SUPPLEMENTARY MATERIAL

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TABLE S1. A SELECTION OF BIMOLECULAR COMPLEXES FORMED BETWEEN BORON TRIFLUORIDE AND OTHER SMALL MOLECULES IN THE GAS PHASE

Base	Technique	References	Base	Technique	References
Ne	infrared	6,7	H_2O	UV-PES[b]	14,15
Ar	infrared	6,7	H_2O	UV-PES[b], EELS[c]	20
Ar	MBER[a]	8	H_2S	UV-PES[b]	14,15
Kr	infrared	6,7	H_2S	UV-PES[b], EELS[c]	21
N_2	MBER[a]	8	SO_2	microwave	22
HF	microwave	9	NCCN	microwave	19
HF	infrared	10	NH_3	microwave	17,23,24
HCl	MBER[a]	11	PH_3	microwave	25
CO	MBER[a]	8	HCCCN	infrared	18
CO	infrared	12,13	CH_3F	infrared	26,27
NO	UV-PES[b]	14,15	CH_3CN	UV-PES[b]	14,15
HCN	microwave	16,17	CH_3CN	microwave	28
HCN	infrared	18	CH_3OH	UV-PES[b]	14,15
CO_2	MBER[a]	19	C_5H_5N	UV-PES[b]	29
CS_2	UV-PES[b]	15	$(CH_3)_3N$	microwave	17,30
N_2O	microwave	19	$(C_2H_5)_2O$	UV-PES[b]	14,15

[a] MBER – molecular beam electric resonance spectroscopy.
[b] UV-PES – ultraviolet photoelectron spectroscopy.
[c] EELS – electron energy loss spectroscopy.

TABLE S2. A SELECTION OF BIMOLECULAR COMPLEXES FORMED BETWEEN BORON TRIFLUORIDE AND OTHER SMALL MOLECULES DETECTED BY MATRIX ISOLATION SPECTROSCOPY

Base	Matrix	References	Base	Matrix	References
N_2	Ar	31	CH_3F	Ar	26
CO	Ar	31	CH_3CN	Ar	46
CO	Ar, N_2	32,33	CH_3CN	Ar,Xe,N_2	47
CO_2	Ar, N_2	34	CH_3CN	Ne,N_2	48
N_2O	Ar, N_2	35	CD_3CN	Ar	49
H_2O	Ar	36	CH_3NC	Ar	50
H_2O,D_2O	Ar	37	CH_2CHF	Ar	51
H_2O	N_2	38	$(CH_3)_2O$	Ar	36
H_2O	Ne	39	$(CH_3)_2O$	Ar,N_2	32,52,53
H_2S	Ar	36	$(CH_3)_2S$	Ar,N_2	52,53
SO_2	Ar, N_2	32,40	$(CH_3)_2CHF$	Ne	54
BF_3	Ar,Kr	41	C_6H_5CN	Ar	55
BF_3	Ar	42,43	$(C_2H_5)_2O$	Ar	37,56
NH_3	Ar	44,45	$(CF_3CH_2)_2O$	Ar	37,56
NH_3	Ar,N_2	32	$(CH_3)_3CCN$	Ar	55

TABLE S3. A SELECTION OF BIMOLECULAR COMPLEXES FORMED BETWEEN BORON TRIFLUORIDE AND OTHER SMALL MOLECULES DETECTED BY INFRARED SPECTROSCOPY IN CRYOGENIC SOLUTIONS

Base	Solvent	References	Base	Solvent	References
N_2	Ar	57	cyclopropene	Ar,N_2	66
CO	Ar	58,59	cyclopropane	Ar,N_2	67
OCS	Ar	60	propene	Ar,N_2	64
COF_2	Ar,Kr,N_2	61	methylene cyclopropane	Ar	68
C_2H_2	Ar	62,63	*cis*-2-butene	Ar	69
CH_3F	Ar,Kr	26	*trans*-2-butene	Ar	69
C_2H_4	Ar,N_2	64	2-methyl propene	Ar	69
CH_2CHF	Ar	51	methyl cyclopropane	Ar,N_2	70
propyne	Ar	62,63	cyclopentene	Ar	71
allene	Ar,N_2	65			

