

Supporting Information

Schmidt et al. 10.1073/pnas.1213083110

SI Text

Electronic Structure Calculations

All electronic structure calculations were carried out using the Molpro suite of programs (1). The potential energy surfaces (PESs) for the $1-3^1A'$, $1-3^1A''$, $1-3^3A'$, and $1-3^3A''$ electronic states were calculated using the multiconfiguration reference internally contracted configuration interaction (MRCI) method (2, 3) based on wave functions obtained from full-valence complete active space self-consistent field (CASSCF) (4, 5) calculations. The correction of Langhoff and Davidson (6) was applied for size-extensive energies and to take into account the approximate effect of higher excitations. Dunning's aug-cc-pVQZ (7) orbital basis set was used. The calculations were done separately for the $^1A'$, $^1A''$, $^3A'$, and $^3A''$ states without state averaging over symmetry or spin.

The PESs were defined on a grid spanning $1.7a_0 \leq r_1 \leq 7.0a_0$, $1.7a_0 \leq r_2 \leq 3.2a_0$, and $30^\circ \leq \alpha \leq 180^\circ$, with spacings between $0.1a_0$ and $0.5a_0$ for the bond lengths and between 5° and 10° for the bond angle. The two C-O bond lengths are r_1 and r_2 , and the O-C-O bond angle is α , with $\alpha = 180^\circ$ corresponding to linear carbon dioxide. The grid was extended to $r_1 = 10a_0$ using an exponential extrapolation described by Schmidt et al. (8). Points for which $r_2 > r_1$ were obtained by symmetry.

The transition dipole moments (TDMs) were calculated at the same level of theory on a small grid centered around the Franck–

Condon region. In the calculations of the TDMs of the $^1A''$ states B and C, the lowest $^1A'$ and three lowest $^1A''$ states were included in the CASSCF and MRCI calculations, whereas for the A state TDM, only the three lowest $^1A'$ states were taken into account.

To describe predissociation by transitions to the triplet states, spin-orbit (SO) coupling matrix elements $\langle ^1\Xi | H_{\text{SO}}^\xi | ^3\Xi(m_s) \rangle$ were determined, where H_{SO}^ξ ($\xi = x, y$, and z) are the Cartesian components of the SO operator, $m_s = 0, \pm 1$ is the spin projection quantum number, and $^1\Xi$ and $^3\Xi(m_s)$ are singlet and triplet electronic wave functions, respectively (9). The coupling elements were calculated at the CASSCF/d-aug-cc-pVTZ level of theory using the approach described by Berning et al. (10). The calculations were carried out on a grid covering the interaction region, with r_1 and r_2 varied from $2.0a_0$ to $4.5a_0$ with varying step sizes between $0.2a_0$ and $0.5a_0$ and α varied from 180° to 60° in steps of 10° .

The potential energies, TDM functions, and SO coupling elements between grid points were interpolated using 3D cubic splines. The different datasets can be obtained from one of the authors (J.A.S.) on request.

Calculated Cross-Sections

The calculated cross-sections for $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$, $^{12}\text{C}^{16}\text{O}^{17}\text{O}$, $^{12}\text{C}^{16}\text{O}^{18}\text{O}$, and $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ at temperatures between 120 K and 395 K are provided as ASCII files in [Datasets S1, S2, S3, S4, S5, and S6](#).

1. Werner H-J, et al. (2010) Molpro, version 2010.1, a package of ab initio programs. Available at www.molpro.net. Accessed June 6, 2013.
2. Werner H-J, Knowles PJ (1988) An efficient internally contracted multi-configuration reference configuration interaction method. *J Chem Phys* 89(9):5803–5814.
3. Knowles PJ, Werner H-J (1988) An efficient method for the evaluation of coupling coefficients in configuration interaction calculations. *Chem Phys Lett* 145(6):514–522.
4. Werner H-J, Knowles PJ (1985) A second order multi-configuration SCF procedure with optimum convergence. *J Chem Phys* 82(11):5053–5063.
5. Knowles PJ, Werner H-J (1985) An efficient second-order MC SCF method for long configuration expansions. *Chem Phys Lett* 115(3):259–267.
6. Langhoff SR, Davidson ER (1974) Configuration interaction calculations on the nitrogen molecule. *International Journal of Quantum Chemistry* 86(1):61–72.
7. Dunning TH, Jr. (1989) Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J Chem Phys* 90(2):1007–1023.
8. Schmidt JA, Johnson MS, McBane GC, Schinke R (2012) The ultraviolet spectrum of OCS from first principles: Electronic transitions, vibrational structure and temperature dependence. *J Chem Phys* 137(5):054313, 10.1063/1.4739756.
9. Schinke R, Schmidt JA, Johnson MS (2011) Photodissociation of N_2O : Triplet states and triplet channel. *J Chem Phys* 135(19):194303, 10.1063/1.3660349.
10. Berning A, Schweizer M, Werner H-J, Knowles PJ, Palmieri P (2000) Spin-orbit matrix elements for internally contracted multi-reference configuration interaction wave functions. *Mol Phys* 98(21):1823–1833, 10.1080/00268970009483386.

