

Supporting information for: Supporting Information

For: A Pathway to Diphosphorus from the Dissociation of Photoexcited Tetrphosphorus

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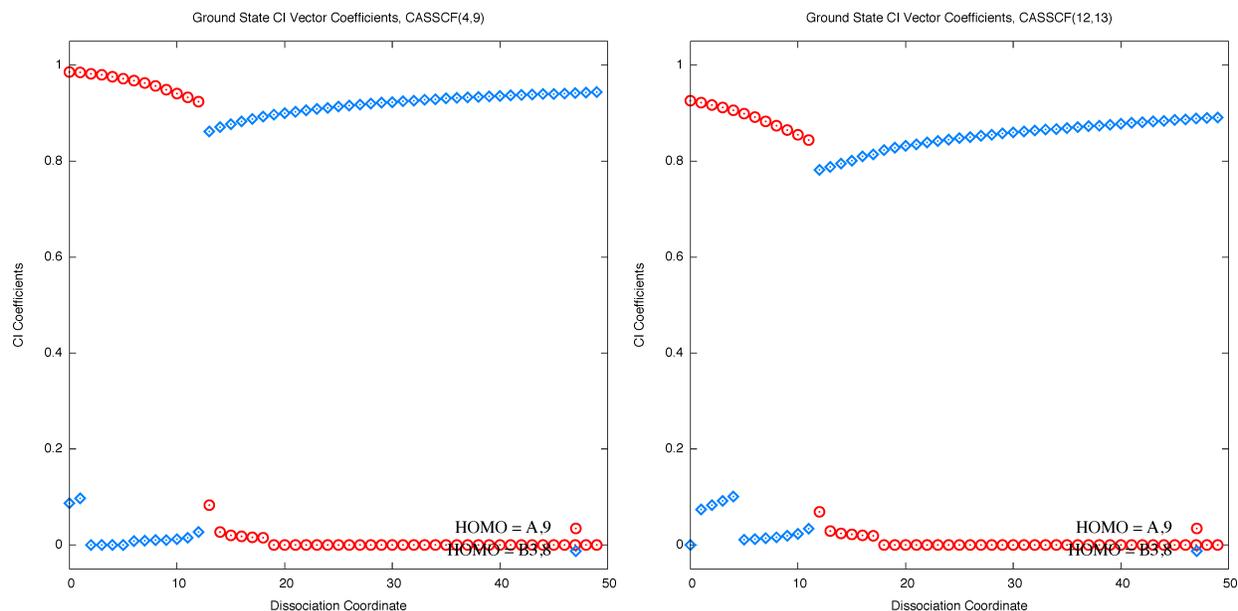


Figure S1: CI vector coefficients of the P4 ground state along the direct dissociation coordinate. The largest CI coefficient corresponds to a closed-shell electron configuration with either the (A,9) orbital doubly occupied or the (B3,8) orbital doubly occupied. There is an abrupt switch from (A,9) double occupation to (B3,8) double occupation which corresponds to the intersection between the A(1) and A(3) electronic states (Figure 2 in paper, $x = 12$). The behavior of the CI coefficients does not change when going from a CASSCF(4,9) calculation (left panel) to a CASSCF(12,13) calculation (right panel), indicating that the ground state is largely single-reference in character and does not involve any excitations from the lower-lying occupied orbitals.

