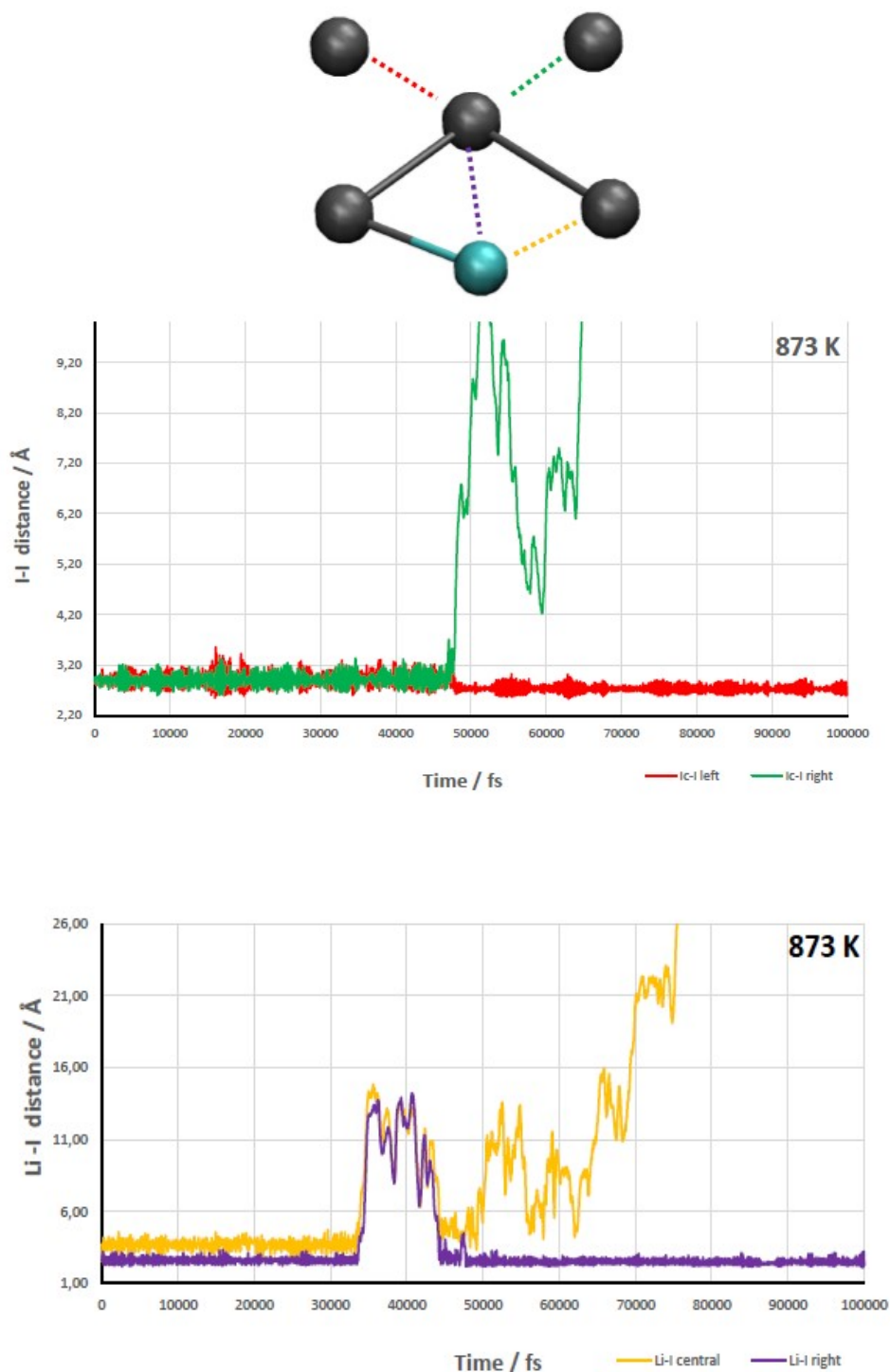
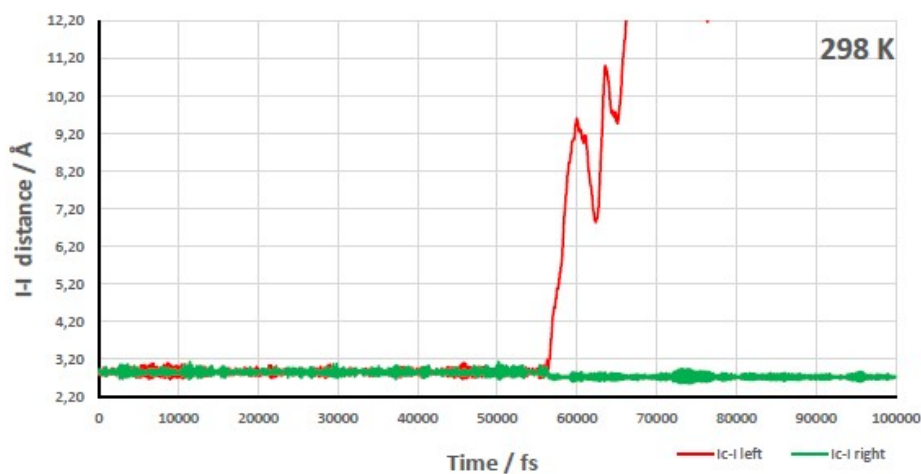
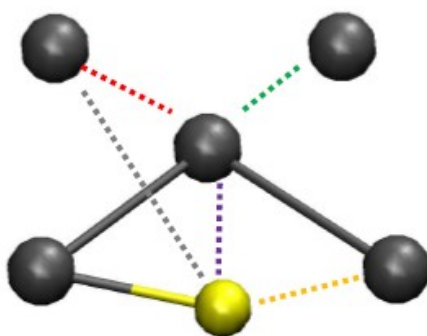


