

Organic Compounds

Chapter 3

Burning Coal-Mining Heaps as an Organo-chemical Laboratory: Interesting Trace Compounds and Their Potential Sources

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Abstract

A continuation of research on the composition of complex gaseous emanations in burning post-mining waste heaps of the Upper Silesian Basin, Poland, brought new data for a large group of relatively weakly studied fumarolic vents. It concerns admixing gases either semi-quantified from *in situ* recorded FTIR spectra or proposed via qualitative analysis of their derivative residual curves. The most likely additional compounds include formaldoxime isocyanate, $\text{HON}=\text{CHNCO}$, ethenol, $\text{C}_2\text{H}_3\text{OH}$, hydrogen isocyanide, HNC , tetrafluoro-*p*-xylylene, $\text{C}_6(\text{CH}_3)_2\text{F}_4$, 1-fluorocyclohexadienyl radical, $\text{C}_6\text{H}_6\text{F}^\cdot$, perfluorinated *p*-benzyne, C_6F_4 , 1,2,4-trioxolane, $\text{C}_2\text{H}_3\text{O}_3$, thioacetaldehyde, CH_3CHS , thiocarbonyl fluoride, dithio-*p*-benzoquinone, *c*-cyanomethanimine, bromomethane, peroxyethyl nitrate, triflic radical, CF_3OSO_3 , and possibly a cyclic C_{10} molecule. Derivatives of freons include CHClF , HCFBr , CF_2I^+ . Organo (semi)metallics include monomethylsilane, titanacyclopropene, CH_3MoH and CH_2MoH_2 , and an indium-acetylene complex. In addition, numerous inorganics may also be present. Possible pathways of the formation of the listed organics are considered.

Keywords: Burning Post-Mining Waste Heaps; Coal Fires; Portable FTIR Gas Analysis; Halogenated Hydrocarbons; Gaseous Organosulfurs; Gaseous Organo (Semi) Metallics.

1. Introduction

Fossil fuel fires are known worldwide. They both concern completely natural environments, e.g., exposed coal or bituminous shale seams, and anthropogenic environments – burning post-coal-mining waste heaps. The latter, herein referred to as BPWHs, are, more or less, permanent elements of coal basins worldwide. This includes numerous objects within both the Upper and Lower Silesian Coal Basins. Spontaneous coal combustion is related to coal oxidation by atmospheric origin, and dependent on atmospheric conditions, coal petrography, occurrence of iron disulfides acting as catalysts, and microbial activity (e.g., [1-5]). Coal remnants and barren rocks undergo degassing and a vast fumarolic vent system is developed. It emits coal-fire gases (CFG). The most important gaseous species emitted, as studied by [6-8] are H₂O and CO₂, with some CH₄ and CO; NO₂ as the major NO_x; thiophene (C₄H₄S), dichloromethane, dichloroethanes and other halohydrocarbons; higher alkanes and, locally, SO₂, NH₃, HCl, propene, furan and/or tetrahydrofuran, acetic acid, some nitriles, aldehydes, SiF₄, trace monoterpenes and freons, CCl₄ and AsH₃, very local thiols and numerous other admixing compounds. The main goal of the current study is to report potential admixing gases in some newly probed vents.

1.1. Sampling sites

Sampling sites are identical to these analyzed for main gases in [8]. They include fumarolic vents from two heap areas in Czerwionka-Leszczyny (CD), Radlin (RD), Bytom-Stroszek (BST), Świętochłowice-Chropaczów (SWC) and Zabrze (ZB), northern part of the USCB; and Rybnik (RCH). Details about these sites are in the literature mentioned.

1.2. Methodology

All the CFG results reported here are obtained using portable Fourier-Transform InfraRed (pFTIR) gas spectrometer, model DX4000 (GASMET/ENVAG), with CALCMET software. The pFTIR method has many advantages over both the Indicatory Tube (IT) and, to some extent, Gas Chromatography. It allows for precise, three-level analysis of chemically complex, hot, aggressive, and ash-bearing gaseous emanations, as shown in [6-8]. The system is also capable of simultaneous measurement of water-soluble inorganic species and hydrocarbons, due to heating of the whole probing line to 180 °C. Composition of the precisely, quantitatively measured major gaseous species, and the second subtype analysis, i.e., external library search mode (ESLM), in the CFG in vents of the aforementioned sites was reported in [6]. In this work results from the third level – qualitative analysis of remaining bands in residual spectra (RSA) are reported. Details on the analytical approach are to be found in the listed literature.

1.3. Results

Results of the ELS are given in Table 1, Table 2 and Table 3. Results of the RSA are juxtaposed in Table 4.

Table 4: Results of residual spectra qualitative pFTIR analysis. Underlined samples have the particular bands more intense.

Band [cm ⁻¹]	Samples	Vibration designations	Literature
4221-4222vw ¹	ZB2o, BT2	H ₂ ?	[9]
4007-4008vw	RD07, ZB1, ZB1A, ZB2, ZB2o, ZB3	activated HHF complex	[10]
3960-3961vw(as/df)	CD6o, CD7, CL2a, CL2aA, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A, RD07, RD07A, RD08NA, RD08k, RD08kA, RD08o, RD11L, RD11o, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1A, BT1o, BT2	HF	[11]
3953-3951vw	CD5	O-H and N-H (in aminonaphthoquinone)	[12]
3929-3930w	CD1o, CD2, CD3, CD5, CD5S, CD6o, CD7, CLd, CLdU, CLdo, CL2a, CL2aA, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A, BT1A, BT1o, BT1o2, BT1o3, BT1o4	H-F stretching (in (HF) ₂); C-H stretching ?	[13]; [14]
3920-3922as	RD07A, RD08NA, RD08k, RD08kA, RD08o, RD11L, RD11o, ZB1, ZB1A, ZB2, ZB2o, ZB3	v≡C-H (in cellulose ether); HF?	[12]
3915-3912vw	CD5, CD7, CL2a, CL2aA, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A, RD07, BT1o3, BT2	OH stretching (in 3-chloro-2-nitrobenzyl alcohol); vHF (in HF complex with CICN)	[12]
3898-3900	CD1, CD1o, CD2, CD3, CLdU, CL2a, SW1oP, RCH1 , RCH1A, BT1	H-bonded OH groups	[12]
3882-3881	CD6o, CD2, CD3, CD7, CLd, CLdA, CLdU, CLdo, SW1, SW1oS, SW1oB, SW1oP, SW1oS, BT1, BT1A, BT1o, BT1o2, BT1o3, BT1o4, BT2	N ₂ or O ₂ ? (or both?)	[15]
3828-3830	(CD1), CD5S, CD5, CD6o, CD7, CLd, CLdA, CLdU, CLdo, CL2a, CL2aA, BT1, BT1A, BT1o, BT1o2, BT1o3, BT1o4, BT2	Mg(OH) ₂	[12]
3814-3816	CD5, <u>SW3</u> , <u>SW3A</u> , RD07, RD07A, BT1	Mg(OH) ₂	[12]

3785-3784w(~sh)	CD5, CD5S, CD6o	Al(OH) ₃ ; Ca(OH) ₂ ; Y(OH) ₃	[16]; [12]; [17]
3782	BT1	Ca(OH) ₂ or Zr(OH) ₄	[12]
3777as	RD07	Ti(OH) ₂ or Ca(OH) ₂ ?	[12]
3768as-3769	(CD1), CD1o, CD2, CD3, CD5S, CD6o, CD7, CLd, CLdA, CLdU, CLdo, CL2a, CL2aA, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A, BT1, BT1A, BT1o, BT1o2, BT1o3, BT1o4, BT2	Ca(OH) ₂ ?	[12]
3750	CLdU, BT1	Al(OH) ₃ ; Sr(OH) ₂	[12]
3728-3730	CLd, CLdA, CLdU, RCH1 , RCH1A	Fe(OH) ₂	[12]
3721-3720w	CD2, CD3, CD5, CD5S, SW1, SW1oB, SW1oP, SW1oS	FeO(OH); Ba(OH) ₂	[18]; [19]
3713	RCH1, RCH1A	OH group (in catechin)	[12]
3700-3698as	CD1, CD1o, CD2, CD3, CD5 (3700), CD5S, CD6o, CD7, SW2, SW2o, SW2o2, SW2o3, SW3, SW3A, RCH1, RCH1A	Zn(OH) ₂ ; Cr(OH) ₂	[12]
3681-3682	CD1, CD2, CD3, CD5, CD5S, CD6o, CD7, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A	Zn(OH) ₂	[12]
3673-3674	CLd, CLdA, CLdU	Ga(OH) ₃ ; CoOH; +1269(CLdU): H ₂ SiO ₃ (metasilicic acid) (?)	[20]; [18]; [21]
3668	CL2aA, ZB1, ZB1A, ZB2, ZB2o, ZB3	Ga(OH) ₂ ? (shf ²)	[12]
3665as	RD08NA, RD08k, RD08kA, RD08o, RD11L, RD11o	Ga(OH) ₂ ?; CrOH	[12]
3662-3663	BT1A, BT1o, BT1o2, BT1o3, BT1o4	Ga(OH) ₂ ?; Cd(OH) ₂ ; CrOH	[12]
3659-3660w(as)	CD1, CD2, CD3, CD5, CD5S, CD6o, CD7, CLdU, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A	Cd(OH) ₂	[12]
3645-3643sh	RCH1, RCH1A, BT1o3	In(OH) ₂	[12]
3642-3639	CD1, BT1A, BT1o4	HON=CHNCO (a nitrile oxide) ?; nonbonded, alcohol- or phenol-included OH group	[12]
3638as-3639as	CD5, CD6o	+~3609: Pb(OH) ₂	[22]
3636-3637	CD1o, (CD2), CD3, CD5S, CD7, SW1, SW1oB, SW1oP, SW1oS, SW2, SW2o, SW2o2, SW2o3, SW3, SW3A	+~2276+1646(CD2,3,7): HON=CHNCO (formaldoxime isocyanate) ; Cu(OH) ₂	[23]; [24]
3618-3621w(as)	CD1, CD1o, CD2, CD5, CD5S, CD6o, CD7, SW1, SW1oB, SW1oP, SW1oS, SW2, SW2o, SW2o2, SW2o3, SW3, SW3A	OH groups; + ~3583(CD5,CD5S,CD6o,CD7): HNC (hydrogen isocyanide)	[12]; [25]

3612-3615	CD7, CLd, CLdA, CLdU, RCH1, RCH1A	+1514(CLd, CLdA): 2,4-C₆H₃OH (2,4-didehydrophenol) (?) ; Tl(OH) ₃	[26]; [20]
3605-3608	(CD1), CD1o, (CD2), CD3, CD5, CD5S, CD6o, SW3, SW3A	Pb(OH) ₄ ; Tl(OH) ₂ ; HOSbO ₂ (metaantimonic acid); +~3640(CD5,6o): Pb(OH) ₂	[22]; [20]; [27]; [22]
3600-3597	CLdU, CLdA	Cl ₂ V(O)OH ?; free OH groups	[12]
3590-3592	CD1, CD2, CD3, CD1o, SW1, SW1oB, SW1oP, SW1oS, SW3, SW3A, RCH1, RCH1A, BT1o2	hypobromous acid? ; OH groups in an alcohol or a phenol	[12]
3581-3582w(as)	CD5, CD5S, CD6o, CD7, CLd, CLdA, BT1A, BT1o3, BT1o4	+ 3620(CD): HNC (hydrogen isocyanide); silanenitrile ?	[12]
3550-3552vw	CD1, CD1o, CD2, CD3, CD5, CD5S, CD6o, CD7, CLd, CLdA, CLdo, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A, BT1A, BT1o, BT1o2	dimeric OH group stretch (or a one in a phenol)	[12]
3528w-3529w	CD1o, CD2, CD3, CD7, CLd, CLdA, CLdU, RCH1, RCH1A, BT1A, BT1o, BT1o2, BT1o3, BT1o4	HOCIO (chlorous acid)	[28]
3134	CL2a, CL2aA	NH ₃ ⁺ symm. stretching; C ₂ H ₂ ⁺ (acetylene ion) (shf)	[29]; [30]
3064-3065	BT1o3, BT1o4	naphthalene	[12]
3062-3060vw	BT1A, BT1o, BT2	naphthalene (?) ; +1668 (BT2): (C₂H₂)In (indium-acetylene complex)	[12]; [31]
3058-3059vw	RD08NA	medial <i>cis</i> or <i>trans</i> C-H stretch in an alkene); NH ₄ ⁺ ion; +1304: bromomethane	[12]; [32]
3042b(df)	BT1o4	cyc-C₃H₅ (cyclopropyl radical)	[33]
3027-3028vw	RD07, BT1o4	CH ₂ asymmetric stretching ? (in a poly(vinylidene fluoride))	[34]
3011-3012	CL2a, CL2aA, RD07, RD07A, RD08N, RD08NA, RD08k, RD08kA, RD08o, RD11L, RD11U, RD11o, ZB1, ZB1A, ZB2, ZB2o, ZB3, ZB3, BT1, BT1A, BT1o, BT1o2, BT1o4, BT2	=CH stretching ?; +1090+~1033 (CL2aA, RCH1; RD and ZB): methane-d2	[32]
2971-2970vw	CD5, RD08NA	<i>cyc</i> -CH ₂ CHCHSi ?; methyl ion	[12]
2963sh	BT2	fluoromethane ; dimethylmercury; cumene ? (undercalculated ?)	[32]; CALCMET
2934-2930vw	RD08NA, BT1, BT1o, BT2	cyclohexene? ; methylene ion	[12]
2902vw	BT1A	CH₂FCI⁺	[35]
2402-2400(w)	CL2a, CL2aA, RD11U, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1, BT1A, BT1o, BT1o3, BT1o4, BT2	SiF _{4-x} + SiH ₄	[12]
2398-2896	BT1o4	H ₂ O ₂ ⁺ (D ₂ O ₂ ⁺)??; ND ₂ F or BF ₂ OH ⁺ ?; SiF _{4-x} + SiH ₄ ?	[12]

2394w-2390w	CD6o, CD2, CD3, CD7, SW1oB, RD07, RD07A, RD08k, RD08kA, RD08o, RD11L, RD11o	BF_2OH^+ ?	[12]
2385-2387(w)	CD1, CD1o(b), CD5, CD5S, CLdA, CLdU, SW1, SW1oB, SW1oP, SW1oS, SW2, SW2o, SW2o2, SW2o3	dicyanoacetylene (2-butynedinitrile); $\nu(\text{C}=\text{N})$ in nitrilium ion / <i>N</i> -alkylacetoneitrilium / acetoneitrilium	[12]
2378-2377	CD1o, SW1, RCH1 , RCH1A	azacyclopropenyldiene (<i>cyc</i> -HC=NC:)?	[12]
2355	CD5, SW2, SW2o, SW2o2, SW2o3	thiirene (<i>cyc</i> -C ₂ H ₂ S)	[12]
2348-2347	CD1, CD1o, CD2, CD3, (CD5S), CD6o, CD7, RCH1 , RCH1A, BT1o2	$^{12}\text{C}^{16}\text{O}_2$?; NO_2^+ ?	[12]
2339-2340	SW1, SW1oB, SW1oP, SW1oS, SW2 , SW2o , SW2o2 , SW2o3 , SW3, SW3A, RD07, RD07A	+1072 (SW2, SW2o, SW2o2, SW2o3): C ₆ F ₄ (perfluorinated <i>p</i>-benzyne)	[36]
2330-2331	RCH1 , RCH1A	CO₂?? (shf); HCCH ⁺ (DCCD ⁺ ; a derivative of acetylene); cyanogen <i>N</i>-oxide ; F₂BNCO (fluoroisocyanatoborane)	[12]
2324sh	CD2, CD3	$\nu(\text{CN})$ in protonated acetoneitrile?	[37]
2316sh ⁴ -2318	CLdU, CLd, CLdA, CLdo, SW1, SW1oB, SW1oP, SW1oS, SW2 , SW2o , SW2o2 , SW2o3 , RCH1 , RCH1A	trifluorosilane?	[12]
2309	SW1oP	diazonium group (aryl-N ⁺ ≡NX ⁻); $\nu(\text{N}=\text{N})$ (diazo groups) in a diphenyldiazomethane ; Brønsted-acid-absorbed acetoneitrile (CD ₃ CN); acetoneitrile (CD ₃ CN); methylphosphine ; HI	[12]
2300(sh)-2304	CD1, CD1o, CD2, CD3, CD5, (CD5S), CD6o, CD7, RCH1A	cyanic acid	[12]
2291sh	SW2, SW2o, SW2o2, SW2o3	C₃BrN (bromocyanoacetylene)	[32]
2287-2285	CD5, SW1, SW1oS, SW2 , SW2o , SW2o2 , SW2o3 , RD08NA	$^{12}\text{C}^{16}\text{O}_2$? or benzene-D ₆ ; cyanic acid? ; HC ₃ O (DC ₃ O) radical; (HF) ₂ ⁺ (D ₂ F ₂ ⁺) radical	[12]
2278-2279	CD2, CD3, CD5S, CD6o, CD7	cyanogen isocyanate ; trifluoroacetoneitrile? (shf); aliphatic nitrile/cyanide; +~3638+1646(CD2,3,7): HON=CHNCO (formaldoxime isocyanate)	[12]; [23]
2269-2270	SW1, SW1oB, SW3, SW3A, RD07, RD08N , RD08k , RD08kA , RD08o , RD11L , RD11o , RD08k, RD08kA, RD08o, RD11L, RD11U, RD11o	iodocyanoacetylene ; isocyanic acid ; an aliphatic nitrile/cyanide or an isocyanate; physisorbed acetoneitrile (CD ₃ CN)	[12]