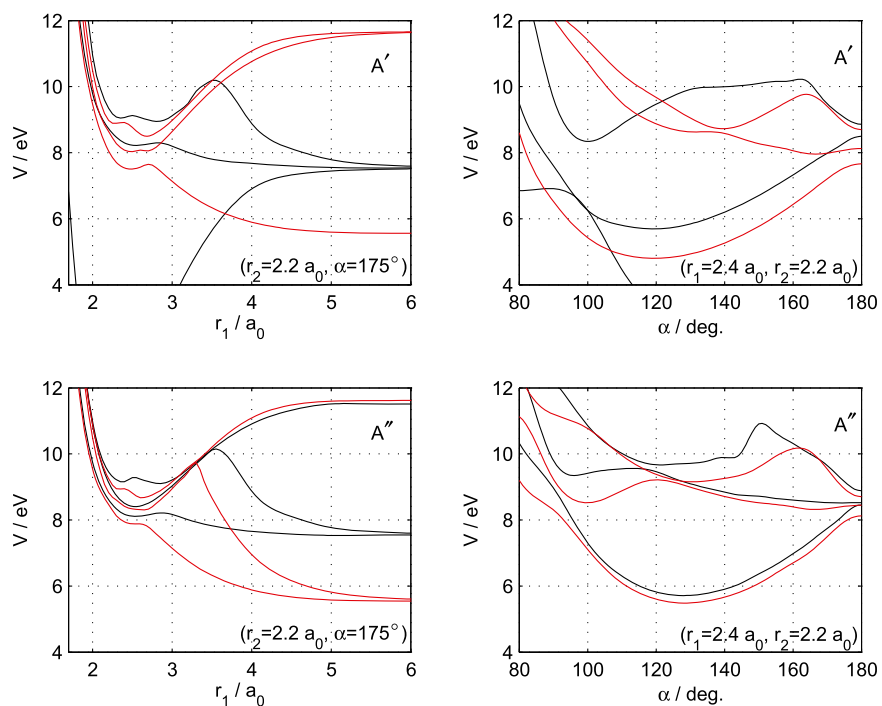


Fig. S1. (Upper Left) PESs for the $1-3^1A'$ states (black) and the $1-3^3A'$ states (red) along r_1 for $r_2 = 2.2a_0$ and $\alpha = 175^\circ$. (Lower Left) Same as in Upper Left but for states of A'' symmetry. (Right) Same as in Left but along the bending coordinate α for $r_1 = 2.4a_0$ and $r_2 = 2.2a_0$. In this figure and in what follows, energy is measured relative to the equilibrium of the X state. deg., degree; V, potential energy.