Figure S3. A square-planar  $I_4^-$  complex, as obtained from a geometry optimization at DFT level, coordinated by a  $Li^+$  cation with selected atom-atom-distances traced over 100 ps of simulation.

Results are taken from the simulation at 600 °C

The presence of a polarizing cation, such as  $Li^+$ , certainly makes a difference already at low temperatures. The  $Li^+-I_4^-$  system was geometrically optimized at DFT level before exposed to the molecular dynamics simulation. The energetically favoured starting position placed the  $Li^+$  ion at one of the edges of the square plane of the polyiodide. During simulation at the three different temperatures, the lithium

cation remains surprisingly much of its time in the square plane defined by the  $\text{I}_4^-$  complex. At 600 °C the disintegrating power of the lithium cation causes fragmentation into a  $\text{Li}^+$ -coordinated  $\text{I}_3^-$  ion and an  $\text{I}_2$  molecule diffusing away from each other. The reactions before the end products form were quite complicated, in which an  $\text{Li-I}$  unit first splits off leaving an  $\text{I}_3^-$  entity behind with the original central iodine atom retaining the role as some sort of coordination centre. However, the initially split-off  $\text{Li-I}$  unit returns to the iodine-atom heap and snatches away an  $\text{I}_2$  unit to form the  $\text{Li}^+-\text{I}_3^-$  and product. The  $\text{I}_2$  part of that cation-coordinated unit shows significant rotational freedom. The 'free' and remaining  $\text{I}_2$  unit diffuses away consisting of the initial central iodine atom together with one of the iodine atoms forming the opposite square edge with respect to the initial lithium-ion coordination.



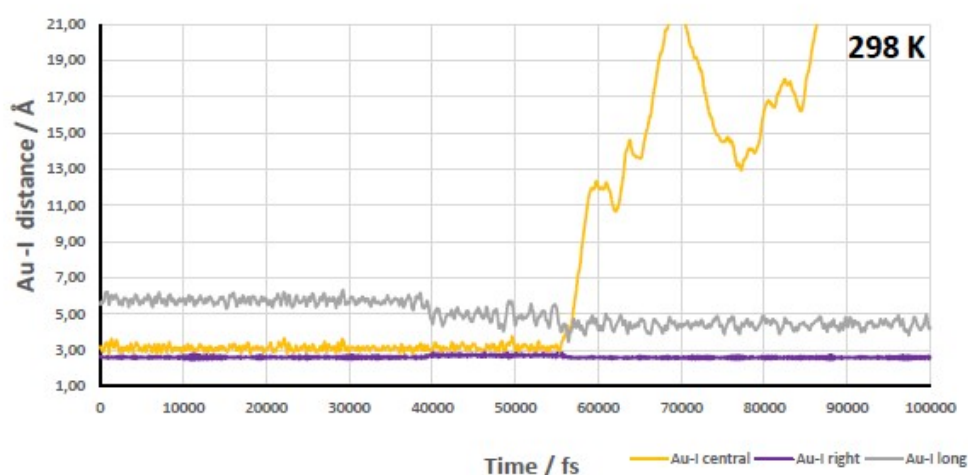


Figure S4. A square-planar  $\text{II}_4^-$  complex coordinated by an  $\text{Au}^+$  cation, as obtained from a geometry optimization at DFT level. Results are taken from the simulation at 25 °C

$\text{Au}^+$  interacts significantly with the  $\text{II}_4^-$  complex already from start and challenges its integrity by almost immediately forming a close to linear  $\text{AuI}_2^-$  fragment at the plane edge of interaction. After about 55 ps of simulation an  $\text{AuI}(\text{I}_2)$  unit splits off an  $\text{I}_2$  molecule. Just as for the  $\text{Li}^+-\text{II}_4^-$  system, the  $\text{I}_2$  molecule that separates away is formed by the initial central iodine atom of the  $\text{II}_4^-$  complex and one of the iodine atoms at the opposite edge of cation interaction. It is notable that the  $\text{I}_2$  ligand coordinated to  $\text{Au}^+$  appears to form already after about 40 ps, thus preceding the separation from the other  $\text{I}_2$  entity by about 15 ps. The simulations at higher temperatures show similar results, albeit the separation into the same type of fragments takes place at much shorter simulation times, already after 5-10 ps at 300 °C and at less than 5 ps at 600 °C.



**REFERENCES**

1. W. Humphrey, A. Dalke and K. Schulten, *J. Molec. Graphics*, 1996, **14**, 33-38.