2255-2252	SW1, SW1oB, SW1oP, SW1oS, SW2, SW2o, SW2o2, SW2o3, RD08NA , BT1, BT1A, BT1o	difluorosilane? (shf); disubstituted alkyne or an aliphatic nitrile/cyanide or a(n) (iso)cyanate	[12]
2248-2246	RD08N, BT1o3, BT1o4	m-hydroxybenzotrile (C≡N stretching); aliphatic nitrile/cyanide or a cyanate	[12]
2239-2241	CL2aA, RD08k, RD08kA, RD08o, RD11L, RD11o, BT2	tribromosilane ; nitrile group (e.g., in acrylonitrile) or an aromatic nitrile/cyanide or a(n) (iso)cyanate	[12]
2232-2231sh	ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1	CHNO (DNCO); Cu(CO) ₂ ⁺ or CuCO ⁺ ; an aromatic nitrile/cyanide or an isocyanate	[12]
2076-2075vw(as)	SW2, SW2o, SW2o2, SW2o3, BT1o2	Ge ₂ H ₆ (digermene); +1915(SW): C₁₀ (cyclic) ; C₆N₄⁻ (tetracyanoethylene anion) ; MgNC (magnesium isocyanide)	[32]; [38]; [39]; [40]
2072-2070vw	RD07, BT1A, BT1o, BT1o3, BT1o4, BT2	H₂C=BH (an organoborane) ; S=C=N-CH₃ (methylisothiocyanate) ; BrNC (bromine isocyanide); BFO (boron monofluoride monoxide)	[41]; [12]; [42]; [43]
2053vw (as)-2050	SW2, SW2o, SW2o2, SW2o3, RD07, RD07A, BT1A, BT1o, BT1o2, BT1o3, BT1o4, BT2	v _{as} (NCS) ?; AuCO; INC (iodine isocyanide); C₄H (butadiynyl radical)	[44]; [45]; [46]; [47]
1915vw	CD5, SW2, SW2o, SW2o2, SW2o3	HgH ₂ ?; a transition metal carbonyl; HSiF (monofluorosilylene) radical (shf); +2075(SW): C₁₀ (cyclic)	[12]; [48]; [38]
1901		CBrO; carbonylsilene (shf); ZrCO; B ₂ O ₂ ; Be ₂ H ₂ ; Cu(CO) ₂ (shf); a transition metal carbonyl	[12]
1890-1891	CD5, CD6o, CD7, (SW2, SW2o, SW2o2, SW2o3, RCH1, RCH1A), RD07, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1o2, BT1o3	ZnH ₂ ; Cu(CO) ₂ ; alane (AlH ₃); NCCO radical; Mo(CO) ₂ ; VCO; methyl-d-3-stannane?; Si(CCH) ₂ ; TiCO; SbH ₃ ; SiH ₃ HgH (shf); a transition metal carbonyl	[12]
1868-1870	CD1o, (CD2), (CD3), CD5, CD6o, CD7, (RCH1, RCH1A), RD08NA, BT1A, BT1o2, BT1o3, BT1o4	c-(NO) ₂ (a dimer); Mo(CO) ₃ ; CO group in a 5-member-ring anhydride or transition metal carbonyl	[12]
1860-1863	RD07, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1	formyl radical or SiH ₃ HgH or c-CH ₃ C(O)OO (acetyl peroxy radical); HGeBr	[12]; [49]
1846vw-1843	CD5, CD6o, CD7, BT1o2, BT1o3, BT1o4	Ag(CO) ₂ ; SnH ₃ ; nitrosyl fluoride; isonitrosyl chloride; cyc-C ₈ ; ethynyl radical; SiH ₃ ; CO group in an organic anhydride or transition metal carbonyl	[12]
1830(as)	CD1o, (CD2), (CD3), CD5, CD6o, CD7, CLdU, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A, RD07, RD07A, RD08N , RD08k, RD08kA, RD08o, RD11L, RD11U, RD11o, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1, BT1A, BT1o2, BT1o3, BT1o4, BT2	Ag(CO) ₂ ; MoH ₄ ; phosgene (shf); benzoylperoxy radical ?; Mn(CO) ₂ (shf); 2-propynylidyne; CO group in a n organic anhydride or transition metal carbonyl; +964 (RD11U): CH₃MoH	[12]; [50]

1806-1809	CD1o, (CD2), (CD3), CD5, CD6o, CD7, CLdU, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A, RD07, RD07A, RD08N , ZB1, ZB1A , ZB2, ZB2o, ZB3 , BT1, BT1o, BT1o2, BT1o3, BT1o4, BT2	Mn(CO); nitrosyl iodide; Fe(NO) ₂ ? (shf); V(CO); CO group in an acyl halide or in an organic anhydride or transition metal carbonyl	[12]
1790-1791	(CD2), CD3, CD5, CD6o, CD7, RCH1, RCH1A, RD08NA, BT1o, BT1o2, BT1o3, BT1o4	<i>c</i> -(NO) ₂ ; Ti(CO); diazomethyl radical ; BF ₃ ⁺ ; <i>l</i> -CrC ₃ ; (HgH) ₂ ; HGeNH ₂ ; Mn(CO); CO group in an acyl halide or in an open-chain acid anhydride; +1760: CH₂MoH₂	[12]
1783-1782	ZB1, ZB1A, ZB2, ZB2o, ZB3, BT2	Fe(CO); diazomethyl radical (HCNN); formyl chloride (CHClO); (HHg) ₂ ?; tricarbon hydride ?	[51]; [52]; [53]; [54]; [55]
1777-1774	CD1o, CD2, CD3, CD6o, CD7, CLdA, CLdU, CLdo, CL2a, SW1, SW1oB, SW1oP, SW1oS, RCH1 , RCH1A , BT1, BT1o, BT1o2, BT1o3, BT1o4	(HHg) ₂ or CO group in a ring anhydride; V(CO) (shf)	[12]
1760-1762b(as)	CD1o, CD2, CD3, CD7, CLdU, CL2a, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A, RD07A, RD08N , RD08NA, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1, BT1A, BT1o, BT1o2, BT1o3, BT1o4, BT2	(<i>t</i> -(NO) ₂ or CO group in an alkyl carbonate or N ₂ O ₄ (shf)); +1790: CH₂MoH₂	[12]; [50]
1752	CD5, CD6o	Zn ₂ H ₂ ; <i>t</i> -ClNO ₂ (chlorine nitrite, <i>trans</i> isomer); W(CO) ₂ ; HAg(H ₂); HFeF	[56]; [57]; [58]; [59]; [60]
1747-1745	CD7, CLd, CLdA, (BT1), BT1A, BT1o, BT1o2, BT1o3, BT1o4, BT2	MoH ₄ ; phosgene (shf); benzoylperoxy radical ?; Mn(CO) ₂ (shf); 2-propynylidyne; CO group in an organic anhydride or transition metal carbonyl; C ₄ S radical;	[12]; [61]
1737-1741	CD1o, CD2, CD3, CD7, CLd, CLdU, CL2a, CL2aA, SW1, SW1oB, SW1oP, SW1oS, SW2 , SW2o , SW2o2 , SW2o3 , SW3 , SW3A , RCH1 , RCH1A	<i>t</i> -(NO) ₂ ; Zn ₂ H ₂ ; MoH₂ ; [GeH₃] ; HFeCl; CH ₃ OFeH; [2H4]acetaldehyde?; B ₂ N ₂ ??; C ₇ ?; an aldehyde or ester or alkyl carbonate or CO group in an organic acid anhydride; +1150 (RCH): [2H4]acetaldehyde	[12]; [32]
1729as-1730	CD5, CD6o, RD08N , RD08k, RD08kA, RD08o, RD11L, RD11U, RD11o, BT1o, BT1o2, BT1o3, BT1o4, BT2	MoH ₂ (shf); SnCO; difluorovinylidene (1,1-difluoroethene)-acetone adduct (C ₄ H ₂ F ₂)?; diazasilene; CH ₃ MoH; Al ₂ (CO) ₂ ; an aldehyde or ester; +1304(CD5;RD;BT1): HO ₂ NO ₂ (peroxynitric acid)	[12]; [62]
1721vw	RD07A, BT1	GeH ₃ ⁻ ; +1297 (RD07a): C₂H₅OONO₂ (peroxyethyl nitrate) ; N ₂ O ₅ ; Fe(CO) ₂ ⁻ ; Th(CO) ₂ ; Mo(CO) ₂ ; Ce(CO) ₂	[12]; [63]; [64]; [65]; [66]; [58]; [67]

1715-1712	CD1o, (CD2), CD3, CD7, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A, BT1A, BT1o, BT1o2, BT1o2, BT1o4	+1304(BT1): HNO ₃ ; HFe ₂ OH; HFe ₂ F; Mn(NO) ₃ ; ClNO ₂ (chlorine nitrite); V(NO) ₃ ; FONO (FNO ₂ ; “nitrosyl hypofluorite”)	[68]; [69]; [60]; [70]; [71]; [72]; [73]
1706w	CD5	AlH ₃ ⁻ ; Mn(NO) ₂ ; SiCO ⁻	[74]; [75]; [76]
1697vw-1700	CD6o, CLd, CLdA, CLdU, CLdo, CL2aA, SW1, SW1oB, SW1oP, SW1oS, SW3, SW3A, RCH1, RCH1A	N ₂ O ₃ (O=N-O-N=O isomer); C ₄ ; PbH ₃ ; a carboxylic acid or a ketone or aldehyde	[12]
1690(sh)-1691	CD1o, CD2, CD3, CD5, CD6o, CD7, CL2a, BT1A, BT1o, BT1o2, BT1o3, BT1o4, BT2	N ₂ O ₃ (O=N-O-N=O isomer); UCO ⁻	[77]; [78]
1679-1677	CLd, CLdA, BT1A, BT1o4	MoH ₃ ; NiNO; AgNO; alkenyl C=C stretch or amide group or a quinone (or conjugated ketone); +1513(CLd, CLdA): C ₆ S ₄ O ₂ (dithio-<i>p</i>-benzoquinone)	[12]; [79]
1673-1676	CD1o, CD2, CD3, CLdU, CL2a, SW1, SW1oB, SW1oP, SW1oS, SW3, SW3A, RCH1 , RCH1A , BT1, BT1A, BT1o, BT1o2, BT1o3	V(CO) (shf); MoH ₃ ; NiNO; AgNO; alkenyl C=C stretch or amide group or a quinone or conjugated ketone); +1327+1321(CD1o): H ¹⁵ NO ₃ ; +1528(CD2;RCH): Au(NO) ₂ ?	[12]; [32]; [80]
1666-1669	CD5, CD6o, CD7, RD07, ZB1 , ZB1A, ZB2, ZB2o, ZB3, BT2	GeH₂ ; CCS (thioxoethenylidyne) radical; (fluoromethylidyne)phosphine; alkenyl C=C stretch or amide group or an open-chain imino compound; F ₂ C=C radical (difluorovinylidene) ; shf); +1227 (CD7): Al ₂ H ₂ (H(<i>cyc</i> -AlHAl)); +3062 (BT2): (C ₂ H ₂) In (indium-acetylene complex)	[12]; [81]; [31]
1660sh-1662sh	CD1o, CD2, CD3, RCH1, RCH1A, RD08N , BT1o, BT1o2, BT1o4	BF ₂ OD ⁺ ; alkenyl C=C stretch or amide group or an open-chain imino compound	[12]
1651-1652	CLd, CLdA, CLdU, CLdo, SW1, SW1oB, SW1oP, SW1oS, SW3, SW3A	alkenyl C=C stretch or amide group or an open-chain imino compound	[12]
1645as-1642	(CD1o), CD2, CD3, CD5, CD6o, CD7, RCH1, RCH1A, RD08NA, BT1, BT1A, BT1o, BT1o4, BT2	alkenyl C=C stretch or amide group or a quinone (or conjugated ketone) or an open-chain imino compound; <i>c</i>-HONO ; +~2276+~3638(CD2,3,7): HON=CHNCO (formaldoxime isocyanate)	[12]; [23]
1639-1636	RD07, RD07A, RD08N , ZB1 , ZB1A, ZB2, ZB2o, ZB3	CrNO; Cu(NO) ₂ ; alkenyl C=C stretch or amide group a quinone (or conjugated ketone) or an organic nitrate or open-chain imino compound; +1605(RD08N): CrH ₂	[12]; [82]
1612-1613	CD5, (RD07, RD07A), RD08k, RD08kA, RD08o, RD11L, RD11U, RD11o, ZB1 , ZB1A, ZB2, ZB2o, ZB3	<i>c</i>-cyanomethanimine ?; Cu(NO) ₂ ; <i>bicyc</i> -C ₆ H ₃ F ₂ N? (2,6-difluorophenylnitrene – a fluorinated azirine) ?; a quinone (or conjugated ketone) or an open-chain imino or azo compound	[12]

1605	RD08N	+~1640: CrH ₂ ; VNO; HSnOH; CH₂BCl (chloromethylboron)	[82]; [72]; [83]; [84]
1590vw-1591	CD6o, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1	MgH ₂ or MnH ₂ or HMgOH or Ni(NO) ₂ ⁻ or difluoromethylene cation or formyl methyl iminoxy radical	[85]; [12]
1588	CD5	CF₂⁺ (difluoromethylene cation); CH₃C(=NO)CHO (formyl methyl iminoxy radical); MgH ₂	[86]; [87]; [84]
1581w-1583as	RCH1, RCH1A, RD07, RD07A, ZB1, ZB1A, ZB2, ZB2o, ZB3	TiH ₃	[88]
1572-1576w	CD1, CD1o, CD2, CD3, CD7, CLd, CLdA, CLdU, CLdo, CL2aA, SW1, SW1oB, SW1oP, SW1oS, SW2, SW2o, SW2o2, SW2o3, RCH1, RCH1A , BT1, BT1o2, BT1o4, BT2	difluoronitroxide radical; carboxylate group; +1267: monomethylsilane (deuterated); cis-1,2-dichloroethene-d2	[12]
1568(as)-1567	CD5, CD6o, BT1o	+1777: (HHg) ₂ or CO group in a ring anhydride; +1669(CD): ONSNO (N ₂ O ₂ S); NOH ? (nitrosyl hydride); NbH ₂ ; H ₂ NbO; SeNO; <i>c</i> -HSNO (thionitrous acid); CH₃NHCH₂NO (methyl(nitrosomethyl)amine); SnNO	[12]; [89]; [90]; [91]; [92]; [93]; [94]; [95]
1553-1551	CD1o, CD2, CD3, CLd, CLdA, CLdo, CL2aA, SW1, SW1oB, SW1oP, SW1oS, SW2, SW2o, SW2o2, SW2o3, SW3, SW3A, RCH1, RCH1A , BT1, BT1o, BT1o2, BT1o4	methyl(nitrosomethyl)amine (CH ₃ NHCH ₂ -NO); Cu(NO) ₂ ; phenylnitrene radical (PhN); phenoxy radical? ; NH bend in a secondary amine or carboxylate group or a nitro-aliphatic or nitro-aryl	[12]
1547	SW3, SW3A	C ₄ ; HCr(H ₂); HMgCH₂F (a Grignard compound); CH ₃ InH (monomethylindium hydride)	[96]; [97]; [98]; [99]
1537	CLd, CLdA, CLdU, CLdo, SW1, SW1oB, SW1oP, SW1oS	H ₂ I ₂ ⁺ ; HTiOH	[100]; [101]
1530-1528	CD2, CD5, RCH1, RCH1A , BT1o4	+1676(CD2;RCH): Au(NO) ₂ ; HZrOH	[80]; [102]
1520-1522	SW1, SW1oB, SW1oP, SW1oS, SW3, SW3A	1,3-butadiene (deuterated); Cd ₂ H; GeD ₄ (germane, deuterated); SNO (nitrogen oxide sulfide); CrNO ⁻ ; Ag ₂ H ⁻	[32]; [103]; [75]; [59]
1518	CLdU	t-OCCO⁻ (C₂O₂⁻; acetylenediolate anion?); 1,2-C₆F₄(NO)₂ (1,2-dinitrosobenzene); In ₂ H ₂ ; HHgOH; ZrH ₂ ; CuH ₂ ⁻	[104]; [105]; [106]; [107]; [108]; [109]
1514	CLd, CLdA	+1679(CLd, CLdA): C ₆ S ₄ O ₂ (dithio-<i>p</i>-benzoquinone); CH₂CHO (vinoxy radical) ; (NS)F ₃ (thiazyl trifluoride); F ₂ P(O)N (difluoronitrosophosphine); SF ₅ O ₃ radical; HAsF ₂ (monofluoroarsine); +3612: 2,4-C₆H₃OH (2,4-didehydrophenol) (?)	[79]; [110]; [32]; [111]; [112]; [113]; [26]

