Photodetachment to the ground state of C_2H ($X\,^2\Sigma^+$) involves ejecting an electron from an s−like σ orbital (approximately $5\sigma_g$ in symmetry character), whereas detachment to the excited $\tilde{A}\,^2\Pi$ state occurs from a p−like π orbital (approximately $1\pi_u$ in character). Therefore, the electron anisotropies may be described using the mixed s-p model,[76]

$$\beta_{sp}(\epsilon) = \frac{2(1-\gamma_p)B_1\epsilon + \gamma_p(2A_1^2\epsilon^2 - 4A_1\epsilon\cos\delta_{2,0})}{(1-\gamma_p)B_1\epsilon + \gamma_p(1+2A_1^2\epsilon^2)} \tag{11}$$

where ϵ is the electron kinetic energy and γ_p is the fraction of p character of the detachment orbital described as

$$|\psi\rangle = \sqrt{1-\gamma_p}|s\rangle + \sqrt{\gamma_p}|p\rangle \tag{12}$$

A_1 and B_1 in Eq. (11) are the generalized Hanstorp[REF1] coefficients describing the assumed Wigner-like[REF2] relative scalings of the radial transition dipole matrix elements for different allowed detachment channels. Specifically, $A_1\epsilon$ describes the energy-dependent ratio of the $p \rightarrow d$ and $p \rightarrow s$ transition amplitudes, while $B_1\epsilon$ corresponds to the $s \rightarrow p$ and $p \rightarrow s$ cross-section ratio.[76] It can be shown that under certain approximations $B_1/A_1 = 8/3$.[REF3] Finally, $\delta_{2,0}$ in Eq. (11) is the phase shift between the s and d partial waves, which in most cases of anion photodetachment is assumed to be small, corresponding to $\cos\delta_{2,0} \approx 1$.

From Eq. (11) it can be seen that detachment from a pure s orbital ($\gamma_p = 0$) will have a positive anisotropy ($\beta = +2$), whereas detachment from a pure p orbital ($\gamma_p = 1$) will have a negative anisotropy for electron kinetic energies $\epsilon < 2/A_1$. Therefore, measuring the anisotropy can help determine the electronic character of each individual transition, which may be compared to the calculated symmetries in Figure 3. The anisotropy parameters were measured for every detachment wavelength and prominent transition in the C_2H^- photoelectron spectra from this work, and are presented in Figure 5. Fitting Eq. (11) to the anisotropy parameters from $^2\Pi$ state detachment, with $\gamma_p = 0.9$ produces a Hanstorp coefficient of $A_1 = 0.66(4)$ eV^{-1}.

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REF2. Wigner, E. P., On the behavior of cross sections near thresholds. *Phys. Rev.* **1948,** *73*, 1002-1009.

REF3. Sanov, A.; Grumbling, E. R.; Goebbert, D. J.; Culberson, L. M., Photodetachment anisotropy for mixed s-p orbitals: 8/3 and other fractions. *J. Chem. Phys.* **2013,** *138*, 054311.