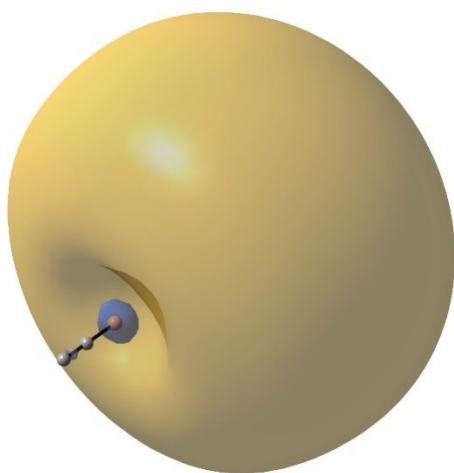


## Supporting Information for

### Probing the Coupling of A Dipole-Bound Electron with the Molecular Core

Joseph Czekner, Ling Fung Cheung, G. Stephen Kocheril, and Lai-Sheng Wang\*

*Brown University, Department of Chemistry, 324 Brook Street, Providence, RI 02912, USA*



**Figure S1.** The calculated wave function of the dipole-bound excited state of  $C_2P^-$ , based on theoretical calculations using the  $\omega$ B97XD functional<sup>S1</sup> and the daug-cc-pVTZ basis set<sup>S2</sup> augmented with an additional  $s$  and  $p$  function in Gaussian 09.<sup>S3</sup>

## Experimental Details

The  $C_2P^-$  anions were produced by laser ablation of a disk target composed of graphite, red phosphorus, and bismuth (served both as a binder and a source of  $Bi^-$  for spectral calibration). The laser-induced plasma was cooled by a He carrier gas containing 10% Ar at a backing pressure of 10 atm to initiate nucleation. The nascent clusters were entrained in the carrier gas and underwent a supersonic expansion. The negatively-charged clusters were extracted from the cluster beam and analyzed by time-of-flight mass spectrometry. Mixed C-P clusters with different stoichiometries were observed. The  $C_2P^-$  anions of current interest were mass selected and photodetached using a Deyang dye laser system in the interaction zone of a multi-lens imaging system.<sup>S4</sup> Photoelectrons were extracted and projected onto a pair of 75-mm diameter micro-channel plates coupled to a phosphor screen and recorded using a charge-coupled device camera. The PE images were analyzed using the maximum entropy method (MEVELER).<sup>S5</sup> The PE spectra were calibrated using the known detachment energies of  $Au^-$  and  $Bi^-$  with various photon energies; the laser wavelengths were calibrated with a Bristol 821 wavelength meter. Typical kinetic energy (KE) resolution of the imaging lens is  $1.2 \text{ cm}^{-1}$  for low KE electrons ( $5.1 \text{ cm}^{-1}$ ) and  $\sim 0.6\% \Delta KE/KE$  for high KE electrons (above 2 eV).<sup>S4</sup>

## Photoelectron Angular distributions (PADs)

Angular distributions of photoelectrons are useful to analyze the angular momentum of the detached photoelectron. PADs can be quantified using the anisotropy parameter,  $\beta$ , as shown in Eq. 1:

