Supporting Information for Negative Ion Photoelectron Spectroscopy Confirms the Prediction that *D*_{3h} Carbon Trioxide (CO₃) Has a Singlet Ground State

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Contents: Optimized geometries, electronic energies, zero-point vibrational energies, and imaginary frequencies for all of the CO₃ electronic states discussed in this manuscript, computed with the aug-cc-pVTZ basis set, using B3LYP, CCSD(T), and (16/13)CASPT2 calculations. Figure S1 contains the CCSD(T) simulation of the triplet region of the NIPE spectrum of $(CO)_3$ ⁻⁻ and the assignment of the vibrational progressions in it; Figure S2 shows the calculated NIPE spectrum, with the lines in the stick spectrum in Figure S1, convoluted with Gaussians; and Figure S3 shows how the appearance of the simulation in Figure 3 is modified by choosing a different value of the energy difference between the 0,0 bands in the two lowest energy triplet states. (9 pages).

Computational Results Obtained with the aug-cc-pVTZ Basis Set

²A₂' *D*_{3h} CO₃⁻⁻

| Calculation | r (C-O) (Å) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|-------------|---------------|----------------|----------------------------------------------|
| B3LYP | 1.271 | -263.9222805 | 0.011866 | none |
| CCSD(T) | 1.275 | -263.4670286 | 0.011895 | none |
| (16/13)CASPT2 | 1.275 | -263.43314103 | | |

¹A₁' *D*_{3h} CO₃

| Calculation | r (C-O) (Å) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|-------------|--------------|----------------|----------------------------------------------|
| B3LYP | 1.248 | -263.7367756 | 0.012555 | none |
| CCSD(T) | 1.260 | -263.3149962 | 0.009030 | <i>i</i> 472.8, <i>i</i> 471.8 |
| (16/13)CASPT2 | 1.262 | -263.2835297 | | |

¹A₁ Cyclic C_{2v} CO₃

| Calculation | r (C=O) (Å) r (C-O2,O3) (Å) O2-C-O3 (degs.) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|---------------------------------------------------|--------------|----------------|----------------------------------------------|
| B3LYP | 1.171 1.332 72.2° | -263.7581828 | 0.013798 | none |
| CCSD(T) | 1.177 1.335 74.9° | -263.3238361 | 0.013559 | none |
| (16/13)CASPT2 | 1.177 1.335 75.2° | -263.2870987 | | |

| Calculation | <i>r</i> (C-O1) (Å) <i>r</i> (C-O2,O3) (Å) O2-C-O3 (degs.) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|------------------------------------------------------------------|--------------|----------------|----------------------------------------------|
| B3LYP | 1.222 1.265 104.3° | -263.7357529 | 0.012145 | <i>i</i> 325.8 |
| CCSD(T) | 1.200 1.308 97.3° | -263.3125831 | 0.011440 | i588.2 |
| (16/13)CASPT2 | 1.201 1.304 96.3° | -263.2729976 | | |

 ${}^{1}A_{1}C_{2v}$ Transition Structure Connecting ${}^{1}A_{1}$ ' D_{3h} CO₃ with ${}^{1}A_{1}$ Cyclic C_{2v} CO₃

Triplet States at D_{3h} Geometries

${}^{3}E_{x}' ({}^{3}B_{2} in C_{2v})$

| Calculation | r (C-O) (Å) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|-------------|--------------|----------------|----------------------------------------------|
| B3LYP | 1.272 | -263.7383853 | | |
| CCSD(T) | 1.272 | -263.2846319 | | |
| (16/13)CASPT2 | 1.279 | -263.2439122 | | |

${}^{3}E_{y}'$ (${}^{3}A_{1}$ in C_{2v})

| Calculation | r (C-O) (Å) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|-------------|--------------|----------------|----------------------------------------------|
| B3LYP | 1.272 | -263.7382524 | | |
| CCSD(T) | 1.272 | -263.2854436 | | |
| (16/13)CASPT2 | 1.279 | -263.2456959 | | |

 ${}^{3}E_{x}$ " (${}^{3}A_{2}$ in C_{2v})

| Calculation | r (C-O) (Å) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|-------------|--------------|----------------|----------------------------------------------|
| B3LYP | 1.272 | -263.7351999 | | |
| CCSD(T) | 1.272 | -263.3939565 | | |
| (16/13)CASPT2 | 1.278 | -263.2515274 | | |

 ${}^{3}E_{y}''$ (${}^{3}B_{1}$ in C_{2v})

| Calculation | r (C-O) (Å) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|-------------|--------------|----------------|----------------------------------------------|
| B3LYP | 1.273 | -263.7377894 | | |
| CCSD(T) | 1.272 | -263.2839086 | | |
| (16/13)CASPT2 | 1.279 | -263.2513398 | | |

$^{3}A_{2}' (^{3}2B_{1} \text{ in } C_{2v})$

| Calculation | r (C-O) (Å) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|-------------|--------------|----------------|----------------------------------------------|
| B3LYP | 1.293 | -263.7181717 | 0.011599 | none |
| CCSD(T) | 1.295 | -263.2697866 | 0.011541 | none |
| (16/13)CASPT2 | 1.296 | -263.2262484 | | |

