Electronic Supplementary Information (ESI)

The $HKrCCH\cdots CO_2$ complex: an *ab initio* and matrix-isolation study

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Table S1. Contraction scheme of the augmented correlation consistent valence basis set L2a_3 as compared to the aug-cc-pVTZ basis set.

Basis set	Kr atom contraction scheme	C, O atoms contraction scheme	H atom contraction scheme
L2a_3	{7s,6p,4d,2f}/{26s,21p,14d,4f}	{5s,4p,3d,2f}/{17s,11p,6d,4f}	{4s,3p,2d}/{11s,6p,4d}
aug-cc-pVTZ	{7s,6p,4d,2f}/{21s,14p,10d,2f}	{5s,4p,3d,2f}/{11s,6p,3d,2f}	{4s,3p,2d}/{6s,3p,2d}

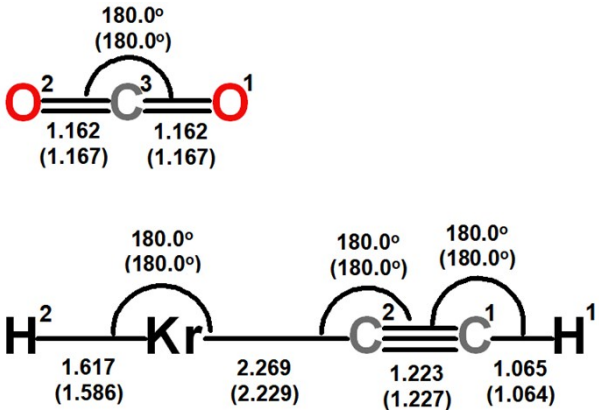

Fig. S1. Structures of the CO_2 and HKrCCH molecules obtained at the CCSD(T)/L2a_3 level of theory (the structural parameters obtained at the MP2/L2a_3 level of theory are shown in parentheses). The distances are in Å.

Table S2. Cartesian atomic coordinates, dipole moments, and total energies for the HKrCCH and CO_2 monomers and HKrCCH···CO_2 complexes (computed at the CCSD(T)/L2a_3 and MP2/L2a_3 level of theory).

MP2/L2a_3 computations				
HKrCCH monomer ($C_{\infty v}$ symmetry)				
Cartesian atomic coordinates, Å	1	0.00000000	0.00000000	2.79597777
	6	0.00000000	0.00000000	1.73190866
	6	0.00000000	0.00000000	0.50539413
	36	0.00000000	0.00000000	–1.72355311
	1	0.00000000	0.00000000	–3.30972746
Dipole moment, D	3.054325			
E, hartree	–2865.937215			
E_0, hartree[a]	–2865.912993			

CO_2 monomer ($D_{\infty h}$ symmetry)	
Cartesian atomic coordinates, Å	6 0.00000000 0.00000000 0.00000000 8 0.00000000 0.00000000 1.16683831 8 0.00000000 0.00000000 –1.16683831
Dipole moment, D	0.000000
E, hartree	–188.479478
E_0, hartree[a]	–188.467916
HKrCCH···CO_2 complex (C_s symmetry)	
Cartesian atomic coordinates, Å	1 –1.93561701 –1.97201522 0.00000000 6 –1.59283129 –0.96418152 0.00000000 6 –1.20138234 0.19982002 0.00000000 36 –0.39941809 2.29290951 0.00000000 1 0.17428014 3.75632408 0.00000000 6 1.64100010 –1.10303859 0.00000000 8 1.38507819 –2.23926860 0.00000000 8 1.92889029 0.02945032 0.00000000
Dipole moment, D	3.210245
E, hartree	–3054.423895
E_0, hartree[a]	–3054.388159
CCSD(T)/L2a_3 computations	
HKrCCH monomer ($C_{\infty v}$ symmetry)	
Cartesian atomic coordinates, Å	1 0.00000000 0.00000000 –2.81673797 6 0.00000000 0.00000000 –1.75129387 6 0.00000000 0.00000000 –0.52878262 36 0.00000000 0.00000000 1.73994058 1 0.00000000 0.00000000 3.35687389
Dipole moment, D	3.062463
E, hartree	–2865.987526
E_0, hartree[a]	–2865.964920

