Generation and Characterization of the C$_3$O$_2^-$ Anion with an Unexpected Unsymmetrical Structure

Lina Wang*, Sudip Pan*, Bo Lu, Xuelin Dong, Hongmin Li, Guohai Deng, Xiaqing Zeng, Mingfei Zhou,* and Gernot Frenking*

anie_202013921_sm_miscellaneous_information.pdf
Supporting Information

1. Experimental and computational details
2. Figures S1 – S5
3. Tables S1 – S2
Experimental and computational details

The 1064 nm fundamental of a Nd:YAG laser (Continuum, Minilite II, 10 Hz repetition rate and 6 ns pulse width) was used to ablate bulk metal targets to produce metal atoms and electrons, which were co-deposited with C$_3$O$_2$/Ne mixtures onto a CsI window at 4 K. Bulk metal targets including Be, Mg, Ca, B, Si, Ge, Sn, Pb, Sb, Bi, Fe, Co, Cu, Ag and Au were used. In general, matrix samples were deposited for 30 minutes at a rate of 4-8 mmol/h. The C$_3$O$_2$/Ne mixtures were prepared in a stainless steel vacuum line using standard manometric technique. After sample deposition, infrared spectra of the resulting samples were recorded on a Bruker V80 spectrometer at a 0.5 cm$^{-1}$ resolution between 4000 and 450 cm$^{-1}$ using a liquid nitrogen cooled broad band HgCdTe (MCT) detector. Bare mirror backgrounds, recorded prior to sample deposition were used as references in processing the sample spectra. The spectra were subjected to baseline correction to compensate for infrared light scattering and interference patterns. Samples were annealed to different temperatures and cooled back to 4 K for spectral acquisition. For selected samples, photo-excitations were performed through a quartz window mounted on the assembly.

Carbon suboxide was prepared according to literature by heating a mixture of malonic acid (107 mg, 1.03 mmol) and excessive P$_2$O$_5$ (1.057 g, 7.45 mmol) at 140 °C in a glass vessel (25 mL), which was connected to the dynamic vacuum line (0.1 pa) through a poly(tetrafluoroethylene) Young-valve. All the volatile products were condensed in a liquid nitrogen trap and then purified by fractional distillation through three successive cold U-traps at -120, -130, and -196 °C. Pure carbon suboxide (57 mg, 0.84 mmol) was retained in the middle trap as a white solid, and its quality was checked by gas-phase IR spectroscopy (Bruker, Tensor 27). $^{13}$C(CO)$_2$ was prepared using the $^{13}$C-labeled malonic acid (2-13C, 99.0%, Cambridge Isotope Laboratories, Inc.).

The geometries and vibrational spectra of the molecules were optimized at the CCSD(T)-Full/def2-TZVPPD level.$^{[1]}$ All structures are minima on the potential
energy surface. These calculations were carried out with Gaussian 16.[2] The NBO calculations were carried out with the version 6.0.[3]

The bonding situation of C₃O²⁻ was further analyzed by means of an energy decomposition analysis (EDA)[4] together with the natural orbitals for chemical valence (NOCV)[5] method by using the ADF 2018.105 program package.[6] The EDA-NOCV calculations[7] were carried out at the M06-2X/TZ2P level using the CCSD(T)-Full/def2-TZVPPD optimized geometries. TZ2P is a triple-ζ quality basis set augmented by two sets of polarization functions.[8] In this analysis, the intrinsic interaction energy (ΔE_{int}) between two fragments can be divided into three energy components as follows:

\[ ΔE_{\text{int}} = ΔE_{\text{elstat}} + ΔE_{\text{Pauli}} + ΔE_{\text{orb}} \]  

(1).

The electrostatic ΔE_{elstat} term represents the quasiclassical electrostatic interaction between the unperturbed charge distributions of the prepared fragments, the Pauli repulsion ΔE_{Pauli} corresponds to the energy change associated with the transformation from the superposition of the unperturbed electron densities of the isolated fragments to the wavefunction, which properly obeys the Pauli principle through explicit antisymmetrization and renormalization of the production wavefunction. The orbital term ΔE_{orb} is originated from the mixing of orbitals, charge transfer and polarization between the isolated fragments, which can be further decomposed into contributions from each irreducible representation of the point group of the interacting system as follows:

\[ ΔE_{\text{orb}} = \sum_r ΔE_r \]  

(2).

