Supplemental Information:

On the impact of large-amplitude mode truncation in anharmonic frequency calculations

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1 Computational details

Harmonic frequency calculations have been performed with CFOUR version 1[1] and MOLPRO version 2018.1[2, 3]. Prior to each harmonic or anharmonic frequency calculation, the geometry was optimised. Symmetry was enabled in all calculations, except for the MOLPRO calculations on CH_3OH and NH_2OH. Anharmonic quartic force fields were computed from analytic Hessians, using PyPES with default settings. Masses of the following isotopes were used: ^{1}H, ^{2}H≡D, ^{11}B, ^{12}C, ^{14}N, ^{16}O, ^{19}F, ^{27}Al, ^{28}Si, ^{31}P, ^{32}S, ^{121}Sb and ^{209}Bi. Keyword specifications used in each calculation are listed below:

Type of calculation	Program	Keywords
CCSD(T) Hessian	CFOUR	FROZEN_CORE=ON SCF_CONV=9 CC_CONV=9 CC_PROGRAM=ECC ABCDTYPE=AOBASIS LINEQ_CONV=9 GEO_CONV=9 GEO_METHOD=NR VIB=EXACT
CCSD(T)-F12 Hessian	MOLPRO	{GThresh,OptStep=6.d-5,OptGrad=1.d-8,Energy=1.d-10,Zero=1.d-16} {Optg,Gaussian,GRMS=1.d-7,SRMS=1.d-7} {Mass,Iso} {Frequencies}
Anharmonic force field	PyPES	CFOUR_ZMAT ZMAT, DO_NUM_DIFF_NM True, DLVL_CART 4, FF_NM_TO_CNM (4)->(4), FF_CNM_TO_NM (4)->(6), SAVE_FF_NM True
VCI	PyVCI	DLVL 6, EXC_LVL 10 (or 9)

2 Fundamental wavenumbers

2.1 Computation of low-resolution band centres for NH_3, H_2O_2/D_2O_2 and CH_3OH

Due to the symmetric double-well potentials of the ammonia inversion / hydrogen peroxide torsion, the vibrational energy levels are split into two levels, labelled according to their parity as + and −. The low-resolution band centre of vibration i is computed as

$$\begin{aligned} 2\bar{\nu}_i &= (W_i^+ - W_{\text{g.s.}}^-) + W_i^- \\ &= (E_i^+ - E_{\text{g.s.}}^-) + (E_i^- - E_{\text{g.s.}}^+), \end{aligned} \tag{1}$$

where W is the term value relative to the vibrational ground state, whereas E includes zero-point energy. For methanol, the three-fold torsional degeneracy results in one A and two E levels. Here, the low-resolution band centre is computed as

$$\begin{aligned} 3\bar{\nu}_i &= 2\nu_i(E) + \nu_i(A) \\ &= 2W_i(E) - 2W_{\text{g.s.}}(E) + W_i(A) \\ &= 2E_i(E) - 2E_{\text{g.s.}}(E) + E_i(A) - E_{\text{g.s.}}(A). \end{aligned} \tag{2}$$

2.2 Part I – Tetratomics

Table S1: Fundamental wavenumbers for all 24 tetratomic molecules in our benchmarking set. Computational (ν_{lit}) and, when available, high-resolution gas phase (ν_{expt}) literature data (references in brackets), and in this work computed VCI(10) fundamentals ($\nu^{(10)}$) and their respective convergence errors (δ_{cvge}) are shown in cm^{-1}. Low-resolution band centres are shown for NH_3 and H_2O_2/D_2O_2 (see footnotes).

	Fundamental	ν_{expt}	ν_{lit}	$\nu^{(10)}$				$\delta_{\text{cvge}} = \nu^{(10)} - \nu^{(9)}$			
				ν_{ref}	$\tilde{\nu}_{\text{harm}}$	ν_{drop}	$\tilde{\nu}_{\text{drop}}$	ν_{ref}	$\tilde{\nu}_{\text{harm}}$	ν_{drop}	$\tilde{\nu}_{\text{drop}}$
Group (A)											
NH_3[a]	ν_1 A_1 s str	3336.2 [4]	3342.5 [5]	3344.7	3337.3	3347.6	3353.4	−5.6	1.3	0.0	0.0
	ν_2 A_1 inversion	949.9 [6]	951.2 [5]	951.9	992.7			−0.5	−0.4		
	ν_3 E a str	3443.4 [7]	3449.0 [5]	3453.1	3450.2	3462.3	3462.0	0.0	−0.1	0.0	0.0
	ν_3 E a str	3443.4 [7]	3449.0 [5]	3453.1	3450.2	3462.3	3462.0	0.0	−0.1	0.0	0.0
	ν_4 E bend	1626.4 [8]	1628.7 [5]	1629.2	1624.3	1630.4	1631.6	0.0	0.0	0.0	0.0
	ν_4 E bend	1626.4 [8]	1628.7 [5]	1629.2	1624.3	1630.4	1631.6	0.0	0.0	0.0	0.0
PH_3	ν_1 A_1 s str	2321.1 [9]	2321.0 [10]	2323.1	2324.1	2325.9	2325.7	0.0	0.0	0.0	0.0
	ν_2 A_1 inversion	992.1 [11]	991.9 [10]	991.8	998.2			0.0	0.0		
	ν_3 E a str	2326.9 [9]	2325.8 [10]	2327.8	2330.8	2332.8	2332.3	0.0	0.0	0.0	0.0
	ν_3 E a str	2326.9 [9]	2325.8 [10]	2327.8	2330.8	2332.8	2332.3	0.0	0.0	0.0	0.0
	ν_4 E bend	1118.3 [11]	1118.9 [10]	1119.7	1120.2	1119.9	1119.6	0.0	0.0	0.0	0.0
	ν_4 E bend	1118.3 [11]	1118.9 [10]	1119.7	1120.2	1119.9	1119.6	0.0	0.0	0.0	0.0
SbH_3	ν_1 A_1 s str	1890.5 [12]	1893.8 [13]	1894.2	1896.0	1897.5	1897.3	0.0	0.0	0.0	0.0
	ν_2 A_1 inversion	782.2 [12]	798.9 [13]	798.4	803.0			0.0	0.0		
	ν_3 E a str	1894.5 [12]	1899.1 [13]	1899.8	1901.9	1903.5	1903.1	0.0	0.0	0.0	0.0
	ν_3 E a str	1894.5 [12]	1899.1 [13]	1899.8	1901.9	1903.5	1903.1	0.0	0.0	0.0	0.0
	ν_4 E bend	827.9 [12]	836.8 [13]	836.8	837.4	836.5	836.1	0.0	0.0	0.0	0.0
	ν_4 E bend	827.9 [12]	836.8 [13]	836.8	837.4	836.5	836.1	0.0	0.0	0.0	0.0
BiH_3	ν_1 A_1 s str	1733.3 [14]	1742.4 [13]	1742.7	1745.6	1746.7	1746.6	0.0	0.0	0.0	0.0
	ν_2 A_1 inversion	726.7 [14]	733.9 [13]	733.4	738.3			0.0	0.0		
	ν_3 E a str	1734.5 [14]	1746.3 [13]	1746.7	1749.2	1750.5	1750.1	0.0	0.0	0.0	0.0
	ν_3 E a str	1734.5 [14]	1746.3 [13]	1746.7	1749.2	1750.5	1750.1	0.0	0.0	0.0	0.0
	ν_4 E bend	751.2 [14]	759.5 [13]	759.3	760.3	759.1	758.7	0.0	0.0	0.0	0.0
	ν_4 E bend	751.2 [14]	759.5 [13]	759.3	760.3	759.1	758.7	0.0	0.0	0.0	0.0
SiH_3^-	ν_1 A_1 s str		1840.7 [15]	1840.4	1838.1	1839.1	1838.5	0.0	0.0	0.0	0.0
	ν_2 A_1 inversion		844.1 [15]	844.2	844.4			0.0	0.0		
	ν_3 E a str		1821.5 [15]	1824.5	1828.8	1828.9	1828.1	0.0	0.0	0.0	0.0
	ν_3 E a str		1821.5 [15]	1824.5	1828.8	1828.9	1828.1	0.0	0.0	0.0	0.0
	ν_4 E bend		937.8 [15]	941.0	939.6	940.1	939.8	0.0	0.0	0.0	0.0
	ν_4 E bend		937.8 [15]	941.0	939.6	940.1	939.8	0.0	0.0	0.0	0.0

[a] Low-resolution experimental and computational literature band centres are computed according to Eq. 1. Pairs of (W_i^+, W_i^-) are listed in cm^{-1}:
Expt:
$W_{\text{g.s.}} = (0, 0.79)$,[6] $W_1 = (3336.11, 3337.10)$, $W_2 = (932.43, 968.12)$, $W_3 = (3443.68, 3443.99)$ and $W_4 = (1626.28, 1627.37)$.
Lit:
$W_{\text{g.s.}} = (0, 0.8)$,[5] $W_1 = (3342.4, 3343.3)$, $W_2 = (933.8, 969.5)$, $W_3 = (3449.2, 3449.6)$ and $W_4 = (1628.6, 1629.7)$.