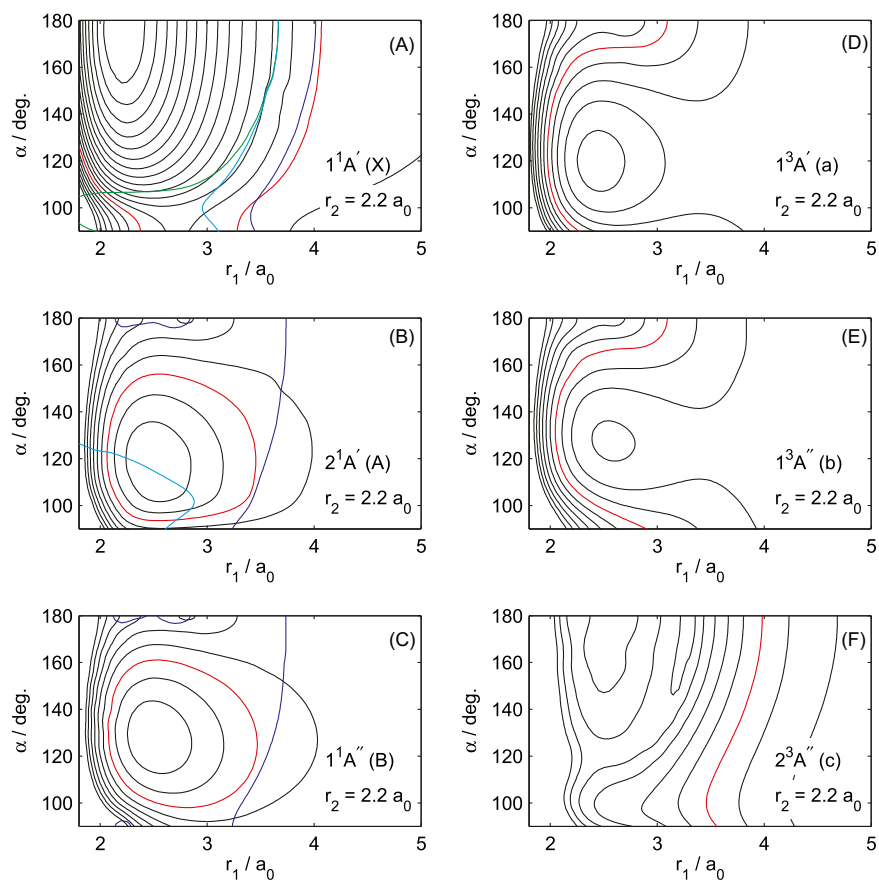


Fig. S2. 2D contour representations of the $1^1A'$ (X) state (A), $2^1A'$ (A) state (B), $1^1A''$ (B) state (C), $1^3A'$ (a) state (D), $1^3A''$ (b) state (E), and $2^3A''$ (c) state (F) for $r_2 = 2.2a_0$. The spacing between the contours is 0.5 eV, and the red contours represent 7.0 eV. The other colored curves mark the intersecting seam between the singlet states and the a (green), b (cyan), and c (blue) states, respectively.

