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Electronic Supplementary Information

Reactions of the radiation-induced electrons with carbon dioxide in inert cryogenic films: matrix tuning of the excess electron interactions in solids

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Table S1. Absorption maxima (wavenumber, cm^{-1}) observed after deposition of different inert matrices doped with CO$_2$. The bands assigned to dimer are in italics.

	Ne	**Ar**	**Xe**	**N$_2$**	**Literature data**		
					Ne^a	**Ar^{b,c}**	**N$_2$^{b}**
			^{12}CO$_2$				
$\upsilon_1+\upsilon_3$		3708.0–3700.4	3697.4–3692.0			3706.8–3699.5	3714.5–3711.6
$2\upsilon_2+\upsilon_3$		3602.6–3597.4	3592.7–3587.9			3602.9–3596.9	3609.1–3607.0
υ_3	2347.8	2345.5	2336.0		2347.6	*2347.7* 2345.0 2344.8 *2342.0* 2340.2 2339.0 *2239.9* 2339.1	2349.0 *2351.1* *2349.2*
υ_2	667.8 664.6	663.2 654.9	659.2		668.2 667.2	*664.4* 663.8 663.7 663.5 663.4 661.9 *659.9*	662.3
			^{13}CO$_2$				
$\upsilon_1+\upsilon_3$	3631.5–3628.7	3627.6–3618.7	3616.0–3613.0	3632.6		3626.9–3618.4	3632.2
$2\upsilon_2+\upsilon_3$	3526.6–3524.1 *3510.1*	3515.9–3511.4	3503.7–3503.5	3520.5		3515.8–3511.9	3520.3
υ_3	2281.8 2272.8 2264.6 *2276.8* *2261.0*	2279.6 2274.3 2268.5 2262.1 2256.4	2271.7 2269.3 2254.4 2252.0	2283.2 2273.9 2265.7	2281.8	*2282.0* 2279.2 2278.5 *2276.5* 2274.7 *2274.5* 2273.7 2273.6	2283.1 *2285.2* *2282.3*
υ_2	648.9	644.2	642.7	643.5	649.1	*645.5*	643.5

641.0	638.4	640.6		648.7	645.0	
636.0		637.2			644.8	
					644.6	
					644.5	
					643.2	
						641.2

Taken from: [a] M. Zhou and L. Andrews, *J. Chem. Phys.*, 1999, **110**, 6820–6826.
[b] M. Zhou and L. Andrews, *J. Chem. Phys.*, 1999, **110**, 2414–2422.
[c] A.Schriver, L. Schriver-Mazzuoli and A. A. Vigasin, *Vib. Spectrosc.*, 2000, **23**, 83–94.