Table S1: *Continued.*

	Fundamental	ν_{expt}	ν_{lit}	$\nu^{(10)}$				$\delta_{\text{cvge}} = \nu^{(10)} - \nu^{(9)}$			
				ν_{ref}	$\tilde{\nu}_{\text{harm}}$	ν_{drop}	$\tilde{\nu}_{\text{drop}}$	ν_{ref}	$\tilde{\nu}_{\text{harm}}$	ν_{drop}	$\tilde{\nu}_{\text{drop}}$
Group (B)											
BF_3	ν_1 A_1' s str		887.6 [16]	887.9	886.8	889.7	889.7	0.0	0.0	0.0	0.0
	ν_2 A_2'' oop	691.2 [17]	696.2 [16]	696.2	693.7			0.0	0.0		
	ν_3 E' a str	1454.0 [18]	1469.6 [16]	1470.3	1472.0	1472.8	1472.8	0.0	0.0	0.0	0.0
	ν_3 E' a str	1454.0 [18]	1469.6 [16]	1470.2	1472.6	1472.8	1472.8	0.0	0.0	0.0	0.0
	ν_4 E' bend	479.4 [19]	480.6 [16]	480.9	479.4	480.4	480.4	0.0	0.0	0.0	0.0
	ν_4 E' bend	479.4 [19]	480.6 [16]	480.9	479.1	480.4	480.4	0.0	0.0	0.0	0.0
CF_3^+	ν_1 A_1' s str		1044.5 [16]	1044.8	1043.5	1046.5	1046.5	0.0	0.0	0.0	0.0
	ν_2 A_2'' oop		812.6 [16]	812.7	812.4			0.0	0.0		
	ν_3 E' a str		1682.8 [16]	1683.5	1685.7	1686.9	1686.9	0.0	0.0	0.0	0.0
	ν_3 E' a str		1682.8 [16]	1683.5	1687.8	1686.9	1686.9	0.0	0.0	0.0	0.0
	ν_4 E' bend		592.6 [16]	593.0	591.5	592.7	592.7	0.0	0.0	0.0	0.0
	ν_4 E' bend		592.6 [16]	593.0	591.2	592.7	592.7	0.0	0.0	0.0	0.0
AlF_3	ν_1 A_1' s str		689.5 [20]	689.0	689.7	686.4	686.4	0.0	0.0	0.0	0.0
	ν_2 A_2'' oop		301.1 [20]	301.3	300.2			0.0	0.0		
	ν_3 E' a str		951.8 [20]	951.2	951.6	951.6	951.6	0.0	0.0	0.0	0.0
	ν_3 E' a str		951.8 [20]	951.2	951.2	951.6	951.6	0.0	0.0	0.0	0.0
	ν_4 E' bend		241.4 [20]	241.4	240.8	241.1	241.1	0.0	0.0	0.0	0.0
	ν_4 E' bend		241.4 [20]	241.4	240.7	241.1	241.1	0.0	0.0	0.0	0.0
SiF_3^+	ν_1 A_1' s str		853.3 [20]	852.8	853.8	850.9	850.9	0.0	0.0	0.0	0.0
	ν_2 A_2'' oop		356.7 [20]	356.8	356.1			0.0	0.0		
	ν_3 E' a str		1187.9 [20]	1187.2	1187.8	1188.0	1188.0	0.0	0.0	0.0	0.0
	ν_3 E' a str		1187.9 [20]	1187.2	1187.4	1188.0	1188.0	0.0	0.0	0.0	0.0
	ν_4 E' bend		307.2 [20]	307.2	306.5	307.0	307.0	0.0	0.0	0.0	0.0
	ν_4 E' bend		307.2 [20]	307.2	306.5	307.0	307.0	0.0	0.0	0.0	0.0
SO_3	ν_1 A_1' s str		1067.0 [21]	1066.9	1071.7	1066.5	1066.5	0.0	0.0	0.0	0.0
	ν_2 A_2'' oop	497.6 [22]	498.6 [21]	496.4	500.4			0.0	0.0		
	ν_3 E' a str	1391.5 [23]	1396.3 [21]	1396.3	1397.6	1398.5	1398.5	0.0	0.0	0.0	0.0
	ν_3 E' a str	1391.5 [23]	1396.3 [21]	1396.3	1398.2	1398.5	1398.5	0.0	0.0	0.0	0.0
	ν_4 E' bend	530.1 [22]	528.1 [21]	528.3	527.2	528.0	528.0	0.0	0.0	0.0	0.0
	ν_4 E' bend	530.1 [22]	528.1 [21]	528.3	527.3	528.0	528.0	0.0	0.0	0.0	0.0
H_2CO	ν_1 A_1 CH_2 s str	2782.5 [24]	2781.7 [25]	2784.1	2782.0	2788.2	2788.2	0.0	0.0	0.0	0.0
	ν_2 A_1 CO str	1746.0 [26]	1744.6 [25]	1744.9	1748.5	1748.5	1748.5	0.0	0.0	0.0	0.0
	ν_3 A_1 CH_2 bend	1500.2 [26]	1499.1 [25]	1499.3	1491.3	1499.9	1499.9	0.0	0.0	0.0	0.0
	ν_4 B_1 oop	1167.3 [26]	1166.1 [25]	1166.1	1149.0			0.0	0.0		
	ν_5 B_2 CH_2 a str	2843.3 [24]	2842.4 [25]	2845.0	2847.0	2851.8	2851.8	0.0	0.0	0.0	0.0
	ν_6 B_2 CH_2 rock	1249.1 [26]	1245.6 [25]	1245.5	1237.4	1242.2	1242.2	0.0	0.0	0.0	0.0
H_2SiO	ν_1 A_1 SiH_2 s str		2171.0 [27]	2171.4	2171.2	2174.7	2174.7	0.0	0.0	0.0	0.0
	ν_2 A_1 SiO str		1206.9 [27]	1207.1	1209.0	1209.0	1209.0	0.0	0.0	0.0	0.0
	ν_3 A_1 SiH_2 bend		994.3 [27]	994.6	991.2	995.0	995.0	0.0	0.0	0.0	0.0
	ν_4 B_1 oop		690.9 [27]	690.6	684.9			0.0	0.0		
	ν_5 B_2 SiH_2 a str		2191.3 [27]	2192.1	2194.2	2196.4	2196.4	0.0	0.0	0.0	0.0
	ν_6 B_2 SiH_2 rock		680.1 [27]	680.1	676.8	678.3	678.3	0.0	0.0	0.0	0.0

Table S1: *Continued.*

	Fundamental	ν_{expt}	ν_{lit}	$\nu^{(10)}$				$\delta_{\text{cvge}} = \nu^{(10)} - \nu^{(9)}$			
				ν_{ref}	$\tilde{\nu}_{\text{harm}}$	ν_{drop}	$\tilde{\nu}_{\text{drop}}$	ν_{ref}	$\tilde{\nu}_{\text{harm}}$	ν_{drop}	$\tilde{\nu}_{\text{drop}}$
Group (C)											
HOOH[b]	ν_1 A OH s str	3608.2 [28]	3609.1 [29]	3593.0	3590.2	3607.3	3607.3	−2.8	−14.7	−0.1	−0.1
	ν_2 A s bend	1391.4 [30]	1392.4 [29]	1393.7	1388.4	1385.1	1385.1	0.3	0.0	0.0	0.0
	ν_3 A OO str	866.2 [31]	866.3 [29]	868.3	867.2	867.0	867.0	−0.4	0.4	0.0	0.0
	ν_4 A torsion	307.0 [32]	307.7 [29]	367.8	408.1			−13.4	−0.1		
	ν_5 B OH a str	3609.0 [33]	3610.3 [29]	3602.8	3602.9	3608.9	3608.9	0.4	−0.4	0.0	0.0
	ν_6 B a bend	1269.2 [30]	1269.1 [29]	1279.6	1287.6	1281.6	1281.6	−1.0	−0.1	0.0	0.0
DOOD[c]	ν_1 A OD s str		2667.2 [29]	2665.0	2663.2	2666.3	2666.3	−2.3	−0.6	0.0	0.0
	ν_2 A s bend		1026.2 [29]	1026.0	1023.5	1023.0	1023.0	−0.1	−0.4	0.0	0.0
	ν_3 A OO str		869.3 [29]	870.2	870.0	869.7	869.7	−0.2	−0.1	0.0	0.0
	ν_4 A torsion	229.1 [34]	230.1 [29]	267.7	288.1			−1.5	−0.8		
	ν_5 B a str		2666.6 [29]	2663.8	2664.3	2665.6	2665.6	−0.4	−0.4	−0.1	−0.1
	ν_6 B OD a bend		945.4 [29]	950.5	957.5	955.0	954.9	−0.3	−0.1	0.0	0.0
HSOH	ν_1 A OH str	3625.6 [35]	3625.9 [36]	3615.7	3618.4	3633.3	3633.3	−2.6	−1.9	0.0	0.0
	ν_2 A SH str	2538.0[d] [37]	2544.4 [36]	2548.0	2545.8	2546.1	2546.1	−1.4	−0.9	0.0	0.0
	ν_3 A SOH bend		1174.0 [36]	1184.0	1188.7	1178.5	1178.5	−0.5	−0.3	0.0	0.0
	ν_4 A OSH bend		1007.7 [36]	1016.3	1007.8	1007.0	1007.0	21.5	−0.5	0.0	0.0
	ν_5 A SO str		760.0 [36]	761.0	763.6	763.4	763.4	−0.7	−0.4	0.0	0.0
	ν_6 A torsion		443.0 [36]	480.3	506.4			−1.0	−0.4		

[b,c] Low-resolution band centres for HOOH and DOOD computed from tunnelling split energy levels (see footnote [a]):
Expt (HOOH):
$W_{\text{g.s.}} = (0, 11.44)$,[32] $W_1 = (3609.8, 3617.95)$, $W_2 = (1395.88, 1398.32)$, $W_3 = (865.94, 877.93)$, $W_4 = (254.55, 370.89)$, $W_5 = (3610.66, 3618.84)$, $W_6 = (1264.58, 1285.12)$.
Lit (HOOH):
$W_{\text{g.s.}} = (0, 11.3)$,[29] $W_1 = (3610.6, 3618.8)$, $W_2 = (1394.9, 1401.1)$, $W_3 = (866.0, 877.8)$, $W_4 = (255.4, 371.3)$, $W_5 = (3611.8, 3620.0)$, $W_6 = (1264.5, 1285.0)$.
Expt (DOOD):
$W_{\text{g.s.}} = (0, 1.93)$[34] and $W_4 = (208.87, 251.26)$.
Lit (DOOD):
$W_{\text{g.s.}} = (0, 1.9)$[29] and $W_4 = (210.1, 251.9)$.

[d] Beckers *et al.* report a low-resolution value of 2538,[38] which is corroborated by the high-resolution value 2537.9869(12)[36] from the dissertation[37] of O. Baum.