TABLE S4. A SELECTION OF THEORETICAL STUDIES OF BIMOLECULAR COMPLEXES FORMED BETWEEN BORON TRIFLUORIDE AND OTHER SMALL MOLECULES

Base	Theory/basis set	References	Base	Theory/basis set	References
Ne	MP2,MP4/LANL2DZ	73	CH_3SH	MP2/6-311++G(d,p)	99
Ar	MP2,MP4/LANL2DZ	73	CH_3CHO	various	95,111,118
Kr	MP2,MP4/LANL2DZ	73	CH_3COF	MP2/6-311++G(d,p)	111
Xe	MP2,MP4/LANL2DZ	73	CH_3NH_2	MP2/6-311++G(d,p)	106
H_2	MP2/6-311G(2df,2pd),TZ2p	74	CH_3PH_2	MP2/6-311++G(d,p)	109
N_2	various	75-78	$CH_3C{\equiv}CH$	MP2/6-31+G(d)	62,63
F_2	MP2/6-31+G(d),6-31++G(d,p)	79	$CH_2{=}C{=}CH_2$	MP2/various	65
Cl_2	MP2/6-31+G(d),6-31++G(d,p)	79	c-$(CH)_2CH_2$[b]	DFT,MP2/various	66
Br_2	MP2/6-31+G(d),6-31++G(d,p)	79	$CH_2CH{=}CHO$[c]	SCF/6-31G(d)	95
HF	various	9,79-84	$HCOOCH_3$	SCF/6-31G(d)	95
HCl	various	79,83	C_2H_5F	SCF/various	82
HBr	MP2/6-31+G(d),6-31++G(d,p)	79	$(CH_3)_2O$	various	89,95,97,99,119-121
ClF	MP2/6-31+G(d),6-31++G(d,p)	79	$(CF_3)_2O$	AM1	121
BrF	MP2/6-31+G(d),6-31++G(d,p)	79	$(CH_3)_2S$	SCF,MP2/various	99,120
BrCl	MP2/6-31+G(d),6-31++G(d,p)	79	$CH_3CH{=}CH_2$	MP2/6-31+G(d)	64
CO	various	33,59,75,85-89	c-$(CH_2)_3$[d]	MP2/6-31+G(d)	67

BF	SCF/4-31G	75	c-$(CH)_4O$[e]	SCF/6-31G(d)	95
NO	SCF/3-21G	14,15	$(CH_3)_2CO$	various	95,111,112,118
CO_2	MP2/6-31G(d)	88	c-$(CH_2)_2C{=}CH_2$[f]	DFT/6-311++G(d,p)	68
CS_2	SCF/3-21G	14	$(CH_3)_2NH$	MP2/6-311++G(d,p)	106
HCN	various	17,45,76,89-93	$(CH_3)_2PH$	MP2/6-311++G(d,p)	109
FCN	MP2/6-31G(d)	45,76	c-$(CH_2)_3O$[g]	SCF/6-31G(d)	95
N_2O	MP2/6-31G(d)	45,94	CH_3CH_2CHO	MP2/6-31G(d)	112
OCS	MP2/6-31+G(d)	60	C_5H_5N	SCF/3-21G	29
H_2O	various	14,15,20,38,95-99	CH_3COOCH_3	SCF/6-31G(d)	95
H_2S	various	14,15,98,99	$CH_2{=}C(CH_3)CHO$[h]	MP2/TZ2P	89
SO_2	MP2/6-31G(d)	22	$CH_3CH{=}CHCHO$[i]	SCF/6-31G(d)	95
C_2H_2	various	62,63,74	$CH_2{=}CHCOCH_3$[j]	SCF/6-31G(d)	95
C_2N_2	MP2/various	76,78,100	$(CH_3)_2CHF$	DFT,MP2/aug-cc-pVTZ	54
BF_3	SCF/4-31G,6-31G(d)	42,101,102	C_6H_6	SCF/STO-3G	81
NH_3	various	17,24,45,89,97,103-106	c-C_5H_6O[k]	SCF/STO-3G	115
NF_3	SCF,MP2/6-31G(d),6-31+G(d)	107	$CH_3CH{=}CHCH_3$[l]	DFT/MP2/6-311++G(d,p)	69
PH_3	various	103,105,108,109	$CH_3CH{=}CHCH_3$[m]	DFT/MP2/6-311++G(d,p)	69
H_2CO	various	95,110-112	$(CH_3)_2C{=}CH_2$[n]	DFT/MP2/6-311++G(d,p)	69
H_2CS	MP2/6-311++G(d,p)	111	c-$(CH_2)_2CHCH_3$[o]	DFT,MP2/various	70
F_2CO	DFT,MP2/various	61,111	$CH_2{=}CHCOOCH_3$[p]	SCF/6-31G(d)	95