1500-1498vw	CD1, CD1o, CD2, CD3, CD7, CLd, CLdA, CLdU, CLdo, CL2aA, SW1, SW1oB, SW1oP, SW1oS, SW2, SW2o, SW2o2, SW2o3, SW3, SW3A, RCH1, RCH1A, BT1, BT1A, BT1o3, BT1o4	SNS⁺ (dithioammonium); vinyl titanium hydride; O ₂ F??; phenanthrene? (sfh) or triphenylene ; a nitro-aryl ; nitrosyl cyanide	[12]; [114]
1490vw(sh)	CD5, CD6o	<i>o</i>-C₆F₄ (<i>o</i>-tetrafluorobenzene); O ₂ F; Si(NO) ₂ (shf); VH ₂ ; Ge ₂ H ₆ (digermane)	[115]; [116]; [117]; [118]; [32]
1482-1481(vw)	RD07, RD07A, RD08N, RD08k, RD08kA, RD08o, RD11L, RD11U, RD11o, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT2	HSeOH ?; + 1468: Ge ₂ H ₄ or nitromethyl radical ?; +1463: Ge(NO) ₂	[12]; [119]; [120]
1473-1475	(CD1o), (CD2), (CD3), CD5, CD6o, CD7, RCH1, RCH1A, BT1A, BT1o3	H₂BC₂H₃ (vinylborane); Ge ₂ H ₄ ; CCIP ((chloromethylidene)phosphine) (shf); F ₂ PO ⁺	[121]; [119]; [122]; [123]
1471	SW1, SW1oB, SW1oP, SW1oS	<i>p</i>-C₆F₄I (iodotetrafluorobenzene); HSiCN (cyanosilylene); H₂BC₂H₃ (vinylborane); Mg ₂ H	[36]; [124]; [121]; [125]
1467-1468	CLd, CLdA, CLdU, (ZB1, ZB1A, ZB2, ZB2o, ZB3), BT1, BT2	+1408(ZB): YH ₂	[126]
1460w	CD1o, CD2, (CD3), CL2aA, SW2, SW2o, SW2o2, SW2o3, SW3, SW3A, RCH1, RCH1A	YH ₂ ; methylene ion or an inorganic carbonate; MgNO; 3,5-C₆H₃CH₃ (5-methyl-1,3-didehydrobenzene) ?	[12]
1450	SW1, SW1oB, SW1oP, SW1oS	HGaCl ₂ ; H ₂ GaCl ₂ GaH ₂	[127]; [128]
1440-1443	CD1, (CD2), (CD3), CD5, CD6o, CD7, CLd, CLdA, CLdU, CLdo, RCH1, RCH1A, RD07, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1, BT2	triphenylene ; ClO ₂ *; dihydroxycarbene?; an inorganic carbonate; benzyl radical?	[12]
1430-1428	CD1, CD2, CD3, CD1o, CD5, CD6o, CD7, CLd, CLdA, CLdo, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A, RD07, RD07A, RD08NA, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1, BT1A, BT1o3, BT1o4, BT2	ClO₂*; HAlCl₂; Si₂H₄ (disilane, Si₂D₄); Tl ₂ H ₂ ; CNiS ₂ ⁺ ; difluorovinylidene? ; cyanomethyl radical (in the RDT samples); an inorganic carbonate or NH ₄ ⁺ ion; Be ₂ H ₅ ; +1406: GaH ₂ Cl; +928 (CD5, CD7, ZB3): C₆H₆F ; +1429(CD5, RD07, RD08N; ZB): PO ₂ Cl (phosphenic chloride); +~1320(CD1o, CD2, CD3): CF₂I⁺ ; +1408(ZB): GaH ₂ Cl	[12]; [129]; [130]; [131]; [132]
1412sh	RCH1, RCH1A	CH ₃ BeO; H ₃ SbO (stibine oxide)	[133]; [134]
~1408	ZB1, ZB1A, ZB2, ZB2o, ZB3	HO(NO)SO ₂ ? (nitrososulfonic acid); OH group in phenol or a tertiary alcohol or a compound with carboxylate group or an organic sulphone or NH ₄ ⁺ ion; +1430(ZB): GaH ₂ Cl; BCIS (chlorothioxoborane); +1468(ZB): YH ₂	[12]; [132]; [135]; [126]

1406-1407as	(CD5), CD6o, CD7, RD07, BT2; BT2	benzyl radical ?; CF_2Cl^+ ; $\text{HO}(\text{NO})\text{SO}_2$ (nitrososulfonic acid); HThO ; H_2UO_2 ; HZnCl	[136]; [137]; [138]; [139]; [140]
1397-1400	CD1, CD1o, CD2, CD3, CD6o, CLd, CLdA, CLdU, CLdo, CL2aA, SW1, SW1oB, SW1oP, SW1oS, RCH1, RCH1A , BT1, BT1o3, BT1o4	YH_2 ; iodosomethane ?; PbH_3 ; HYOH ; OH group in phenol or a tertiary alcohol or carboxylate group or an organic sulphone or sulphate or NH_4^+ ion; CHBrF^+ ; +1152(RCH): $\text{H}_2\text{Ti}(\text{C}_2\text{H}_2)$ (titanacyclopropene)	[12]; [35]; [141]
1389	CD7	SO_3 ; $(\text{F}_2)\text{BF}_2$?; GaH_3 (gallane)	[32]; [142]; [143]
1381	ZB1, ZB1A, ZB2, ZB2o, ZB3	SAuCS ; $(\text{H}_2)\text{YH}_2$; HCuOH ; AlNO^- ; C_2S_4^+	[144]; [126]; [69]; [145]; [146]
1372(vw)-1374	CD1o, CLd, CLdA, CLdU	SO_2 ; FNS (thiazyl fluoride) ; NSCN (thiazyl cyanide) ; PNS (thiazylidene phosphane) ; F_2PN (difluoro-λ^3-phosphinonitrile) ; F_2CSO (difluorosulfine) ; $(\text{CH}_2)=\text{PCI}$ (methylenephosphine chloride, 1-phosphaethene) ; <i>cyc</i>-H_2COC: (oxiranylidene) ; PbH_3 ; ZnH_2	CALCMET; [32]; [147]; [148]; [149]; [150]; [151]; [152]; [153]; [154]
1368	CD7	thiocarbonyl fluoride (CSF_2); CHF^+ ; CH_3UH (uranium methylidene dihydride); $\text{HY}(\text{OH})_2$	[32]; [155]; [156]; [157]
1360-1358	ZB1, ZB1A, ZB2, ZB2o, ZB3, BT2	thioacetaldehyde ?; SbH_3 ?; OH group in phenol or a tertiary alcohol or CN group (stretch) in an aromatic tertiary amine or a nitro-aliphatic or a sulphonate or an inorganic nitrate; CHF^+ or sulfine (CH_2SO) or SiD_3HgD (SiH_3HgH) or $(\text{REE})\text{NO}$ or WD_3 ; ; $\text{H}_2\text{B}=\text{OCH}_3$ (methoxyborane)	[12]; [158]
1350(vw)-1351	CD1o, CLd, CLdA, CLdU, CLdo, <u>CL1</u>	pentacene ; C_6Cl_6 ?; methyne ion or phenol or a tertiary alcohol (OH group) or an aromatic amine (CN group) or a nitro-aliphatic or nitro-aryl or an organic phosphate or sulphonate or an inorganic nitrate	[12]
1346w(as)	BT2	+1358: thioacetaldehyde ; UH_3 ; $\text{HCu}(\text{H}_2)$; HNiOCH_3 (an intermediate methoxy compound); difluoroethyne	[159]; [160]; [109]; [161]
1342-1345	RD08N, RD08k, RD08kA, RD08o, RD11L, RD11U, RD11o, ZB1, ZB1A, ZB2, ZB2o, ZB3	thioacetaldehyde ?; <i>cyc</i> -FeNO; C-NH bond (in a thiazolidine); Mn_2H_4 ; Cu_2H_2 ; methyne ion or an aromatic amine (CN group) or a nitro-aryl or an organic phosphate or sulphonate; HGeCl ; +1306(RD11U;ZB): Al_2H_4 (dialane)	[12]; [74]
1340-1341	RD07A	Cu_2H_2 ; <i>cyc</i> -FeNO; HGeCl ; Mn_2H_4 ; phenol or a tertiary alcohol (OH group) or an aromatic amine (CN group) or a nitro-aryl or an organic phosphate	[12]
1329-1327	CD1o, CLd, CLdA, CLdU, CLdo, <u>CL1</u> , ZB1, ZB1A, ZB2, ZB2o, ZB3, BT2	2,4,6-trinitrene-1,3,5-triazine ; phenol or a tertiary alcohol (OH group) or an aromatic amine (CN group) or a nitro-aryl or an organic phosphate or dialkyl/aryl sulphone; +1672+1321(CD1o): H^{15}NO_3	[12]; [32]

1320-1321vw	CD1o, CD2, CD3	<i>cyc</i> -O ₄ ⁺ ; HCdCl; +1327+1672(CD1o): H ¹⁵ NO ₃ ; PO ₂ ; +~1433 (shf?): CF ₂ I ⁺	[162]; [140]; [32]; [163]; [131]
1303w-1305as	CD5, RD08NA, RD11U, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1, BT1A, BT1o, BT1o2	Sb ₂ H; POCl ₃ ; HOCCOH (dihydroxyacetylene, ethynediol); +~1712(BT): HNO ₃ ; +1728(CD5;RD;BT): HO₂NO₂ (peroxynitric acid); +3056(RD08NA): bromomethane; +~1346(RD11U;ZB): Al ₂ H ₄ (dialane)	[164]; [12]; [165]; [68]; [32]; [74]
1300(as)-1301	CL2a, CL2aA, BT2	CClF ₃ ⁺ (and others below); Sb ₂ H; +1244: GaH ₂ ; PbH ₄ ; Cl ₂ PO radical; H ₂ GeCl radical	[131]; [164]; [166]; [167]; [62]; [168]
1298as	RD07 , RD07A, BT1o3	CClF ₃ ⁺ ; +1719 (RD07A): C ₂ H ₅ OONO ₂ (peroxyethyl nitrate); In ₂ H ₆ ; H ₂ InNH ₂ ; SiH ₃ AlH	[131]; [63]; [169]; [170]; [171]
1282-1280	RD07, RD07A, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1A, BT1o	HAIOH or HSO ₂ (hydroxysulfinyl) or NC(<i>cyc</i> -C=NC:) (a dicyanocarbene isomer) or CF ₃ OSO ₃ radical or AlON or INO ₂ (iodine nitrite) or difluorocyclopropenone ; +1150 (RD07): C*HCIF radical	[12]; [172]
1266(vw)-1269	CD5, CD6o, CD7, CLdU, CLdo, CL2a, CL2aA, SW2, SW2o, SW2o2, SW2o3, (SW3), (SW3A), RCH1, RCH1A, RD07, RD07A, RD08N, RD08k, RD08kA, RD08o, RD11L, RD11U, RD11o, RD08NA, ZB1, ZB1A, ZB2, ZB2o, ZB3, BT1, BT1A, BT1o, BT1o2, BT1o3, BT2	F₂C=C radical (difluorovinylidene); methyne ion or an aromatic primary amine (CN group stretch) or an organic nitrate or phosphate ; +~1572: monomethylsilane (deuterated); benzyl radical?; +1080 (RD07, RD07A; ZB): <i>p</i>-(CF₂)₂C₆H₄ (tetrafluoro-<i>p</i>- xylylene) ; +1149(RD07): HCFBr radical ; +~1300 (CL2a, CL2aA, BT2): GaH ₂ ; +~3676(CLdU): H ₂ SiO ₃ (metasilicic acid) (?)	[12]; [272]; [172]; [166]; [21]
1243-1241	CL2a, CL2aA, RD07, RD07A, (ZB1, ZB1A, ZB2, ZB2o, ZB3), BT1o, BT2	cyclobutadiene or nitrogen dioxide anion or dihydroxycarbene? or HCl₃OSi (trichlorosilanol) or P ₄ O ? or CH₃Cl⁺ or CF₂Br₂⁺ or BiH ₃ or CH ₃ MoH ? or CH ₃ CoH ? or Ca₂H₂ or H ₂ Ca(OH); <i>t,t</i>-HOCOH (dihydroxycarbene)	[12]; [173]
1220	CL2a, CL2aA, (RD07)	CHCl₃ ; C₆H₅CCl (phenylchlorocarbene); <i>c</i>-HN=CHCN (<i>c</i>-cyanomethanimine); CH₃SiCl (chloromethylsilane); CH₃SiBr (bromomethylsilane); CH₃SiI (iodomethylsilane); PbH ₃ ; HNdO; <i>t</i>-(NO)₂ ; GeH ₃ ⁻ ; ClClO ₂ (chloryl chloride)	[32]; [174]; [175]; [176]; [177]; [178]; [153]; [179]
1198vw	RD07	F₂C=(<i>cyc</i>-C₃H₂) (fluorinated methylenecyclopropene) ; CCl₂⁺ (a dihalocarbene cation) ; PO ₂ ; N ₂ O ₂ ; HMnOH; OZrC=S	[180]; [181]; [182]; [183]; [69]; [184]
1159-1158	SW2, SW2o, SW2o2, SW2o3, RD08N	<i>t</i>-1,3-difluoroethene; CBrF (bromofluoromethylene); CS₂ ; CrH ₂ ; SiF ₃ ⁺ ; CH ₃ Nbh; HSnOH; S ₂ O (disulfur monoxide)	[32]; [35]; [185]; [82]; [186]; [187]; [188]; [189]

