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Supporting Information

Infrared Spectroscopy of $Be(CO_2)_4^+$ in the Gas Phase: Electron Transfer and C–C Coupling of CO_2

Yang Yang, Yangyu Zhou, Xiaoyang Jin, Guanjun Wang, Mingfei Zhou*

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysts and Innovative Materials, Fudan University, Shanghai 200438, China. Email: mfzhou@fudan.edu.cn

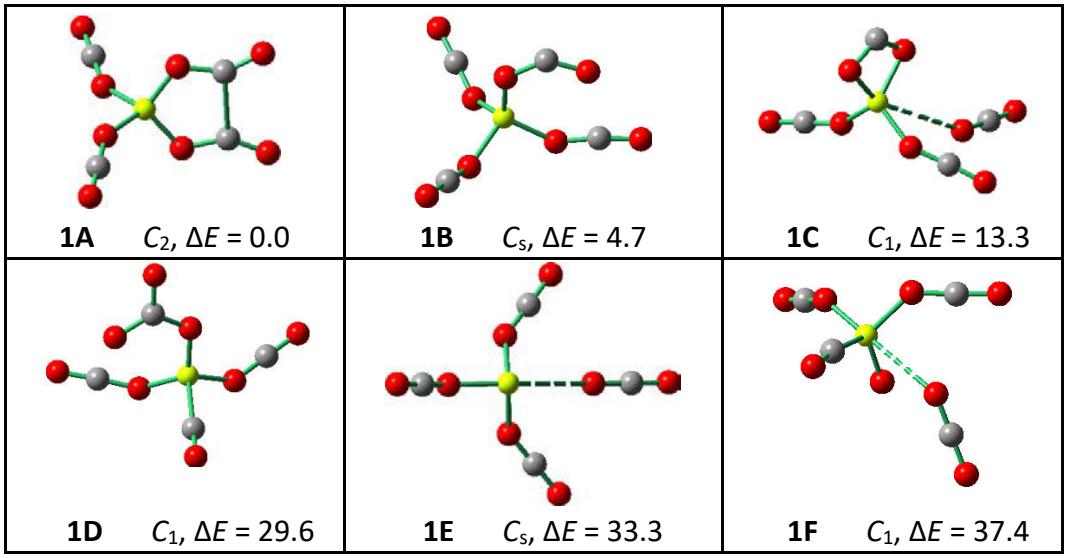


Fig. S1 Calculated geometries and relative energies (kcal mol^{-1}) of the $Be(CO_2)_4^+$ isomers in the doublet spin state at the B3LYP-D3/aug-cc-pVTZ level of theory.