HCOF	MP2/6-311++G(d,p)	111	c-$(CH_2)_4O$[q]	SCF/6-31G(d)	95
HCCCN	MP2/6-31G(d,p)	76,78	$(CH_3)_3N$	various	17,89,97,103,106
CH_3F	SCF,MP2/various	26,54,82,113	$(CH_3)_3P$	MP2/various	103,108,109
CH_3Cl	MP2/6-311++G(d,p)	113	C_6H_5CN	DFT/various	122
CH_2NH	MP2/6-311++G(d,p)	111	c-$(CH)_2(CH_2)_3$[r]	MP2/various	71
NH_2OH	MP2/6-311++G(d,p)	114	$(CH_3)_3CF$	DFT,MP2/aug-cc-pVTZ	54
C_2H_4	MP2/various	64,74	C_6H_5CHO	MP2/ TZ2P 6-31G(d)	89,118
CH_2CHF	MP2/6-31+G(d)	51	$(CH_3)_2C=CHCHO$[s]	SCF/6-31G(d)	95
c-$(CH)_2C=O$[a]	SCF/STO-3G	115	$(C_2H_5)_2O$	AM1,SCF/3-21G	14,15,56
CH_3CN	various	14,15,89,93,100,116	$(CF_3CH_2)_2O$	AM1	56
CH_3NC	DFT/6-311++G(d,p)	50	$(C_2F_5)_2O$	AM1	56
CH_2FCN	DFT/aug-cc-pVTZ	117	$(CH_3)_3CCN$	DFT/various	122
CH_2ClCN	DFT/aug-cc-pVTZ	117	$CH_2=C(CH_3)COOCH_3$[t]	MP4/STO-3G	123
CH_2BrCN	DFT/aug-cc-pVTZ	117	c-C_6H_8O[u]	SCF/6-31G(d)	95
CH_3OH	various	14,15,95,99			

[a] cyclopropenone
[b] cyclopropene
[c] acrolein
[d] cyclopropane
[e] furan
[f] methylene cyclopropane
[g] oxetane
[h] 2-methyl acrolein
[i] 2-butenal
[j] 3-buten-2-one
[k] dimethyl cyclopropenone
[l] *cis*-2-butene
[m] *trans*-2-butene
[n] 2-methyl propene
[o] methyl cyclopropane
[p] methyl propenoate
[q] tetrahydrofuran
[r] cyclopentene
[s] 3-methyl-2-butenal
[t] methyl methacrylate
[u] 7-oxanorbornene

TABLE S5. A SELECTION OF BIMOLECULAR COMPLEXES FORMED BETWEEN NITROUS ACID AND OTHER SMALL MOLECULES IN CRYOGENIC MATRICES