1150vw	RCH1, RCH1A, RD07	CFI_2^+ ; NdH_3 ; ThNH_3 (thorimine); +1737 (RCH): [2H4]acetaldehyde ; +1283 (RD07): C*HCIF radical ; CHBr_3 (tribromomethane) ; F_2OP^- ; +1266(RD): HCFBr radical ; +1397(RCH): $\text{H}_2\text{Ti}(\text{C}_2\text{H}_2)$ (deuterated; titanacyclopropene)	[190]; [191]; [192]; [32]; [172]; [32]; [123]; [141]
1128sh(w)	CD7	HVOH; <i>cyc</i> -(CeH) ₂ ; NbH_2 ; AlO_2 ; +~1669: <i>cyc</i> - Al_2H_2 ; <i>cyc</i> - C_5Cl_4 (tetrachlorocyclopentadienylidene)	[101]; [191]; [90]; [193]; [81]; [194]
1122w(sh)-1120w	CD5, RD07, RD08N, ZB1, ZB1A, ZB2, ZB2o, ZB3	SOBr_2 (thionyl bromide); CBrCl^+ ; $\text{CH}_2=\text{PCI}$ (a phosphalkene) ; $(\text{CH}_3)_2\text{Si}=\text{NH}$ (1,1-dimethylsilanimine) ; +1429: PO_2Cl (phosphenic chloride)	[32]; [86]; [151]; [195]; [130]
1119-1120	CLdo, CL2a, CL2aA, SW2, SW2o, SW2o2, SW2o3, (SW3), (SW3A), RCH1, RCH1A, RD07, RD07A	+~1078 (RD07, RD07A): ethenol	[196]
1112vw-1110	SW1, SW1oB, SW1oP, SW1oS, RD08NA, RD08k, RD08kA, RD08o, RD11L, RD11U, RD11o	ClO_2 ; CuO_4 (O_2CuO_2); CuO_5 ($\text{OCuO}_2(\text{O}_2)$); <i>cyc</i> - YO_3 ; <i>cyc</i> - LaO_4 ; CH_3TiH (an insertion compound); ZrH_3 ; $\text{HZr}(\text{O})\text{OH}$; $\text{HCr}(\text{H}_2)$; FCSF (fluoro(fluloromethylidene)-λ^4-sulfane) ; <i>t,t</i>-HOCOH (dihydroxycarbene) ; HMg_2OH ; <i>cyc</i> - CrNO	[197]; [198]; [199]; [200]; [201]; [108]; [202]; [97]; [173]; [203]
1098w	RCH1, RCH1A	CBrF_2 ; PF_3^+ ; SnD_3^- ; Ag_2H ; HZrOH ; LiO_2 (lithium superoxide); <i>cyc</i> - AlO_2 ; CCl_3NO_2 (chloropicrin)	[131]; [123]; [153]; [59]; [102]; [204]; [205]; [206]
1088w-1090w	CD5, CD6o, CD7, CLd, CLdA, CLdo, CL2a , CL2aA, RCH1A, RD07, RD07A, RD08N , RD08k, RD08kA, RD08o, RD11L, RD11U, RD11o, ZB1, ZB1A, ZB2, ZB2o, ZB3	+1013: $(\text{F}_2\text{N})\text{AuF}$; +~1033~3013 (CL2aA, RCH1; RD and ZB): methane-d ₂ ; BCl_3^+ ; BHCl_2 (dichloroborane)	[207]; [32]; [208]
1081-1080sh	RD07, RD07A, ZB1, ZB1A, ZB2, ZB2o, ZB3	CBrCl_2F (bromodichlorofluoromethane) ; NaO_2 ; AlNO ; VH_2 ; In_2H_2 ; HInOH ; Cd_2H ; <i>cyc</i> - TlO_2 ; TiH_2 ; HTiC_2H_3 (vinyltitanium monohydride) ; $\text{H}_2\text{CCl-Cl}$; +~1118 (RD07, RD07A): ethenol ; +1267 (RD07, RD07A; ZB): <i>p</i>-(CF_2)₂C_6H_4 (tetrafluoro-<i>p</i>-xylylene)	[32]; [209]; [145]; [118]; [106]; [16]; [56]; [210]; [56]; [211]; [196]; [272] [36]
1072w	SW2, SW2o, SW2o2, SW2o3, RCH1, RCH1A	<i>t</i> - HNOH ; +~2337 (the SW samples): C_6F_4 (perfluorinated <i>p</i>-benzyne) ; MnD_2^- ; CH_3IO (iodosomethane) ; CH_3SO (methylsulfinyl radical) ; DPbO (HPbO)	[212]; [36]; [213]; [214]; [215]; [188]
1066w	CLdU	Mg_2H ; HCS_2 ; SnH_2^-	[125]; [216]; [153]

1060w	RCH1, RCH1A	+~1584: Mg ₂ H ₄ ; HBaOH; hydroxyacetonitrile ; 1,2,4-cyc-C₂H₄O₃ (an ethylene ozonide); cyc-C₃HCl (chlorinated cyclopropenylidene); (2-ClC₆H₄)CH (2-chlorophenyl) carbene); UH ₄ ; GaBH ₆ (gallaborane); +1035: CeH ₂ ⁺	[125]; [217]; [218]; [219]; [220]; [221]; [159]; [222]; [191]
1037as- 1034as	CL2aA, SW2, SW2o, SW2o2, SW2o3, RCH1, RCH1A, RD07, RD07A, RD08N , RD08k, RD08kA, RD08o, RD11L, RD11U, RD11o, RD08k, RD08kA, RD08o, RD11L, RD11U, RD11o, ZB1, ZB1A, ZB2, ZB2o, ZB3	NF ₃ ; +1082 (RD07, RD07A, ZB1, ZB1A, ZB2, ZB2o, ZB3): CH₂OCH₂OO (1,2,4-trioxolane); +1281 +1244 (RD07, RD07A, ZB): CF₃OSO₃ (triflic) radical; propargyl fluoride (C ₃ H ₃ F); +1090+~3013 (CL2aA, RCH1; RD and ZB): methane-d ₂ ; +1060 (RCH1, RCH1A): CeH ₂ ⁺	[32]; [223]; [224]; [32]; [191]
1032-1034w	CD6o, CD7, CLd, CLdA, CLdU, CL2a, RCH1A	methanol ?; NF ₃ ?; cyclohexane (ring vibrations) or an aliphatic phosphate or an organic siloxane or silicone or an inorganic sulphate or phosphate or silicate	[12]
1012-1011	SW2, SW2o, SW2o2, SW2o3; RD07, RD11U, ZB1, ZB1A, ZB2, ZB2o, ZB3	HOOb; CBrCl ₂ F; C₂Cl₄⁺ ; +1090: (F ₂ N)AuF; CuCH ₂ (copper methylene); CuO ₂ ; CHSi (silicon methylidyne); BS ₂	[225]; [131]; [226]; [207]; [227]; [228]; [229]
976vw	RCH1, RCH1A	CBr₂Cl⁺ ; NCrO; CHNSi ; CH ₃ UH; FeO ₃ ; SF ₄ ⁺ ; Cu ₂ D ₂ ; IOClO; 2H-azirine	[230]; [203]; [124]; [156]; [231]; [123]; [232]; [233]; [234]
966vw	RD11U	Se ₂ O ₂ (cyc-(SeOSe)=O); Ga ₂ O ₂ ; CrO ₂ S; BCl ₂ ; H ₂ O ₂ ; +1830: CH₃MoH	[235]; [236]; [237]; [238]; [239]; [50]
925-928vw	CD5, CD7, (ZB3)	dimethylsilanol ; germanol (GeH ₃ OH); SiCl ₃ OCl; OF ₂ ; Al ₂ H ₄ ; Li(C₆H₆) ; P ₂ F ₄ (F ₃ P=PF); (Cl₂)CCl••Cl ; <i>t</i> -ClC(O)OO (peroxychloroformyl radical); +1428: C₆H₆F ; H ₃ Si (silyl radical); CD7: SO ₂ F ₃ ; FNC (“fluorine cyanide”)	[240]; [241]; [242]; [32]; [243]; [244]; [235]; [246]; [32]; [247]; [129]; [248]; [25]
920vw	SW2, SW2o, SW2o2, SW2o3	methyl-d ₃ -stannane?; (H ₂)LaH ₂ ; H₃Si(cyc-CSiCH) ; cyc-(HC=NCH)CN ; CNbO; <i>cyc</i> -Ti ₂ H ₂ ; SF ₅ O ₂ radical; WO ₃ ; Ga ₂ H ₂	[32]; [126]; [124]; [249]; [250]; [251]; [112]; [252]; [253]
911vw	ZB3, BT1o4	GeCl ₄ ; vinyl-1,2-butadiene	CALCMET; [254]

¹ weak, very weak, diffuse, broad, shoulder; ² shifted against the literature-derived position; ³ other (important) bands missing; expected organic compounds are given in bold; some data is for deuterated molecules.

It is noteworthy that the above table only list proposal trace gaseous species. At least some of them are transient molecules potentially related to photochemical reactions at the heap

surfaces. The cited literature often concerns noble-gas matrix-isolated compounds and laser-ablated precursors. Thus, the listed proposals should be treated with care.

2. Discussion: Chance of the Occurrence And Potential Sources of Selected Trace Organic Gases

Bromomethane, CH₃Br

Observation of bromomethane (methyl bromide) is not a surprise, especially that it is reported, together with chloromethane, as “the most abundant halogenated hydrocarbon” in the atmosphere (e.g., [255]). Interestingly, exactly this compound was detected, exclusively, at the very same vent using the IT method. This observation is somewhat in opposition to the suggestion of the mentioned authors that bromomethane is “mainly of nonindustrial origin” (although they mention biomass burning as one of its sources). Although Br₂ was not detected in any CFGs studied, I₂ was. Thus, a reaction involving methanol, Br₂ and S (or H₂S), is credible:



The compound is degraded by photochemically generated OH[·] groups and is slowly hydrolysed by water [257].

CHClF, HCFBr, and CF₂I[·]

These molecules, or radicals, are undoubtedly derivatives of their parent freon-type molecules like dichloromethane, chloromethane, CFC-11, and HCFC-22. In our former study similar ions were detected, e.g., dichlorodifluoromethane anion. Such ions are important in studies of ozone depletion, as at least some CFCs may liberate Cl atoms (e.g., [258]).

cyc-C₁₀

This is one of the linear molecules obtained via photodetachment from its relative anion, C₁₀⁻ [38]. Both molecules result from carbon vaporization, i.e., a graphite rod bombardment by Cs cations. A similar molecule, C₄, was previously tentatively detected in the CFGs [7]. It is a matter of debate if C₁₀ could be formed via ring opening of ten-carbon compounds well-known to occur in the exhalative environment of the BPWHs like naphthalene, C₁₀H₈.

c-cyanomethanimine, CH₂=N-CN

This unstable compound, important in astrobiochemical studies, may be formed via pyrolysis of dimethylcyanamide, (CH₃)₂NCN [259]. It is one of many nitriles detected in the CFGs [7-8], and an isomer of HCN. [260] generated its *N*-homologue from two heterocycles: 1,5-trimethylenetetrazole, (CH₂)₃N(N=N-N)C (by removal of N₂ and ethene, at 500-800 °C) and

ditetrazolopyrazine, $(\text{CH}_2)_2\text{C}(=\text{N}-\text{N}=\text{N}-\text{N})_2$ (by removal of 2N_2 , at 600-850 °C). Combustion of *N,N*-dimethylcyanamide may also be used. The *N* isomer of cyanomethanimine is said to be theoretically more stable than both HCN and another isomer – iminoacetonitrile. However, this does not seem to be true for the BPWH environment. Nevertheless, the mentioned reactions seem to be plausible to explain the occurrence of the compound in question there.

Dithio-*p*-benzoquinone (thio-*para*-benzoquinone; DpBQ) $\text{C}_6\text{S}_4\text{O}_2$

This compound was obtained by [261], alongside with *p*-benzoquinone, monothiol-*p*-benzoquinone, and 1,5-hexadiene, during thermal decomposition of 1,4-di(heteroallyl)-substituted benzenes, $\text{C}_6\text{H}_4(\text{XCH}_2\text{CH}=\text{CH}_2)_2$ ($\text{X} = \text{O}, \text{S}$), at 797 °C. According to [79], DpBQ may also be formed via photolysis or vacuum pyrolysis (at 800 °C) from $[\text{C}_4(\text{CO})_2][\text{S}(\text{CO})\text{S}]_2$, that is most likely 1,3,5,7-tetrathia-*s*-indacene-4,8-dione, by removal of 2 CO. The temperatures reported are easily reachable in the BPWHs and are typical for high-temperature pyrolysis, or similar processes, taking place at depth. At once, a rich S source in the CFG would be available in the form of abundant heterocycle thiophene, $\text{C}_4\text{H}_4\text{S}$. Identification of dithio-*para*-benzoquinone brings to mine detection of hexathiophane (thiepane), $(\text{CH}_2)_6\text{S}$ in an organic pyrolysate deposited in a vent of one of the BPWHs studied [7]. Both compounds, as thiophene, may act as precursors to common elemental sulfur crystals of the local fumaroles.

Ethenol

Ethenol, or *syn*-vinyl alcohol is related to acetaldehyde – a common admixing constituent of the CFGs – via tautomerization (e.g., [262]). The process needs very high temperature and low pressure, but may be achieved in the environment in question due to catalytic role of photochemistry. Vinyl compounds are expected to be enriched in the CFGs, as vinyl chloride is one of the major Cl species there. Another route to ethenol is dehydration of ethylene glycol [263] which, however, was not observed yet. [196] produced ethenol via thermal decomposition of some alcohols and aldehydes. One such reaction, taking place at ~650 °C with optimum at 750 °C, involves ethene and acetaldehyde at the first stage, with additional acetylene formed at the second one. Ethenol was also obtained from *b*-butyraldehyde, *n*-butanol, and *n*-propanol. Most of these molecules were identified in the CFG, mainly involving the ESLM.

1-fluorocyclohexadienyl radical, $\text{C}_6\text{H}_6\text{F}$

The radical, or addition complex, is a relatively long-lasting product of a microwave-discharge, or photochemically formed F atoms with benzene, although at very low temperatures. As such conditions are very different for these in the BPWHs, such radical, if present, must have been formed following another chemical path, or is also to be formed at normal and/or elevated temperatures. It is likely in a recombination relation with fluorobenzene [129]. A similar complex is known as benzene fluoride, $\text{C}_6\text{H}_6\text{F}^-$.

Formaldoxime isocyanate, HO-N=CH-N=C=O

This is one of the compounds formed in long-time experimental gas-phase pyrolysis of chloroglyoxime, N(OH)=CH-(Cl)C=N(OH). By removing HCl from the latter, an intermediate nitriloxide, HO-N=C(H)-C≡N→O is formed [23]. Irradiation of the latter produces the compound in question. Formaldoxime – an oxime of formaldehyde – may itself be formed via interaction of hydroxylamine, NH₂OH, and formaldehydes [264]. Amines do occur in the CFGs studied.

Hydrogen isocyanide, HNC

The observation of this compound is expected, as its major tautomer – hydrogen cyanide – is one of the most common cyanides detected in the CFGs studied, at various vents and heaqqps, by both the FTIR and IT techniques. A well known interstellar molecule, it is extraterrestrially formed via, e.g., dissociative recombination of protonated hydrogen cyanide, HNCH⁺, and H₂NC⁺ [265]. However, it may also be formed as an intermediate in combustion of its tautomer [266].

Monomethylsilane, (CH₃)SiH₃ (MMS)

This is yet another silane derivative detected in the CFGs after SiF₄ (fully quantitative analysis), carbonosilylene, diazasilene, difluorosilane, dimethylsilanimine, disilane, tribromosilane, trichlorosilane, trifluorosilane, silanenitrile [7], and other potential Si compounds from this study: bromo- and iodomethylsilane, monofluorosilylene radical, metasilicic acid, methylsilanediylene (methylsilylene, HSiCH₃), trichlorosilanol, silicon methylidyne, and Si(NO)₂, to mention some. In the light of such a potential of a wealth of Si-bearing gases, a monosubstituted silane is not an oddity. Of a particular interest is methylsilylene. Interestingly, it was preliminarily detected, alongside with MMS, in two CL samples and one RD sample. It is a major product of MMS combustion (i.e., static pyrolysis, at 340-440 °C and 40-400 Torr; [270]), according to the reaction of 1,1-H₂ elimination:



A silene compound may be formed in 1,2-H₂ elimination (at 427 °C)

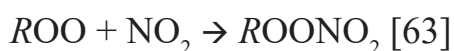
**Perfluorinated p-benzyne, C₆F₄**

Also known as 1,4-didehydro-2,3,5,6-tetrafluorobenzene, it is yet another compound originally isolated in a noble gas matrix by [36]. Its generation was achieved by destabilization of 1,3,4,6-tetrafluoro-hex-3-ene-1,5-diyne, (CCF₃)₂(CF)₂, although it could theoretically also

be formed photochemically from 1,4-diiodo-2,3,5,6-tetrafluorobenzene and by irradiation of 2,3,5,6-tetrafluoroterephthaloyl diiodide. The latter process, however, takes place at very low temperature. Reactions allowing formation of similar compounds are known as Bergmann cyclization. Occurrence of C_6F_4 in the CFG is reliable due to the two-method-confirmed occurrence of benzene and suspected presence of *o*-tetrafluorobenzyne, hexafluorobenzene, and iodofluorobenzene, among others.

Peroxyethyl nitrate (PEN), $C_2H_5OONO_2$

This and similar compounds may be formed in the following reaction (taking place at P close to ambient):



Where $R = C_nH_{2n+1}$, $n=1-6$. The precursor phase is an alkane- NO_2 mixture. Both these constituents are frequent components in the CFG. [63] also reported similar peroxy nitrates, as major N species, among products of photolysis of mixtures of Cl_2 , NO_2 , and alkanes. [271] also explored reaction of $C_2H_5O_2$ (ethylperoxy radical) with NO_2 and found PEN, too. They suggest this compounds to be important in urban atmospheres, thus making discovery of it in the CFG more reliable. What is important, the reaction takes place at ambient temperature. The more, other peroxy compounds may be present in the CFG, including acetyl peroxy, benzoylperoxy and peroxychloroformyl radicals, and the conjugate acid relative of the PEN.