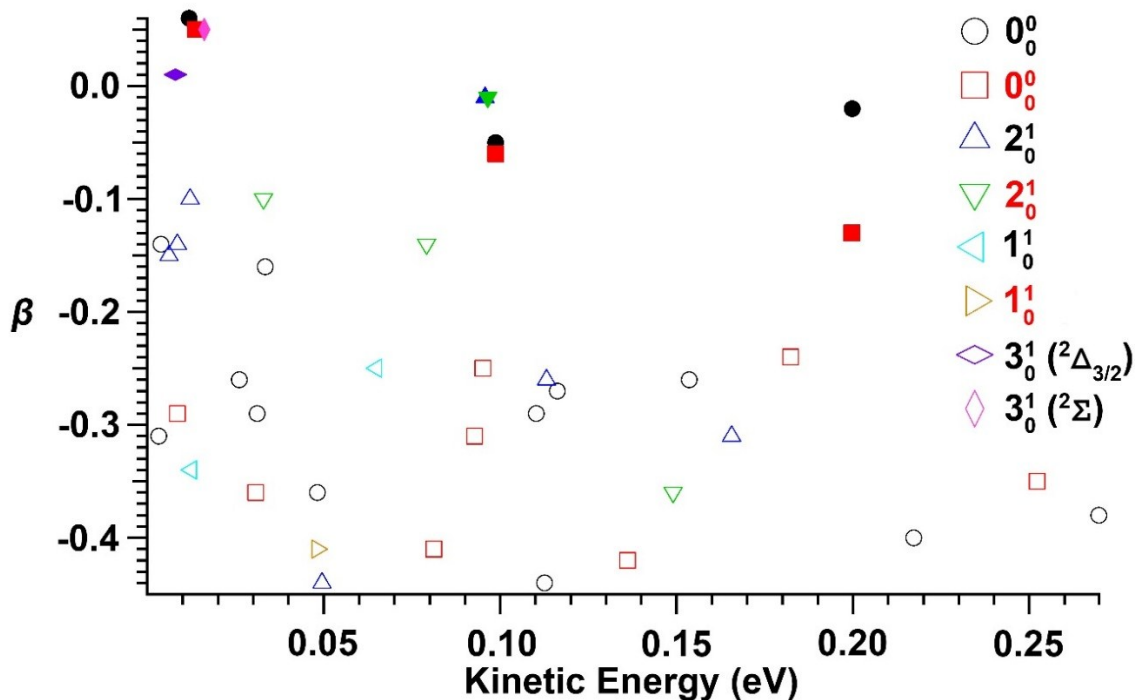
$$d\sigma/d\Omega = \sigma_{\text{Tot}}/4\pi[1 + \beta P_2(\cos\theta)] \quad (1)$$

Here  $\sigma_{\text{Tot}}$  is the total cross section,  $P_2$  is the second order Legendre polynomial, and  $\theta$  is the angle of the outgoing electron relative to the laser polarization.<sup>S6</sup> The PAD can be approximated by

$$I(\theta) \sim [1 + \beta P_2(\cos\theta)] \quad (2)$$

where  $\beta$  can have any value between -1 and 2. This model works reasonably well for single-photon detachment from randomly oriented particles. Therefore, if an electron is detached from an atomic  $s$ -orbital ( $l = 0$ ) the outgoing electron will have one unit of angular momentum ( $l = 1$ ) and the resulting  $\beta$  value will be 2. Because molecular orbitals can be approximated as a linear

combination of atomic orbitals, interpreting  $\beta$  for a molecular system is not a trivial process.<sup>S7</sup> However, we can use the angular distributions to differentiate between resonant and non-resonant photoelectron spectra, particularly at higher electron kinetic energies (above 0.05 eV) where threshold effects are less noticeable. Resonantly-enhanced features are found to be nearly isotropic with  $\beta \sim 0$ . The angular distributions of the main features in Fig. 3, Fig. S2, and Fig. S3 have been analyzed and the beta values are shown in Fig. S4.



**Figure S2.** Beta values of the main vibrational features in the PE spectra in Fig. 1 and Fig. 4. Solid shapes denote enhanced peaks in the dipole-bound resonant spectra, which are all nearly isotropic ( $\beta \sim 0$ ).

## References

- S1. D. E. Woon and T. H. Dunning Jr., *J. Chem. Phys.*, 1994, **100**, 2975-2988.
- S2. J. D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.* 2008, **10**, 6615-6620.
- S3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, R. J. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsugi, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuga, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 09, Revision C.01*; Gaussian Inc.: Wallingford CT, 2016.
- S4. I. Léon, Z. Yang, H. T. Liu, and L. S. Wang, *Rev. Sci. Instrum.* 2014, **85**, 083106.
- S5. B. Dick, *Phys. Chem. Chem. Phys.* 2014, **16**, 570-580.
- S6. J. Cooper and R. N. Zare, *J. Chem. Phys.* 1968, **48**, 942-943.
- S7. A. Sanov and R. Mabbs, *Int. Rev. Phys. Chem.* 2008, **27**, 53-85.