Partner molecule	Major type of interaction	References	Partner molecule	Major type of interaction	References
Xe	OH…Xe	124	NH_3	OH…N	136
N_2	OH…N	124,125	CH_4	OH…H_3CH	137
HF	FH…O(H)	126	SiH_4	Si…O(H)	137
HCl	ClH…O(H)	126,127	GeH_4	Ge…O(H)	137
CO	OH…C	125,128	C_2H_4	OH…π	138
NO	OH…N	129	CH_2=CCl_2	OH… π, OH…Cl	139
CO_2	OH…O	130	CH_2NOH	ONOH…N(OH)CH_2, H_2CNOH…N(O)OH	140
CS_2	OH…S	130	CH_2=C=CH_2	OH… π, CH…N(O)OH	141
H_2O	ONOH…OH_2	131	$(CH_3)_2S$	OH…S	142
SO_2	OH…O	132,133	$(CH_3)_2CO$	OH…O	143
NO_2	OH…O	134	CH_3SSCH_3	OH…S	142
C_2H_2	OH…π	135	$(C_2H_5)_2O$	OH…O	143

TABLE S6. COMPUTED VIBRATIONAL SPECTRUM OF BF_3.HONO COMPLEX STRUCTURE **1** (C_s)

Symmetry species	Mode	Wavenumber/cm^{-1}		Intensity/ km mol^{-1}	Approximate description[a]
		Harmonic	Anharmonic		
a′	ν_1	3708.1	3533.6	147.5	ν(OH)
	ν_2	1655.7	1617.1	85.6	ν(N=O)
	ν_3	1403.8	1395.0	231.3	$\nu_a(BF_3)$
	ν_4	1337.5	1289.5	344.4	δ(HON)
	ν_5	901.9	821.2	168.1	ν(N-O)
	ν_6	862.3	854.7	9.0	$\nu_s(BF_3)$
	ν_7	674.6	640.7	78.8	δ(ONO)
	ν_8	597.2	611.2	264.5	$\delta_s(BF_3)$
	ν_9	473.9	469.6	8.7	$\delta_a(BF_3)$
	ν_{10}	202.8	156.2	4.1	*l*(geared)
	ν_{11}	126.4	101.1	1.5	*l*(antigeared)
	ν_{12}	56.6	55.0	15.5	ν(B...N)
a″	ν_{13}	1459.4	1441.1	397.6	$\nu_a(BF_3)$
	ν_{14}	658.4	589.4	83.6	γ(HON)
	ν_{15}	470.0	464.1	4.8	$\delta_a(BF_3)$
	ν_{16}	273.3	194.6	13.1	*l*(geared)
	ν_{17}	95.5	71.5	2.1	γ(OH...F)
	ν_{18}	40.3	14.1	0.5	*l*(antigeared)

[a] ν – stretching, δ – in-plane bending, γ – out-of-plane bending, *l* – libration, s – symmetric, a – antisymmetric.

TABLE S7. COMPUTED VIBRATIONAL SPECTRUM OF BF_3.HONO COMPLEX STRUCTURE **2** (C_1). ALL MODES ARE OF a SYMMETRY

Mode	Wavenumber/cm^{-1}		Intensity/ km mol^{-1}	Approximate description[a]
	Harmonic	Anharmonic		
ν_1	3745.9	3563.4	96.5	ν(OH)
ν_2	1713.3	1716.8	163.9	ν(N=O)
ν_3	1446.1	1403.6	393.7	$\nu_a(BF_3)$
ν_4	1426.1	1384.3	391.6	$\nu_a(BF_3)$
ν_5	1222.7	1135.3	120.5	δ(HON)
ν_6	871.9	855.8	7.4	$\nu_s(BF_3)$
ν_7	738.8	690.5	52.8	ν(N-O)
ν_8	623.9	598.8	116.9	$\delta_s(BF_3)$
ν_9	585.3	549.9	156.4	δ(ONO)
ν_{10}	476.8	464.6	75.8	$\delta_a(BF_3)$
ν_{11}	470.5	466.2	6.6	$\delta_a(BF_3)$
ν_{12}	430.4	332.0	288.5	γ(HON)
ν_{13}	166.4	176.1	7.6	*l*(geared)
ν_{14}	153.9	163.8	7.1	*l*(geared)
ν_{15}	101.2	72.1	26.2	ν(B...O)
ν_{16}	88.6	87.1	6.0	γ(B...OH)
ν_{17}	53.8	45.5	5.9	*l*(antigeared)
ν_{18}	26.6	28.9	0.6	*l*(antigeared)

[a] ν – stretching, δ – in-plane bending, γ – out-of-plane bending, *l* – libration, s – symmetric, a – antisymmetric.