Tetrafluoro-*p*-xylylene (TFpX), $(C_6H_4)(CHF_2)_2$

This compound was isolated in a noble gas matrix by [272]. Its formation is due to vacuum pyrolysis of octafluoro[2.2]paracyclophane. The compound was also found to rearrange into heptafulvene. Vapor deposition, in turn, turns it into parylene, $[(C_6H_4)(CF_2)_2]_n$, that is stable at elevated temperatures, i.e., 240 °C. Rearrangement of TFpX produces tetrafluoroheptafulvene, $(C_7H_4)F_2(CHF_2)$, while [1,2]-F shift (F atom migration) leads to fluorocarbene, $(C_6H_4)F(:CF)(CHF_2)$. Interestingly, some carbene compounds may be present in the CFG, too, including dihydroxycarbene, (2-chlorophenyl)carbene, phenylchlorocarbene, and a dihalocarbene cation. The parent molecule, *p*-xylylene, is very reactive, easily undergoing polymerization and oligomerization. As a derivative of benzene, such compound is likely to exist in the CFG.

Thioacetaldehyde, CH_3CHS

A member of the thial group, known as ethanethial and acetothialdehyde, it is an unstable molecule. Polymerization of thials, e.g., thioformaldehyde, leads to cyclic organosulfurs [273]. Such a reaction may possibly be responsible for the occurrence of molecules like thiirene in the CFG. The latter authors obtained the compound via pyrolysis of 1,3,5-trimethyl-*s*-trithiane and hexamethyl *s*-trithiane, at 500-600 °C. Interestingly, [274] reports another route: (1) matrix

photolysis of either thiirane, $(\text{CH}_2)_2\text{S}$, or ethanesulfonyl chloride, $\text{CH}_3\text{CH}_2\text{SOCl}$, or (2) flash photolysis of allyl ethyl sulfide, $\text{CH}_3\text{CHSCH}_2\text{CH}=\text{CH}_2$. The pyrolysis experiments of the latter authors were conducted at 800 or 900 °C depending on the routes.

Thiocarbonyl fluoride (TCF), CSF_2

It is a sulfur analogue of carbonyl fluoride. [275] prepared it from silyl trifluoromethyl sulfide, SiH_8SCF_3 , in reaction with NH_3 (a gas common in the CFG) or NaF. What is important, it is said to be stable not only at room temperature, but up to 300 °C, its occurrence in the CFG is thus very likely. However, what may be important from our point of view, [276] generated it from a carbene – difluorocarbene, reacted with S_8 allotrope of sulfur. This allotrope is identical with the mineral known as native sulfur, occurring in abundance in the BPWH vents. TCF is also a product of interaction of bis(trifluoromethyl)mercury with sulfur. This reaction is interesting in relation to possible occurrence of SiH_3HgH in the CFG. Interestingly, TCF interacts with silica to give SiF_4 and COS [275], both products being also known to occur in the CFG. [277] reports another, simple route, that is pyrolysis of 2,2,4,4,-tetrafluoro-1,3-dithietane, $(\text{CF}_2)_2(\mu\text{-S})_2$, generated from thiophosgene, $(\text{CCl}_2)_2((\mu\text{-S})_2)$. Dithietane and thiophosgene are compounds similar or relative to thiirene, thiophene, and phosgene, known or suspected to occur in the CFG.

Titanacyclopropene (TCP), $\text{H}_2\text{Ti}(\text{C}_2\text{H}_2)$

Observation of more than a single band of, potentially, this cyclometalloorganic compound, is important, as it may confirm the existence of organometallics in the CFG and may shed light on the mode of gaseous transfer of metals from the fire zones into the surrounding environment. [141] obtained this molecule, alongside with vinyltitanium monohydride, via interaction of ground-state Ti^0 atoms with ethene, in argon, and selective electronic excitation of the metal. [278] have prepared both TCP and titanacyclopropane, by reacting titanium(IV) isopropoxide, $\text{Ti}(\text{Oi-Pr})_4$, *n*-butyllithium and alkynes, in tetrahydrofuran, at 0 °C. In the case of the unsaturated species, the saturated one was acting as the immediate precursor. [279] obtained a propyl derivative of TCP by reacting diisopropoxy(η^2 -propene)titanium with an alkyne. They do not report exact temperature of this particular process, but is likely a low-temperature one. Possibility of such a process at high temperatures typical for the BPWHs is unknown.

Triflic radical, CF_3OSO_3

Spectroscopic study confirming the existence of this radical was done by [224]. They generated the radical via low-pressure flash thermolysis of a peroxide radical dimer $\text{CF}_3\text{OS}(\text{O})_2\text{OOS}(\text{O})_2\text{OCF}_3$. However, the radical is also known to arise when CF_3O – the trifluoromethoxy radical formed by degradation of the CF_3 group in freons and a major actor

in their atmospheric fate – and SO_2 are combined to form CF_3OSO_2 (trifluoromethoxy sulfonyl radical), which is then slowly oxidized. Their study is of a great importance, because the radical is photolysed to SO_3 – a possible route for SO_2 to SO_3 oxidation in the atmosphere. According to the authors the triflic radical was previously unknown to exist. Its possible occurrence in the CFG is thus important from the environmental protection point of view.

1,2,4-trioxolane

Also known as ethylene ozonide, it may be formed via interaction of ethene and ozone. It is thus yet another compound important from the point of view of atmospheric-environmental studies. The intermediate molecule is CH_2OO^* , known as Criegee intermediate, and formaldehyde. The latter is quite frequent in the CFG. 1,2,4-trioxolane decays into formic anhydride, $(\text{CHO})_2\text{O}$, and hydrogen [223]. [267] reports formation of some trioxolanes via Griesbaum coozolonylation of oxime ether/ketone pairs. According to [268], 1,2,4-trioxolane is prone to self-decompose, to a triplet biradical, via “a spin intersystem crossing process and O-O bond cleavage”. Trioxolanes may be for an important add to the oxygen-bearing heterocycles in the CFG, represented by furan and tetrahydrofuran. Another such compound, detected in a Portuguese BPWH by [269] is 1,4-dioxane.

3. Other Molecules

Below are various molecules with slight less occurrence probability, or the ones with less evident fit to the CFG spectra.

(C₂H₂)In (indium-acetylene complex)

Indium is a very rare element, but may be enriched in various BPWH materials. As shown by [280], its concentration in the local pyrometamorphic rocks may reach 430 ppm, which is a large concentration for this element. As the burning process is known of mobilization of various elements, it is reliable to expect some organoindium compounds in the CFG. Indeed, some exhalative sulfate minerals have shown up to 220 ppm In. This is in accordance to the relatively high affinity of In to coals, with Coal Affinity Index (CAI) of 3.7 ppm as compared to 0.04 ppm mean (Clarke) concentration [281]. To obtain the complex, [31] used indium outgassed at 900 °C – a temperature easily reachable at the burnout stage of the heap burning phenomenon. They suggest the complex to bear μ -In bonding. A similar complex, In-C₂H₂-O, formed by semihydrogenation of acetylene on In₂O₃, is reported by [282] to show a strong chemisorption towards the alkyne. Another related compound, potentially occurring in another heap's fumaroles, is monomethylindium. Other reduced In species in the CFG may include In₂H₂ and In₂H₆.

CH₃MoH (methylmolybdenum hydride) and CH₂MoH₂ (methylidenemolybdenum hydride)

Molybdenum is a typical coal-enriched element, even though its CAI is 1.1 ppm as compared to the Clarke value of 2.2 ppm [281]. Still, gas deposition (desublimation or similar processes) of minerals with species-defining Mo in the BPWH, e.g., in the form of ilsemannite, Mo₃O₈·nH₂O are known [280]. A recent discovery of the new mineral hasanovite, KNa(MoO₂)(SO₄)₂, at the famous Ravat fire site in Tajikistan [283] confirms this phenomenon. Organomolybdenum and other gaseous Mo species are thus expected in the CGF. [50] obtained the two title complexes via activation of methane by laser-ablated Mo atoms. Alongside with methylidynemolybdenum hydride, they are formed via C-H insertion that is achieved thanks to excited Mo atoms. The three complexes are interdependent via α-H transfers. It is important to notice, that Mo hydrides, namely MoH₂, MoH₃ and MoH₄, were tentatively detected in the CFG, alongside with other reduced species like Mo(CO)₂ and Mo(CO)₃.

2,4-didehydrophenol (hydroxybenzyne, cyclohexa-1,3-dien-5-yn-1-ol), C₆H₃(OH)

[26] obtained this *meta*-aryne (*m*-benzyne) via photochemical decarboxylation of a carbene, (C₄H₃(CO)C:)(COOH), in argon matrix, at T = 10 K. The compound obtained is a diradical. It is yet another potential carbenic molecule to exist in the CFG. [284] found a similar way to obtain the title compound(s). They used photodecarboxylation of *p*-benzoquinone diazide carboxylic acids, (CRCOC(COOH)(CH)₂CN₂).

Other organic compounds that were tentatively detected via the RSA method in the CFG include (1) radicals: butadiynyl, cyclopropyl, and methylsulfinyl; (2) halogenated hydrocarbons: bromofluoromethylene, 1,3-difluoroethene, chloroform, fluorinated methylenecyclopropane, fluoromethane, *p*-iodotetrafluorobenzene, propargyl fluoride; (3) oxygen-bearing heterocycles: oxiranylidene; (3) amines: methyl(nitrosomethyl)amine; (4) other organonitrogens: 2*H*-azirine, chloropicrin; (4) organosulfurs: difluorosulfine, fluoro(fluoromethylidyne)-λ⁴-sulfane, methylisothiocyanate; (3) organoborons: H₂C=BH and chloromethylboron; (4) organosilicon compounds: 1,1,-dimethylsilanimine, dimethylsilanol; chloro-, bromo- and/or iodomethylsilane; (5) organophosphorus compounds: 1-phosphaethene, (chloromethylidyne) phosphine, difluoro-λ³-phosphonitrile; (4) bromine isocyanide, fluorine isocyanide; (7) organometallics: lithium-benzene complex, HMgCH₂F Grignard-type compound, vinyl titanium hydride, HNiOCH₃, and CH₃UH.

Inorganic compounds preliminarily observed include: (1) hydrides: Al₂H₂ and Al₂H₄; GaH₂ and GaH₂Cl; YH₂, CeH₂⁺; and (HHg)₂; (2) sulfur and nitrogen compounds: sulfur monoxide, thiazyl fluoride, nitrogen sulfide oxide, N₂O₂S, peroxyntic and nitric acid; (3) nitrosyls: Ge(NO)₂, Au(NO)₂; (3) silicon compounds: metasilicic acid; (4) phosphorus compounds: PO₂Cl; and (5) (F₂N)AuF and Pb(OH)₂.

4. Conclusions

An obvious weakness of the (FT)IR's RSA method is its usual basing on single bands. Although the CALCMET software is supposed to calculate the precise (major) gas contents, one cannot be fully convinced on its infallibility, i.e., some undercalculated intensities may likely result in tiny remnant signals in the residual spectra. This is especially true for the bands in the 3000-3900 cm^{-1} range, that is, one of the major absorption ranges of H_2O . On the other hand, there are quite numerous compound proposals in the RSA based on more than a single band. Many of the listed proposals are based on the literature data related to matrix isolation at low temperatures, laser ablation and similar harsh-condition experiments. However, a question arises if matrix isolation spectroscopy necessary for the formation of the particular compounds or, rather, is simply a method to identify and stabilize the otherwise unstable and transient molecules. Thus, at least some of the literature-reported processes, or some similar routes, are suspected to be able to also take place at higher temperatures typical for the BPWHs.

The results presented show that the BPWHs may stand for a very complex organic-chemical laboratory. Complex nature of the waste rocks and very high dynamics of the combustion and related processes may invoke formation of numerous interesting compounds that are otherwise known from very different geological environments, both terrestrial and extraterrestrial ones.

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6. References

1. Cebulak, S., Smieja-Król, B., Tabor, A., Misz, M., Jelonek, I., Jelonek, Z., 2015. Oksyreaktywna Analiza Termiczna (OTA) – dobra i tania metoda oceny samozapalności węgla na składowiskach – wstępne wyniki badań. Wydawnictwo Geologiczne, Warszawa, 135–138 (in Polish)
2. Wagner, M., 1980. Przemiany termiczne węgla kamiennego w strefach pożarów hałd kopalnianych. Zeszyty Naukowe Akademii Górniczo-Hutniczej Geologia, 6(2), 5–14 (in Polish).
3. Kim, A.G., 2007. Greenhouse gases generated in underground coal-mine fires In: Stracher, G.B. (ed.), Geology of Coal Fires: Case Studies from Around the World. Rev. Eng. Geol., XVIII, 1–13.
4. Srebrodolskiy, B.I., 1989. Tainy Sezonnkh Mineralov. Nauka, Moscow (in Russian)
5. Sokol, E.V., Maksimova, N.V., Nigmatulina, E.N., Sharygin, V.V., Kalugin, V.M., 2005. Combustion Metamorphism. Publishing House of the SB RAS, Novosibirsk, 312 pp. (in Russian, with parts in English)
6. Kruszewski, Ł., 2021. Fossil Fuel Fires: A Forgotten Factor of Air Quality [Online First]; in: Air Quality [Working Title]. IntechOpen, DOI: 10.5772/intechopen.96294, 23 pp.; <https://www.intechopen.com/online-first/fossil-fuel-fires-a-forgotten-factor-of-air-quality>
7. Kruszewski, Ł., Fabiańska, M.J., Ciesielczuk, J., Segit, T., Orłowski, R., Motyliński, R., Moszumańska, I., Kusy, D., 2018. First multi-tool exploration of a gas-condensate-pyrolysate system from the environment of burning coal mine

heaps: An in situ FTIR and laboratory GC and PXRD study based on Upper Silesian materials. *Science of the Total Environment*, 640-641, 1044-1071; DOI: 10.1016/j.scitotenv.2018.05.319

8. Kruszewski, Ł., Fabiańska, M.J., Segit, T., Kusy, D., Motyliński, R., Ciesielczuk, J., Deput, E., 2020. Carbon-nitrogen compounds, alcohols, mercaptans, monoterpenes, acetates, aldehydes, ketones, SF₆, PH₃, and other fire gases in coal-mining waste heaps of Upper Silesian Coal Basin (Poland) – a re-investigation by means of in-situ FTIR external database approach. *Sci. Total Env.*, 698, 134274, doi: 10.1016/j.scitotenv.2019.134274

9. Crouch, D.J., 1999. Synthesis and molecular properties of zwitterionic adducts of TCNQ and other related compounds. D.Ph. thesis, Sheffield Hallam University, 310 pp.

10. Al-Abbasi, O., Modeling the Non-Equilibrium Behavior of Chemically Reactive Atomistic Level Systems Using Steepest-Entropy-Ascent Quantum Thermodynamics. D.Ph. thesis, Faculty of the Virginia Polytechnic Institute and State University, 142 pp.

11. Chuprov, L.A., Sennikov, P.G., Tokhadze, K.G., Ignatov, S.K. Schrems, O., 2006. High-Resolution Fourier-Transform IR Spectroscopic Determination of Impurities in Silican Tetrafluoride and Silane Prepared from It. *Inorg. Mat.*, 42(8), 924–931.

12. Lindstrom, P.J., Mallard, W.G., 2016. NIST Chemistry WebBook, NIST standard reference database number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, and references therein (to be found in [7]); <http://webbook.nist.gov> (retrieved December 16, 2016).

13. Yamada, Y., Mikami, N., Ebata, T., 2008. Relaxation dynamics of NH stretching vibrations of 2-aminopyridine and its dimer in a supersonic beam. *PNAS*, 105(35), 12690–12695.

14. Bora, M., Benoy, S.M., Tamuly, J., Saikia, B.A., 2020. Ultrasonic-assisted chemical synthesis of activated carbon from low-quality subbituminous coal and its preliminary evaluation towards supercapacitor applications. *J. Environ. Chem. Eng.*, 9, 104986 (20 pp.).

15. Minenko, M., Jodl, H.-J., 2006. Fourier transform infrared studies of the N₂-O₂ binary system, *Fiz. Nizk. Temp.*, 32(11), 1382–1401.

16. Hauge, R.H., Kauffman, J.W., Margrave, J.L., 1980. Infrared matrix-isolation studies of the interactions and reactions of Group 3A metal atoms with water. *J. Am. Chem. Soc.*, 102(19), 6005.

