Electronic Supplementary Information for: Chlorine Gas and Anion Radical Reactivity in Molten Salts and the Link to Chlorobasicity

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S1 Figures

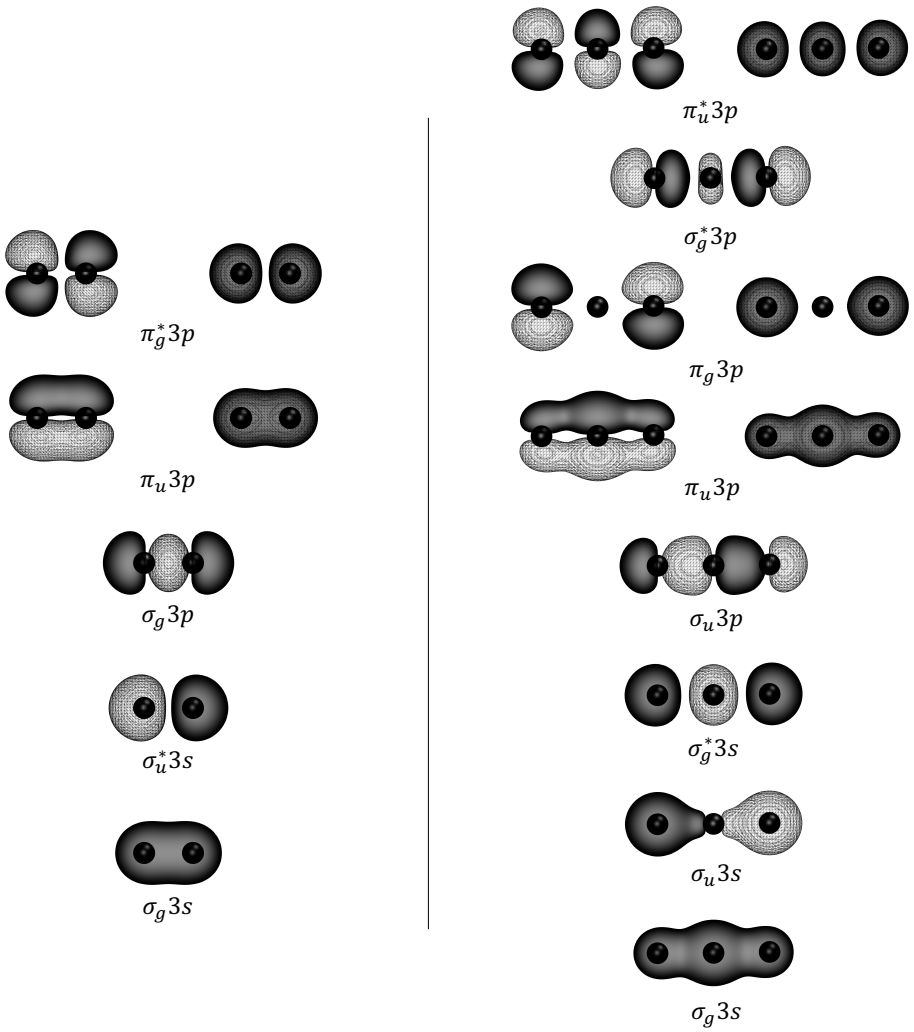
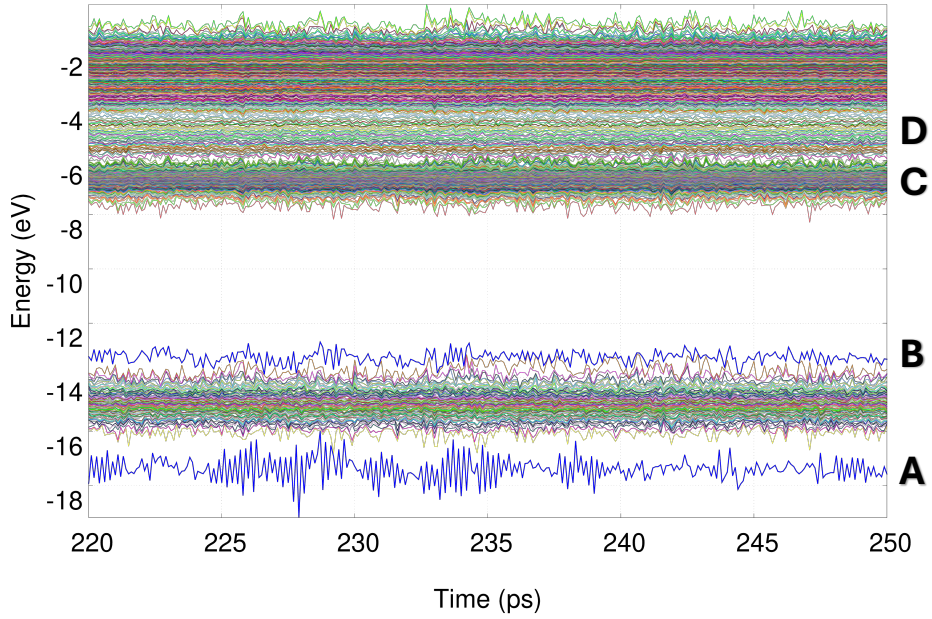