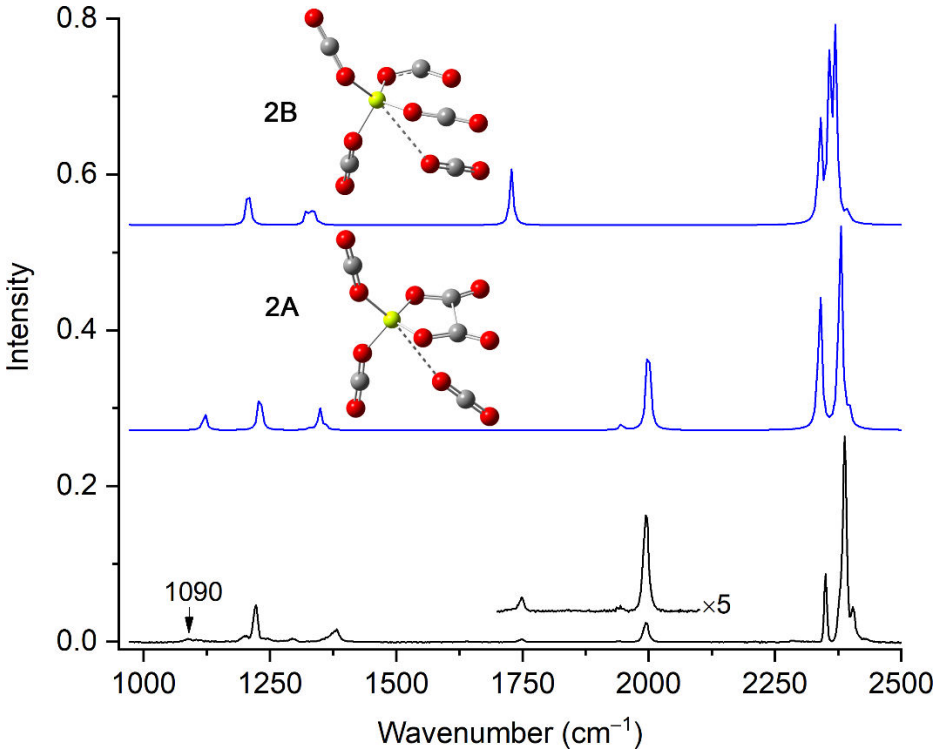


Fig. S2 Experimental infrared spectrum (black) and simulated vibrational spectra (blue) of $Be(CO_2)_5^+$ cation. The simulated spectra were obtained from scaled harmonic frequencies and intensities for the two lowest-lying structural isomers (**2A** and **2B**) calculated at the B3LYP-D3/aug-cc-pVTZ level.

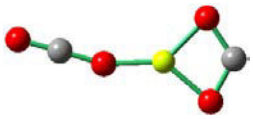
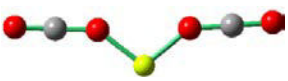
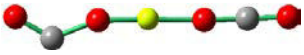
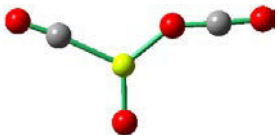
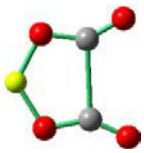
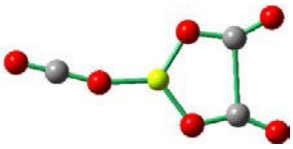
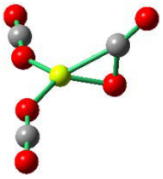
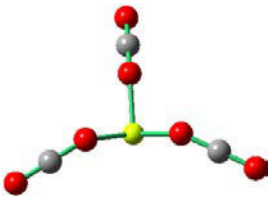
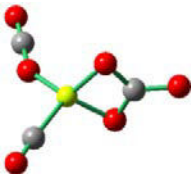
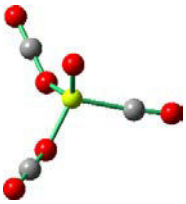
$BeCO_2^+$	 $C_{\infty v}$, ΔE = 0.0	 C_{2v}, ΔE = 6.0	 $C_{\infty v}$, ΔE = 7.6
$Be(CO_2)_2^+$	 C_s, ΔE = 0.0	 C_{2v}, ΔE = 7.1	 C_s, ΔE = 10.1
	 C_s, ΔE = 14.9	 C_{2v}, ΔE = 17.3	 C_{2v}, ΔE = 22.8
$Be(CO_2)_3^+$	 C_s, ΔE = 0.0	 C_{2v}, ΔE = 0.4	 C_s, ΔE = 5.7
	 C_{3v}, ΔE = 20.0	 C_s, ΔE = 22.0	 C_s, ΔE = 24.7

Fig. S3 Calculated geometries and relative energies (kcal mol^{-1}) of different isomers of $Be(CO_2)_n^+$ (n = 1-3) in the doublet spin state at the B3LYP-D3/aug-cc-pVTZ level of theory.