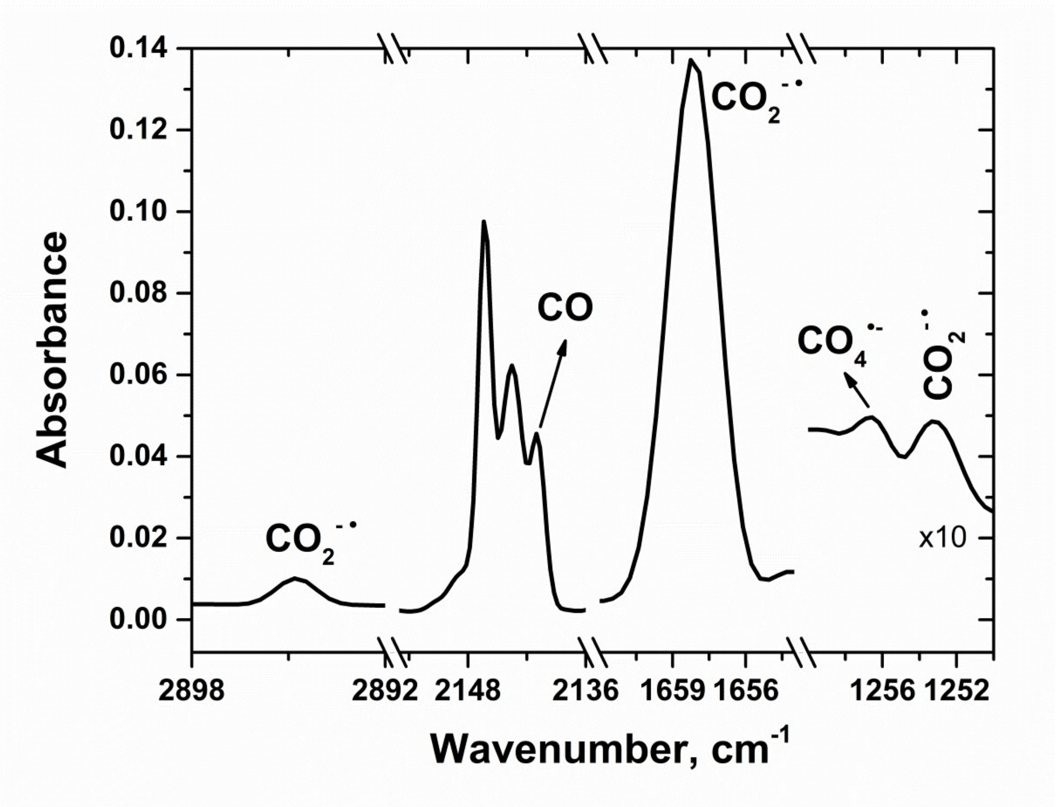

Figure S1. Fragments of difference FTIR spectrum of $^{12}CO_2$/Ne (1/1000) sample showing the effect of the irradiation with X-rays to the absorbed dose of 9.7 kGy.

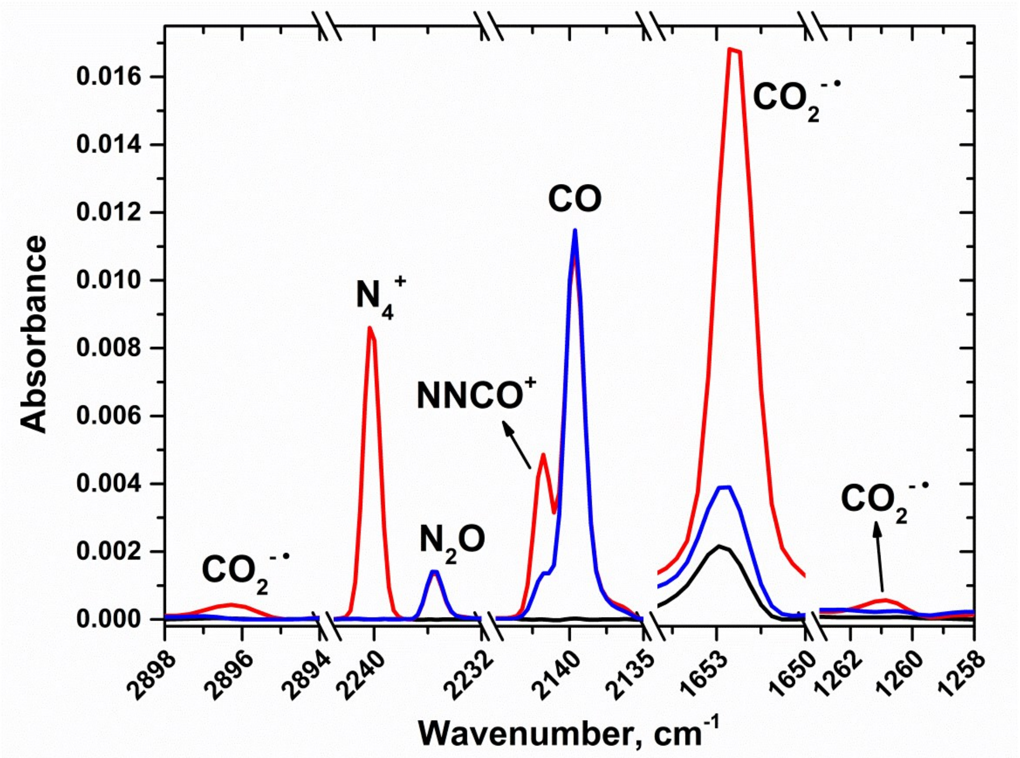

Figure S2. Fragments of FTIR spectra of $^{12}CO_2/N_2$ (1/1000) system after deposition (black line), irradiation with X-rays to the absorbed dose of 3.2 kGy (red line) and subsequent photolysis at 400 nm (blue line) at 6 K.

