Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Formation of dimethylketene and methacrolein by reaction of the CH radical with acetone

Supporting Information

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Geometry optimization calculations were performed for the series of ketenes, ketene, methylketene, dimethylketene and ethylketene Using Gaussian 09 software[1] at the HF/6-31G(d,p) level. The HOMO-1, HOMO, LUMO and LUMO+1 are plotted for each compound. One can see that unlike the series of acetylenes studied by Xu et al,[2] additional substitution onto the ketene frame does not significantly impact the wavefunction character for the series of frontier orbitals. Furthermore, none of the normally unoccupied orbitals display the g-wave (ℓ=4) character that leads to the very strong shape resonance observed in 2-butyne. These observations, along with the similar shape observed for each ketene shape resonance, support the scaling of the photoionization cross sections for the substituted ketenes to the peak in the ketene shape resonance.

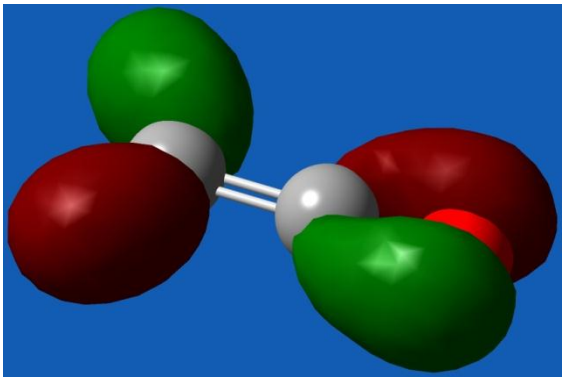

Figure S1. Ketene HOMO-1

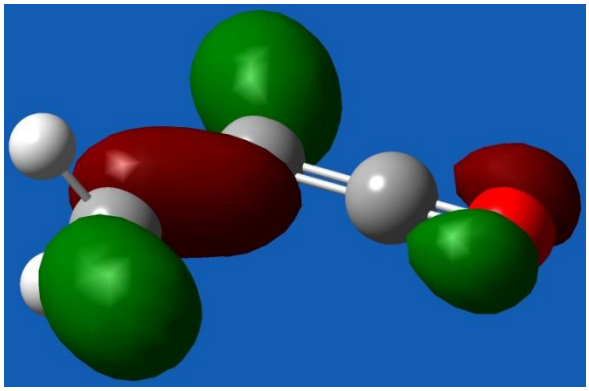

Figure S2. Methylketene HOMO-1

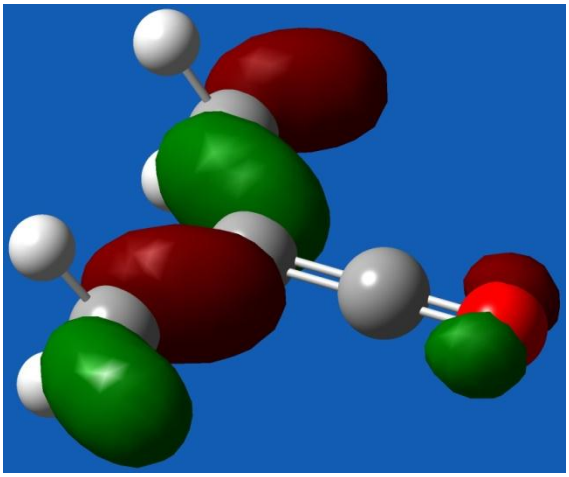

Figure S3. Dimethylketene HOMO-1

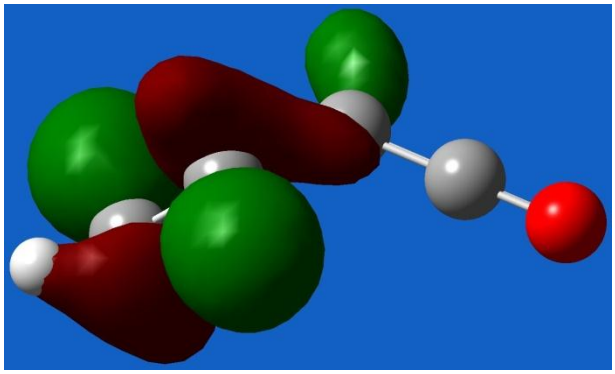

Figure S4. Ethylketene HOMO-1

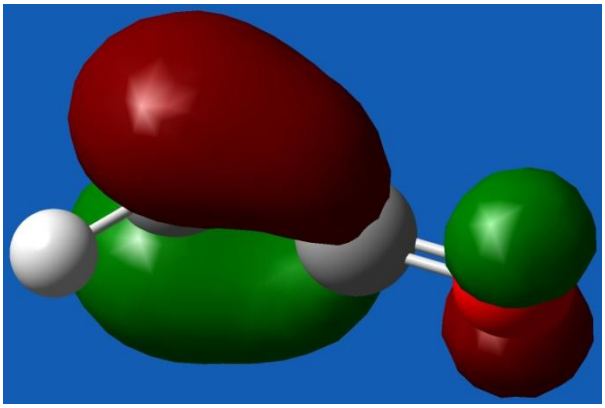

Figure S5. Ketene HOMO

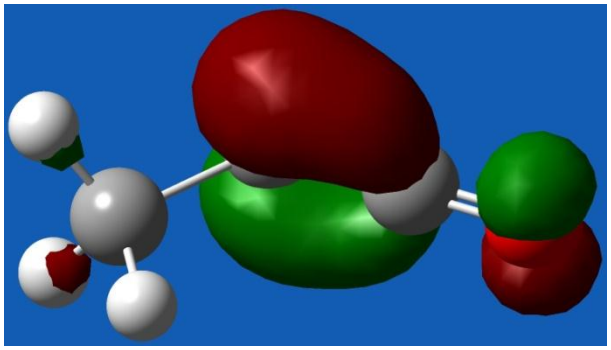

Figure S6. Methylketene HOMO

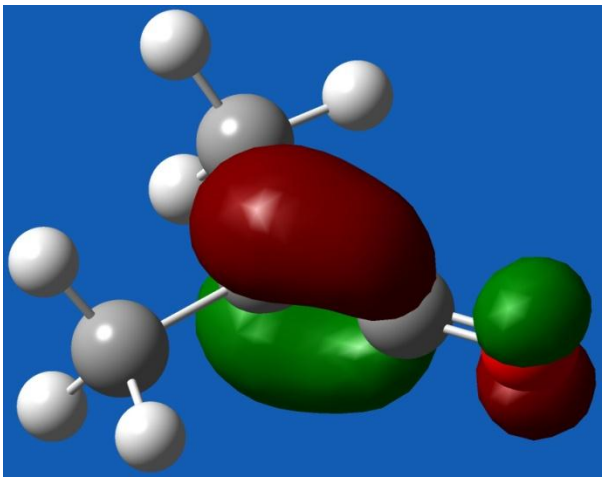

Figure S7. Dimethyl Ketene HOMO

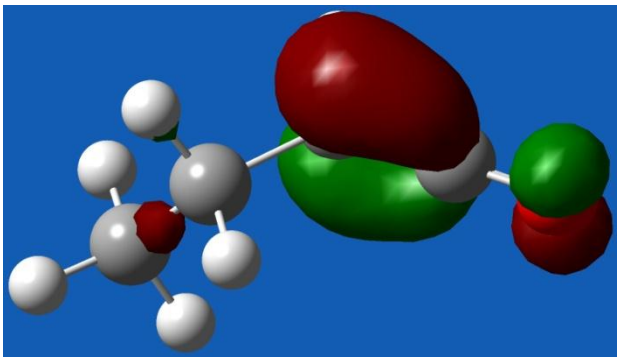

Figure S8. Ethyl Ketene HOMO

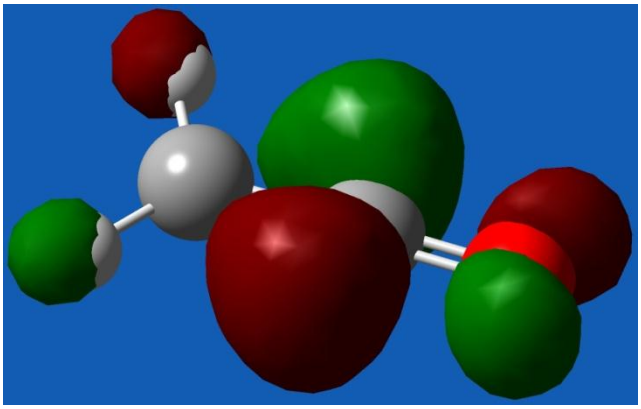

Figure S9. Ketene LUMO