TABLE S8. COMPUTED VIBRATIONAL SPECTRUM OF BF_3.HONO COMPLEX STRUCTURE **3** (C_s)

Symmetry species	Mode	Wavenumber/cm^{-1}		Intensity/ km mol^{-1}	Approximate description[a]
		Harmonic	Anharmonic		
a′	ν_1	3746.5	3564.7	120.3	ν(OH)
	ν_2	1633.5	1603.3	94.7	ν(N=O)
	ν_3	1455.0	1431.9	396.2	$\nu_a(BF_3)$
	ν_4	1310.0	1265.2	211.0	δ(HON)
	ν_5	888.5	846.6	127.2	ν(N-O)
	ν_6	875.6	853.7	87.2	$\nu_s(BF_3)$
	ν_7	679.3	656.6	10.4	δ(ONO)
	ν_8	635.9	632.7	371.2	$\delta_s(BF_3)$
	ν_9	473.7	471.5	11.1	$\delta_a(BF_3)$
	ν_{10}	132.2	115.9	4.3	*l*(geared)
	ν_{11}	83.5	74.8	8.7	ν(B...O)
	ν_{12}	52.7	50.2	1.2	*l*(antigeared)
a″	ν_{13}	1448.2	1427.0	403.6	$\nu_a(BF_3)$
	ν_{14}	614.3	571.9	98.4	γ(HON)
	ν_{15}	473.7	471.4	10.7	$\delta_a(BF_3)$
	ν_{16}	133.9	120.6	0.2	γ(B...ON)
	ν_{17}	58.5	64.8	3.4	*l*(geared)
	ν_{18}	26.2	31.4	9.1	*l*(antigeared)

[a] ν – stretching, δ – in-plane bending, γ – out-of-plane bending, *l* – libration, s – symmetric, a – antisymmetric.

TABLE S9. COMPUTED VIBRATIONAL SPECTRUM OF BF_3.HONO COMPLEX STRUCTURE **4** (C_s)

Symmetry species	Mode	Wavenumber/cm^{-1}		Intensity/ km mol^{-1}	Approximate description[a]
		Harmonic	Anharmonic		
a′	ν_1	3749.5	3568.0	115.3	ν(OH)
	ν_2	1639.1	1606.6	91.0	ν(N=O)
	ν_3	1452.0	1428.8	394.6	$\nu_a(BF_3)$
	ν_4	1300.5	1254.5	174.9	δ(HON)
	ν_5	882.5	869.0	11.8	$\nu_s(BF_3)$
	ν_6	861.7	812.4	162.9	ν(N-O)
	ν_7	672.8	657.4	112.7	$\delta_s(BF_3)$
	ν_8	633.8	620.1	181.2	δ(ONO)
	ν_9	472.0	470.3	8.7	$\delta_a(BF_3)$
	ν_{10}	97.5	90.1	1.2	*l*(geared)
	ν_{11}	94.4	85.7	5.6	ν(B...O)
	ν_{12}	59.6	62.9	1.2	*l*(antigeared)
a″	ν_{13}	1455.6	1433.6	402.3	$\nu_a(BF_3)$
	ν_{14}	605.8	569.7	99.4	γ(HON)
	ν_{15}	474.6	473.2	12.4	$\delta_a(BF_3)$
	ν_{16}	149.2	132.5	6.6	γ(B...ON)
	ν_{17}	54.8	54.9	4.1	*l*(geared)
	ν_{18}	32.2	46.7	0.5	*l*(antigeared)

[a] ν – stretching, δ – in-plane bending, γ – out-of-plane bending, *l* – libration, s – symmetric, a – antisymmetric.