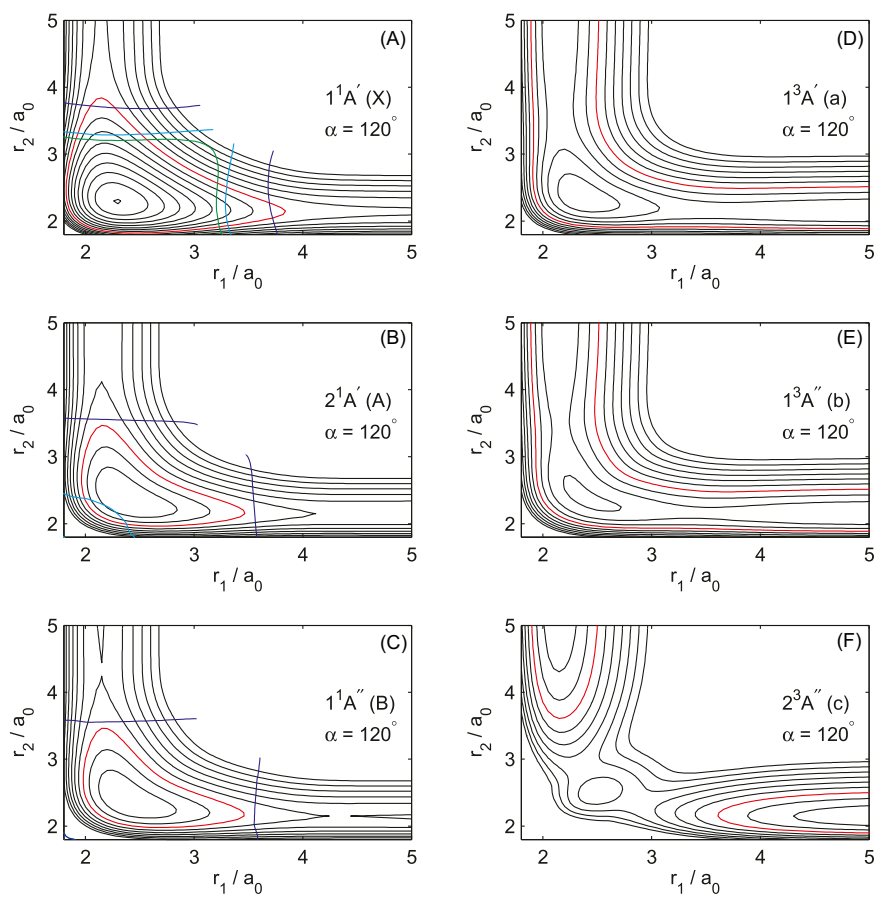


Fig. S3. 2D contour representations of the $1^1A'$ (X) state (A), $2^1A'$ (A) state (B), $1^1A'$ (B) state (C), $1^3A'$ (a) state (D), $1^3A''$ (b) state (E), and $2^3A''$ (c) state (F) for $\alpha = 120^\circ$. The spacing between the contours is 0.5 eV, and the red contours represent 7.0 eV. The other colored curves mark the intersecting seam between the singlet states and the a (green), b (cyan), and c (blue) states, respectively.

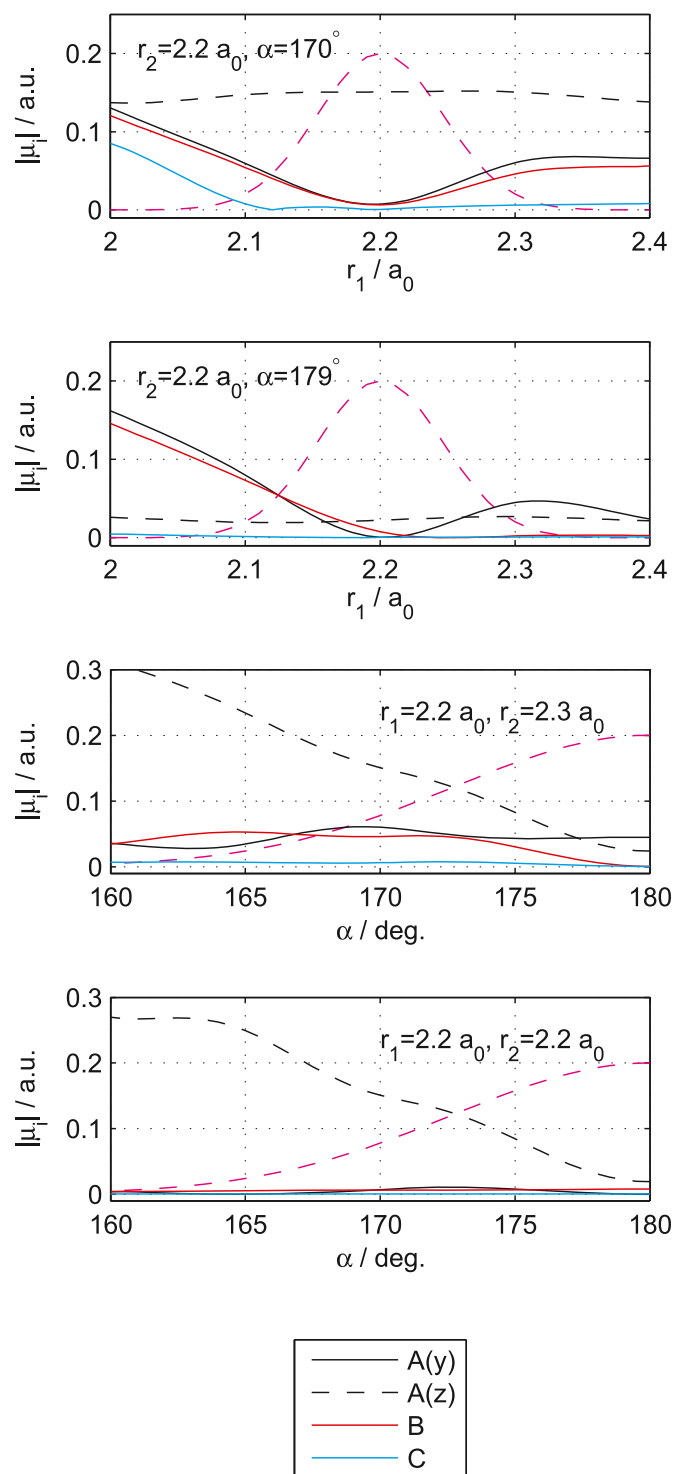


Fig. S4. Cuts along r_1 and α of the TDMs between the electronic ground state and the different excited states. The broken manganese line is a Gaussian with a FWHM identical to that of the ground state vibrational wave function. a.u., atomic units.