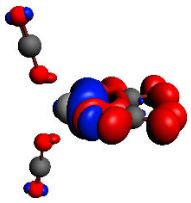
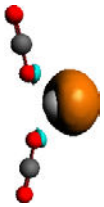
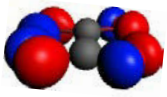
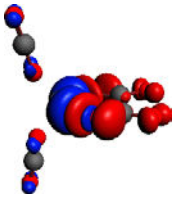
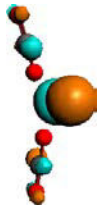
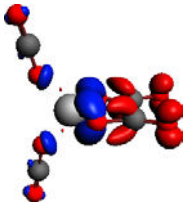
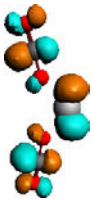
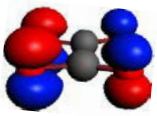
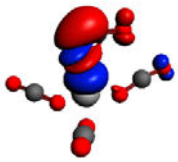
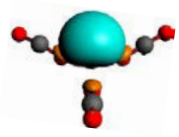
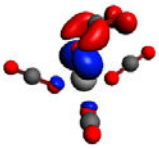
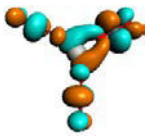
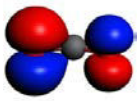
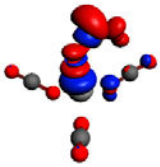
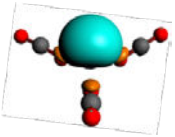
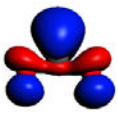
1A		
Deformation densities $\Delta\rho$	$[Be(CO_2)_2^{2+}]$ (S)	$[C_2O_4^{-}]$ (D)
		
$\Delta\rho_{(1)}$, $\Delta E_{orb(1)}$ = −45.6; $\lvert v_1 \rvert$ = 0.44	LUMO	HOMO-3
		
$\Delta\rho_{(2)}$, $\Delta E_{orb(2)}$ = −45.6; $\lvert v_2 \rvert$ = 0.40	LUMO+1	HOMO
		
$\Delta\rho_{(3)}$, $\Delta E_{orb(3)}$ = −19.4; $\lvert v_3 \rvert$ = 0.30	LUMO+2	HOMO-2
1B		
Deformation densities $\Delta\rho$	$[Be(CO_2)_3^{2+}]$ (S)	$[CO_2^{-}]$ (D)
		
$\Delta\rho_{(1)}$, $\Delta E_{orb(1)}$ = −41.2; $\lvert v_1 \rvert$ = 0.45	LUMO	HOMO
		
$\Delta\rho_{(2)}$, $\Delta E_{orb(2)}$ = −16.1; $\lvert v_2 \rvert$ = 0.28	LUMO+2	HOMO-1
		
$\Delta\rho_{(3)}$, $\Delta E_{orb(3)}$ = −15.7; $\lvert v_3 \rvert$ = 0.22	LUMO	SOMO

Fig. S4 Plot of deformation densities $\Delta\rho$ of the pairwise orbital interactions and the associated fragment orbitals at the BP86/TZ2P//B3LYP-D3/aug-cc-pVTZ level. Isosurface values are 0.002 a.u. The eigenvalues give the size of the charge migration in e. The direction of the charge flow of the deformation densities is red→blue.

Table S1 Calculated vibrational frequencies and intensities (km mol^{-1}) of the six lowest-lying $Be(CO_2)_4^+$ isomers at the B3LYP-D3/aug-cc-pVTZ level.