Table S1: *Continued.*

	Fundamental	ν_{expt}	ν_{lit}	$\nu^{(10)}$				$\delta_{\text{cvge}} = \nu^{(10)} - \nu^{(9)}$			
				ν_{ref}	$\tilde{\nu}_{\text{harm}}$	ν_{drop}	$\tilde{\nu}_{\text{drop}}$	ν_{ref}	$\tilde{\nu}_{\text{harm}}$	ν_{drop}	$\tilde{\nu}_{\text{drop}}$
Group (D)											
t-HNNH	ν_1 A_g NH s str		3033.3 [39]	3036.5	3042.6	3044.3	3044.3	−0.1	−0.1	−0.1	−0.1
	ν_2 A_g NH s bend		1579.4 [39]	1579.7	1584.8	1582.0	1582.0	0.0	0.0	0.0	0.0
	ν_3 A_g NN str		1519.3 [39]	1519.3	1524.3	1524.1	1524.1	0.0	0.0	0.0	0.0
	ν_4 A_u torsion	1288.6 [40]	1294.2 [39]	1294.2	1318.5			0.0	0.0		
	ν_5 B_u NH a str	3120.3 [40]	3125.0 [39]	3114.8	3117.8	3123.8	3123.8	−0.1	−0.1	−0.1	−0.1
	ν_6 B_u NH a bend	1316.4 [40]	1317.5 [39]	1317.9	1323.1	1316.0	1316.0	0.0	0.0	0.0	0.0
c-HSiOH[e]	ν_1 A' OH str		3676.2 [41]	3662.0	3666.4	3681.9	3681.9	−2.7	−3.0	−0.1	−0.1
	ν_2 A' SiH str		1891.0 [41]	1872.6	1878.5	1870.5	1870.5	0.9	2.0	−0.3	−0.3
	ν_3 A' a bend		939.0 [41]	948.1	954.4	946.1	946.1	−0.7	−2.6	−0.2	−0.2
	ν_4 A' SiO str		841.1 [41]	841.6	842.4	842.7	842.7	−0.3	−0.2	−0.1	−0.1
	ν_5 A' s bend		727.0 [41]	745.5	754.7	738.3	738.3	−2.2	0.1	−0.1	−0.1
	ν_6 A'' torsion		599.6 [41]	626.7	652.2			−0.5	−1.5		
t-HSiOH	ν_1 A' OH str		3673.1 [41]	3665.9	3663.6	3678.0	3678.0	14.8	−0.3	0.0	0.0
	ν_2 A' SiH str		1950.0 [41]	1951.3	1954.3	1955.0	1955.0	−0.3	−0.2	−0.1	−0.1
	ν_3 A' s bend		929.9 [41]	940.4	952.9	941.3	941.3	0.1	−0.5	−0.3	−0.3
	ν_4 A' SiO str		836.9 [41]	837.6	839.3	839.1	839.1	−0.3	−0.2	−0.1	−0.1
	ν_5 A' a bend		788.4 [41]	797.7	801.8	792.5	792.5	−0.6	−0.4	−0.3	−0.3
	ν_6 A'' torsion		632.7 [41]	652.4	687.1			−1.0	−0.6		
c-DSiOD	ν_1 A' OD str		2713.1 [41]	2711.0	2711.3	2717.0	2717.0	0.6	−0.2	0.0	0.0
	ν_2 A' SiD str		1372.8 [41]	1375.0	1362.3	1374.8	1374.8	−0.3	−0.2	−0.1	−0.1
	ν_3 A' SiO str		838.4 [41]	838.6	839.0	839.6	839.6	−0.1	−0.1	0.0	0.0
	ν_4 A' a bend		718.2 [41]	721.2	725.3	720.8	720.8	−0.2	−0.2	−0.1	−0.1
	ν_5 A' s bend		523.4 [41]	528.5	534.2	526.5	526.5	−0.3	−0.2	−0.1	−0.1
	ν_6 A'' torsion		450.2 [41]	458.6	474.5			−0.4	−0.3		
t-DSiOD	ν_1 A' OD str		2709.7 [41]	2707.9	2706.8	2712.6	2712.6	−0.1	−0.1	0.0	0.0
	ν_2 A' SiD str		1423.6 [41]	1425.8	1429.5	1427.4	1427.4	−0.2	−0.2	−0.1	−0.1
	ν_3 A' SiO str		834.7 [41]	835.0	836.3	836.2	836.2	−0.1	−0.1	0.0	0.0
	ν_4 A' s bend		705.3 [41]	707.3	714.6	709.5	709.5	−0.2	−0.1	−0.1	−0.1
	ν_5 A' a bend		573.4 [41]	576.2	578.9	574.1	574.1	−0.2	−0.1	−0.1	−0.1
	ν_6 A'' torsion		469.2 [41]	475.9	496.0			−0.4	−0.3		
c-HOCO	ν_1 A' OH str		3452.3 [42]	3442.7	3441.6	3449.4	3449.4	−1.0	3.2	−0.1	−0.1
	ν_2 A' C=O str		1824.1 [42]	1830.1	1823.4	1823.9	1823.9	8.5	0.0	0.0	0.0
	ν_3 A' COH bend		1280.2 [42]	1296.6	1289.3	1275.8	1275.8	−0.7	−0.3	0.0	0.0
	ν_4 A' C−O str		1042.4 [42]	1048.2	1050.3	1049.9	1049.9	−0.2	−0.4	0.0	0.0
	ν_5 A' OCO bend		601.2 [42]	602.9	603.2	600.0	600.0	−0.9	−0.1	0.0	0.0
	ν_6 A'' torsion		540.2 [42]	588.9	596.8			−1.0	−0.8		
t-HOCO[f]	ν_1 A' OH str	3635.7 [43]	3641.0 [44]	3627.8	3632.3	3650.5	3650.5	3.5	1.8	−0.1	−0.1
	ν_2 A' C=O str	1852.6 [45]	1862.0 [44]	1861.0	1861.4	1861.6	1861.6	−0.7	−0.3	0.0	0.0
	ν_3 A' COH bend		1212.7 [44]	1224.8	1228.6	1219.5	1219.5	−0.1	−0.3	−0.1	−0.1
	ν_4 A' C−O str		1052.0 [44]	1049.7	1054.2	1053.2	1053.2	−0.8	−0.4	0.0	0.0
	ν_5 A' OCO bend		616.0 [44]	619.1	618.6	615.5	615.5	−0.6	−0.4	0.0	0.0
	ν_6 A'' torsion		475.4 [44]	541.6	572.2			−5.1	−2.0		
c-DOCO	ν_1 A' OD str		2551.6 [42]	2551.2	2547.8	2550.2	2550.2	0.0	0.0	0.0	0.0
	ν_2 A' C=O str		1827.5 [42]	1826.7	1826.4	1827.2	1827.2	0.0	0.0	0.0	0.0
	ν_3 A' C−O str		1123.1 [42]	1123.5	1124.9	1125.5	1125.5	0.0	0.0	0.0	0.0
	ν_4 A' COD bend		960.9 [42]	969.9	944.1	960.1	960.1	−0.2	−0.2	0.0	0.0
	ν_5 A' OCO bend		539.8 [42]	541.7	542.4	540.2	540.2	0.0	0.0	0.0	0.0
	ν_6 A'' torsion		446.9 [42]	471.2	478.6			−0.1	−0.1		
t-DOCO[g]	ν_1 A' OD str	2684.1 [46]	2685.1 [44]	2687.4	2689.8	2693.8	2693.8	−0.7	1.2	0.0	0.0
	ν_2 A' C=O str	1851.6 [45]	1859.8 [44]	1859.1	1859.5	1859.8	1859.8	−0.1	−0.2	0.0	0.0
	ν_3 A' C−O str		1086.4 [44]	1087.4	1090.3	1090.0	1090.0	−0.1	−0.1	0.0	0.0
	ν_4 A' COD bend		902.6 [44]	905.9	910.5	906.3	906.3	−0.1	−0.1	0.0	0.0
	ν_5 A' OCO bend		590.1 [44]	593.2	593.2	589.6	589.6	−0.1	−0.1	0.0	0.0
	ν_6 A'' torsion		368.0 [44]	401.1	422.5			−0.5	−0.4		

[e] Consistent with results by Martin[41], we observe a strong Fermi resonance between ν_2 and $2\nu_3$, where the resonant is located at 1857.9 (ν_{lit}), 1904.7 (ν_{ref}) and 1901.8 ($\nu_{\text{drop}}/\tilde{\nu}_{\text{drop}}$), indicating an inverse assignment to Ref. [41].

[f] In Ref. [47] reported VCI data on the CcCRE QFF for *t*-HOCO are incorrect,[44] instead CcCR-based values are taken from Ref. [44].

[g] No CcCRE-based VCI data for *t*-DOCO are reported in the literature.

Table S2: From V_{ref} computed transition wavenumbers (cm^{-1}) and percentage wavefunction contributions P (squared VCI coefficients) from respective VCI basis functions, as a function of VCI excitation level for states that become near-degenerate with: the OSH bending fundamental of HSOH (ν_4), the OH stretching fundamental of t-HSiOH (ν_1), the symmetric NH stretching fundamental of NH_3 (ν_1), the terminal C=O stretching fundamental of c-HOCO (ν_2) and the OH torsional fundamental of HOOH (ν_4). States are automatically grouped according to their leading wavefunction coefficients. Bolded values indicate logical regroupings of states and associated transition frequencies that could plausibly be assigned as fundamentals.

V_{ref}		VCI(8)	VCI(9)	VCI(10)
HSOH	Fundamental	**1002.3**	994.8	**1016.3**
	$P(\nu_4)$	87%	48%	52%
	$P(2\nu_6)$	8%	39%	37%
	Resonant	1040.4	**1016.1**	992.9
	$P(\nu_4)$	9%	40%	44%
	$P(2\nu_6)$	72%	24%	44%
NH_3	Fundamental	**3345.1**	**3344.7**	3339.2
	$P(\nu_1)$	69%	69%	38%
	$P(3\nu_2)$	$< 1\%$	$< 1\%$	24%
	Resonant	3539.5	3432.3	3352.6
	$P(\nu_1)$	$< 1\%$	$< 1\%$	31%
	$P(3\nu_2)$	52%	55%	32%
	$P(5\nu_2)$	19%	14%	6%
HOOH	Fundamental	**382.4**	**381.2**	367.8
	$P(\nu_4)$	86%	85%	67%
	$P(\nu_1 + 8\nu_4)$		$< 1\%$	7%
	Resonant			428.1
	$P(\nu_4)$			18%
	$P(\nu_1 + 8\nu_4)$			30%

V_{ref}		VCI(8)	VCI(9)	VCI(10)
t-HSiOH	Fundamental	**3666.3**	3651.0	**3665.9**
	$P(\nu_1)$	89%	42%	57%
	$P(3\nu_3 + \nu_4)$	$< 1\%$	$< 1\%$	2%
	$P(8\nu_6)$	$< 1\%$	21%	$< 1\%$
	Resonant		3675.7	3661.2
	$P(\nu_1)$		25%	28%
	$P(3\nu_3 + \nu_4)$		20%	13%
	$P(8\nu_6)$		11%	$< 1\%$
c-HOCO	Fundamental	**1821.9**	**1821.7**	1830.1
	$P(\nu_2)$	68%	66%	59%
	$P(\nu_5 + 2\nu_6)$	8%	9%	23%
	Resonant	1840.0	1837.9	1815.9
	$P(\nu_2)$	21%	22%	29%
	$P(\nu_5 + 2\nu_6)$	41%	39%	30%

Table S3: From $\tilde{V}_{\text{harm}}$ computed transition wavenumbers (cm^{-1}) and percentage wavefunction contributions P (squared VCI coefficients) from respective VCI basis functions for the symmetric OH stretch of HOOH (ν_1) which becomes near-degenerate with $2\nu_2 + \nu_3$, as a function of VCI excitation level. VCI eigenstates are automatically grouped according to their leading basis state wavefunction coefficients.