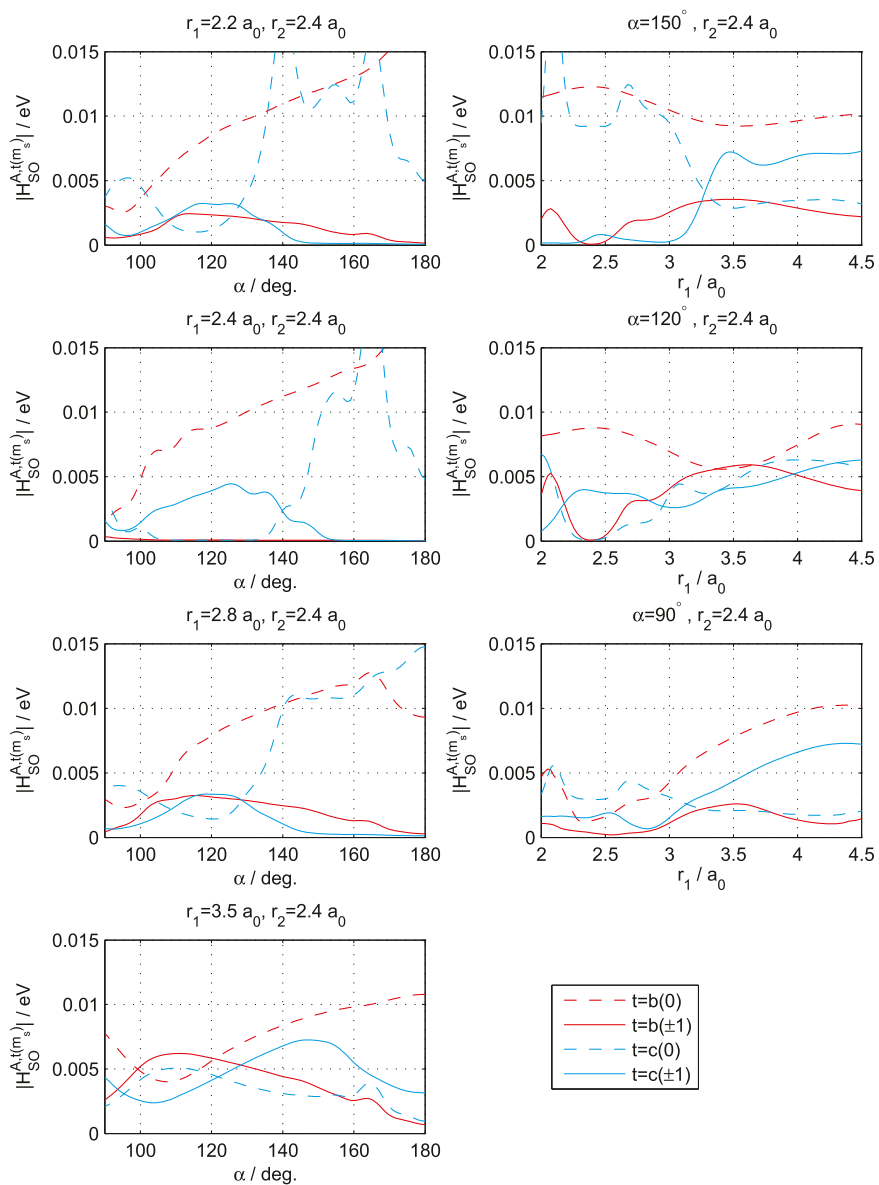


Fig. S5. Cuts along r_1 and α of the SO coupling elements between the A state and the b and c states.