Isomer **1A**	Isomer **1B**	Isomer **1C**	Isomer **1D**	Isomer **1E**	Isomer **1F**
10.5 (0)	19.9 (2.5)	16.5 (0.3)	13.2 (3.2)	5.4 (0.2)	21.9 (0.1)
16.6 (0.4)	30.1 (0)	21.4 (0.4)	35.8 (0.2)	22.5 (0.4)	30.7 (0.1)
37.0 (2.6)	35.4 (0.5)	33.2 (0.3)	44.2 (1.8)	34.9 (0)	34.9 (0.1)
37.5 (0.1)	46.8 (1.3)	34.7 (0.5)	50.0 (0.3)	44.1 (0.3)	45.3 (0.4)
80.0 (0)	52.5 (1.0)	49.0 (0.6)	58.9 (0.8)	55.3 (0.4)	58.0 (2.9)
88.6 (0.6)	63.5 (0.3)	55.2 (3.0)	94.8 (5.9)	64.3 (0.5)	63.6 (0.6)
167.7 (0)	125.4 (15.1)	86.4 (0.7)	111.1 (1.6)	68.0 (0)	75.3 (1.0)
172.5 (0.1)	166.8 (3.2)	89.7 (0.9)	120.8 (2.5)	71.2 (3.4)	84.3 (7.4)
179.6 (0.4)	169.0 (0.1)	101.2 (4.9)	154.9 (6.9)	92.3 (0)	100.1 (12.6)
208.8 (2.4)	194.9 (5.8)	165.9 (0.4)	191.4 (1.0)	98.6 (0.5)	119.5 (3.1)
263.0 (0.8)	210.5 (1.1)	180.9 (2.9)	228.4 (7.0)	106.7 (0.5)	133.7 (1.0)
275.1 (0.1)	217.9 (0.8)	194.0 (5.6)	240.7 (7.2)	173.7 (0.7)	173.7 (0.3)
353.4 (1.6)	254.6 (4.3)	265.5 (7.0)	318.5 (5.2)	191.2 (1.1)	226.6 (11.3)
419.0 (0.5)	289.7 (1.3)	334.1 (0.4)	335.7 (5.4)	218.2 (0.9)	234.9 (20.5)
446.7 (4.8)	378.2 (5.8)	398.3 (0.2)	356.2 (6.0)	445.5 (25.3)	321.5 (3.3)
523.2 (79.5)	539.3 (105.1)	473.1 (21.7)	474.9 (54.9)	490.4 (125.9)	337.5 (13.5)
582.1 (450.3)	559.1 (377.4)	623.5 (53.8)	548.9 (128.7)	499.8 (250.4)	391.2 (8.7)
630.9 (6.1)	629.7 (18.5)	630.3 (29.0)	580.1 (148.2)	583.7 (28.2)	540.3 (192.8)
632.1 (60.2)	636.9 (43.6)	636.6 (100.7)	635.4 (3.1)	584.9 (27.0)	547.1 (368.2)
642.2 (4.6)	637.9 (49.7)	648.2 (27.9)	639.7 (72.5)	590.9 (24.8)	636.5 (13.6)
645.8 (0.3)	644.2 (245.3)	665.7 (28.9)	646.8 (184.2)	615.3 (0)	640.0 (69.7)
650.8 (22.9)	660.1 (36.1)	669.8 (6.7)	654.5 (25.8)	618.6 (91.2)	661.1 (21.8)
689.5 (172.8)	663.8 (149.2)	690.6 (374.1)	683.1 (167.3)	622.6 (52.3)	662.2 (71.9)
841.2 (336.1)	744.9 (78.2)	845.5 (423.0)	792.1 (40.7)	666.9 (28.3)	664.3 (58.5)
928.4 (299.8)	964.3 (211.7)	880.1 (1.1)	932.8 (52.8)	672.6 (27.6)	670.1 (37.7)
1145.9 (122.1)	1230.1 (305.7)	1370.9 (16.0)	1111.2 (284.9)	1367.7 (16.2)	1079.6 (153.4)
1261.9 (320.2)	1356.7 (127.2)	1386.7 (171.6)	1295.1 (26.5)	1371.7 (39.4)	1366.8 (23.2)
1388.9 (152.3)	1374.5 (122.0)	1390.1 (59.4)	1359.3 (100.6)	1372.1 (74.2)	1368.1 (109.0)
1400.8 (30.5)	1387.0 (15.1)	1405.4 (1.8)	1375.2 (71.5)	1385.3 (4.3)	1379.5 (46.8)
2008.4 (44.7)	1784.2 (412.3)	1516.8 (454.2)	1530.3 (447.9)	2406.1 (1176.0)	2319.5 (75.2)
2063.8 (797.8)	2424.5 (1114.9)	2410.1 (875.8)	2331.9 (49.0)	2428.9 (1188.7)	2404.2 (871.4)
2450.4 (1638.5)	2438.7 (1236.8)	2451.2 (1470.1)	2435.0 (1263.5)	2434.7 (1739.1)	2434.0 (1280.5)
2469.3 (166.8)	2464.4 (114.7)	2469.5 (180.9)	2454.3 (312.8)	2464.1 (45.6)	2453.9 (368.2)

Table S2 Charge analysis of $Be(CO_2)_4^+$ with Mulliken, Hirshfeld, and VDD along with NPA and AIM charge analysis at the B3LYP/aug-cc-pVTZ level.

