# Supplementary Information

# The dicarbon bonding puzzle viewed with photoelectron imaging

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**SUPPLEMENTARY DISCUSSION**

Rotational band models for the $C_2(X^1\Sigma_g^+) \leftarrow C_2^-(X^2\Sigma_g^+)$ and $C_2(a^3\Pi_u) \leftarrow C_2^-(X^2\Sigma_g^+)$ electronic transitions have been constructed using methods similar to those developed by Buckingham *et al.* [1]. The anion $^2\Sigma_g^+$ and ground neutral $^1\Sigma_g^+$ states belong to Hund's case (b), where there is negligible spin-orbit coupling. The positions of the rotational lines of the anion $^2\Sigma_g^+$ state are given by the formula of Mulliken [2],

$$F_{1,2} = BN(N+1) \pm \frac{1}{2}\gamma N,$$
(1)

where $F_1$ and $F_2$ are the doublet fine structure components, $B$ is the rotational constant, $N$ is the total rotational (minus spin) angular momentum quantum number, and $\gamma$ is the spin-rotation splitting constant ($= 0.001274 \text{ cm}^{-1}$ [3]). For the neutral ground state, where there is no spin splitting, the levels are simply given by, $F = BN(N+1)$.

The excited $^3\Pi_u$ state of the neutral belongs to Hund's case (a) as it experiences strong spin-orbit (LS) coupling. For triplet $\Pi$ states, the rotational levels are given by [4],

$$F_1 = B\left[J(J+1) - \sqrt{Z_1} - 2Z_2\right],$$
(2)

$$F_2 = B\left[J(J+1) + 4Z_2\right],$$
(3)

$$F_3 = B\left[J(J+1) + \sqrt{Z_1} - 2Z_2\right],$$
(4)

with the values $Z_1$ and $Z_2$ defined as,

$$Z_1 = Y(Y-4) + \frac{4}{3} + 4J(J+1),$$
(5)

$$Z_2 = \frac{1}{3Z_1}\left[Y(Y-1) - \frac{4}{9} - 2J(J+1)\right],$$
(6)

where $B$ is the rotational constant of the molecule, $Y$ is the ratio of the spin-orbit and rotational constants $Y = A_{\text{SO}}/B$, and $J$ is the total angular momentum quantum number.

The intensity of each rotational transition may be calculated using the method of Ref. [1], which employs Wigner $3j$-symbols to describe the angular momentum couplings involved in the transitions. For the ground state $C_2(X^1\Sigma_g^+) \leftarrow C_2^-(X^2\Sigma_g^+)$ photodetachment, the intensity $Q$-factor for a case-(b) to case-(b) transition is,

$$Q = (2N'+1)\begin{pmatrix} N' & j_{\text{t}} & N'' \\ -\Lambda' & \Delta\Lambda & \Lambda'' \end{pmatrix}^2,$$
(7)

where $j_{\text{t}}$ is a variable ranging from $|\ell - 1|$ to $\ell$, and $\Lambda$ is the axial component of the orbital angular momentum. For transitions to the ground state of $C_2$, $\Lambda' = \Lambda'' = \Delta\Lambda = 0$.

Similarly, the rotational transition intensities involved in the excited state $C_2(a^3\Pi_u) \leftarrow C_2^-(X^2\Sigma_g^+)$ photodetachment may be calculated using the $Q$-factor for a case-(b) to case-(a) transition,

$$Q = \frac{2J'+1}{2S'+1}\sum_{\chi=j_{\text{t}}-1/2}^{j_{\text{t}}+1/2} (2\chi+1)\begin{pmatrix} j_{\text{t}} & S' & \chi \\ \Delta\Lambda & \Sigma' & \Lambda'' - \Omega' \end{pmatrix}^2 \begin{pmatrix} J' & \chi & N'' \\ -\Omega' & \Omega' - \Lambda'' & \Lambda'' \end{pmatrix}^2,$$
(8)

where $S'$ is the spin of the neutral, $\Sigma'$ is the axial component of the spin, and $\Omega'$ is the projection of the total electronic angular momentum of the molecular state onto the molecular axis. For detachment yielding $C_2(a^3\Pi_u)$, $S' = 1$, $\Lambda' = 1$, $\Lambda'' = 0$, $\Delta\Lambda = 1$, and $\Omega' = \Lambda' + \Sigma'$.

The rotational model defined above was fitted to the experimental photoelectron spectrum, as shown in Fig. **??**. Fitting the model yields an anion rotational temperature of T=197(2) K, while the Gaussian full-width half-maximum (FWHM) of each transition gives an energy resolution of $\Gamma_{X^1\Sigma} = 17(1) \text{ cm}^{-1}$ and $\Gamma_{a^3\Pi} = 19(1) \text{ cm}^{-1}$, which are consistent with expectations for the spectrometer at kinetic energies of $\epsilon \sim 0.5$ eV.

The above rotational model is fitted to the experimental photoelectron spectrum in Fig. 4. This provides an accurate determination of the band head origin, allowing for precise determination of spectroscopic constants, as presented in Supplementary Table I.

**SUPPLEMENTARY TABLES**

Supplementary Table I: Molecular constants ($cm^{-1}$) of $C_2$ and $C_2^-$.

|  |  | HR-PEI | Previous Work |
|---|---|---|---|
| $C_2^-$ $X^2\Sigma_g^+$ | B | 1.746(1) | $1.7468(5)^a$ |
|  | $\omega_e$ | 1782(2) | $1781.189(18)^a$ |
| $C_2$ $X^1\Sigma_g^+$ | EA | 26,396(3) | $26,360(50)^b$ |
|  | B | 1.820(1) | $1.8198(4)^c$ |
| $C_2$ $a^3\Pi_u$ | $T_e$ | 718(1) | $718.318(1)^d$ |
|  | $A_{SO}$ | −14.6(6) | $−15.272(3)^d$ |
|  | B | 1.635(4) | $1.6324(6)^d$ |

[a] from infrared study of Rehfuss *et al.* [5]
[b] from photoelectron spectroscopy of Lineberger *et al.* [6]
[c] from infrared study of Davis *et al.* [7]
[d] from flame-emission spectroscopy of Amiot *et al.* [8]

**SUPPLEMENTARY REFERENCES**

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