The combination of the EDA with NOCV[9] enables the partition of the total orbital interactions into pairwise contributions of the orbital interactions which is very vital to get a complete picture of the bonding. The charge deformation Δρ_{kl}(r), resulting from the mixing of the orbital pairs \( \psi_k(r) \) and \( \psi_l(r) \) of the interacting fragments presents the amount and the shape of the charge flow due to the orbital interactions (Equation 3), and the associated energy term ΔE_{orb} provides with the size of stabilizing orbital energy originated from such interaction (Equation 4).
Since we used a metahybrid functional, which has energy contributions that cannot be assigned to the three EDA terms, the calculations give a physically unspecified addition terms $\Delta E_{\text{Metahybrid}}$, which is rather small. More details about the EDA-NOCV method and its application are given in recent reviews articles\(^9\).

References

[1] a) G. D. Purvis III, R. J. Bartlett, \textit{J. Chem. Phys.} \textbf{1982}, 76, 1910; b) J. A. Pople, M. Head-Gordon, K. Raghavachari, \textit{J. Chem. Phys.} \textbf{1987}, 87, 5968; c) T. H. Dunning Jr., \textit{J. Chem. Phys.} \textbf{1989}, 90, 1007; d) R. A. Kendall, T. H. Dunning Jr., R. J. Harrison, \textit{J. Chem. Phys.} \textbf{1992}, 96, 6796; e) F. Weigend, R. Ahlrichs, \textit{Phys. Chem. Chem. Phys.}, \textbf{2005}, 7, 3297-305.

[2] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[3] E. D. Glendening, C. R. Landis, C.F. Weinhold, \textit{F. J. Comput. Chem.} \textbf{2013}, 34, 1429.

[4] T. Ziegler, A. Rauk, \textit{Theor. Chim. Acta} \textbf{1977}, 46, 1-10.

[5] a) M. Mitoraj, A. Michalak, \textit{Organometallics} \textbf{2007}, 26, 6576; b) M. Mitoraj, A. Michalak, \textit{J. Mol. Model.} \textbf{2008}, 14, 681.

[6] a) ADF2018, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The
Netherlands, http://www.scm.com; b) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S. J. A. Van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931.

[7] a) A. Michalak, M. Mitoraj, T. Ziegler, *J. Phys. Chem. A* **2008**, *112*, 1933; b) M. P. Mitoraj, A. Michalak, T. Ziegler, *J. Chem. Theory Comput.* **2009**, *5*, 962.

[8] E. van Lenthe, E. J. Baerends, *J. Comput. Chem.* **2003**, *24*, 1142.