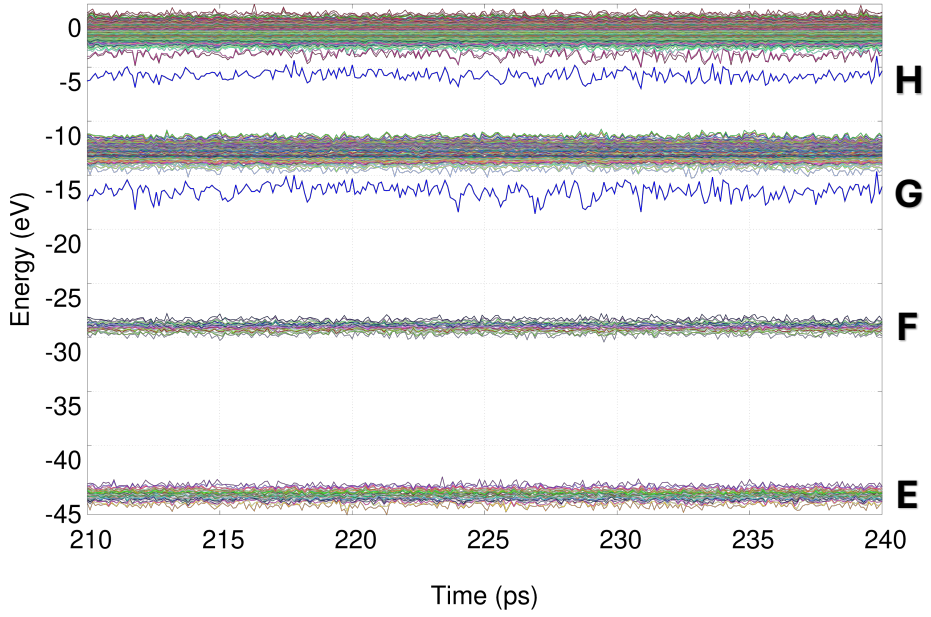
Figure S.1: For Cl_2 (left) and Cl_3^- (right), gas phase MO diagram highlighting relevant orbitals; computed using the Gaussian09 Revision D01 Software.[1] All structures were optimized using the B3LYP functional and the def2TZVP basis set.

Figures S.2 highlight selected states of the system, some of which we refer to in the main text. In Figure S.2a, for $ZnCl_2$, label A indicates $\sigma_g 3s$ of Cl_2, B mostly coincides with $\sigma_u^* 3s$ of Cl_2, C is a liquid band for which states at lower energy are associated with the extended MOs presented in Figure 2 of the main text; in the region denoted by D we often find orbitals with the tetrahedral pattern that one could associate with $ZnCl_4^{2-}$ units. For the case of the eutectic mixture in Fig-

ure S.2b, E corresponds to s orbitals on Li^+, F corresponds to s orbitals on K^+, G and H correspond to $\sigma_g 3s$ and $\sigma_u 3p$ of Cl_3^-, respectively.



(a) $ZnCl_2$



(b) LiCl-KCl eutectic mixture

Figure S.2: Liquid-phase MO diagrams for 30 ps segments in our bulk phase simulations highlighting the identity of important states or bands with letters on the right side of each figure. An explanation of the labels is given in the text.

Being able to identify molecular orbitals of Cl_2 and Cl_3^- as separated from those of the melt is important for analysis presented in the main text.

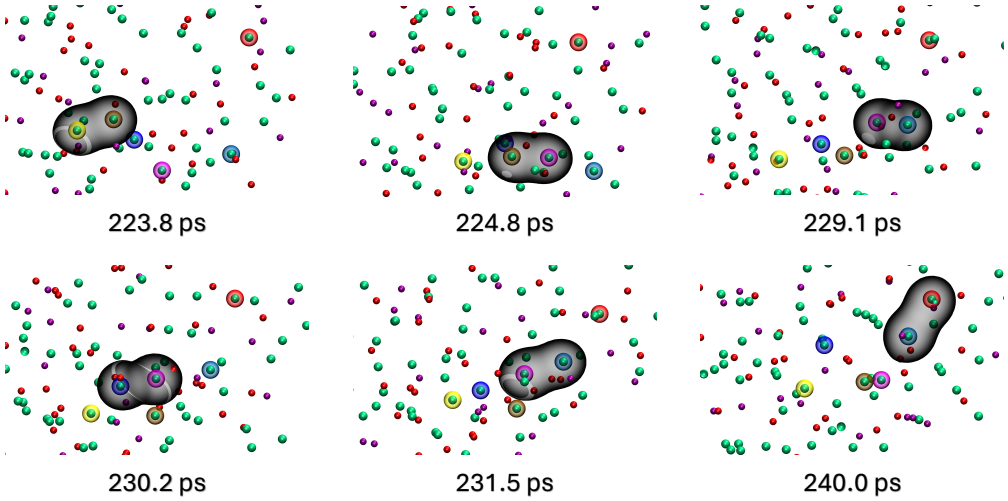


Figure S.3: The figure shows snapshots from the eutectic mixture in which Cl_2 is formed. Some Cl atoms or Cl^- ions are highlighted with a colored shell to identify species that along the trajectory were, are, or will become part of the Cl_2 molecule. Notice that as opposed to the case of the $ZnCl_2$ melt where atoms in the Cl_2 molecule do not change with time, in the eutectic mixture these are in constant exchange.

References

(1) Frisch, M. J. et al. Gaussian 09 Revision D.01. Gaussian Inc., Wallingford CT 2013.