$\tilde{V}_{\text{harm}}$		VCI(8)	VCI(9)	VCI(10)
HOOH	Fundamental	3596.9	3604.9	3590.2
	$P(\nu_1)$	43%	53%	39%
	$P(2\nu_2 + \nu_3)$	36%	23%	38%
	Resonant	3608.9	3592.7	3600.9
	$P(\nu_1)$	42%	32%	39%
	$P(2\nu_2 + \nu_3)$	29%	45%	28%

2.3 Part II – Pentatomics and hexatomics

Table S4: Fundamental wavenumbers for methyleneimine (CH_2NH), hydroxylamine (NH_2OH) and formaldoxime (CH_2NOH). Computational anharmonic (ν_{lit}) and high-resolution gas phase (ν_{expt}) literature data (references in brackets), harmonic (ω), and computed VCI(9) fundamentals ($\nu^{(9)}$) are shown in cm^{-1}. All reported VCI(9) fundamentals are converged to within $0.1\,\text{cm}^{-1}$, if not stated otherwise. s and a refer to symmetric and antisymmetric combinations, respectively.

	Fundamental			ω [a]		$\nu^{(9)}$			ν_{lit} [b]		ν_{expt} [c]	
				CC	CC-F12	ν_{ref}	ν_{drop}	$\tilde{\nu}_{\text{drop}}$				
CH_2NH	ν_1	A'	NH str	3435.1	3449.6	3280.7[d]	3288.5[d]	3288.5[d]	3275.3	[48]	3262.6	[49]
	ν_2	A'	CH_2 a str	3150.9	3156.3	3026.6	3028.0	3027.7	3029.7	[48]	3024.5	[50]
	ν_3	A'	CH_2 s str	3050.5	3052.6	2912.4	2915.0	2915.2	2909.5	[48]	2914.2	[50]
	ν_4	A'	CN str	1666.5	1675.7	1636.3	1638.9	1639.4	1636.6	[48]	1638.3	[51]
	ν_5	A'	CH_2 scissor	1475.5	1480.6	1450.2	1451.2	1451.4	1447.8	[48]	1452.0	[52]
	ν_6	A'	CNH bend	1375.1	1380.6	1347.2	1347.7	1347.0	1340.1	[48]	1344.3	[52]
	ν_7	A'	CH_2 rock	1067.1	1072.7	1059.2	1058.3	1057.6	1053.6	[48]	1058.2	[53]
	ν_8	A''	NH torsion	1148.7	1155.7	1128.4			1124.8	[48]	1127.0	[53]
	ν_9	A''	CH_2 wag	1071.2	1078.9	1064.0	1062.0	1060.4	1059.9	[48]	1060.8	[53]
NH_2OH	ν_1	A'	OH str	3826.5	3845.3		3663.0	3663.0			3649.9	[54]
	ν_2	A'	NH_2 s str	3444.7	3458.5		3291.2[e,f]	3303.9[e,g]			3294.2	[54]
	ν_3	A'	NH_2 scissor	1663.2	1669.7		1608.4	1608.2			1604.5	[54]
	ν_4	A'	NOH bend	1402.7	1409.1		1360.8	1360.7			1353.3	[54]
	ν_5	A'	NH_2 wag	1154.9	1157.0		1116.0	1114.8			1115.5	[54]
	ν_6	A'	NO str	920.2	937.1		900.2	900.1			895.2	[54]
	ν_7	A''	NH_2 a str	3529.6	3544.4		3361.2	3361.2			3358.8	[54]
	ν_8	A''	NH_2 twist	1327.2	1336.1		1298.2	1298.3			1294.5	[54]
	ν_9	A''	OH torsion	406.7	410.2						386.0	[54]
CH_2NOH	ν_1	A'	OH str	3823.3	3842.0		3663.9	3663.9			3650.3	[55]
	ν_2	A'	CH_2 a str	3245.9	3252.9		3111.1	3111.1			3109.7	[55]
	ν_3	A'	CH_2 s str	3115.4	3118.1		2974.4	2974.4			2974.2	[55]
	ν_4	A'	CN str	1677.3	1687.7		1642.8	1642.8			1639.5	[56]
	ν_5	A'	CH_2 scissor	1446.2	1451.6		1410.2	1410.2			1410.5	[56]
	ν_6	A'	NOH bend	1343.1	1350.6		1315.0	1315.0			1319.0	[56]
	ν_7	A'	CH_2 rock	1172.5	1182.3		1162.0	1161.9			1157.3	[57]
	ν_8	A'	NO str	906.2	924.7		897.5	897.5			892.6	[56]
	ν_9	A'	CNO bend	528.8	533.8		529.5	529.5			530.0	[57]
	ν_{10}	A''	CH_2 wag	961.5	968.5		957.0	957.0			952.6	[58]
	ν_{11}	A''	NOH wag	785.0	791.2		776.5	776.5			772.8	[57]
	ν_{12}	A''	OH torsion	404.7	413.4						397.7	[57]

[a] This work: CC = fc-CCSD(T)/aVTZ; CC-F12 = fc-CCSD(T)-F12a/VTZ-F12

[b] VCI at CCSD(T)-F12a/aVTZ

[c] Experimental data for CH_2NH and CH_2NOH are compactly summarised in Ref. [56].

[d] Fermi resonance between ν_1 and $2\nu_4$:
ν_{ref}: $3280.7\,\text{cm}^{-1}$ (81% ν_1, 4% $2\nu_4$) and $3260.0\,\text{cm}^{-1}$ (4% ν_1, 81% $2\nu_4$)
ν_{drop}: $3288.5\,\text{cm}^{-1}$ (81% ν_1, 4% $2\nu_4$) and $3265.1\,\text{cm}^{-1}$ (4% ν_1, 82% $2\nu_4$)
$\tilde{\nu}_{\text{drop}}$: $3288.6\,\text{cm}^{-1}$ (81% ν_1, 4% $2\nu_4$) and $3266.3\,\text{cm}^{-1}$ (4% ν_1, 82% $2\nu_4$)

[e] Strong resonance mixing between ν_2, $3\nu_5$ and $2\nu_3$:
ν_{drop}: $3309.5\,\text{cm}^{-1}$ (27% ν_2, 37% $3\nu_5$, 6% $2\nu_3$), $3291.2\,\text{cm}^{-1}$ (45% ν_2, 21% $3\nu_5$, 3% $2\nu_3$) and $3193.7\,\text{cm}^{-1}$ (12% ν_2, 78% $2\nu_3$)
$\tilde{\nu}_{\text{drop}}$: $3303.9\,\text{cm}^{-1}$ (50% ν_2, 19% $3\nu_5$, 9% $2\nu_3$), $3282.9\,\text{cm}^{-1}$ (21% ν_2, 41% $3\nu_5$) and $3193.3\,\text{cm}^{-1}$ (12% ν_2, 78% $2\nu_3$)

[f] $\nu^{(9)} - \nu^{(8)}$ convergence uncertainty: $1.2\,\text{cm}^{-1}$

[g] $\nu^{(9)} - \nu^{(8)}$ convergence uncertainty: $1.8\,\text{cm}^{-1}$

Table S5: Fundamental transition wavenumbers (ν) and tunnel splittings ($\Delta = \nu(E) - \nu(A) + \Delta_{\text{g.s.}}$) for methanol ($CH_3OH$) in the molecular symmetry group representation G_6. Experimental references are shown in brackets, see footnotes on how transition wavenumbers were obtained. All reported values are in units of cm^{-1}.

Methanol (G_6)			Ref. [59]			Ref. [60]			Expt.			
			$\nu(A)$	$\nu(E)$	Δ	$\nu(A)$	$\nu(E)$	Δ	$\nu(A)$	$\nu(E)$	Δ	Ref.
g.s.	A_1/E				8.8			8.7			9.12	[61]
ν_1	A_1/E	OH str	3680.2	3677.9	6.5	3675.0	3673.2	6.9	3685.32	3682.49	6.29	[62]
ν_2	A_1/E	CH_3 a str	3005.2	2993.6	−2.8	2986.3	2976.9	−0.7	3006.99	2994.61	−3.26	[63]
ν_3	A_1/E	CH_3 s str	2844.4	2841.2	5.6	2839.5	2839.9	9.1	2844.72	2844.67	9.07	[64]
ν_4	A_1/E	CH_3 a bend	1484.0	1469.9	−5.3	1483.8	1472.4	−2.7	1486.08	1474.14	−2.82	[65]
ν_5	A_1/E	CH_3 s bend	1450.2	1449.0	7.6	1446.8	1446.8	8.7	1453.32	1452.96	8.76	[65]
ν_6	A_1/E	COH bend	1321.0	1337.1	24.9	1321.9	1333.2	20.0	1320.63	1335.20	23.69	[66]
ν_7	A_1/E	CH_3 rock	1074.0	1069.8	4.6	1079.9	1078.8	7.6	1074.66	1070.15	4.61	[67]
ν_8	A_1/E	CO str	1031.0	1030.6	8.4	1026.3	1028.1	10.5	1034.37	1033.53	8.27	[67]
ν_9	A_2/E	CH_3 a str	2956.5	2943.7	−4.0	2961.5	2949.4	−3.4	2966.64	2952.04	−5.48	[68]
ν_{10}	A_2/E	CH_3 a bend	1465.0	1451.5	−4.7	1475.1	1462.2	−4.2	1481.45	1464.80	−7.53	[65]
ν_{11}	A_2/E	CH_3 rock	1159.9	1143.6	−7.5	1156.5	1142.4	−5.4	1163.97	1147.35	−7.50	[67]

Low-resolution band centres are computed for each fundamental according to Eq. 2:

g.s. Moruzzi *et al.*[61] report Taylor expansion coefficients for absolute term energies in Tabs. 8.1 (A) and 8.3 (E). From these, we compute the ground state term values $E_{\text{g.s.}}(A) = 128.7822\,cm^{-1}$ and $E_{\text{g.s.}}(E) = 137.9036\,cm^{-1}$, yielding a zero-point splitting of $\Delta_{\text{g.s.}} = 9.12\,cm^{-1}$. For consistency, this value is used to compute E transitions for all other vibrational fundamentals.

