Supplementary Information

Table S1. Band centers (cm^{-1}), band limits (cm^{-1}) and integrated intensities for the molecules with available spectrum in PNNL database.

Molecule	Band center	Band limits	Integral	Integrated Intensity*	
				$atm^{-1}\,cm^{-2}$	$km\,mol^{-1}$
CO	2142	2030 – 2245	0.0108817	250.6	61.7
F_2CO	1944	1850 – 2000	0.0732902	1687.5	415.4
Cl_2CO	1827	1780 – 1890	0.0465606	1072.1	263.9
HCOOH	1776	1700 – 1820	0.0610520	1405.3	345.9
CH_3COOH	1790	1700 – 1850	0.0542142	1248.2	307.3
Acetone	1740	1650 – 1850	0.0260469	599.7	147.6
Acetaldehyde	1745	1650 – 1900	0.0247776	570.5	140.4
Formaldehyde	1745	1660 – 1820	0.0137370	316.3	77.9
Glycolaldehyde	1754	1650 – 1825	0.0227784	524.5	129.1
Glyoxal	1731	1661 – 1808	0.0255018	587.1	144.5
Methylglyoxal	1731	1691 – 1773	0.0284755	654.7	161.2
Diacetyl	1729	1690 – 1769	0.0318350	732.4	180.3

* – The two units are shown since ($atm^{-1}\,cm^{-2}$) is preferred by PNNL and ($km\,mol^{-1}$) is the most common in outputs of *ab initio* packages like Gaussian, Gamess–UK and CFOUR. The conversion factor between them is 1/4.0623.

Table S2. Individual charge, charge transfer and counterpolatization contributions to the carbonyl stretching intensity, at QCISD/cc–pVTZ, in $km\,mol^{-1}$.

Molecule	C^2	CT^2	CP^2	2xCxCT	2xCxCP	2xCTxCP	Total
CO	210.3	213.2	68.8	–423.5	240.5	–242.2	67.1
F_2CO	611.2	444.0	301.9	–1041.9	859.1	–732.2	442.2
Cl_2CO	237.8	90.6	139.6	–293.6	364.3	–224.8	313.9
Br_2CO	183.7	25.1	79.0	–135.8	240.9	–89.1	303.8
HFCO	330.5	265.0	244.3	–571.2	475.3	–483.9	260.1
HClCO	209.8	148.2	110.3	–270.7	302.3	–176.7	323.2
HBrCO	187.1	208.8	91.5	–177.3	254.2	–179.4	384.8
HCOOH	421.5	323.7	269.7	–732.2	613.7	–565.6	330.8
H_2CO_3	855.3	650.3	348.0	–1491.6	1090.9	–951.1	501.9
CH_3COOH	420.1	304.7	255.7	–614.0	471.3	–543.7	294.1
Acetone	173.6	104.1	85.1	–268.8	242.9	–188.1	148.8
Acetaldehyde	168.4	125.2	98.6	–246.0	225.1	–221.7	149.5
Formaldehyde	153.9	130.3	64.3	–283.2	199.0	–183.0	81.2
Glycolaldehyde	151.0	136.7	96.2	–241.0	204.8	–229.3	118.4
Glyoxal	331.2	358.0	188.2	–647.2	455.2	–517.7	167.8
Methylglyoxal	326.4	316.4	178.6	–633.8	465.0	–472.7	179.9
Diacetyl	327.1	305.0	182.0	–630.8	484.8	–464.5	203.5

Table S3. CCTCP contributions to the carbonyl stretching intensity in different levels of theory, in km mol^{-1}.