17. Wang, X., Andrews, L., 2006a. Infrared Spectra and Density Functional Calculations for M(OH)_{2,3} and HOMO Molecules and M(OH)₂⁺ Cations (M = Y, La). *J. Phys. Chem. A*, 110(12), 4157–4168.

18. Wang, X., Andrews, L., 2006b. Infrared Spectra of M(OH)_{1,2,3} (M = Mn, Fe, Co, Ni) Molecules in Solid Argon and the Character of First Row Transition Metal Hydroxide Bonding. *J. Phys. Chem. A*, 110(33), 10035–10045.

19. Wang, X., Andrews, L., 2005a. Infrared Spectra and Electronic Structure Calculations for the Group 2 Metal M(OH)₂ Dihydroxide Molecules. *J. Phys. Chem. A*, 109(12), 2782–2792.

20. Wang, X., Andrews, L., 2007. Infrared Spectroscopic Observation of the Group 13 Metal Hydroxides, M(OH)_{1,2,3} (M = Al, Ga, In, and Tl) and HAl(OH)₂. *J. Phys. Chem. A*, 111(10), 1860–1868.

21. Withnall, R., Andrews, L., 1985. Matrix reactions of silane and oxygen atoms. Infrared spectroscopic evidence of silanol, silanone, and silanoic and silicic acid molecules. *J. Phys. Chem.*, 89(15), 3261.

22. Wang, X., Andrews, L., 1985b. Infrared Spectra of M(OH)_{1,2,4} (M = Pb, Sn) in Solid Argon. *J. Phys. Chem. A*, 109(40), 9013–9020.

23. Maier, G., Teles, J.H., 1987. Isolierung und Photoisomerisierung von einfach substituierten Nitriloxiden. *Angew. Chem.*, 99(2), 152 (in German).

24. Wang, X., Andrews, K., 2005c. Infrared Spectra and Structures of the Coinage Metal Dihydroxide Molecules. *Inorg. Chem.*, 44(24), 9076–9083.
25. Milligan, D.E., Jacox, M.E., 1976. Spectroscopic Study of the Vacuum-Ultraviolet Photolysis of Matrix-Isolated HCN and Halogen Cyanides. Infrared Spectra of the Species CN and XNC. *J. Chem. Phys.*, 47(1), 278.
26. Bucher, G., Sander, W., Kraka, E., Cremer, D., 1992. 2,4-Didehydrophenol --- erster IR-spektroskopischer Nachweis eines meta-Arins. *Angew. Chem.*, 104(9), 1225 (in German).
27. Andrews, L., Moores, B.W., Fonda, K.K., 1989. Matrix infrared spectra of reaction and photolysis products of stibine and ozone. *Inorg. Chem.*, 28(2), 290.
28. Johnsson, K., Engdahl, A., Nelander, B., 1996. IR and Photodecomposition Spectroscopic Study of HOClO and HClO₂ in Argon Matrices. *J. Phys. Chem.*, 100, 3923–3926.
29. Kumar, S., 2016. Vibrational Study of Aspartic Acids. *AKGEC Int. J. Technol.*, 7(1), 60–64.
30. Forney, D., Jacox, M.E., Thompson, W.E., 1992. The vibrational spectra of molecular ions isolated in solid neon: HCCH⁺ and HCC⁻. *J. Mol. Spectrosc.* 153(1-2), 680.
31. Burkholder, T.R., Andrews, L., 1999. Matrix Infrared Spectra of Aluminum, Gallium, and Indium Complexes with Acetylene. *Inorg. Chem.*, 32, 2491–2496.
32. Shimanouchi, T. 1972. Tables of Molecular Vibrational Frequencies Consolidated Volume II. *J. Phys. Chem. Ref. Data*, 6(3), 993–1102.
33. Dong, F., Davis, S., Nesbitt, D.J., 2006. Slit Discharge IR Spectroscopy of a Jet-Cooled Cyclopropyl Radical: Structure and Intramolecular Tunnelling Dynamics. *J. Phys. Chem. A*, 110(9), 3059.
34. Nallasamy, P., Mohan, S., 2005. Vibrational spectroscopic characterization of poly(vinylidene fluoride). *Ind. J. Pure Appl. Phys.*, 43, 821–827.
35. Prochaska, F.T., Andrews, L., 1980. Infrared and visible absorption spectra and photochemistry of the CH₂FX⁺, CHF₂X⁺, F--H•••(CHX)⁻, and X--H•••(CHF)⁻ molecular ions in solid argon. *J. Chem. Phys.*, 73(6), 2651.
36. Wenk, H.H., Balster, A., Sander, W., Hrovat, D.A., Borden, W.T., 2001. Matrix Isolation of Perfluorinated p-Benzyne. *Angew. Chem. Int. Ed.*, 40(12), 2295–2298.
37. Bordiga, S., Lamberti, C., Bonino, F., Travert, A., Thibault-Starzyk, F., 2015. Probing zeolites by vibrational spectroscopies. *Chem. Soc. Rev.*, 44, 7262–7341.
38. Freivogel, P., Grutter, M., Forney, D., Maier, J.P., 1997. Infrared bands of mass-selected carbon chains C_n (n = 8 – 12) and C_n⁻ (n = 5–10, 12) in neon matrices. *Chem. Phys.*, 216, 401–406.
39. Smith-Gicklhorn, A.M., Frankowski, M., Bondybey, V.E., 2002. Tetracyanoethylene, its ions and ionic fragments. *Phys. Chem. Chem. Phys.*, 4(5), 1425.
40. Lanzisera, D.V., Andrews, L., 1997. Reactions of Laser-Ablated Mg, Ca, Sr, and Ba Atoms with Hydrogen Cyanide in Excess Argon. Matrix Infrared Spectra and Density Functional Calculations on Novel Isocyanide Products. *J. Phys. Chem. A*, 101(50), 9666.
41. Hassanzadeh, P., Hannachi, Y., Andrews, L., 1993. Pulsed Laser Evaporated Boron Atom Reactions with Methane. 2. Infrared Spectra of H₂CBH₂, H₂CBH, HCBH, and HBCBH in Solid Argon. *J. Phys. Chem.*, 97, 6418–6424.
42. Jacox, M.E., Thompson, W.E., 2007. Infrared spectra of ClCN⁺, ClNC⁺, and BrCN⁺ trapped in solid neon. *J. Chem. Phys.*, 126(24), 244311.
43. Snelson, A., 1972. *High Temp. Sci.*, 4, 141

44. Davidson, G., 2005. Spectroscopic Properties of Inorganic and Organometallic Compounds. Vol. 37, 1st ed., Royal Society of Chemistry, 202 pp.
45. Liang, B., Andrews, L., 2000. Reactions of Laser-Ablated Ag and Au Atoms with Carbon Monoxide Matrix Infrared Spectra and Density Functional Calculations on $\text{Ag}(\text{CO})_n$ ($n = 2, 3$), $\text{Au}(\text{CO})_n$, ($n = 1, 2$) and $\text{M}(\text{CO})_{n+}$ ($n = 1-4$; $\text{M} = \text{Ag, Au}$). *J. Phys. Chem. A*, 104(40), 9156–9164.
46. Fraenkel, R., Haas, Y., 1993. Photolysis of ICN in a cryogenic matrix. *Chem. Phys. Lett.*, 214(2), 234–240.
47. Dismuke, K.I., Graham, W.R.M., Weltner, W.Jr., 1975. Optical and ESR spectra of the C_4H radical in rare gas matrices at 4K. *J. Mol. Spectrosc.*, 57(1), 127.
48. Ismail, Z.K., Fredin, L., Hauge, R.H., Margrave, J.L., 1998. Matrix isolation studies of the reactions of silicon atoms. II. Infrared spectrum and structure of matrix-isolated fluorosilylene: HWiF . *J. Chem. Phys.*, 77(4), 1626.
49. Isabel, R.J., Guillory, W.A., 1972. Ultraviolet Photolysis of GeH_3Br ; Infrared Spectra of Matrix-Isolated GeH_2Br and GeHBr . *J. Chem. Phys.*, 57(3), 1116.
50. Cho, H.-G., Andrews, L., 2005. Infrared Spectra of $\text{CH}_3\text{-MoH}$, $\text{CH}_2\text{=MoH}_2$, and CH:MoH_3 Formed by Activation of CH_4 by Molybdenum Atoms. *J. Am. Chem. Soc.*, 127(22), 8226–8231.
51. Zhou, M., Andrews, L., 1999. Reactions of laser-ablated iron atoms and cations with carbon monoxide: Infrared spectra of FeCO^+ , $\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_x$, and $\text{Fe}(\text{CO})_x^-$ ($x=1-4$) in solid neon. *J. Chem. Phys.*, 110(21), 10370.
52. Ogilvie, J.F., 1968. Vibrational absorption of the trapped diazomethyl radical. *Can. J. Chem.*, 46(14), 2472.
53. Hisatsune, I.C., Heicklen, J., 1973. *Can. J. Spectrosc.*, 18, 77.
54. Wang, X., Andrews, L., 2005d. Mercury dihydride forms a covalent molecular solid. *Phys. Chem. Chem. Phys.*, 7(5), 750.
55. Jacox, M.E., Milligan, D.E., 1974. Matrix isolation study of the vacuum ultraviolet photolysis of allene and methylacetylene. Vibrational and electronic spectra of the species C_3 , C_3H , C_3H_2 , and C_3H_3 . *Chem. Phys.*, 4(1), 45.
56. Wang, X., Andrews, L., 2004a. Infrared Spectra of Zn and Cd Hydride Molecules and Solids. *J. Phys. Chem. A*, 108(50), 11006.
57. Tevault, D.E., Smardzewski, R.R., 1977. Matrix reactions of chlorine atoms with NO_2 molecules. *J. Chem. Phys.*, 67(8), 3777.
58. Andrews, L., Zhou, M., Gutsev, G.L., 2003a. Reactions of Laser-Ablated Mo and W Atoms, Cations, and Electrons with CO in Excess Neon: Infrared Spectra and Density Functional Calculations on Neutral and Charged Unsaturated Metal Carbonyls. *J. Phys. Chem. A*, 107(7), 990.
59. Wang, X., Andrews, L., Manceron, L., Marsden, C., 2003b. Infrared Spectra and DFT Calculations for the Coinage Metal Hydrides MH , $(\text{H}_2)\text{MH}$, MH_2 , M_2H , M_2H^- , and $(\text{H}_2)\text{CuHCu}$ in Solid Argon, Neon, and Hydrogen. *J. Phys. Chem. A*, 107(41), 8492–8505.
60. Kauffman, J.W., Hauge, R.H., Margrave, J.L., 1984a. Reactions of Iron Atoms and Iron Dimers with Methane, Ammonia, and Hydrogen Fluoride in Low Temperature Matrices. *High Temp. Sci.*, 17, 237.
61. Szczepanski, J., Hodyss, R., Fuller, J., Vala, M., 1999. Infrared Absorption Spectroscopy of Small Carbon-Sulfur Clusters Isolated in Solid Ar. *J. Phys. Chem. A*, 103(16), 2975–2981.
62. Niki, H., Maker, P.D., Savage, C.M., Breitenbach, L.P., 1977. Fourier transform IR spectroscopic observation of pernitric acid formed via $\text{HOO} + \text{NO}_2 \rightarrow \text{HOONO}_2$. *Chem. Phys. Lett.*, 45(3), 564–566.
63. Niki, H., Maker, P.D., Savage, C.M., Breitenbach, L.P., 1978. FTIR spectroscopic observation of peroxyalkyl nitrates

formed via $\text{ROO} + \text{NO}_2 \rightarrow \text{ROONO}_2$. *Chem. Phys. Lett.*, 55(2), 289.

64. Fateley, W.G., Bent, H.A., Crawford, B.Jr., 1959. Infrared Spectra of the Frozen Oxides of Nitrogen. *J. Chem. Phys.*, 31(1), 204.

65. Zhou, M., Chertihin, G.V., Andrews, L., 1998. Reactions of laser-ablated iron atoms with carbon monoxide: Infrared spectra and density functional calculations of Fe_xCO , $\text{Fe}(\text{CO})_x$, and $\text{Fe}(\text{CO})_x^-$ ($x=1,2,3$) in solid argon. *J. Chem. Phys.*, 109(24), 10893.

66. Li, J., Bursten, B.E., Zhou, M., Andrews, L., 2001. A Combined Theoretical and Experimental Study of the Reaction Products of Laser-Ablated Thorium Atoms with CO: First Identification of the CThO , CThO^- , OThCCO , $\text{OTh}(\eta^3\text{-CCO})$, and $\text{Th}(\text{CO})_n$ ($n = 1-6$) Molecules. *Inorg. Chem.*, 40, 5448-5460.

67. Zhou, M., Jin, X., Li, J., 2006. Reactions of Cerium Atoms and Dicerium Molecules with CO: Formation of Cerium Carbonyls and Photoconversion to CO-Activated Insertion Molecules. *J. Phys. Chem. A*, 110(34), 10206.

68. McGraw, G.E., Bernitt, D.L., Hisatsune, I.C., 1965. Vibrational Spectra of Isotopic Nitric Acids. *J. Chem. Phys.* 42(1), 237.

69. Kauffman, J.W., Hauge, R.H., Margrave, J.L., 1985. Studies of reactions of atomic and diatomic chromium, manganese, iron, cobalt, nickel, copper, and zinc with molecular water at 15 K. *J. Phys. Chem.*, 89(16), 3541.

70. Andrews, L., Wang, X., 2002a. Infrared Spectra and Density Functional Calculations for Early First-Row Transition Metal Nitrosyls in Solid Neon. *J. Phys. Chem. A*, 106(7), 1196.

71. Janowski, B., Knauth, N.-D., Martin, J., 1977. Chlornitrit, ein metastabiles Zwischenprodukt der Reaktion von Dichlormonoxid mit Nitrosylchlorid. *Ber. Bunsenges. Phys. Chem.*, 81(12), 1262 (in German).

72. Zhou, M., Andrews, L., 1999. Reactions of Laser-Ablated Vanadium Atoms with Nitric Oxide. Infrared Spectra and Density Functional Calculations on NVO , $\text{V}-\eta^1\text{-NO}$, $\text{V}-(\eta^1\text{-NO})_2$, $\text{V}-(\eta^1\text{-NO})_3$, and $\text{V}-\eta^2\text{-NO}$. *J. Phys. Chem. A*, 103(4), 478-484.

73. Smardzewski, R.R., Fox, W.B., 1974. Infrared spectroscopic evidence for matrix isolated 'nitrosyl hypofluorite', an isomer of nitryl fluoride. *J. Chem. Phys.*, 60(8), 2980.

74. Andrews, L., Wang, X., 2004a. Infrared Spectra of Dialanes in Solid Hydrogen. *J. Phys. Chem. A*, 108(19), 4202.

75. Andrews, L., Wang, X., 2002b. Infrared Spectra and Density Functional Calculations for Early First-Row Transition Metal Nitrosyls in Solid Neon. *J. Phys. Chem. A*, 106(7), 1196.

76. Zhang, L., Dong, J., Zhou, M., 2000. Matrix infrared spectra and quantum chemical calculations of the MCO^- ($\text{M}=\text{Si}, \text{Ge}, \text{Sn}$) anions. *J. Chem. Phys.*, 113(19), 8700.

77. Varretti, E.L., Pimentel, G.C., 1971. Isomeric Forms of Dinitrogen Trioxide in a Nitrogen Matrix. *J. Chem. Phys.*, 55(8), 3813.

78. Zhou, M., Andrews, L., Li, J., Bursten, B.E., 1999. Reaction of Laser-Ablated Uranium Atoms with CO: Infrared Spectra of the CUO , CUO^- , OUCCO , $(\eta^2\text{-C}_2)\text{UO}_2$, and $\text{U}(\text{CO})_x$ ($x = 1-6$) Molecules in Solid Neon. *J. Am. Chem. Soc.*, 121(41), 9712-9721.

79. Maier, G., Schrot, J., Reisenauer, H.P., Frenking, G., Jonas, V., 1992. Cyclische C_6S_6 -Isomere --- Matrixspektroskopische und theoretische Untersuchungen. *Chem. Ber.*, 125(1), 126.

80. Citra, A., Wang, X., Andrews, L., 2002. Reactions of Laser-Ablated Gold with Nitric Oxide: Infrared Spectra and DFT Calculations of AuNO and $\text{Au}(\text{NO})_2$ in Solid Argon and Neon. *J. Phys. Chem. A*, 106(14), 3287-3293.