ν_1 Hunt *et al.*[62] list relative term values in Tabs. 1 (A) and 2 (E): $W_1(A) = 3685.3222\,cm^{-1}$ and $W_1(E) = 3691.6122\,cm^{-1}$.

ν_2 Xu *et al.*[63] report both, absolute term values for the ground state ($E_{\text{g.s.}}(A) = 127.817\,cm^{-1}$ and $E_{\text{g.s.}}(E) = 136.939\,cm^{-1}$) and ν_2 ($E_2(A) = 3134.804\,cm^{-1}$ and $E_2(E) = 3131.549\,cm^{-1}$) in Tab. 4. We obtain relative term values as $W_2(A/E) = E_2(A/E) - 127.817\,cm^{-1}$.

ν_3 Hunt *et al.*[64] report transition wavenumbers $\nu_3(A) = (2844.72 \pm 0.01)\,cm^{-1}$ and $\nu_3(E) = (2844.67 \pm 0.05)\,cm^{-1}$ in Tab. 2.

ν_4 Temsamani *et al.*[65] report absolute term values for ν_4, ν_5 and ν_{10} in Tab. 7. For ν_4 they report values of $E_4(A) = 1614.19\,cm^{-1}$ and $E_4(E) = 1611.37\,cm^{-1}$. In Tab. 4 they report a zero-point energy of $E_{\text{g.s.}}(A) = 128.1069\,cm^{-1}$ which they calculated with constants reported by Xu and Hougen[69]. We obtain relative term values as $W_i(A/E) = E_i(A/E) - 128.1069\,cm^{-1}$.

ν_5 See ν_4. $E_5(A) = 1581.43\,cm^{-1}$ and $E_5(E) = 1590.19\,cm^{-1}$.

ν_6 Lees *et al.*[66] report transition wavenumbers for ν_6 in Tab. 1: $\nu_6(A) = 1320.633\,cm^{-1}$ and $\nu_6(E) = 1335.199\,cm^{-1}$.

ν_7 Lees *et al.*[67] re-fitted Fourier coefficients for ν_7, ν_8, ν_{11} and other vibrational states. Using their coefficients in Tab. 2, we obtain relative term values of $W_7(A) = 1074.661\,cm^{-1}$ and $W_7(E) = 1079.269\,cm^{-1}$.

ν_8 See ν_7. $W_8(A) = 1034.373\,cm^{-1}$ and $W_8(E) = 1042.646\,cm^{-1}$.

ν_9 Wang and Perry[68] report absolute term values for ν_2, ν_3 and ν_9 ($E_9(A) = 3094.75\,cm^{-1}$ and $E_9(E) = 3089.27\,cm^{-1}$). The zero-point energy is computed by constants reported by Xu and Hougen[69]. We obtain relative term values as $W_i(A/E) = E_i(A/E) - 128.1069\,cm^{-1}$.

ν_{10} See ν_4. $E_{10}(A) = 1609.65\,cm^{-1}$ and $E_{10}(E) = 1602.03\,cm^{-1}$.

ν_{11} See ν_7. $W_{11}(A) = 1163.970\,cm^{-1}$ and $W_{11}(E) = 1156.465\,cm^{-1}$.

Table S6: Fundamental transition wavenumbers (cm^{-1}) for methanol (CH_3OH) in the single-reference point group symmetry representation C_s. Low-resolution computational and experimental literature values ($\bar{\nu}$), harmonic (ω) and single-reference VCI(9) fundamental transition wavenumbers ($\nu^{(9)}$) are shown. All reported VCI(9) fundamentals are converged to within $0.1\,cm^{-1}$, if not stated otherwise.

Methanol (C_s)			ω [a]		$\nu^{(9)}$		$\bar{\nu}$		
			CC	CC-F12	ν_{drop}	$\tilde{\nu}_{\text{drop}}$	Ref. [59]	Ref. [60]	Expt.
ν_1	A'	OH str	3843.6	3864.0	3685.6	3685.6	3678.7	3673.8	3683.4
ν_2	A'	CH_3 a str	3128.3	3137.1	3002.9	3002.7	2997.5	2980.0	2998.7
ν_3	A'	CH_3 s str	3010.9	3016.1	2840.9	2840.7	2842.3	2839.8	2844.7
ν_4	A'	CH_3 a bend	1522.8	1521.0	1475.5	1475.1	1474.6	1476.2	1478.1
ν_5	A'	CH_3 s bend	1484.1	1484.6	1448.3	1448.4	1449.4	1446.8	1453.1
ν_6	A'	COH bend	1379.2	1382.5	1347.9	1347.8	1331.7	1329.4	1330.3
ν_7	A'	CH_3 rock	1082.3	1089.2	1067.2	1067.1	1071.2	1079.2	1071.7
ν_8	A'	CO str	1053.6	1061.3	1033.3	1033.4	1030.7	1027.5	1033.8
ν_9	A''	CH_3 a str	3069.2	3076.3	2953.0[b,c]	2952.1[b,c]	2948.0	2953.4	2956.9
ν_{10}	A''	CH_3 a bend	1512.3	1510.8	1464.5	1464.0	1456.0	1466.5	1470.4
ν_{11}	A''	CH_3 rock	1175.9	1180.9	1155.7	1155.5	1149.0	1147.1	1152.9

[a] This work: CC = fc-CCSD(T)/aVTZ; CC-F12 = fc-CCSD(T)-F12a/VTZ-F12

[b] Very strong resonance mixing between ν_9 and $\nu_4 + \nu_5$:
ν_{drop}: $2953.0\,cm^{-1}$ (33% ν_9, 44% $\nu_4 + \nu_5$) and $2921.7\,cm^{-1}$ (28% ν_9, 35% $\nu_4 + \nu_5$)
$\tilde{\nu}_{\text{drop}}$: $2952.1\,cm^{-1}$ (35% ν_9, 52% $\nu_4 + \nu_5$) and $2921.3\,cm^{-1}$ (27% ν_9, 37% $\nu_4 + \nu_5$)

[c] $\nu^{(9)} - \nu^{(8)}$ convergence uncertainty: $0.2\,cm^{-1}$

3 R matrices

In the following, **R** matrices (see main text, Eq. 4) are reported for all investigated molecular topologies (group D similar to group B), where **R** contains elements $R_{ij} = \partial\tilde{Q}_i/\partial S_j$. The internal coordinate labels SPF, BA, DA and SOOP stand for Simons-Parr-Finlan, bond angle, dihedral angle and sine of out-of-plane angle, respectively. ν_i denotes the i^{th} normal mode.

3.1 Tetratomic examples: NH_3, SO_3 and H_2O_2

Cartesian coordinates (Angst)				
1	N	0.00	0.00	0.07
2	H	-0.46	0.82	-0.31
3	H	-0.48	-0.80	-0.31
4	H	0.94	-0.01	-0.31

Redundant internal coordinates		Connectivity
S_1	SPF	(1-2)
S_2	SPF	(1-3)
S_3	SPF	(1-4)
S_4	BA	(2-1-3)
S_5	BA	(2-1-4)
S_6	BA	(3-1-4)

R matrix for V_{ref}/~V_{harm}/V_{drop}

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6
1	A_1	s stretch	-47	-47	-47	-3	-3	-3
2	A_1	inversion	-1	-1	-1	40	40	40
3	E	a stretch	47	14	-61	1	0	-1
3	E	a stretch	-43	63	-19	0	-1	1
4	E	a bend	1	2	-3	40	-30	-10
4	E	a bend	3	-2	-1	12	29	-41

R matrix for ~V_{drop}

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6
1	A_1	s stretch	-49	-49	-49	139	139	139
3	E	a stretch	47	14	-61	1	0	-1
3	E	a stretch	-43	63	-19	0	-1	1
4	E	a bend	1	2	-3	40	-30	-10
4	E	a bend	3	-2	-1	12	29	-41

Cartesian coordinates (Angst)				
1	S	0.00	0.00	0.00
2	O	1.43	0.00	0.00
3	O	-0.71	-1.23	0.00
4	O	-0.71	1.23	0.00

Redundant internal coordinates		Connectivity
S_1	SPF	(1-2)
S_2	SPF	(1-3)
S_3	SPF	(1-4)
S_4	BA	(2-1-3)
S_5	BA	(2-1-4)
S_6	BA	(3-1-4)
S_7	SOOP	(1-2-4-3)

R matrix for V_{ref}/~V_{harm}/V_{drop}

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6	S_7
1	A_1'	s stretch	266	266	266	0	0	0	0
2	A_2''	oop	0	0	0	0	0	0	-504
4	E'	a bend	121	9	-129	162	-11	-151	0
4	E'	a bend	-80	144	-65	81	-181	100	0
3	E'	a stretch	1	241	-242	-6	6	0	0
3	E'	a stretch	279	-140	-139	-3	-3	6	0

R matrix for ~V_{drop}

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6	-
1	A_1'	s stretch	266	266	266	0	0	0	-
3	E'	a stretch	1	241	-242	-6	6	0	-
3	E'	a stretch	279	-140	-139	-3	-3	6	-
4	E'	a bend	121	9	-129	162	-11	-151	-
4	E'	a bend	-80	144	-65	81	-181	100	-

Cartesian coordinates (Angst)				
1	H	-0.90	-0.79	-0.49
2	O	-0.73	0.00	0.03
3	O	0.73	0.00	0.03
4	H	0.90	0.79	-0.49

Redundant internal coordinates		Connectivity
S_1	SPF	(1-2)
S_2	SPF	(2-3)
S_3	SPF	(3-4)
S_4	BA	(1-2-3)
S_5	BA	(2-3-4)
S_6	DA	(1-2-3-4)

R matrix for V_{ref}/~V_{harm}/V_{drop}

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6
1	A	OH_2 s stretch	-53	4	-53	1	1	0
2	A	s bend	-4	-88	-4	-53	-53	-4
3	A	OO stretch	3	329	3	-1	-1	-3
4	A	torsion	0	-17	0	1	1	-52
5	B	OH_2 a stretch	53	0	-53	0	0	0
6	B	a bend	-1	0	1	-52	52	0