CO_2 monomer ($D_{\infty h}$ symmetry)	
Cartesian atomic coordinates, Å	6 0.00000000 0.00000000 0.00000000 8 0.00000000 0.00000000 1.16352534 8 0.00000000 0.00000000 –1.16352534
Dipole moment, D	0.000000
E, hartree	−188.497934
E_0, hartree[a]	−188.486374
HKrCCH···CO_2 complex (C_s symmetry)	
Cartesian atomic coordinates, Å	1 –1.96887262 1.95863874 0.00000000 6 –0.95900414 1.61739708 0.00000000 6 0.20317647 1.23419505 0.00000000 36 2.32228773 0.39279738 0.00000000 1 3.80276685 –0.21099262 0.00000000 6 –1.13191438 –1.65163321 0.00000000 8 –2.26580271 –1.40002656 0.00000000 8 –0.00263719 –1.94037586. 0.00000000
Dipole moment, D	3.247826
E, hartree	–3054.492058
E_0, hartree[a]	–3054.457080

[a] ZPVE corrected value

Table S3. Effect of BSSE and ZPVE corrections on the interaction energies in the HKrCCH···CO_2 complex.

Level of theory	Interaction energies, kcal mol^{-1}			
	No corrections	BSSE corrected	ZPVE corrected	ZPVE and BSSE corrected
MP2/L2a_3	–4.52	–3.95	–4.55	–3.98
CCSD(T)/L2a_3	–4.14	–3.67	–3.63	–3.16

Table S4. Effective minimal basis set (EMBS) and Generalized Atomic Polar Tensor (GAPT) charges for the HKrCCH···CO_2 complex as computed at the MP2/L2a_3 and CCSD(T)/L2a_3 levels of theory. Corresponding values for the HKrCCH and CO_2 monomers are given in parentheses.

Atom[a]	MP2/L2a_3		CCSD(T)/L2a_3	
	EMBS charges	GAPT charges	EMBS charges	GAPT charges
H^1	0.142 (0.139)	0.189 (0.188)	0.146 (0.144)	0.184 (0.181)
C^1	–0.164 (–0.148)	–0.477 (–0.479)	–0.169 (–0.153)	–0.505 (–0.507)
C^2	–0.673 (–0.659)	–0.480 (–0.464)	–0.655 (–0.641)	–0.344 (–0.321)
Kr	0.876 (0.870)	1.246 (1.232)	0.858 (0.850)	1.152 (1.126)
H^2	–0.183 (–0.202)	–0.453 (–0.475)	–0.181 (–0.199)	–0.464 (–0.479)
C^3	0.759 (0.732)	1.002 (1.061)	0.778 (0.752)	1.059 (1.131)
O^1	–0.358 (–0.366)	–0.489 (–0.531)	–0.368 (–0.376)	–0.521 (–0.566)
O^2	–0.400 (–0.366)	–0.537 (–0.531)	–0.409 (–0.376)	–0.561 (–0.566)

[a] See Fig. S1 for atom labeling

Table S5. Calculated harmonic frequencies (cm^{-1}) and IR intensities (km/mol, in parentheses) of the HKrCCH···CO_2 complex and the corresponding values of HKrCCH and CO_2 monomers computed at the MP2/L2a_3 level of theory.

Complex	Assignment	Monomers
3453.0 (36.4)	C–H str.	3637.7 (9.0)
2415.1 (474.1)	CO_2 antisymm. str.	2413.3 (583.4)
1947.8 (6.6)	C≡C str.	2182.3 (24.4)
1636.0 (2040.7)	H–Kr str.	1563.3 (2197.5)
1332.7 (0.4)	CO_2 sym. str.	1329.6 (0.0)
715.4 (0.5)	in-plane bend. HKrC	714.4 (1.3)
713.8 (0.7)	out-of-plane bend. HKrC	714.4 (1.3)
666.0 (23.7)	out-of-plane bend. CO_2	666.0 (22.6)
651.0 (34.5)	out-of-plane bend. HCC	646.1 (40.5)
648.4 (63.0)	in-plane bend. HCC	646.1 (40.5)
643.6 (25.6)	in-plane bend. (CO_2 + HCC)	666.0 (22.6)
322.4 (184.5)	C–Kr str.	303.2 (163.1)
151.2 (20.2)	in-plane bend. KrCC	112.5 (17.1)
115.2 (17.4)	out-of-plane bend. KrCC	112.5 (17.1)
97.4 (3.2)	Intermol. vibr.	–
91.4 (0.1)	Intermol. vibr.	–
53.3 (1.5)	Intermol. vibr.	–
32.8 (0.4)	Intermol. vibr.	–