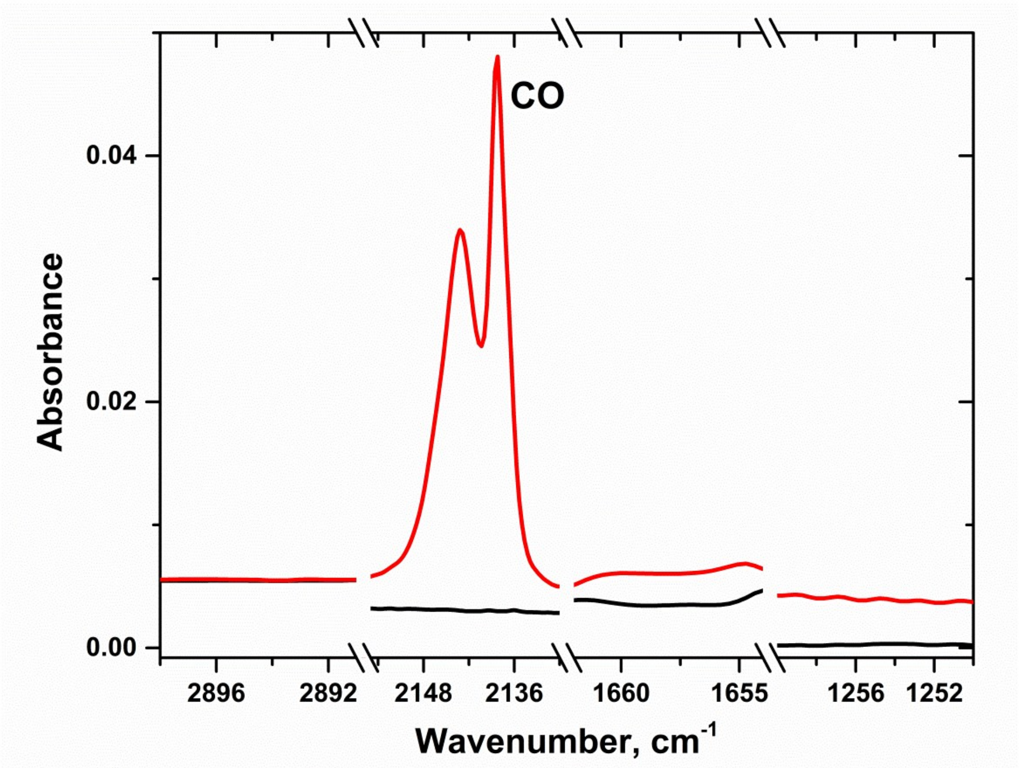

Figure S3. Fragments of FTIR spectra of $^{12}CO_2$/Ar (1/300) matrix after deposition (black line) and irradiation with X-rays to the absorbed dose of 41.4 kGy (red line) at 6 K.

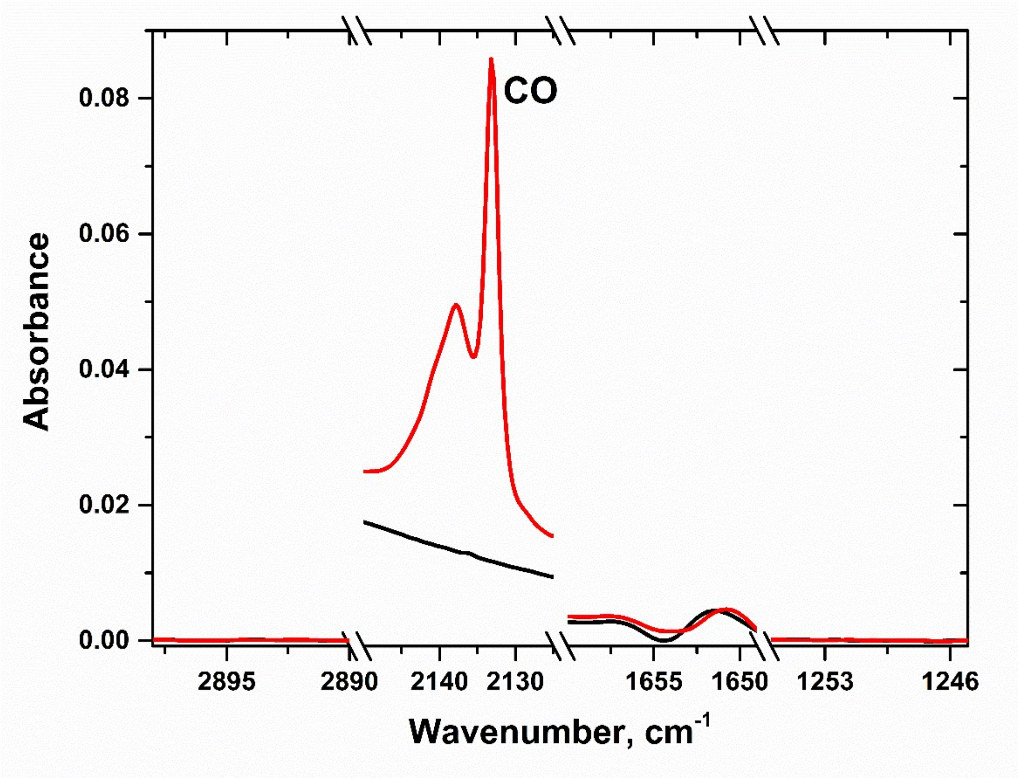

Figure S4. Fragments of FTIR spectra of $^{12}CO_2$/Xe (1/300) matrix after deposition (black line) and irradiation with X-rays to the absorbed dose of 42 kGy (red line) at 6 K.