R matrix for ~V_{drop}

ν_i		Label	S_1	S_2	S_3	S_4	S_5	-
1	A	OH_2 s stretch	-53	4	-53	1	1	-
2	A	s bend	-4	-87	-4	-53	-53	-
3	A	OO stretch	3	330	3	-1	-1	-
5	B	OH_2 a stretch	53	0	-53	0	0	-
6	B	a bend	-1	0	1	-52	52	-

3.2 Pentatomics: CH_2NH and NH_2OH

Cartesian coordinates (Angst)				
1	C	0.00	0.03	-0.63
2	N	0.00	0.03	0.64
3	H	0.00	-0.93	0.99
4	H	0.00	0.99	-1.15
5	H	0.00	-0.87	-1.25

Redundant internal coordinates		
		Connectivity
S_1	SPF	(1-2)
S_2	SPF	(1-4)
S_3	SPF	(1-5)
S_4	SPF	(2-3)
S_5	BA	(2-1-4)
S_6	BA	(2-1-5)
S_7	BA	(4-1-5)
S_8	BA	(1-2-3)
S_9	DA	(4-1-2-3)
S_{10}	DA	(5-1-2-3)
S_{11}	SOOP	(1-2-5-4)

R matrix for $V_{ref}/\sim V_{harm}/V_{drop}$

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
1	A'	NH stretch	6	3	-4	-80	-1	1	0	-2	0	0
2	A'	CH_2 a stretch	2	-75	37	-4	0	0	0	0	0	0
3	A'	CH_2 s stretch	-6	39	76	-3	0	-1	1	-1	0	0
4	A'	CN stretch	208	9	9	6	-8	-11	19	6	0	0
5	A'	CH_2 scissor	182	5	4	5	22	14	-36	10	0	0
6	A'	CNH bend	10	-9	8	-3	-28	31	-3	-56	0	0
7	A'	CH_2 rock	20	-4	6	-2	-45	46	-1	53	0	0
8	A''	NH torsion	0	0	0	0	0	0	0	0	40	21
9	A''	CH_2 wag	0	0	0	0	0	0	0	0	41	-48

R matrix for $\sim V_{drop}$

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_{11}	-
1	A'	NH stretch	6	3	-4	-80	-1	1	0	-2	0	-
2	A'	CH_2 a stretch	2	-75	37	-4	0	0	0	0	0	-
3	A'	CH_2 s stretch	-6	39	76	-3	0	-1	1	-1	0	-
4	A'	CN stretch	208	9	9	6	-8	-11	19	6	0	-
5	A'	CH_2 scissor	182	5	4	5	22	14	-36	10	0	-
6	A'	CNH bend	10	-9	8	-3	-28	31	-3	-56	0	-
7	A'	CH_2 rock	20	-4	6	-2	-45	46	-1	53	0	-
9	A''	CH_2 wag	0	0	0	0	0	0	0	0	-154	-

Cartesian coordinates (Angst)				
1	N	0.00	-0.01	-0.74
2	O	0.00	-0.01	0.71
3	H	0.00	-0.95	0.91
4	H	0.81	0.56	-0.97
5	H	-0.81	0.56	-0.97

Redundant internal coordinates		
		Connectivity
S_1	SPF	(1-2)
S_2	SPF	(1-4)
S_3	SPF	(1-5)
S_4	SPF	(2-3)
S_5	BA	(2-1-4)
S_6	BA	(2-1-5)
S_7	BA	(4-1-5)
S_8	BA	(1-2-3)
S_9	DA	(4-1-2-3)
S_{10}	DA	(5-1-2-3)

R matrix for $V_{ref}/\sim V_{harm}/V_{drop}$

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
1	A'	OH stretch	-3	-1	-1	76	0	0	0	0	0	0
2	A'	NH_2 s stretch	2	-57	-57	-1	0	0	-3	0	-1	1
3	A'	NH_2 scissor	38	1	1	2	27	27	-34	12	-9	9
4	A'	NOH bend	-91	-3	-3	-4	-13	-13	-9	-66	-9	9
5	A'	NH_2 wag	101	1	1	2	41	41	10	-32	19	-19
6	A'	NO stretch	304	3	3	3	-8	-8	-6	2	-6	6
7	A''	NH_2 a stretch	0	56	-56	0	-1	1	0	0	0	0
8	A''	NH_2 twist	0	-5	5	0	-55	55	0	0	2	2
9	A''	OH torsion	0	1	-1	0	-3	3	0	0	-31	-31

R matrix for $\sim V_{drop}$

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	-	-
1	A'	OH stretch	-3	-1	-1	76	0	0	0	0	-	-
2	A'	NH_2 s stretch	2	-57	-57	-1	-1	-1	-4	0	-	-
3	A'	NH_2 scissor	38	1	1	2	24	24	-44	12	-	-
4	A'	NOH bend	-91	-3	-3	-4	-17	-17	-19	-66	-	-
5	A'	NH_2 wag	101	1	1	2	48	48	31	-32	-	-
6	A'	NO stretch	304	3	3	3	-10	-10	-12	2	-	-
7	A''	NH_2 a stretch	0	56	-56	0	-1	1	0	0	-	-
8	A''	NH_2 twist	0	-5	5	0	-55	55	0	0	-	-

3.3 Hexatomics: CH_2NOH and CH_3OH

Cartesian coordinates (Angst)				
1	N	-0.37	0.21	-0.33
2	O	-0.37	-0.55	0.86
3	C	0.83	0.45	-0.70
4	H	-1.32	-0.67	1.03
5	H	1.69	0.09	-0.14
6	H	0.94	1.04	-1.60

Redundant internal coordinates		
		Connectivity
S_1	SPF	(1-2)
S_2	SPF	(1-3)
S_3	SPF	(2-4)
S_4	SPF	(3-5)
S_5	SPF	(3-6)
S_6	BA	(2-1-3)
S_7	BA	(1-2-4)
S_8	BA	(1-3-5)
S_9	BA	(1-3-6)
S_{10}	BA	(5-3-6)
S_{11}	DA	(3-1-2-4)
S_{12}	DA	(2-1-3-5)
S_{13}	DA	(2-1-3-6)

R matrix for V_{ref}/~V_{harm}/V_{drop}

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}
1	A'	OH str	2	1	-76	1	0	0	0	0	0	0	0	0	0
2	A'	CH_2 a str	3	2	0	40	-73	1	0	0	0	0	0	0	0
3	A'	CH_2 s str	-1	-8	0	75	42	-1	0	0	0	0	0	0	0
4	A'	CN str	-27	209	-1	11	8	-9	-19	-4	-8	12	0	0	0
5	A'	CH_2 scissor	41	-56	2	-1	3	18	36	-20	-14	33	0	0	0
6	A'	NOH bend	23	164	3	2	7	22	57	0	19	-19	0	0	0
7	A'	CH_2 rock	-51	-16	0	-9	9	35	-21	-45	43	2	0	0	0
8	A'	NO str	331	82	5	-2	7	28	1	-15	19	-4	0	0	0
9	A'	CNO bend	-90	-109	-9	3	-10	-230	15	-35	30	5	0	0	0
10	A"	CH_2 wag	0	0	0	0	0	0	0	0	0	0	0	51	-40
11	A"	NOH wag	0	0	0	0	0	0	0	0	0	0	-10	35	61
12	A"	OH torsion	0	0	0	0	0	0	0	0	0	0	71	13	5

R matrix for ~V_{drop}

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	-	S_{12}	S_{13}
1	A'	OH str	2	1	-76	1	0	0	0	0	0	0	-	0	0
2	A'	CH_2 a str	3	2	0	40	-73	1	0	0	0	0	-	0	0
3	A'	CH_2 s str	-1	-8	0	75	42	-1	0	0	0	0	-	0	0
4	A'	CN str	-27	209	-1	11	8	-9	-19	-4	-8	12	-	0	0
5	A'	CH_2 scissor	41	-56	2	-1	3	18	36	-20	-14	33	-	0	0
6	A'	NOH bend	23	164	3	2	7	22	57	0	19	-19	-	0	0
7	A'	CH_2 rock	-51	-16	0	-9	9	35	-21	-45	43	2	-	0	0
8	A'	NO str	331	82	5	-2	7	28	1	-15	19	-4	-	0	0
9	A'	CNO bend	-90	-109	-9	3	-10	-230	15	-35	30	5	-	0	0
10	A"	CH_2 wag	0	0	0	0	0	0	0	0	0	0	-	51	-40
11	A"	NOH wag	0	0	0	0	0	0	0	0	0	0	-	37	62

Cartesian coordinates (Angst)				
1	O	0.69	-0.06	0.00
2	C	-0.73	0.01	0.00
3	H	-1.10	-1.01	0.00
4	H	1.04	0.83	0.00
5	H	-1.11	0.52	-0.89
6	H	-1.11	0.52	0.89

Redundant internal coordinates		
		Connectivity
S_1	SPF	(1-2)
S_2	SPF	(1-4)
S_3	SPF	(2-3)
S_4	SPF	(2-5)
S_5	SPF	(2-6)
S_6	BA	(2-1-4)
S_7	BA	(1-2-3)
S_8	BA	(1-2-5)
S_9	BA	(1-2-6)
S_{10}	BA	(3-2-5)
S_{11}	BA	(3-2-6)
S_{12}	BA	(5-2-6)
S_{13}	DA	(4-1-2-3)
S_{14}	DA	(4-1-2-5)
S_{15}	DA	(4-1-2-6)

R matrix for V_{ref}/~V_{harm}/V_{drop}

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}
1	A'	OH str	-3	76	-1	0	0	1	0	0	0	0	0	0	0	0	0
2	A'	CH_3 a str	-1	1	80	-19	-19	-1	0	0	0	1	1	-1	0	0	0
3	A'	CH_3 s str	-4	0	-29	-58	-58	0	0	1	1	0	0	-1	0	0	0
4	A'	CH_3 a bend	1	1	-1	1	1	7	16	-13	-13	-12	-12	33	0	12	-12
5	A'	CH_3 s bend	-31	-1	2	1	1	-1	-25	-22	-22	25	25	20	0	-3	3
6	A'	COH bend	37	4	10	-4	-4	56	32	-13	-13	0	0	-4	0	-13	13
7	A'	CH_3 rock	-211	-2	1	-6	-6	-40	36	-23	-23	4	4	4	0	-14	14
8	A'	CO str	-242	-5	-7	-3	-3	28	-33	10	10	4	4	4	0	10	-10
9	A"	CH_3 a str	0	0	0	60	-60	0	0	-1	1	1	-1	0	1	0	0
10	A"	CH_3 a bend	0	0	0	2	-2	0	0	-14	14	27	-27	0	16	-9	-9
11	A"	CH_3 rock	0	0	0	9	-9	0	0	52	-52	0	0	0	20	-10	-10
12	A"	torsion	0	0	0	0	0	0	0	-4	4	-1	1	0	-23	-20	-20

