Supporting Information for

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

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Figure S1. The calculated wave function of the dipole-bound excited state of C_2P^-, based on theoretical calculations using the ωB97XD functional\(^{S1}\) and the daug-cc-pVTZ basis set\(^{S2}\) augmented with an additional s and p function in Gaussian 09.\(^{S3}\)
Experimental Details

The C$_2$P$^-$ 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$_2$P$^-$ 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. 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 (MEVELE). 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 cm$^{-1}$ for low KE electrons (5.1 cm$^{-1}$) and ~0.6% ΔKE/KE for high KE electrons (above 2 eV).

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:

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

(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. The PAD can be approximated by

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

(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.\textsuperscript{87} 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.

![Graph showing beta values](image)

**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