81. Chertihin, G.V., Andrews, L., 1993. Reactions of pulsed-laser ablated aluminum atoms with hydrogen: infrared

- spectra of aluminum hydride (AlH, AlH₂, AlH₃, and Al₂H₂) species. *J. Phys. Chem.* 97(40), 10295.
82. Xiao, Z.L., Hauge, R.H., Margrave, J.L., 1992. Reactions and photochemistry of chromium and molybdenum with molecular hydrogen at 12 K. *J. Phys. Chem.*, 96(2), 636.
83. Kauffman, J.W., Hauge, R.H., Margrave, J.L., 1982. ACS Symposium Ser. 179, American Chemical Society, Washington D.C.
84. Lanzisera, D.V., Andrews, L., 2000. Reactions of Laser-Ablated Boron Atoms with Methyl Halides in Excess Argon. Infrared Spectra and Density Functional Calculations on CH₃BX, CH₂BX, and CHBX (X = F, Cl, Br). *J. Phys. Chem. A*, 104(41), 9295–9301.
85. Shayesteh, A., Appadoo, D.R.T., Gordon, I., Bernath, P.F., 2003. The vibration—rotation emission spectrum of MgH₂. *J. Chem. Phys.*, 119(15), 7785.
86. Andrews, L., Keelan, B.W., 1979. Infrared spectra, structure, and bonding in the dihalocarbene cations in solid argon. *J. Am. Chem. Soc.*, 101(13), 3500.
87. Harrison, J.A., Frei, H., 1994. Visible Light-Induced Oxygen Transfer from Nitrogen Dioxide to Ethyne and Propyne in a Cryogenic Matrix. 1. Identification of Products. *J. Phys. Chem.*, 98(47), 12142–12151.
88. Chertihin, G.V., Andrews, L., 1994. Reactions of Laser Ablated Ti Atoms with Hydrogen during Condensation in Excess Argon. Infrared Spectra of the TiH, TiH₂, TiH₃, and TiH₄ Molecules. *J. Am. Chem. Soc.*, 116(18), 8322.
89. Jacox, M.E., Milligan, D.E., 1973. Matrix-isolation study of the reaction of H atoms with NO. *J. Mol. Spectrosc.*, 48(3), 536.
90. Van Zee, R.J., Li, S., Weltner, W.Jr., 1995. V, Nb, and Ta hydride molecules in deuterium and rare-gas matrices: Infrared and electron spin resonance spectra. *J. Chem. Phys.*, 102(11), 4367.
91. Zhou, M., Dong, J., Zhang, L.N., Qin, Q.Z., 2001. Reactions of Group V Metal Atoms with Water Molecules. Matrix Isolation FTIR and Quantum Chemical Studies. *J. Am. Chem. Soc.*, 123(1), 135–141.
92. Andrews, L., Hassanzadeh, P., Lanzisera, D.V., Brabson, G.D., 1996a. Reactions of selenium in a quartz Discharge Tube. Infrared Spectra and Density Functional Theory Calculations of New Selenium-Nitrogen and Selenium-Silicon Species in Solid Argon. *J. Phys. Chem.*, 100(41), 16667.
93. Muller, R.P., Murata, S., Nonella, M., Huber, J.R., 1984a. HNO, an Intermediate in (Light-induced) Rearrangement Reactions of Nitrosooxy Compounds and Nitrosamines. *Helv. Chim. Acta*, 67(4), 953.
94. Muller, R.P., Nonella, M., Russegger, P., Huber, J.R., 1984b. UV-, VIS- nad IR-light-induced isomerization of HSNO in a low-temperature matrix. *Chem. Phys.*, 87(3), 351.
95. Xu, Q., Jiang, L., 2006. Infrared Spectra of the M(NO)_n (M = Sn, Pb; n = 1, 2) and PbNO- Molecules. *Inorg. Chem.*, 45(21), 8648 – 8654.
96. Shen, L.N., Graham, W.R.M., 1989. Observation of an infrared frequency of the C₄ molecule. *J. Chem. Phys.*, 91(8), 5115.
97. Wang, X., Andrews, L., 2003a. Chromium Hydrides and Dihydrogen Complexes in Solid Neon, Argon, and Hydrogen: Matrix Infrared Spectra and Quantum Chemical Calculations. *J. Phys. Chem. A*, 107(4), 570.
98. Bare, W.D., Andrews, L., 1998. Formation of Grignard Species from the Reaction of Methyl Halides with Laser-Ablated Magnesium Atoms. A Matrix Infrared Study of CH₃MgF, CH₃MgCl, CH₃MgBr, and CH₃MgI. *J. Am. Chem. Soc.*, 120(29), 7293–7301.
99. Himmel, H.-J., Downs, A.J., Greene, T.M., Andrews, L., 2000. Matrix Photochemistry of Gallium and Indium Atoms (M) in the Presence of Methane: Formation and Characterization of the Divalent Species CH₃MH and Univalent

Species CH₃M. *Organometallics*, 19(6), 1060–1070.

100. Lugez, C.L., Jacox, M.E., Johnson, R.D.III, 1999. Vibrational spectra of molecular ions isolated in solid neon. XV. Infrared spectroscopic evidence for NeHF⁺ and HFFH⁺. *J. Chem. Phys.*, 110(11), 5037.

101. Kauffman, J.W., Hauge, R.H., Margrave, J.L., 1985. Reactions of atomic scandium, titanium, and vanadium with molecular water at 15 K. *J. Phys. Chem.*, 89(16), 3547.

102. Zhou, M., Zhang, L., Dong, J., Qin, Q., 2000. Reactions of Group IV Metal Atoms with Water Molecules. Matrix Isolation FTIR and Theoretical Studies. *J. Am. Chem. Soc.*, 122(3), 10680.

103. Tchir, P.O., Spratley, R.D., 1975. The Photolysis of Matrix Isolated cis-Thionylimide. 1. The Identification and Infrared Spectra of cis-HOSN, HSNO, and SNO. *Can. J. Chem.*, 53(15), 2318–2330.

104. Jacox, M.E., Thompson, W.E., 1989. The Production and Spectroscopy of Molecular Ions Isolated in Solid Neon. *Res. Chem. Intermed.*, 12(1), 33.

105. Dunikin, I.R., Lynch, M.A., Boulton, A.J., Henderson, N., 1991. 1,2-Dinitrosobenzene in argon matrices at 14 K. *J. Chem. Soc., Chem. Comm.*, 17, 1178.

106. Himmel, H.-J., Manceron, L., Downs, A.J., Pullumbi, P., 2002. Characterization and Photochemistry of the Gallium and Indium Subhydrides Ga₂H₂ and In₂H₂. *Angew. Chem. Int. Ed.*, 41(5), 796.

107. Macrae, V.A., Greene, T.M., Downs, A.J., 2004a. Matrix studies of the thermal and photolytic reactions of Zn, Cd and Hg (M) atoms with H₂O: formation and characterisation of the adduct M···OH₂ and photoproduct HMOH. *Phys. Chem. Chem. Phys.*, 6(19), 4586.

108. Chertihin, G.V., Andrews, L., 1995. Reactions of laser-ablated Zr and Hf atoms with hydrogen. Matrix infrared spectra of the MH, MH₂, MH₃, and MH₄ molecules. *J. Phys. Chem.*, 99(41), 15004.

109. Andrews, L., Wang, X., 2003. Infrared Spectra and Structures of the Stable CuH₂⁻, AgH₂⁻, AuH₂⁻, and AuH₄⁻ Anions and the AuH₂ Molecule. *J. Am. Chem. Soc.*, 125(38), 11751–11760.

110. Jacox, M.E., 1982a. The reaction of F atoms with acetaldehyde and ethylene oxide. Vibrational spectra of the CH₃CO and CH₂CHO free radicals trapped in solid argon. *Chem. Phys.*, 69(3), 407.

111. Zeng, X., Beckers, H., Willner, H., Neuhaus, P., Grote, D., Sander, W., 2009. Difluorophosphoryl Nitrene F₂P(O)N: Matrix Isolation and Unexpected Rearrangement to F₂PNO. *Chem. Eur. J.*, 15, 13466.

112. Kronberg, M., von Ahsen, S., Willner, H., Francisco, J.S., 2004. The SF₅O_x Radicals, x=0-3. *Angew. Chem. Int. Ed.*, 44(2), 253.

113. Andrews, L., McInnis, T.C., 1991. Cocondensation reaction of arsine and fluorine matrix infrared spectrum of fluoroarsine. *Inorg. Chem.*, 30(15), 2990.

114. Maier, G., Reisenauer, H.P., Eckwert, J., Naumann, N., De Marco, M., 1997. *Angew. Chem.*, 109, 1795.

115. Wenk, H.H., Sander, W., 2001. Matrix Isolation and Spectroscopic Characterization of Perfluorinated ortho- and meta-Benzynes. *Chem. Eur. J.*, 7(9), 1837.

116. Arkell, A., 1965. Matrix Infrared Studies of Compounds. II. The O₂F radical. *J. Am. Chem. Soc.*, 87(18), 4057–4062.

117. Zhou, M., Jiang, L., Xu, Q., 2004. Reactions of Silicon Atoms with NO. Experimental and Theoretical Characterization of Molecules Containing Si, N and O. *J. Phys. Chem. A*, 108(44), 9521.

118. Xiao, Z.L., Hauge, R.H., Margrave, J.L., 1991. Reactions of vanadium and titanium with molecular hydrogen in krypton and argon matrices at 12 K. *J. Phys. Chem.*, 95(7), 2696.

119. Wang, X., Andrews, L., Kushto, G.P., 2002b. Infrared Spectra of the Novel Ge₂H₂ and Ge₂H₄ Species and the Reactive GeH_{1,2,3} Intermediates in Solid Neon, Deuterium and Argon. *J. Phys. Chem. A*, 2002, 106(24), 5809–5816.
120. Chou, J.-B., Bahou, M., Lee, Y.P.-, Rayner, D., Simard, B., 2005. Isomers of GeNO and Ge(NO)₂: Production and infrared absorption of GeNO and ONGeNO in solid Ar. *J. Chem. Phys.*, 123(5), 054321.
121. Andrews, L., Lanzisera, D.V., Hassanzadeh, P., Hannachi, Y., 1998. Reactions of Laser-Ablated Boron Atoms with Ethylene and Ethane. Infrared Spectra and DFT Calculations for Several Novel BC₂H_x (x = 1, 2, 3, 4, 5) Molecules. *J. Phys. Chem. A.*, 102(19), 3259–3267.
122. McNaughton, D., Bruget, D.N., 1993. The Infrared Spectrum of Chlorophosphaethyne, ClC≡P. *J. Mol. Spectrosc.*, 161(2), 336.
123. Lugez, C.L., Irikura, K.K., Jacox, M.E., 1998a. Experimental and ab initio study of the infrared spectra of ionic species derived from PF₅, PF₃, and F₃PO and trapped in solid neon. *J. Chem. Phys.*, 108(20), 8381.
124. Maier, G., Reisenauer, H.P., Egenolf, H., Glatthaar, J., 1998. Reaction of Silicon Atoms with Hydrogen Cyanide: Generation and Matrix-Spectroscopic Identification of CHNSi and CNSi Isomers. *Eur. J. Org. Chem.*, 1307.
125. Wang, X., Andrews, L., 2004b. Infrared Spectra of Magnesium Hydride Molecules, Complexes, and Solid Magnesium Dihydride. *J. Phys. Chem. A.*, 108(52), 11511.
126. Wang, X., Chertihin, G.V., Andrews, L., 2002c. Matrix Infrared Spectra and DFT Calculations of the Reactive MH_x (x = 1, 2, and 3), (H₂)MH₂, MH₂⁺, and MH₄⁻ (M = Sc, Y, and La) Species. *J. Phys. Chem. A*, 106(40), 9213–9225.
127. Koppe, R., Tacke, M., Schnöckel, H., 1991. Infrarotspektroskopischer Nachweis von monomerem HGaCl₂ in festem Argon. *Z. Anorg. Allg. Chem.*, 605(1), 35 (in German).
128. Pulham, C., Downs, A.J., Goode, M.J., 1995. The vibrational spectra of natural and perdeuterated monochlorogallane, H₂Ga(μ-Cl)₂GaH₂, and an empirical harmonic potential function. *Spectrochim. Acta A Mol. Spect.*, 51(5), 767–777.
129. Jacox, M.E., 1982b. Reaction of fluorine atoms with benzene. Vibrational spectrum of the 1-fluorocyclohexadienyl radical intermediate trapped in solid argon. *J. Phys. Chem.*, 86(5), 670.
130. Ahlrichs, R., Ehrhard, C., Lakenbrink, M., Schunck, S., Schnöckel, H., 1986. Molecular PO₂Cl: matrix IR investigations and ab initio SCF calculations. *J. Am. Chem. Soc.*, 108(13), 3596.
131. Prochaska, F.T., Andrews, L., 1978. Matrix photoionization studies of trifluoromethyl halide systems. Infrared spectra of the CF₃⁺, CF₂X⁺, and CF₃X⁺ cations in solid argon. *J. Am. Chem. Soc.*, 100(7), 2102.
132. Köppe, R., Schnöckel, H., 1992. Molecular GaH₂Cl: matrix infrared spectrum and ab initio investigations. *J. Chem. Soc. Dalton Trans.*, 23, 3393.
133. Huang, Z., Chen, M., Zhou, M., 2004. Matrix Isolation Infrared Spectroscopic and Theoretical Study of the Reactions Beryllium Atoms with Methanol. *J. Phys. Chem. A*, 108(16), 3390.
134. Andrews, L., Moores, B.W., Fonda, K.K., 1989. Matrix infrared spectra of reaction and photolysis products of stibine and ozone. *Inorg. Chem.*, 28(2), 290.
135. August, J.A., Aziz, S., Kroto, H.W., Suffolk, R.J., 1988, unpublished data.
136. Jacox, M.E., 1978. Matrix isolation study of the interaction of excited argon atoms with CF₂Cl₂, CF₂ClBr, and CF₂Br₂. Infrared spectra of the CF₂Cl⁺ and CF₂Br⁺ molecular ions. *Chem. Phys. Lett.*, 54(1), 176.
137. Wierzejewska, M., Olbert-Majkut, A., 2003. Photolysis of Matrix Isolated HONO/SO₂ System. Identification and Infrared Spectra of Nitrososulfonic Acid HO(NO)SO₂ and Hydroxysulfonyl HOSO₂ Radical. *J. Phys. Chem. A*, 107(50), 10944–10952.