R matrix for ~V_{drop}

ν_i		Label	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	-	-	-
1	A'	OH str	-3	76	-1	0	0	1	0	0	0	0	0	0	-	-	-
2	A'	CH_3 a str	-1	1	80	-19	-19	-1	0	0	0	1	1	-1	-	-	-
3	A'	CH_3 s str	-4	0	-29	-58	-58	0	0	1	1	0	0	-1	-	-	-
4	A'	CH_3 a bend	1	1	-1	1	1	7	11	-10	-10	-18	-18	43	-	-	-
5	A'	CH_3 s bend	-31	-1	2	1	1	-1	-24	-23	-23	27	27	17	-	-	-
6	A'	COH bend	37	4	10	-4	-4	56	38	-17	-17	6	6	-14	-	-	-
7	A'	CH_3 rock	-211	-2	1	-6	-6	-40	43	-26	-26	10	10	-7	-	-	-
8	A'	CO str	-242	-5	-7	-3	-3	28	-38	12	12	-1	-1	12	-	-	-
9	A"	CH_3 a str	0	0	0	60	-60	0	0	-1	1	1	-1	0	-	-	-
10	A"	CH_3 a bend	0	0	0	2	-2	0	0	-9	9	37	-37	0	-	-	-
11	A"	CH_3 rock	0	0	0	9	-9	0	0	57	-57	12	-12	0	-	-	-

References

[1] J. F. Stanton, J. Gauss, L. Cheng, M. E. Harding, D. A. Matthews, P. G. Szalay, CFOUR, Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package, With contributions from A.A. Auer, R.J. Bartlett, U. Benedikt, C. Berger, D.E. Bernholdt, Y.J. Bomble, O. Christiansen, F. Engel, R. Faber, M. Heckert, O. Heun, M. Hilgenberg, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, T. Kirsch, K. Klein, W.J. Lauderdale, F. Lipparini, T. Metzroth, L.A. Mück, D.P. O'Neill, D.R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J.D. Watts and the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see https://www.cfour.de.

[2] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, "Molpro: a general-purpose quantum chemistry program package", *WIREs Comput. Mol. Sci.* **2012**, *2*, 242–253.

[3] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, W. Györffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, S. J. Bennie, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, S. J. R. Lee, Y. Liu, A. W. Lloyd, Q. Ma, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, T. F. Miller III, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, M. Welborn, MOLPRO, version 2018.1, a package of ab initio programs, see https://www.molpro.net, **2018**.

[4] G. Guelachvili, A. H. Abdullah, N. Tu, K. N. Rao, Š. Urban, D. Papoušek, "Analysis of high-resolution Fourier transform spectra of $^{14}NH_3$ at 3.0 μm", *J. Mol. Spectrosc.* **1989**, *133*, 345–364.

[5] S. N. Yurchenko, J. Zheng, H. Lin, P. Jensen, W. Thiel, "Potential-energy surface for the electronic ground state of NH_3 up to 20 000 cm^{-1} above equilibrium", *J. Chem. Phys.* **2005**, *123*, 134308.

[6] Š. Urban, V. Špirko, D. Papoušek, J. Kauppinen, S. P. Belov, L. I. Gershtein, A. F. Krupnov, "A simultaneous analysis of the microwave, submillimeterwave, far infrared, and infrared-microwave two-photon transitions between the ground and ν_2 inversion-rotation levels of $^{14}NH_3$", *J. Mol. Spectrosc.* **1981**, *88*, 274–292.

[7] I. Kleiner, L. R. Brown, G. Tarrago, Q.-L. Kou, N. Picqué, G. Guelachvili, V. Dana, J.-Y. Mandin, "Positions and intensities in the $2\nu_4/\nu_1/\nu_3$ vibrational system of $^{14}NH_3$ near 3 μm", *J. Mol. Spectrosc.* **1999**, *193*, 46–71.

[8] C. Cottaz, I. Kleiner, G. Tarrago, L. R. Brown, J. S. Margolis, R. L. Poynter, H. M. Pickett, T. Fouchet, P. Drossart, E. Lellouch, "Line positions and intensities in the $2\nu_2/\nu_4$ vibrational system of $^{14}NH_3$ near 5-7 μm", *J. Mol. Spectrosc.* **2000**, *203*, 285–309.

[9] O. N. Ulenikov, E. S. Bekhtereva, V. A. Kozinskaia, J.-J. Zheng, S.-G. He, S.-M. Hu, Q.-S. Zhu, C. Leroy, L. Pluchart, "On the study of resonance interactions and splittings in the PH_3 molecule: ν_1, ν_3, $\nu_2+\nu_4$, and $2\nu_4$ bands", *J. Mol. Spectrosc.* **2002**, *215*, 295–308.

[10] R. I. Ovsyannikov, W. Thiel, S. N. Yurchenko, M. Carvajal, P. Jensen, "Vibrational energies of PH_3 calculated variationally at the complete basis set limit", *J. Chem. Phys.* **2008**, *129*, 044309.

[11] A. Ainetschian, U. Häring, G. Spiegl, W. A. Kreiner, "The ν_2/ν_4 diad of PH_3", *J. Mol. Spectrosc.* **1997**, *181*, 99–107.

[12] L. Fusina, G. Di Lonardo, "The Fundamental Bands in the Infrared Spectrum of Stibine (SbH_3)", *J. Mol. Spectrosc.* **2002**, *216*, 493–500.

[13] S. N. Yurchenko, W. Thiel, P. Jensen, "Rotational energy cluster formation in XY_3 molecules: Excited vibrational states of BiH_3 and SbH_3", *J. Mol. Spectrosc.* **2006**, *240*, 174–187.

[14] W. Jerzembeck, H. Bürger, J. Breidung, W. Thiel, "High resolution infrared spectra of the ν_1–ν_4 bands of BiH_3, and ab initio calculations of the spectroscopic parameters", *J. Mol. Spectrosc.* **2004**, *226*, 32–44.

[15] K. Aarset, A. G. Császár, E. L. Sibert III, W. D. Allen, H. F. Schaefer III, W. Klopper, J. Noga, "Anharmonic force field, vibrational energies, and barrier to inversion of SiH_3^-", *J. Chem. Phys.* **2000**, *112*, 4053–4063.

[16] Y. Pak, R. C. Woods, "Anharmonic force fields and spectroscopic properties of BF_3 and CF_3^+ using the coupled cluster method", *J. Chem. Phys.* **1997**, *106*, 6424–6429.

[17] S. Yamamoto, R. Kuwabara, M. Takami, K. Kuchitsu, "Infrared diode laser spectroscopy of the ν_2 band of BF_3", *J. Mol. Spectrosc.* **1986**, *115*, 333–352.

[18] S. Yamamoto, K. Kuchitsu, T. Nakanaga, H. Takeo, C. Matsumura, M. Takami, "Infrared–microwave double resonance spectroscopy of the ν_3 band of BF_3 using a tunable diode laser", *J. Chem. Phys.* **1986**, *84*, 6027–6033.

[19] S. G. W. Ginn, D. Johansen, J. Overend, "The ν_4 bands of $^{10}BF_3$ and $^{11}BF_3$ at high resolution", *J. Mol. Spectrosc.* **1970**, *36*, 448–463.

[20] Y. Pak, E. L. Sibert III, R. C. Woods, "Coupled cluster anharmonic force fields, spectroscopic constants, and vibrational energies of AlF_3 and SiF_3^+", *J. Chem. Phys.* **1997**, *107*, 1717–1724.

[21] J. M. L. Martin, "A fully ab initio quartic force field of spectroscopic quality for SO_3", *Spectrochim. Acta Part A* **1999**, *55*, 709–718.

[22] J. Ortigoso, R. Escribano, A. G. Maki, "The ν_2 and ν_4 IR bands of SO_3", *J. Mol. Spectrosc.* **1989**, *138*, 602–613.

[23] N. F. Henfrey, B. A. Thrush, "The ν_3 band of SO_3 at high resolution", *Chem. Phys. Lett.* **1983**, *102*, 135–138.

[24] A. Perrin, A. Valentin, L. Daumont, "New analysis of the $2\nu_4$, $\nu_4+\nu_6$, $2\nu_6$, $\nu_3+\nu_4$, $\nu_3+\nu_6$, ν_1, ν_5, $\nu_2+\nu_4$, $2\nu_3$, $\nu_2+\nu_6$ and $\nu_2+\nu_3$ bands of formaldehyde $H_2{}^{12}C^{16}O$: Line positions and intensities in the 3.5 μm spectral region", *J. Mol. Struct.* **2006**, *780*, 28–44.

[25] A. Yachmenev, S. N. Yurchenko, P. Jensen, W. Thiel, "A new spectroscopic potential energy surface for formaldehyde in its ground electronic state", *J. Chem. Phys.* **2011**, *134*, 244307.

[26] F. K. Tchana, A. Perrin, N. Lacome, "New analysis of the ν_2 band of formaldehyde ($H_2{}^{12}C^{16}O$): Line positions for the ν_2, ν_3, ν_4 and ν_6 interacting bands", *J. Mol. Spectrosc.* **2007**, *245*, 141–144.

[27] J. Koput, S. Carter, N. C. Handy, "The vibrational–rotational energy levels of silanone", *Chem. Phys. Lett.* **1999**, *301*, 1–9.

[28] W. B. Olson, R. H. Hunt, B. W. Young, A. G. Maki, J. W. Brault, "Rotational constants of the lowest torsional component (^{0}G) of the ground state and lowest torsional component (^{1}G) of the first excited torsional state of hydrogen peroxide", *J. Mol. Spectrosc.* **1988**, *127*, 12–34.

[29] P. Małyszek, J. Koput, "Accurate ab initio potential energy surface and vibration-rotation energy levels of hydrogen peroxide", *J. Comput. Chem.* **2013**, *34*, 337–345.