Table S2. Absorption maxima (wavenumber, cm^{-1}) of the bands of monomer and dimer CO_2 radical anions and their complexes isolated in a neon matrix.

	This work	**Literature data**[a,b,c,d]
$^{12}CO_2^{-\bullet}$	2894.8	2894.6
	1658.2	1658.2
		1657.4
	1632.2	1630.6
	1628.2	1629.8
	1253.2	1253.8
		1252.7
		714.2
		713.6
$^{12}C_2O_4^{-\bullet}$	1864.0	1864.2
	1862.2	1862.0
	1855.2	1854.9
	1852.5	1852.4
		1850.7
		1190.0
	1189.0	1189.2
	1186.1	1186.0

	This work	**Literature data**^{a,b,c,d}
		1185.6
	1184.1	1183.7
		674.0
		679.2
$(^{12}CO_2)_n..(^{12}CO_2)^{-\bullet}$	2326.2	2326.7
	2322.1	2322.1
		2320.3
	1669.3	1670.2
	1665.6	1665.5
		1654.6
	1650.4	1650.6
$^{12}CO_2..O_2^-$	1895.3	1895.2
	1256.6	1256.5
		697.1
$^{13}CO_2^{-\bullet}$	2835.1	2835.0
	1614.3	1614.1
		1613.3
		1238.2
	1237.0	1237.3
		703.0
		702.4
$^{13}C_2O_4^{-\bullet}$		1814.0
	1812.2	1812.0
	1804.3	1803.1
		1801.0
		1182.2
	1180.6	1181.4
	1178.7	1178.4
	1177.0	1176.4
		664.8
$(^{13}CO_2)_n..(^{13}CO_2)^{-\bullet}$		2261.5
		2257.0
		2255.3
		1625.7
	1621.4	1621.2
		1610.7
	1607.0	1607.0
$^{13}CO_2..O_2^-$	1832.8	1832.8
		1835.6
	1247.5	1247.6
		686.4

Taken from: [a] M. E. Jacox and W. E. Thompson, *J. Chem.*

	This work	**Literature data**[a,b,c,d]

Phys., 1989, **91**, 1410–1416.
[b] M. Zhou and L. Andrews, *J. Chem. Phys.*, 1999, **110**, 6820–6826.
[c] W. E. Thompson and M. E. Jacox, *J. Chem. Phys.*, 1999, **111**, 4487–4496.
[d] M. E. Jacox and W. E. Thompson, *J. Phys. Chem.*, 1991, **95**, 2781–2787.

Computational details and results

Molecular geometries were fully optimized (tolerance on gradient: 10^{-7} a.u.) at the UCCSD(T)/L4a_3 level of theory (only the valence electrons are correlated).

Table S3. Contraction scheme of the augmented correlation consistent valence basis set L4a_3 as compared to the aug-cc-pV5Z basis set

Basis	C, O, atoms contraction scheme
L4a_3	{7s,6p,5d,4f,3g,2h}/{20s,14p,8d,6f,5g,4h}
aug-cc-pV5Z	{7s,6p,5d,4f,3g,2h}/{15s,9p,5d,4f,3g,2h}

Computed structures and energies

CO_2, $D_{\infty h}$

```
$molecule
 cartesian
 set=L4a_3
  6    0.00000000   0.00000000   0.00000000
  8    0.00000000   0.00000000   1.16205294
  8    0.00000000   0.00000000  -1.16205294
$end
```

E = -188.4073511295 a.u

CO_2^-, C_{2v}

```
$molecule
 charge=-1 mult=2
 cartesian
 set=L4a_3
  6    0.00000000   0.00000000   0.30781622
  8    1.14630447   0.00000000  -0.15390811
  8   -1.14630447  0.00000000  -0.15390811
$end
```

E =   -188.3824204485 a.u.

Table S4. Calculated geometrical parameters of CO_2 and its radical anion

Molecule	CO bond length, A	OCO angle, degree
CO_2	1.16205	180.000
CO_2-	1.14630	136.121