Triplet States at Geometries Optimized in C_{2v} Symmetry

${}^{3}B_{2}$

| Calculation | r (C-O1) (Å) r(C-O2,O3) (Å) O2-C-O3 (degs) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|--------------------------------------------------|--------------|----------------|----------------------------------------------|
| B3LYP | 1.266 1.276 130.7° | -263.7434042 | 0.0106683 | none |
| CCSD(T) | 1.246 1.294 127.0° | -263.2890362 | 0.008614 | i219.1, i58.5 |
| (16/13)CASPT2 | 1.285 1.274 133.0° | -263.2501237 | | |

³A₁

| Calculation | <i>r</i> (C-O1) (Å) <i>r</i> (C-O2,O3) (Å) O2-C-O3 (degs) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|-----------------------------------------------------------------|--------------|----------------|----------------------------------------------|
| B3LYP | 1.311 1.257 113.7° | -263.7424700 | 0.010196 | i361.6 |
| CCSD(T) | 1.321 1.259 113.7° | -263.2903079 | 0.011433 | none |
| (16/13)CASPT2 | 1.325 1.259 114.2° | -263.2503121 | | |

$^{3}A_{2}$

| Calculation | <i>r</i> (C-O1) (Å) <i>r</i> (C-O2,O3) (Å) O2-C-O3 (degs) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|-----------------------------------------------------------------|--------------|----------------|----------------------------------------------|
| B3LYP | 1.338 1.245 122.0° | -263.7383763 | 0.0105226 | none |
| CCSD(T) | 1.334 1.254 119.2° | -263.2866759 | 0.011428 | none |
| (16/13)CASPT2 | 1.315 1.267 119.7° | -263.2520151 | | |

${}^{3}B_{1}$

| Calculation | <i>r</i> (C-O1) (Å) <i>r</i> (C-O2,O3) (Å) O2-C-O3 (degs) | E (hartrees) | ZPE (hartrees) | imaginary frequencies (cm ⁻¹) |
|---------------|-----------------------------------------------------------------|--------------|----------------|----------------------------------------------|
| B3LYP | 1.274 1.273 120.8° | -263.7378196 | 0.0109566 | i680.3 |
| CCSD(T) | 1.294 1.272 123.0° | -263.2844714 | 0.007471 | i589.9, i509.5 |
| (16/13)CASPT2 | 1.246 1.296 117.5° | -263.2528141 | | |



Figure S1. (a) B3LYP/aug-cc-pVTZ simulated stick spectrum for the ${}^{1}A_{1}$ ' state and CCSD(T)/aug-cc-pVTZ simulated stick spectra for the ${}^{3}A_{1}$ and ${}^{3}A_{2}$ states, superimposed on the experimental spectrum. The 0-0 band for the ${}^{3}A_{2}$ state is aligned with the fourth peak in the ${}^{3}A_{1}$ band with *EBE* = 5.03 eV. Note that B3LYP, rather than CCSD(T), was used to simulate the vibrational structures for the singlet state, because, as discussed in the text, CCSD(T) gives imaginary frequencies for the D_{3h} singlet state, due to artifactural symmetry breaking. (b) Mode assignments for the simulated vibrational structures for each state in (a).



Figure S2. (a) Calculated vibrational structures for formation of the ¹A₁' state (B3LYP) and the ³A₁ and ³A₂ states (CCSD(T)) of CO₃ in the NIPE spectrum of CO₃⁻⁻, superimposed on the experimental NIPE spectrum (red). The positions of the bands in the calculated spectrum have been adjusted for both the singlet (grey) and triplet (blue and green), in order to align the 0,0 bands in the calculated spectrum with the 0,0 bands in the observed spectrum (the 0-0 band for the ³A₂ state is aligned with the fourth peak in the ³A₁ band with *EBE* = 5.03 eV). The spectrum spectrum for ¹A₁', (grey), ³A₁(blue), and ³A₂ (green), convoluted using Gaussian line shapes with 100, 60, and 60 meV full widths at half maxima for each stick is also shown. (b) Overall convoluted spectrum, contributed by the singlet and sum of the two triplets (grey) in (a), superimposed on the experimental 266 spectrum (red).



Figure S3. (a) B3LYP/ aug-cc-pVTZ calculated vibrational structure in the NIPE spectrum of CO_3 , superimposed on the experimental NIPE spectrum (red). The positions of the bands in the calculated stick spectrum for ${}^{1}A_{1}$ ' (grey), ${}^{3}A_{1}$ (blue), and ${}^{3}A_{2}$ (green) have been adjusted, in order to align the 0,0 bands in the calculated spectrum with the 0,0 bands in the observed spectrum. However, in contrast to the case to Figure 3 in the manuscript, the 0-0 peak of ${}^{3}A_{2}$ is aligned with the third peak in the A band with *EBE*

= 4.97 eV, instead of being aligned with the fourth peak with EBE = 5.03 eV in Figure 3. The calculated spectrum, using Gaussian line shapes with, respectively, 100, 60, and 60 meV full widths at half maxima for each stick in ¹A₁', ³A₁, and ³A₂, is also shown. (b) The computed NIPE spectrum (grey), calculated from the sum of the convoluted contributions of the singlet and two triplets in Figure S2a (with the same ratio of ³A₁ over ³A₂ contributions as in Figure 3 in the manuscript), superimposed on the experimental 266 spectrum (red). (c) The computed NIPE spectrum (grey), calculated from the sum of the singlet and two triplets on the experimental 266 spectrum (red). (c) The computed NIPE spectrum (grey), calculated from the sum of the sum of the convoluted contributions of the singlet and two triplets, but with the contribution from ³A₂ only one tenth of that in (b), superimposed on the experimental 266 spectrum (red).