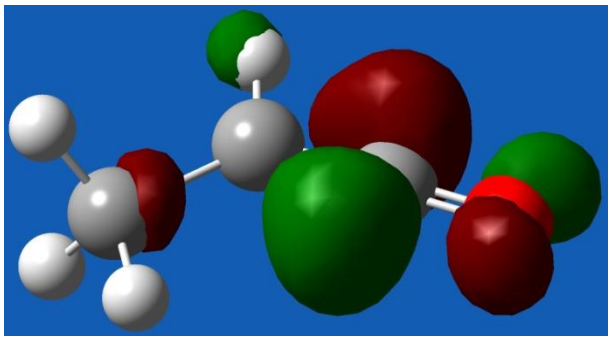

Figure S10. Methylketene LUMO

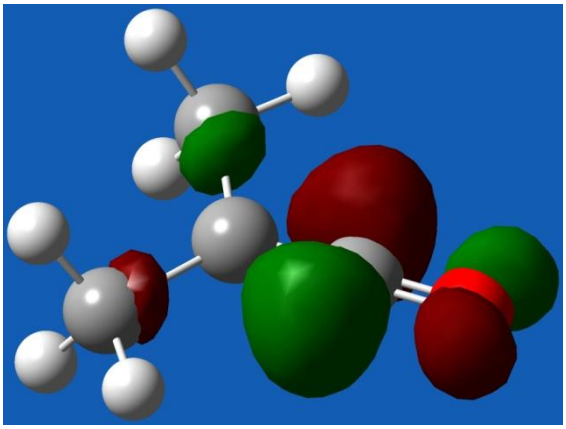

Figure S11. Dimethylketene LUMO

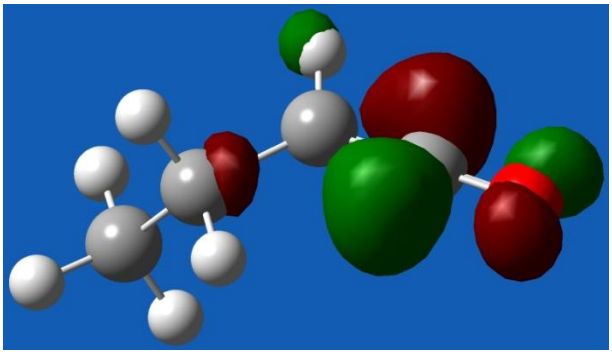

Figure S12. Ethylketene LUMO

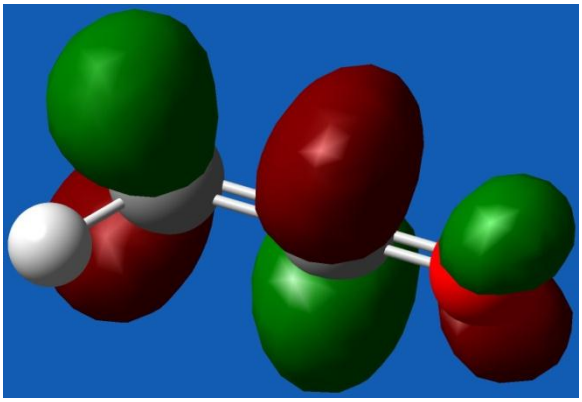

Figure S13. Ketene LUMO+1

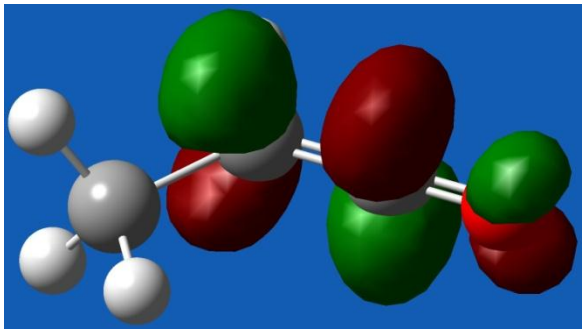

Figure S14. Methylketene LUMO+1

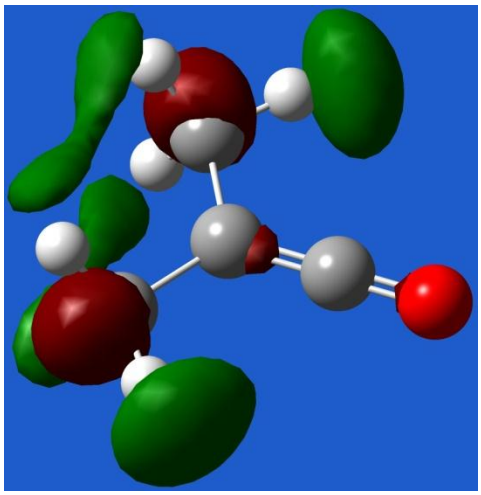

Figure S15. Dimethylketene LUMO+1

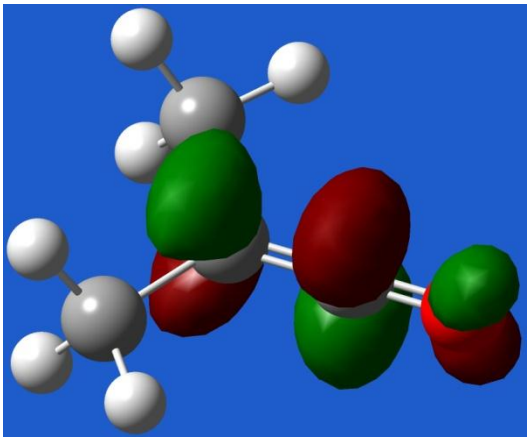

Figure S16. Dimethylketene LUMO+2

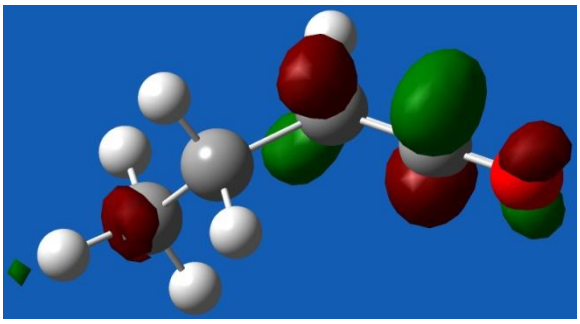

Figure S17. Ethylketene LUMO+1

References:

(1) Frisch, M. J.; Trucks, G. W. S., H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H. *et al.* Gaussian 09, Revision A.1, Gaussian, Inc.: Wallingford CT

(2) Xu, H.; Jacovella, U.; Ruscic, B.; Pratt, S. T.; Lucchese, R. R. *J. Chem. Phys.* **2012**, *136*, 154303.