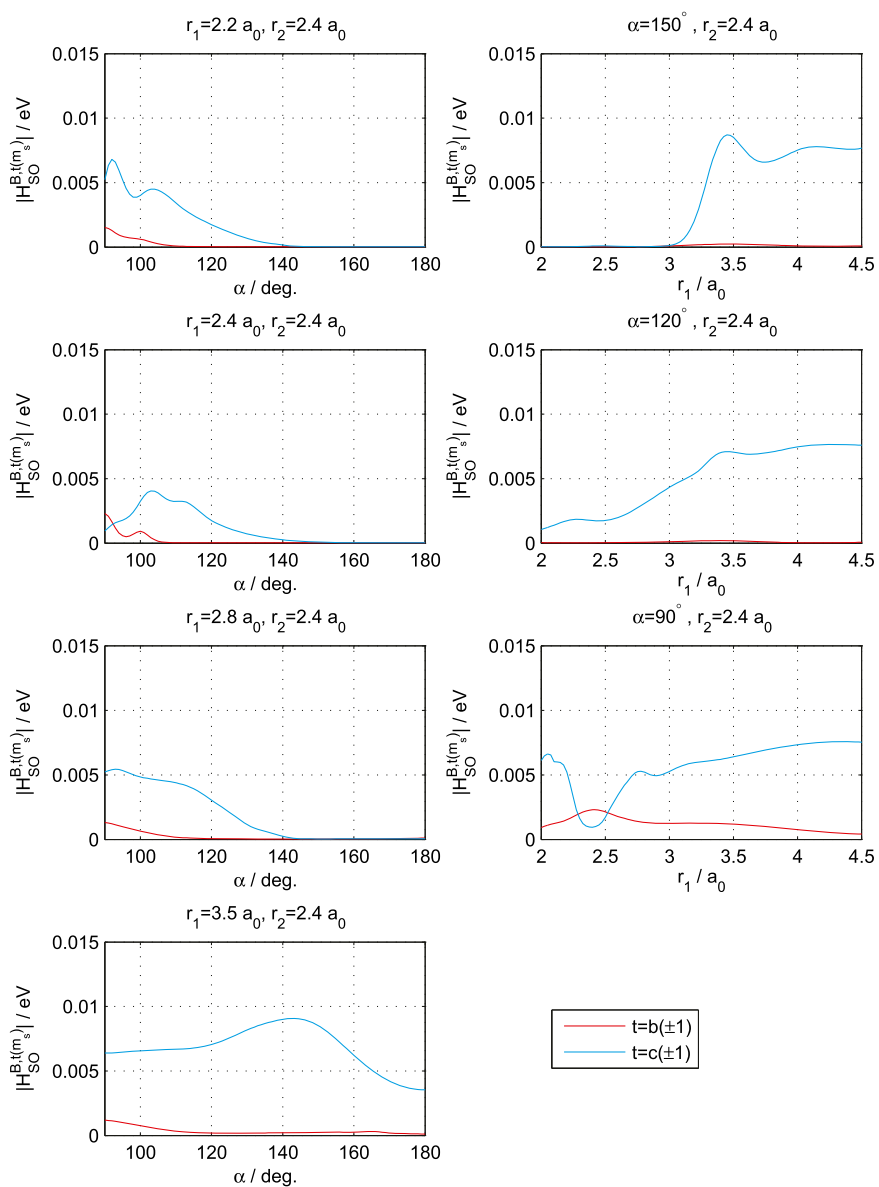


Fig. S6. Cuts along r_1 and α of the SO coupling elements between the B state and the b and c states.