[30] A. Perrin, A. Valentin, J.-M. Flaud, C. Camypeyret, L. Schriver, A. Schriver, P. Arcas, "The 7.9-μm band of hydrogen peroxide: line positions and intensities", *J. Mol. Spectrosc.* **1995**, *171*, 358–373.

[31] C. Camy-Peyret, J.-M. Flaud, J. W. C. Johns, M. Noel, "Torsion-vibration interaction in H_2O_2: First high-resolution observation of ν_3", *J. Mol. Spectrosc.* **1992**, *155*, 84–104.

[32] J.-M. Flaud, C. Camy-Peyret, J. W. C. Johns, B. Carli, "The far infrared spectrum of H_2O_2. First observation of the staggering of the levels and determination of the *cis* barrier", *J. Chem. Phys.* **1989**, *91*, 1504–1510.

[33] W. B. Cook, R. H. Hunt, W. N. Shelton, F. A. Flaherty, "Torsion-rotation energy levels, hindering potential, and inertial parameters of the first excited vibrational state of the antisymmetric OH stretch in hydrogen peroxide", *J. Mol. Spectrosc.* **1995**, *171*, 91–112.

[34] J.-M. Flaud, J. W. C. Johns, Z. Lu, G. Winnewisser, H. Klein, "The torsion-rotation spectrum of D_2O_2", *Can. J. Phys.* **2001**, *79*, 367–374.

[35] O. Baum, T. F. Giesen, S. Schlemmer, "High-resolution infrared measurements on HSOH: Analysis of the OH fundamental vibrational mode", *J. Mol. Spectrosc.* **2008**, *247*, 25–29.

[36] S. N. Yurchenko, A. Yachmenev, W. Thiel, O. Baum, T. F. Giesen, V. V. Melnikov, P. Jensen, "An ab initio calculation of the vibrational energies and transition moments of HSOH", *J. Mol. Spectrosc.* **2009**, *257*, 57–65.

[37] O. Baum, *HSOH : an elusive species with many different traits (PhD thesis)*, 1st ed., Cuvillier, Göttingen, **2008**.

[38] H. Beckers, S. Esser, T. Metzroth, M. Behnke, H. Willner, J. Gauss, J. Hahn, "Low-Pressure Pyrolysis of tBu$_2$SO: Synthesis and IR Spectroscopic Detection of HSOH", *Chem. Eur. J.* **2006**, *12*, 832–844.

[39] J. M. L. Martin, P. R. Taylor, "Accurate ab initio quartic force field for *trans*-HNNH and treatment of resonance polyads", *Spectrochim. Acta Part A* **1997**, *53*, 1039–1050.

[40] F. Hegelund, H. Burger, O. Polanz, "The high-resolution infrared spectrum of the ν_4, ν_5, and ν_6 bands of *trans*-di-imide revisited", *J. Mol. Spectrosc.* **1994**, *167*, 1–10.

[41] J. M. L. Martin, "Anharmonic force fields and accurate thermochemistry of H_2SiO, *cis*-HSiOH, and *trans*-HSiOH", *J. Phys. Chem. A* **1998**, *102*, 1394–1404.

[42] R. C. Fortenberry, X. Huang, J. S. Francisco, T. D. Crawford, T. J. Lee, "Vibrational frequencies and spectroscopic constants from quartic force fields for *cis*-HOCO: The radical and the anion", *J. Chem. Phys.* **2011**, *135*, 214303.

[43] J. T. Petty, C. B. Moore, "Transient Infrared Absorption Spectrum of the ν_1 Fundamental of *trans*-HOCO", *J. Mol. Spectrosc.* **1993**, *161*, 149–156.

[44] X. Huang, R. C. Fortenberry, Y. Wang, J. S. Francisco, T. D. Crawford, J. M. Bowman, T. J. Lee, "Dipole Surface and Infrared Intensities for the *cis*- and *trans*-HOCO and DOCO Radicals", *J. Phys. Chem. A* **2013**, *117*, 6932–6939.

[45] T. J. Sears, W. M. Fawzy, P. M. Johnson, "Transient diode laser absorption spectroscopy of the ν_2 fundamental of *trans*-HOCO and DOCO", *J. Chem. Phys.* **1992**, *97*, 3996–4007.

[46] J. T. Petty, C. B. Moore, "Transient infrared absorption spectrum of the ν_1 fundamental of *trans*-DOCO", *J. Chem. Phys.* **1993**, *99*, 47–55.

[47] R. C. Fortenberry, X. Huang, J. S. Francisco, T. D. Crawford, T. J. Lee, "The *trans*-HOCO radical: Quartic force fields, vibrational frequencies, and spectroscopic constants", *J. Chem. Phys.* **2011**, *135*, 134301.

[48] G. Rauhut, G. Knizia, H.-J. Werner, "Accurate calculation of vibrational frequencies using explicitly correlated coupled-cluster theory", *J. Chem. Phys.* **2009**, *130*, 054105.

[49] L. Halonen, G. Duxbury, "Fourier transform infrared spectrum of CH_2NH: The ν_1 band", *Chem. Phys. Lett.* **1985**, *118*, 246–251.

[50] L. Halonen, G. Duxbury, "High resolution infrared spectrum of methyleneimine, CH_2NH,in the 3 μm region", *J. Chem. Phys.* **1985**, *83*, 2091–2096.

[51] G. Duxbury, H. Kato, M. L. Le Lerre, "Laser Stark and interferometric studies of thioformaldehyde and methyleneimine", *Faraday Discuss. Chem. Soc.* **1981**, *71*, 97–110.

[52] G. Duxbury, M. L. Le Lerre, "Fourier transform infrared spectra of CH_2NH: The ν_5 and ν_6 bands", *J. Mol. Spectrosc.* **1982**, *92*, 326–348.

[53] L. Halonen, G. Duxbury, "The Fourier transform infrared spectrum of methyleneimine in the 10 μm region", *J. Chem. Phys.* **1985**, *83*, 2078–2090.
[54] D. Luckhaus, "The rovibrational spectrum of hydroxylamine: A combined high resolution experimental and theoretical study", *J. Chem. Phys.* **1997**, *106*, 8409–8426.
[55] G. Duxbury, "High-resolution infrared spectrum of formaldoxime (CH_2NOH) in the 3-μm and OH overtone regions", *J. Mol. Spectrosc.* **1988**, *132*, 393–406.
[56] R. A. Bannai, G. Duxbury, "Fourier-transform infrared spectra of formaldoxime: ν_4, ν_5, ν_6, and ν_8 bands", *J. Opt. Soc. Am. B* **1994**, *11*, 170–175.
[57] R. A. Bannai, G. Duxbury, G. Ritchie, S. Klee, "Fourier Transform Infrared Spectra of Formaldoxime: The ν_7, ν_9, ν_{11}, ν_{12}, and $2\nu_{12}$ Bands", *J. Mol. Spectrosc.* **1996**, *178*, 84–92.
[58] G. Duxbury, R. M. Percival, D. Devoy, M. R. M. Mahmoud, "Fourier transform and diode laser spectroscopy of the 10-μm bands of formaldoxime (CH_2NOH)", *J. Mol. Spectrosc.* **1988**, *132*, 380–392.
[59] E. L. Sibert III, J. Castillo-Chará, "Theoretical studies of the potential surface and vibrational spectroscopy of CH_3OH and its deuterated analogs", *J. Chem. Phys.* **2005**, *122*, 194306.
[60] J. M. Bowman, X. Huang, N. C. Handy, S. Carter, "Vibrational Levels of Methanol Calculated by the Reaction Path Version of MULTIMODE, Using an ab initio, Full-Dimensional Potential", *J. Phys. Chem. A* **2007**, *111*, 7317–7321.
[61] G. Moruzzi, B. P. Winnewisser, M. Winnewisser, I. Mukhopadhyay, F. Strumia, *Microwave, infrared, and laser transitions of methanol: atlas of assigned lines from* 0 *to* 1258 cm^{-1}, CRC Press, Boca Raton, London, New York, **1995**.
[62] R. H. Hunt, W. N. Shelton, F. A. Flaherty, W. B. Cook, "Torsion–Rotation Energy Levels and the Hindering Potential Barrier for the Excited Vibrational State of the OH-Stretch Fundamental Band ν_1 of Methanol", *J. Mol. Spectrosc.* **1998**, *192*, 277–293.
[63] L.-H. Xu, X. Wang, T. J. Cronin, D. S. Perry, G. T. Fraser, A. S. Pine, "Sub-Doppler Infrared Spectra and Torsion–Rotation Energy Manifold of Methanol in the CH-Stretch Fundamental Region", *J. Mol. Spectrosc.* **1997**, *185*, 158–172.
[64] R. H. Hunt, W. N. Shelton, W. B. Cook, O. N. Bignall, J. W. Mirick, F. A. Flaherty, "Torsion-rotation absorption line assignments in the symmetric CH-stretch fundamental of methanol", *J. Mol. Spectrosc.* **1991**, *149*, 252–256.
[65] M. A. Temsamani, L.-H. Xu, R. M. Lees, "A rotation–torsion–vibration treatment with three-dimensional internal coordinate approach and additional FTIR spectral assignments for the CH_3-bending fundamentals of methanol", *J. Mol. Spectrosc.* **2003**, *218*, 220–234.
[66] R. M. Lees, L.-H. Xu, J. W. C. Johns, Z.-F. Lu, B. P. Winnewisser, M. Lock, R. L. Sams, "Fourier transform spectroscopy of CH_3OH: rotation–torsion–vibration structure for the CH_3-rocking and OH-bending modes", *J. Mol. Spectrosc.* **2004**, *228*, 528–543.
[67] R. M. Lees, M. Mollabashi, L.-H. Xu, M. Lock, B. P. Winnewisser, "Variations in the torsion-vibration energy structure of CH_3OH from fundamental, overtone, and combination bands of the ν_7, ν_8 and ν_{11} CH_3 rocking and CO stretching modes", *Phys. Rev. A* **2002**, *65*, 042511.
[68] X. Wang, D. S. Perry, "An internal coordinate model of coupling between the torsion and C–H vibrations in methanol", *J. Chem. Phys.* **1998**, *109*, 10795–10805.
[69] L. Xu, J. Hougen, "Global Fit of Torsional-Rotational Transitions in the Ground and First Excited Torsional States of Methanol", *J. Mol. Spectrosc.* **1995**, *173*, 540–551.