Molecule	Method	Basis set	C²	CTCP²	2xCxCTCP	Total
CO	B3LYP	cc–pVDZ	208.0	35.1	–171.0	72.1
		cc–pVTZ	197.7	29.4	–152.5	74.6
		cc–pVQZ^g	202.1	29.8	–155.3	76.6
	M06–2X	cc–pVDZ	219.5	28.9	–159.3	89.1
		cc–pVTZ	213.7	24.7	–145.4	93.0
		cc–pVQZ^g	216.5	24.8	–146.5	94.8
	PBE0	cc–pVDZ	212.8	33.0	–167.5	78.2
		cc–pVTZ	205.7	30.4	–158.2	78.0
		cc–pVQZ^g	210.2	31.3	–162.1	79.3
	MP2	cc–pVDZ	188.2	72.0	–232.8	27.4
		cc–pVTZ	191.1	67.0	–226.4	31.8
		cc–pVQZ^g	196.5	66.6	–228.8	34.3
	QCISD	cc–pVDZ	203.8	40.8	–182.4	62.2
		cc–pVTZ	210.3	39.8	–183.0	67.1
		cc–pVQZ^g	216.6	40.1	–186.5	70.2
	Average		206.2	39.6	–177.2	68.6
	Standard Deviation		9.5	15.8	29.8	21.4
H_2CO	B3LYP	cc–pVDZ	160.7	5.0	–56.9	108.8
		cc–pVTZ	149.5	3.5	–46.0	107.0
		cc–pVQZ^g	164.4	5.2	–58.7	111.0
	M06–2X	cc–pVDZ	175.3	6.3	–66.7	114.9
		cc–pVTZ	168.1	5.5	–60.6	113.0
		cc–pVQZ^g	185.2	7.4	–74.2	118.4
	PBE0	cc–pVDZ	166.6	5.2	–58.9	112.9
		cc–pVTZ	155.2	4.2	–50.9	108.5
		cc–pVQZ^g	169.9	6.0	–64.0	111.9
	MP2	cc–pVDZ	156.3	18.1	–106.3	68.1
		cc–pVTZ	137.6	14.8	–90.3	62.1
		cc–pVQZ^g	154.3	18.7	–107.4	65.6
	QCISD	cc–pVDZ	166.9	12.9	–92.6	87.1
		cc–pVTZ	153.9	11.3	–83.3	81.9
		cc–pVQZ^g	171.7	15.0	–101.4	85.3
	Average		162.2	9.1	–73.3	98.1
	Standard Deviation		11.9	5.5	23.1	20.8
HFCO	B3LYP	cc–pVDZ	286.4	19.8	–44.9	261.3
		cc–pVTZ	295.6	21.8	–46.5	270.9
		cc–pVQZ^g	302.7	23.2	–46.9	279.0
	M06–2X	cc–pVDZ	311.5	18.1	–35.1	294.5
		cc–pVTZ	326.9	20.3	–46.2	300.9
		cc–pVQZ^g	333.4	23.4	–50.3	306.5
	PBE0	cc–pVDZ	297.6	19.3	–39.3	277.7
		cc–pVTZ	300.2	22.2	–46.5	275.9
		cc–pVQZ^g	318.9	25.0	–58.2	285.7
	MP2	cc–pVDZ	290.1	27.3	–91.1	226.3
		cc–pVTZ	311.3	31.2	–108.8	233.7
		cc–pVQZ^g	318.6	32.4	–109.0	242.0
	QCISD	cc–pVDZ	302.8	21.3	–73.5	250.7
		cc–pVTZ	330.5	25.4	–95.8	260.1
		cc–pVQZ^g	340.5	28.2	–101.2	267.6
	Average		311.1	23.9	–66.2	268.9
	Standard Deviation		16.6	4.3	27.3	23.7

Table S4. Dynamic CCTCP atomic contributions for carbon and oxygen at QCISD/cc–pVTZ, in km mol^{-1}.

Molecule	Atom	C²	CTCP²	CxCTCP	CTCPxC	Total
CO	C	120.2	22.7	–52.3	–52.3	38.4
	O	90.1	17.1	–39.2	–39.2	28.8
F_2CO	C	463.8	10.1	–69.3	–67.6	337.0
	O	133.9	4.3	–20.0	–28.5	89.6
Cl_2CO	C	149.8	4.8	22.3	31.7	208.6
	O	87.9	0.5	13.1	3.3	104.8
Br_2CO	C	105.7	12.5	30.2	43.8	192.3
	O	78.0	2.5	22.3	8.7	111.5
HFCO	C	219.0	13.9	–29.0	–19.6	184.3
	O	106.1	6.8	–16.0	–22.1	74.8
HClCO	C	121.0	51.7	12.3	24.4	209.4
	O	84.6	21.4	7.4	–4.3	109.2
HBrCO	C	102.6	76.5	24.4	38.7	242.2
	O	79.8	33.6	17.7	2.8	133.8
HCOOH	C	246.9	14.0	–36.9	–12.1	211.9
	O	114.4	6.7	–19.0	–10.4	91.7
H_2CO_3	C	513.6	21.5	–120.3	–91.2	323.7
	O	154.2	2.4	–36.1	–9.9	110.6
CH_3COOH	C	247.0	8.7	–45.7	–23.5	186.4
	O	110.6	3.3	–19.4	–10.2	84.3
Acetone	C	101.6	0.1	–7.6	0.6	94.6
	O	70.9	0.9	–5.3	–11.8	54.7
Acetaldehyde	C	99.1	–0.3	–5.9	4.7	97.6
	O	69.1	1.0	–4.6	–10.8	54.7
Formaldehyde	C	90.9	3.5	–24.9	–12.8	56.7
	O	64.6	4.7	–17.7	–17.2	34.4
Glycolaldehyde	C	91.4	0.5	–10.6	–4.2	77.2
	O	66.3	2.1	–8.3	–13.5	46.7
Glyoxal	C	183.0	11.7	–52.7	–42.3	99.6
	O	146.5	13.5	–42.5	–45.6	71.8
Methylglyoxal	C	182.5	10.3	–47.2	–37.0	108.6
	O	143.5	11.0	–37.2	–42.5	74.9
Diacetyl	C	185.9	11.2	–40.8	–32.7	123.7
	O	142.4	10.3	–32.4	–39.8	80.4

Table S5. Dynamic atomic contributions to the carbonyl stretch infrared intensities (in km mol^{-1}) calculated in different levels of theory.