[9] a) L. Zhao, M. von Hopffgarten, D. M. Andrada, G. Frenking, *WIREs Comput. Mol. Sci.*, **2018**, *8*, e1345; b) G. Frenking, F. M. Bickelhaupt, in *The Chemical Bond. Fundamental Aspects of Chemical Bonding*, G. Frenking and S. Shaik (Eds), Wiley-VCH, Weinheim, **2014**, p. 121-158; c) G. Frenking, R. Tonner, S. Klein, N. Takagi, T. Shimizu, A. Krapp, K. K. Pandey, P. Parameswaran, *Chem. Soc. Rev.* **2014**, *43*, 5106; e) L. Zhao, M. Hermann, N. Holzmann, G. Frenking, *Coord. Chem. Rev.* **2017**, *344*, 163; f) G. Frenking, M. Hermann, D. M. Andrada, N. Holzmann, *Chem. Soc. Rev.* **2016**, *45*, 1129; g) L. Zhao, M. Hermann, W.H.E. Schwarz, G. Frenking, *Nat. Rev. Chem.* **2019**, *3*, 48; h) L. Zhao, S. Pan, N. Holzmann, P. Schwerdtfeger, G. Frenking, *Chem. Rev.* **2019**, *119*, 8781.
**Figure S1.** IR difference spectra in the 2100-1700 cm\(^{-1}\) region from co-deposition of laser-ablated metal atoms and electrons with isotopic-labeled C\(_3\)O\(_2\) in excess neon (spectrum taken after 10 min of blue light irradiation minus spectrum taken after 30 min of sample deposition at 4K). (a) 0.05% \(^{12}\)C\(_3\)O\(_2\), (b) 0.05% \(^{13}\)C(\(^{12}\)CO)\(_2\), and (c) 0.05% \(^{12}\)C\(_3\)O\(_2\) + 0.05% \(^{13}\)C(\(^{12}\)CO)\(_2\).
**Figure S2.** IR difference spectra in the 1450-1250 and 950-750 cm\(^{-1}\) regions from co-deposition of laser-ablated metal atoms and electrons with isotopic-labeled C\(_3\)O\(_2\) in excess neon (spectrum taken after 10 min of blue light irradiation minus spectrum taken after 30 min of sample deposition at 4K). (a) 0.05% \(^{12}\)C\(_3\)O\(_2\), (b) 0.05% \(^{13}\)C\(^{(12}\)CO\(_2\))\(^-\), and (c) 0.05% \(^{12}\)C\(_3\)O\(_2\) + 0.05% \(^{13}\)C\(^{(12}\)CO\(_2\)).
**Figure S3.** Infrared absorption spectra in the 2150-1350 cm$^{-1}$ region from co-deposition of laser-ablated silver atoms and electrons with 0.05% C$_3$O$_2$ in neon with and without CCl$_4$ doping. (a) without CCl$_4$ doping, after 30 min of sample deposition at 4 K, (b) with 0.025% CCl$_4$ doping, after 30 min of sample deposition at 4 K.
Figure S4. Calculated equilibrium geometries E(CO)$_2$ and E(CO) (E = C$^-$, N, O$^+$) and free CO molecule at the CCSD(T)-Full/def2-TZVPPD level. Bond distances are in Å and bond angles are in degree. The bond dissociation energies are in kcal/mol. The partial natural charges on each atomic centre are given in square brackets.
\[ \Delta \rho \]

\[ \Delta E_{\text{orb}(1\alpha)} = -90.3; |v_{1\alpha}| = 0.45 \]

\[ \Delta \rho_{1\alpha} \]

\[ \Delta E_{\text{orb}(1\beta)} = -111.0; |v_{1\beta}| = 0.51 \]

\[ \Delta \rho_{1\beta} \]

\[ \Delta E_{\text{orb}(1)} = -201.3; |v_{1}| = 0.96 \]

\[ \Delta \rho_{1\alpha+1\beta} \]

\[ \Delta E_{\text{orb}(2)} = -40.9; |v_{2}| = 0.56 \]

\[ \Delta \rho_{2\alpha+2\beta} \]

[CO] (T)

SOMO (v_{1\alpha} = -0.29)

SOMO-1 (v_{1\alpha} = -0.20)

[CO] (T)

SOMO (v_{1\alpha} = 0.56)

SOMO-1 (v_{1\beta} = 0.57)

[C(CO)]\(^{-}\) (D)

SOMO (v_{1\alpha} = -0.03)

HOMO (v_{1\beta} = -0.32)

SOMO (v_{1\beta} = 0.56)

HOMO (v_{1\beta} = -0.20)

HOMO-1 (v_{3} = -0.26)
Figure S5. Plot of the deformation densities $\Delta \rho$ of the individual components of the $\alpha$ and $\beta$ electrons as well as the sum $\alpha+\beta$ and the connected most important fragment orbitals at the M06-2X/TZ2P//CCSD(T)-Full/def2-TZVPPD level, which are associated to the orbital interactions $\Delta E_{\text{orb}(1)} - \Delta E_{\text{orb}(3)}$ in $\text{C}_3\text{O}_2^-$ between the fragments ($^3\Pi$) CO and ($^2\Sigma$) CCO$^-$ as interacting moieties (Table 2). The orbital energy values are given in kcal/mol. The charge flow of the deformation densities is red→blue. The isosurface value is 0.001 au. Charge eigenvalues $|\nu|$ show the total electron movement.
Table S1. EDA-NOCV results at the M06-2X/TZ2P//CCSD(T)-Full/def2-TZVPPD level of $\text{C}_3\text{O}_2^-$ using the fragments CCO$^-$ and the distant CO group in different electronic states as interacting moieties. Energy values are given in kcal/mol.