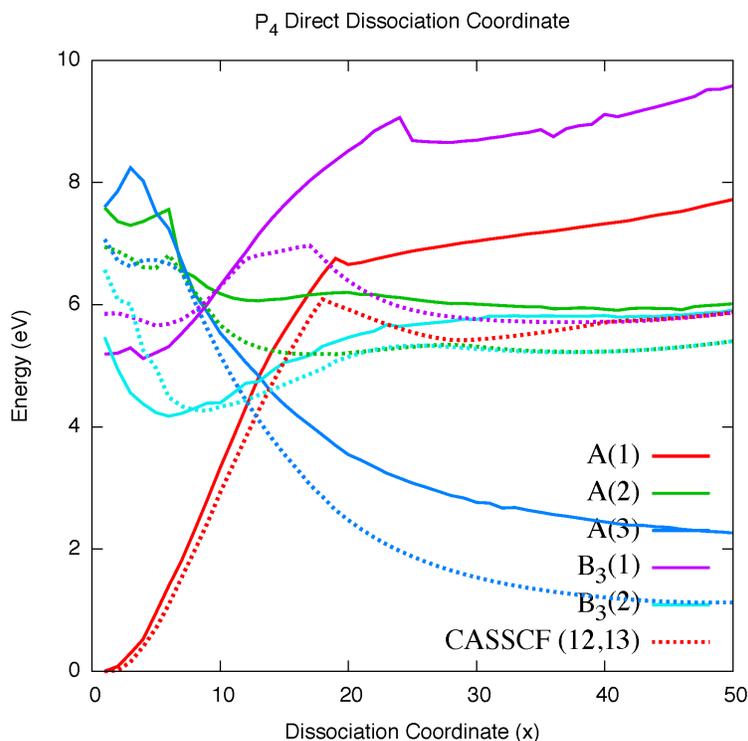


Figure S2: Electronic energies from the CASSCF(12,13) calculation compared to CASSCF(4,9)-RSPT3 (Figure 2 in paper). The qualitative behavior of the lowest-energy states A(1), A(3) and B₃(2) are all the same. The B₃(2) state still exhibits a minimum at small dimer separations. In the dissociation limit, A(3) becomes the ground state, while A(2) and B₃(2) become degenerate excited states; all of this agrees with the CASPT3(4,9) picture.

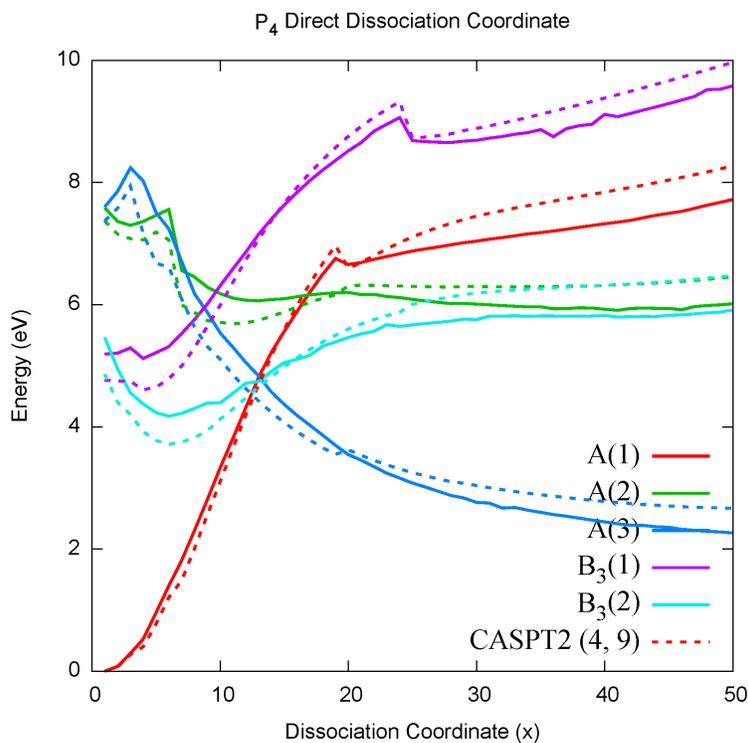


Figure S3: Comparison of RSPT2 and RSPT3 treatments of dynamic correlation. We found CASPT3 to provide more quantitative accuracy in comparing to experiment, as CASPT2 predicts the lowest excitation energy at the Franck-Condon point to be slightly below experiment (4.7 eV vs. 5.1 eV). Nevertheless, the treatment of dynamic correlation does not change the qualitative behavior of the potential surface.