Molecule	Method	Basis set	C	O	Subst.	% C	% O	% (C+O)
CO	B3LYP	cc–pVDZ	41.3	31.0	–	57.1	42.9	100.0
		cc–pVTZ	42.7	32.0	–	57.1	42.9	100.0
		cc–pVQZ[g]	43.8	32.9	–	57.1	42.9	100.0
	M06–2X	cc–pVDZ	51.0	38.2	–	57.1	42.9	100.0
		cc–pVTZ	53.2	39.9	–	57.1	42.9	100.0
		cc–pVQZ[g]	54.2	40.7	–	57.1	42.9	100.0
	PBE0	cc–pVDZ	44.7	33.6	–	57.1	42.9	100.0
		cc–pVTZ	44.6	33.4	–	57.1	42.9	100.0
		cc–pVQZ[g]	45.4	34.0	–	57.1	42.9	100.0
	MP2	cc–pVDZ	15.7	11.8	–	57.1	42.9	100.0
		cc–pVTZ	18.2	13.6	–	57.1	42.9	100.0
		cc–pVQZ[g]	19.6	14.7	–	57.1	42.9	100.0
	QCISD	cc–pVDZ	35.6	26.7	–	57.1	42.9	100.0
		cc–pVTZ	38.4	28.8	–	57.1	42.9	100.0
		cc–pVQZ[g]	40.2	30.1	–	57.1	42.9	100.0
H_2CO	B3LYP	cc–pVDZ	73.2	45.5	–9.8	67.2	41.8	109.0
		cc–pVTZ	73.1	45.4	–11.4	68.3	42.4	110.7
		cc–pVQZ[g]	75.7	47.2	–11.9	68.1	42.5	110.7
	M06–2X	cc–pVDZ	75.4	49.5	–9.9	65.6	43.0	108.6
		cc–pVTZ	75.0	49.5	–11.4	66.3	43.8	110.1
		cc–pVQZ[g]	78.7	51.9	–12.1	66.4	43.8	110.2
	PBE0	cc–pVDZ	75.1	48.0	–10.2	66.5	42.5	109.0
		cc–pVTZ	73.4	47.1	–11.9	67.6	43.4	110.9
		cc–pVQZ[g]	75.6	48.7	–12.3	67.5	43.5	111.0
	MP2	cc–pVDZ	48.2	26.0	–6.0	70.7	38.2	108.8
		cc–pVTZ	45.1	25.4	–8.3	72.5	40.8	113.3
		cc–pVQZ[g]	47.4	27.2	–9.0	72.3	41.4	113.7
	QCISD	cc–pVDZ	60.0	34.8	–7.6	68.8	39.8	108.7
		cc–pVTZ	56.8	34.4	–9.9	69.9	42.3	112.2
		cc–pVQZ[g]	59.4	36.5	–10.5	69.6	42.8	112.3
HFCO	B3LYP	cc–pVDZ	183.4	78.9	–0.8	70.1	30.2	100.3
		cc–pVTZ	189.4	83.6	–1.9	69.9	30.8	100.7
		cc–pVQZ[g]	194.5	86.8	–2.1	69.7	31.1	100.7
	M06–2X	cc–pVDZ	205.7	88.6	0.4	69.8	30.1	99.9
		cc–pVTZ	209.3	92.3	–0.4	69.5	30.6	100.1
		cc–pVQZ[g]	212.8	94.8	–0.9	69.4	30.9	100.3
	PBE0	cc–pVDZ	194.5	83.2	0.1	70.0	29.9	100.0
		cc–pVTZ	193.3	83.7	–0.9	70.0	30.3	100.3
		cc–pVQZ[g]	199.1	87.9	–1.1	69.6	30.8	100.4
	MP2	cc–pVDZ	164.8	60.3	1.4	72.8	26.6	99.4
		cc–pVTZ	168.7	65.0	0.2	72.2	27.8	99.9
		cc–pVQZ[g]	173.7	69.1	–0.6	71.7	28.5	100.2
	QCISD	cc–pVDZ	179.4	69.7	1.8	71.5	27.8	99.3
		cc–pVTZ	184.5	74.9	1.0	70.9	28.8	99.6
		cc–pVQZ[g]	188.7	78.5	0.6	70.5	29.3	99.8