| Energy       | $(^3\Sigma)\ \text{CO} + (^2\Pi)\ \text{CCO}^-$ | $(^3\Pi)\ \text{CO} + (^2\Pi)\ \text{CCO}^-$ | $(^1\Sigma)\ \text{CO} + (^2\Sigma)\ \text{CCO}^-$ | $(^1\Sigma)\ \text{CO} + (^2\Pi)\ \text{CCO}^-$ |
|--------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| $\Delta E_{\text{int}}$ | -230.7                                       | -171.7                                       | -93.7                                         | -58.0                                         |
| $\Delta E_{\text{Pauli}}$ | 258.6                                        | 706.6                                        | 477.1                                         | 624.6                                         |
| $\Delta E_{\text{Metahybrid}}$ | 6.1                                           | 12.4                                         | 11.1                                          | 13.6                                          |
| $\Delta E_{\text{elstat}}^{[a]}$ | -204.1 (41.2%)                                | -304.1 (34.1%)                               | -201.5 (34.6%)                                | -270.7 (38.9%)                                |
| $\Delta E_{\text{orb}}^{[a]}$ | -291.3 (58.8%)                                | -586.5 (65.9%)                               | -380.3 (65.4%)                                | -425.5 (61.1%)                                |

$^{[a]}$The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$. 
Table S2. The Cartesian coordinates of E(CO)$_2$ and E(CO) (E = C, N, O$^+$) at the CCSD(T)-full/def2-TZVPPD level.

| Structure                  | E (au)                  | C                  | O                  | N                  |
|----------------------------|-------------------------|--------------------|--------------------|--------------------|
| CsO$_2$ (Cs, 2A$'$)        | -264.4250819            |                    |                    |                    |
| E                           |                         | -1.275009000       | -0.266329000       | -0.000000000       |
| C                           | 1.241204000             | -0.020308000       | 0.000000000        |                    |
| O                           | -2.416152000            | 0.156474000        | -0.000000000       |                    |
| O                           | 2.441506000             | -0.140087000       | 0.000000000        |                    |
| C                           | 0.000000000             | 0.264787000        | -0.000000000       |                    |
| N(CO)$_2$ (Cs, 2A$'$)      | -281.0422076            |                    |                    |                    |
| E                           |                         | -1.169523000       | -0.329145000       | -0.000000000       |
| C                           | 1.159907000             | 0.035485000        | 0.000000000        |                    |
| O                           | -2.284464000            | 0.054657000        | -0.000000000       |                    |
| O                           | 2.291677000             | -0.217268000       | 0.000000000        |                    |
| N                           | 0.000000000             | 0.437550000        | 0.000000000        |                    |
| O(CO)$_2$ (Cs, 2A$'$)      | -301.1408031            |                    |                    |                    |
| E                           |                         | -1.181504000       | -0.694639000       | -0.000000000       |
| C                           | 1.185079000             | 0.388271000        | 0.000000000        |                    |
| O                           | -2.302426000            | -0.604605000       | -0.000000000       |                    |
| O                           | 2.299745000             | 0.173605000        | 0.000000000        |                    |
| O                           | -0.000000000            | 0.660775000        | -0.000000000       |                    |
| CCO$^-$ (Cs$_v$, 2^\Pi$)   | -151.1599856            |                    |                    |                    |
| E                           |                         | 0.000000000        | 0.000000000        | -1.403670000       |
| C                           | 0.000000000             | 0.000000000        | -0.097366000       |                    |
| O                           | 0.000000000             | 0.000000000        | 1.125777000        |                    |
| NCO (Cs$_v$, 2^\Pi$)       | -167.817456             |                    |                    |                    |
| E                           |                         | 0.000000000        | 0.000000000        | -1.269272000       |
| N                           | 0.000000000             | 0.000000000        | -0.038613000       |                    |
| C                           | 0.000000000             | 0.000000000        | 1.139573000        |                    |
| OC$^+$O (Cs$_v$, 2^\Pi$)   | -187.8917657            |                    |                    |                    |
| E                           |                         | 0.000000000        | 0.000000000        | -1.177329000       |
| O                           | 0.000000000             | 0.000000000        | -0.000183000       |                    |
| C                           | 0.000000000             | 0.000000000        | 1.177466000        |                    |
| O                           | 0.000000000             | 0.000000000        | -0.000183000       |                    |