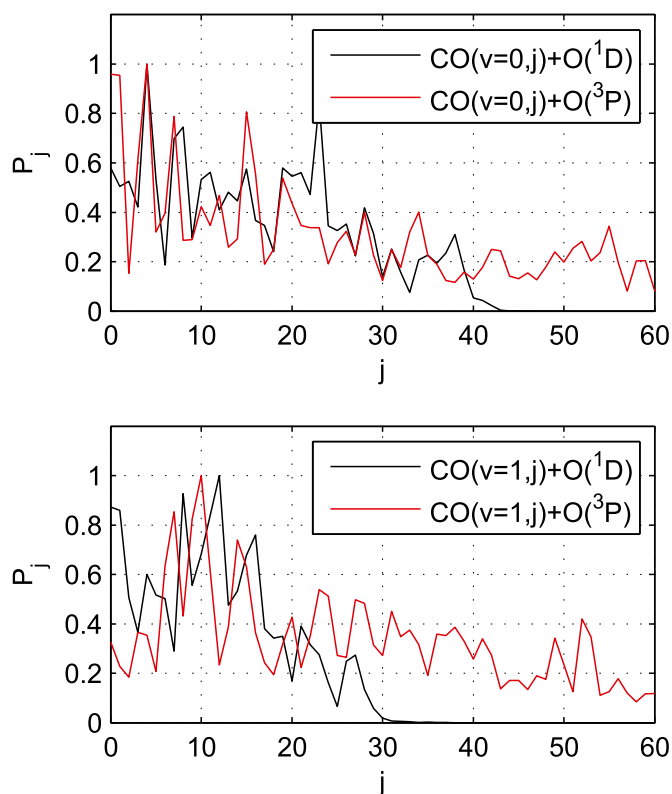


Fig. S7. Rotational distribution of carbon monoxide ($\text{CO}(v=0)$ and $\text{CO}(v=1)$) following dissociation of carbon dioxide at 157 nm in the singlet and triplet channels. P_i , product distribution.

Table S1. Overview of the electronic states

| Abbreviation | $D_{\infty h}$ | C_{2v} | C_s | Asymptotes | V_{vert} | V_{min} | r_{min} | α_{min} |
|--------------|-----------------|----------|----------|------------|-------------------|------------------|------------------|-----------------------|
| X | $1^1\Sigma_g^+$ | 1^1A_1 | $1^1A'$ | (II) | 0 | 0 | 2.197 | 180 |
| A | $1^1\Delta_u$ | 1^1B_2 | $2^1A'$ | (II) | 8.938 | 5.532 | 2.363 | 117.8 |
| B | $1^1\Delta_u$ | 1^1A_2 | $1^1A''$ | (II) | 8.950 | 5.528 | 2.370 | 127.2 |
| C | $1^1\Sigma_u^-$ | 2^1A_2 | $2^1A''$ | (II) | 9.142 | 8.136 | 2.410 | 174.1 |
| A | $3^3\Sigma_u^-$ | 1^3B_2 | $1^3A'$ | (I) | 8.228 | 4.642 | 2.355 | 117.5 |
| D | $3^3\Delta_u$ | 2^3B_2 | $2^3A'$ | (II) | 8.715 | 7.651 | 2.389 | 166.5 |
| B | $3^3\Delta_u$ | 1^3A_2 | $1^3A''$ | (III) | 8.713 | 5.329 | 2.370 | 127.4 |
| C | $3^3\Sigma_u^-$ | 2^3A_2 | $2^3A''$ | (I) | 8.799 | 7.995 | 2.402 | 166.3 |

Adiabatic asymptotes: (I) $\text{CO}(1^1\Sigma^+) + \text{O}(3P)$, (II) $\text{CO}(1^1\Sigma^+) + \text{O}(1D)$, and (III) $\text{CO}(3^1\Pi) + \text{O}(3P)$. All minima are in C_{2v} configurations. CO, carbon monoxide; V_{vert} , vertical excitation energy/eV; V_{min} , potential energy at minimum/eV; r_{min} , r coordinate at minimum/ a_0 ; α_{min} , angle coordinate at minimum of potential/degree.

Table S2. Calculated vibrational energies of the X state compared with experimental values

| Vibrational state | Calculated, cm^{-1} | Experimental, cm^{-1} |
|-----------------------|------------------------------|--------------------------------|
| Zero point energy | 2,518.00 | 2,484.65* |
| (0,0 ⁰ ,0) | 0.0 | 0.0 |
| (0,1 ¹ ,0) | 660.07 | 667.38 |
| (0,2 ⁰ ,0) | 1,375.92 | 1,388.18 |
| (0,2 ² ,0) | 1,322.37 | 1,335.13 |
| (0,3 ¹ ,0) | 2,058.14 | 2,076.84 |
| (0,3 ³ ,0) | 1,986.92 | 2,003.25 |
| (1,0 ⁰ ,0) | 1,272.71 | 1,285.41 |
| (0,0 ⁰ ,1) | 2,328.46 | 2,349.14 |
| (1,1 ¹ ,0) | 1,913.17 | 1,932.47 |

Experimental data are taken from a study by Rothman (1).

*Derived from the harmonic frequencies.

1. Rothman LS (1986) Infrared energy levels and intensities of carbon dioxide. Part 3. *Appl Opt* 25(11):1795–1816.

Other Supporting Information Files

[Dataset S1 \(TXT\)](#)

[Dataset S2 \(TXT\)](#)

[Dataset S3 \(TXT\)](#)

[Dataset S4 \(TXT\)](#)

[Dataset S5 \(TXT\)](#)

[Dataset S6 \(TXT\)](#)