	Mulliken	Hirshfeld	VDD	NPA	AIM
Isomer **1A**					
Be	1.30	0.30	0.22	1.10	1.74
C_2O_4	–0.36	0.01	0.05	–0.47	–0.84
CO_2	0.06	0.70	0.73	0.37	0.08
Isomer **1B**					
Be	1.35	0.30	0.23	1.11	1.74
bent CO_2	–0.37	0.02	0.06	–0.64	–0.83
CO_2	0.02	0.68	0.72	0.53	0.10

Table S3 Coordinates (in Å) and total energies (in Hartree) of the calculated species at the B3LYP-D3/aug-cc-pVTZ level.

$Be(CO_2)_4^+$, Isomer **1A**, E = –769.189579

Be	0.00000000	0.00000000	0.37790300
O	0.00000000	1.30167200	1.45762500
O	0.00000000	-1.30167200	1.45762500
C	0.28322300	2.42394900	1.68775600
O	0.54200200	3.50335500	1.93780700
C	-0.28322300	-2.42394900	1.68775600
O	-0.54200200	-3.50335500	1.93780700
C	-1.03755400	-0.01047500	-1.79832400
O	-1.54119600	-0.01399400	-2.84765200
C	1.03755400	0.01047500	-1.79832400
O	1.54119600	0.01399400	-2.84765200
O	-1.26418000	-0.01629000	-0.55932900
O	1.26418000	0.01629000	-0.55932900

$Be(CO_2)_4^+$, Isomer **1B**, E = –769.1812763

C	-0.61711900	-2.42337400	0.00000000
C	1.20064500	1.16685100	2.30843500
C	1.20064500	1.16685100	-2.30843500
O	0.18142000	-1.53873000	0.00000000
O	-1.24311900	-3.37101800	0.00000000
O	1.23614400	0.50957100	1.32590100
O	1.20064500	1.78767200	3.26157700

O	1.23614400	0.50957100	-1.32590100
O	1.20064500	1.78767200	-3.26157700
C	-2.23615300	0.33883200	0.00000000
O	-2.54028200	-0.81640300	0.00000000
O	-1.05326200	0.88843400	0.00000000
Be	0.24130300	0.11272100	0.00000000

$Be(CO_2)_5^+$, Isomer **2A**, E = –957.866950

Be	-1.03661000	0.31979000	0.00000000
O	-0.44535000	1.89746300	0.00001200
O	-2.70260300	0.62251900	-0.00000100
C	0.50329200	2.59866100	-0.00000100
O	1.38374400	3.31961800	-0.00001300
C	-3.80148800	0.19405900	0.00000500
O	-4.87308100	-0.18961600	0.00001100
C	0.11540800	-1.51931500	-1.03184300
O	0.71831600	-2.38176300	-1.53267300
C	0.11540300	-1.51932800	1.03182600
O	0.71830800	-2.38178300	1.53264700
O	-0.58626500	-0.50231600	-1.26524300
O	-0.58627300	-0.50233300	1.26523400
C	3.35028800	0.05021700	0.00001300
O	2.21398400	0.33387900	0.00000900
O	4.46534800	-0.22878300	0.00001700

$Be(CO_2)_5^+$, Isomer **2B**, E = –957.858800

C	0.56231000	-1.70611500	-1.28674000
C	0.19380800	2.51806900	-0.38153500
C	-3.69687600	-0.10686400	0.06054500
O	-0.35324500	-0.95089500	-1.22297300
O	1.40801200	-2.43690600	-1.49232200
O	-0.56443700	1.65761900	-0.66715000
O	0.89624900	3.37812800	-0.13439000
O	-2.67405000	0.08964000	-0.49910700
O	-4.69969300	-0.29008800	0.56569500
C	0.05996000	-0.99960400	1.83315700
O	0.79129100	-1.76189100	1.27261200
O	-0.77029000	-0.12625800	1.34130100
Be	-1.00951100	0.11098000	-0.13105000
C	3.14503400	0.21809500	0.27111300
O	4.11475900	-0.06875900	0.81694500
O	2.15798400	0.51123400	-0.28749200