138. Liang, B., Andrews, L., Li, J., Bursten, B.E., 2002. Experimental and Theoretical Studies of the Products of Laser-Ablated Thorium Atom Reactions with H₂O in Excess Argon. *J. Am. Chem. Soc.*, 124(23), 6723–6733.
139. Liang, B., Hunt, R.D., Kushto, G.P., Andrews, L., Li, J., Bursten, B.E., 2005. Reactions of Laser-Ablated Uranium Atoms with H₂O In Excess Argon: A Matrix Infrared and Relativistic DFT Investigation of Uranium Oxyhydrides. *Inorg. Chem.*, 44(7), 2159–2168.
140. Macrae, V.A., Green, J.C., Greene, T.M., Downs, A.J., 2004. Thermal and Photolytic Reactions of Group 12 Metal Atoms in HCl-Doped Argon Matrixes: Formation and Characterization of the Hydride Species HMCl (M = Zn, Cd, o*r Hg). *J. Phys. Chem. A.*, 108(44), 9500.
141. Lee, Y.K., Manceron, K., Papai, I., 1997. An IR Matrix Isolation and DFT Theoretical Study of the First Steps of the Ti(0) Ethylene Reaction: Vinyl Titanium Hydride and Titanacyclopentene. *J. Phys. Chem. A.*, 101(50), 9650.
142. Wang, X., Andrews, L., 2011. Quantum-Chemical Calculations and IR Spectra of the (F₂)MF₂ Molecules (M = B, Al, Ga, In, Tl) in Solid Matrices: A New Class of Very High Electron Affinity Neutral Molecules. *J. Am. Chem. Soc.*, 133(11), 3768–3771.
143. Pullumbi, P., Bouteiller, Y., Manceron, L., Mijoule, C., 1994. Aluminium, gallium and indium trihydrides. An IR matrix isolation and ab initui study. *Chem. Phys.*, 185(1), 25.
144. Zeng, A., Kong, Q., Wang, Y., Zhou, M., 2003. Matrix isolation infrared spectroscopic and density functional theoretical studies of the reactions of silver and gold atoms with carbon disulfide. *Chem. Phys.*, 292(1), 111.
145. Andrews, L., Zhou, M., Bare, W.D., 1998. Matrix Infrared Spectra and Density Functional Calculations of Three Al, N, O Isomers. *J. Phys. Chem. A.*, 102(26), 5019.
146. Zhou, M., Andrews, L., 2000. Infrared spectra of the CS₂⁻, CS₂⁺, and C₂S₄⁺ molecular ions in solid neon and argon. *J. Chem. Phys.*, 112(15), 6576.
147. Allaf, A., Suffolk, R.J., 1994. Gas-phase Infrared Spectrum of Thiazyl Cyanide, NSCN. *J. Chem. Res., Synop.* 186.
148. Zeng, X., Beckers, H., Willner, H., Francisco, J.S., 2012. Experimental Observation of the 16-Electron Molecules SPN, SNP, and Cyclic PSN. *Angew. Chem. Int. Ed.*, 51(14), 3334.
149. Zeng, X., Beckers, H., Willner, H., 2009a. Difluoro-λ⁵-Phosphinonitrile F₂P≡N: Matrix Isolation and Photoisomerization into FP=NF. *Angew. Chem. Int. Ed.*, 48(26), 4828.
150. Sander, W., Henn, R., Sundermeyer, W., 1986. Charakterisierung und Photochemie von (Dihalogenmethylen) sulfoxiden, XYC=S=O. *Spectrochim. Acta*, 42A(11), 1281–1287.
151. Ohno, K., Kurita, E., Kawamura, M., Matsuura, H., 1987. Gas-phase infrared spectra of the unstable phosphalkenes CF₂:PH, CF₂:PCF₃, an CH₂:PC: the stretching vibration and force constant. *J. Am. Chem. Soc.*, 109(19), 5614.
152. Maier, G., Reisenauer, H.P., Cibulka, M., 1999. Oxiranylidene. *Angew. Chem.*, 111(1-2), 110.
153. Wang, X., Andrews, L., Chertihin, G.V., Souter, P.F., 2002d. Infrared Spectra of the Novel Sn₂H₂ Species and the Reactive SnH_{1,2,3} and PbH_{1,2,3} Intermediates in Solid Neon, Deuterium, and Argon. *J. Phys. Chem. A*, 106(26), 6302–6308.
154. Shayesteh, A., Appadoo, D.R.T., Gordon, I.E., Bernath, P.F., 2004. Vibration-Rotation Emission Spectra of Gaseous ZnH₂ and ZnD₂. *J. Am. Chem. Soc.*, 126(44), 14356–14357.
155. Andrews, L., Prochaska, F.T., 1979. Infrared spectra of the CH₂F⁺, CHF₂⁺, CHF⁺, and FH⁻ (CHF⁻) molecular ions in solid argon. *J. Chem. Phys.*, 70(10), 4714.
156. Lyon, J.T., Andrews, L., Malmqvist, P.-Å., Roos, B.O., Yang, T., Bursten, B.E., 2007. Infrared Spectrum and Bonding un Uranium Methylidene Dihydride, CH₂=UH₂. *Inorg. Chem.*, 46(12), 4917–4925.

157. Zhang, L., Shao, L., Zhou, M., 2001. Reactions of laser-ablated Y and La atoms with H₂O. Infrared spectra and density functional calculations of the HMO, HMOH and M(OH)₂ molecules in solid argon. *Chem. Phys.*, 272(1), 27.
158. Carpenter, J.D., Ault, B.S., 1992. Matrix isolation study of the reaction of diborane with methanol: spectroscopic characterization of methoxyborane, H₂B=OCH₃. *J. Phys. Chem.*, 96(11), 4288.
159. Souter, P.F., Kushto, G.P., Andrews, L., Neurock, M., 1997. Experimental and Theoretical Evidence for the Formation of Several Uranium Hydride Molecules. *J. Am. Chem. Soc.*, 119(7), 1682.
160. Park, M., Hauge, R.H., Margrave, J.L., 1988. Reactions and Photochemistry of Atomic and Diatomic Nickel with Water at 15K. *High Temp. Sci.*, 25, 1–15.
161. Burger, H., Schneider, W., Sommer, S., Thiel, W., Willner, H., 1991. The vibrational spectrum and rotational constants of difluoroethyne FC_{3/4}CF. Matrix and high resolution infrared studies and ab initio calculations. *J. Chem. Phys.*, 95(8), 5660.
162. Thompson, W.E., Jacox, M.E., 1989. The vibrational spectra of molecular ions isolated in solid neon. II. O⁺4 and O⁻4. *J. Chem. Phys.*, 91(7), 3826.
163. Andrews, L., Withnall, R., 1988. Matrix reactions of oxygen atoms with P₄. Infrared spectra of P₄O, P₂O, PO and PO₂. *J. Am. Chem. Soc.*, 110(17), 5605.
164. Wang, X., Souter, P.F., Andrews, L., 2003. Infrared Spectra of Antimony and Bismuth Hydrides in Solid Matrixes. *J. Phys. Chem. A*, 107(21), 4244.
165. Maier, G., Rohr, C., 1996. Ethynediol: Photochemical Generation and Matrix-spectroscopic Identification. *Liebigs Ann.*, 307.
166. Xiao, Z.L., Hauge, R.H., Margrave, J.L., 1993. Cryogenic reactions of gallium with molecular hydrogen and methane. *Inorg. Chem.*, 32(5), 642.
167. Moores, B.W., Andrews, L., 1989. Oxidation of phosphorus(III) halides by red photolysis of ozone complexes in solid argon. *J. Phys. Chem.*, 93(5), 1902.
168. Isabel, R.J., Guillory, W.A., 1971. Vacuum-Ultraviolet Photolysis of GeH₃Cl; the Infrared Spectrum of Matrix-Isolated GeH₂Cl. *J. Chem. Phys.*, 55(3), 1197.
169. Wang, X., Andrews, L., 2004c. Infrared Spectra of Indium Hydrides in Solid Hydrogen and Neon. *J. Phys. Chem. A*, 108(20), 4440.
170. Himmel, H.-J., Downs, A.J., Greene, T.M., 2000. Thermal and Photochemical Reactions of Aluminum, Gallium, and Indium Atoms (M) in the Presence of Ammonia: Generation and Characterization of the Species M·NH₃, HMNH₂, MNH₂, and H₂MNH₂. *J. Am. Chem. Soc.*, 122(40), 9793–9807.
171. Lefcourt, M.A., Ozin, G.A., 1991. Aluminum(2P)-silane complex and photoreversible oxidative addition/reductive elimination reaction Al(2P){SiH₄} ↔ SiH₃AlH. 2. Al(2P){SiH₄} ↔ SiH₃AlH Reaction. *J. Phys. Chem.*, 95(7), 2623–2628.
172. Prochaska, F.T., Keelan, B.W., Andrews, L., 1979. Infrared spectra of the CHFCl, CHFBr, and CHFI free radicals in solid argon. *J. Mol. Spectrosc.*, 76(1-3), 142.
173. Schreiner, P.R., Reisenauer, H.P., 2008. Spectroscopic Identification of Dihydroxycarbene. *Angew. Chem. Int. Ed.*, 47(47), 7071.
174. Mal'tsev, A.K., Zuev, P.S., Nefedov, O.M., 1985. Direct IR spectra study of phenylchlorocarbene. *Bull. Acad. Sci. USSR (Izv. Akad. Nauk SSSR), Div. Chem. Sci. (Ser. Khim.)*, 34, 2159.
175. Lorencak, P., Raabe, G., Radziszewski, J.J., Wentrup, C., 1986. Iminoacetonitrile, an HCN dimer. I.R. identification

in an argon matrix. *J. Chem. Soc. Chem. Commun.*, 12, 916.

176. Maier, G., Mihm, G., Reisenauer, H.P., Littmann, D., 1984. Hetero- π -Systeme. 9. Über die Beziehungen zwischen Silaethenen und Methylsilylenen. *Chem. Ber.*, 117(7), 2369 (in German).

177. Maier, G., Glatthaar, J., Reisenauer, H.P., 2003. Dihalodimethylsilanes from silicon atoms and methyl halides: a combined matrix-spectroscopic and density functional theory study. *J. Organomet. Chem.*, 686(1-2), 341.

178. Xu, J., Zhou, M., 2006. Reactions of Early Lanthanide Metal Atoms (Nd, Sm, Eu) with Water Molecules. A Matrix Isolation Infrared Spectroscopy and Theoretical Study. *J. Phys. Chem. A*, 110(36), 10575.

179. Mueller, H.S.P., Willner, H., 1992. Synthesis and properties of chloryl chloride, ClClO₂. *Inorg. Chem.*, 31(12), 2527–2534.

180. Kotting, C., Sander, W., Senzlober, M., 1998. Evidence for the Non-Concerted Addition of Difluorovinylidene to Acetylenes. *Chem. Eur. J.*, 4(11), 2360.

181. Fridgen, T.D., Zhang, X.K., Parnis, J.M., March, R.E., 2000. Isomerization and Fragmentation Products of CH₂Cl₂ and Other Dihalomethanes in Rare-Gas Matrices: An electron Bombardment Matrix-Isolation TIR Spectroscopic Study. *J. Phys. Chem. A*, 104(16), 3487–3497.

182. Mielke, Z., McCluskey, M., Andrews, L., 1990. Matrix reactions of P₂ and O₃ molecules. *Chem. Phys. Lett.*, 165(2-3), 146.

183. Jacox, M.E., 1990. The vibrational spectra of molecular ions isolated in solid neon. V. N₂O⁺ and NNO-2. *J. Chem. Phys.*, 93(11), 7622.

184. Baker, A.B., Andrews, L., 2006. Group 4 Transition-Metal Atom Reactions with CS₂ and OCS: Infrared Spectra and Density Functional Calculations of SMCS, SM-(η^2 -CS), SMCO, and OMCS in Solid Argon. *J. Phys. Chem. A*, 110(47), 12785–12792.

185. Halasinski, T.M., Godbout, J.T., Allison, J., Leroi, G.E., 1996. Matrix Isolation and Cold Diffusion of Mass-Selected CS₂⁺ in Neon: Infrared Observation of the Assymmetric Stretch of CS₂⁺ and CS₂⁻. *J. Phys. Chem.*, 100(36), 14865–14871.

186. Jacox, M.E., Irikura, K.K., Thompson, W.E., 1995. Matrix isolation study of the interaction of excited neon atoms with SiF₄: Infrared spectra of SiF₃⁺ and SiF₃⁻. *J. Chem. Phys.*, 103(13), 5308.

187. Cho, H.-G., Andrews, L., 2006. Methane Activation by Laser-Ablated V, Nb, and Ta Atoms: Formation of CH₃-MH, CH₂=MH₂, CH:MH₃⁻, and (CH₃)₂MH₂. *J. Phys. Chem. A*, 110(11), 3886–3902.

188. Teng, Y.-L., Jiang, L., Han, S., Xu, Q., 2007. Matrix-Isolation Infrared Spectroscopic and Density Theory Studies on Reactions of Laser-Ablated Lead and Tin Atoms with Water Molecules. *Bull. Chem. Soc. Japan*, 80(11), 2149.

189. Hopkins, A.G., Daly, F.P., Brown, C.W., 1975. Infrared spectra of matrix isolated disulfur monoxide isotopes. *J. Phys. Chem.*, 79(17), 1849.

190. Keelan, B.W., Andrews, L., 1979. Matrix photoionization of dihalofluoromethanes. Infrared spectra and daughter cations and intramolecular hydrogen-bonded parent anions in solid argon at 15 K. *J. Phys. Chem.*, 83(19), 2488.

191. Willson, S.P., Andrews, L., 2000. Characterization of the Reaction Products of Laser-Ablated Lanthanide Metal Atoms with Molecular Hydrogen. Infrared Spectra of LnH, LnH₂, LnH₃, and LnH₄ Molecules in Solid Argon. *J. Phys. Chem. A*, 104(8), 1640–1647.

192. Wang, X., Andrews, L., Marsden, C.J., 2007. Infrared Spectrum and Structure of Thorimine (HN=Th₂). *Chem. Eur. J.*, 13(19), 5601.

193. Andrews, L., Burkholder, T.R., Yustein, J.T., 1992. Reactions of pulsed-laser evaporated aluminum atoms with

oxygen: infrared spectra of the reaction products in solid argon. *J. Phys. Chem.*, 96(25), 10182.

194. Bell, G.A., Dunkin, I.R., 1985. Tetrachlorocyclopentadienyldiene, indenylidene and fluorenylidene in low-temperature matrices. Ultraviolet and infrared spectra and reactions with carbon monoxide. *J. Chem. Soc. Faraday Trans.*, 2, 81, 725.

195. Kuhn A., Sander, W., 1998. Photochemistry of Dimethylsilyl Azide: Formation and Reactivity of 1,1-Dimethylsilylimine. *Organometallics*, 17(2), 248–254.

196. Koga, Y., Nakanaga, T., Sugawara, K., Watanabe, A., Sugie, M., Takeo, H., Kondo, S., Matsumura, C., 1991. Gas phase infrared spectrum of syn-vinyl alcohol produced by thermal decomposition of several alcohols and aldehydes. *J. Mol. Spectrosc.*, 145(2), 315–322.

197. Hedberg, K., 1951. The Infrared Spectra of Cl₂O and ClO₂. *J. Chem. Phys.*, 19(4), 509.

198. Darling, J.H., Garton-Sprenger, M.B., Ogden, J.S., 1974. Matrix isolation studies on reactions of metal atoms. The characterisation of Cu(O₂)₂ and Cr(O₂)₂. *Sympos. Faraday Soc.*, 8(75).

199. Gong, Y., Zhou, M., 2009. Formation and characterization of the CuO₅, CuO₄ and CuO₄⁻ complexes in solid argon. *Phys. Chem. Chem. Phys.*, 11(38), 8714.

200. Andrews, L., Zhou, M., Chertihin, G.V., Bauschlicher, C.W.Jr., 1999. Reactions of Laser-Ablated Y and La Atoms, Cations and Electrons with O₂. Infrared Spectra and Density Functional Calculations of the MO, MO⁺, MO₂, MO₂⁺, and MO₂⁻ Species in Solid Argon. *J. Phys. Chem. A*, 103(33), 6525–6532.

201. Andrews, L., Cho, H.-G., Wang, X., 2005. Reactions of Methane with Titanium Atoms: CH₃TiH, CH₂=TiH₂, Agostic Bonding, and (CH₃)₂TiH₂. *Inorg. Chem.*, 44(13), 4834–4842.

202. Wang, X., Andrews, L., 2005. Infrared Spectra and Structures for Group 4 Dihydroxide and Tetrahydroxide Molecules. *J. Phys. Chem. A*, 109(47), 10689.

203. Zhou, M., Andrews, L., 1998. Reactions of Laser-Ablated Chromium Atoms with Nitric Oxide: Infrared Spectra of NCrO, Cr-(η¹-NO)_x (x = 1, 2, 3, 4), and Cr-η²-NO in Solid Argon. *J. Phys. Chem. A*, 102(38), 7452–7461.

204. Andrews, L., 1968. Matrix infrared spectrum and bonding in the lithium superoxide molecule, LiO₂. *J. Am. Chem. Soc.*, 90(26), 7368.

205. Serebrennikov, L.V., Osin, S.B., Mal'tsev, A.A., 1982. Infrared spectra of the products of reaction of aluminium, gallium, indium, and thallium with oxygen in an argon matrix. Estimation of the fundamentals, ν₃, in cyclic superoxides of Group III metals. *J. Mol. Struct.*, 81(1-2), 25–33.

206. Wade, E.A., Reak, K.E., Parsons, B.F., Clemes, T.P., Singmaster, K.A., 2002. Photochemistry of chloropicrin in cryogenic matrices. *Chem. Phys. Lett.*, 365(5-6), 473.

207. Gong, Y., Andrews, L., 2012. Matrix Infrared Spectroscopic and Theoretical of the Difluoroamino Metal Fluoride Molecules: F₂NMF (M = Cu, Ag, Au). *Inorg. Chem.*, 51(1), 667–673.

208. Lynds, L., Stern, D.R., 1959. New synthesis of alkylchloroboranes. *J. Am. Chem. Soc.*, 81(18), 5006.

209. Andrews, L., 1976. Ultraviolet absorption studies of the alkali metal atom-oxygen molecule matrix reaction. *J. Mol. Spectrosc.* 61(3), 337.

210. Kelsall, B.J., Carlson, K.D., 1980. Matrix reactions of molecular oxygen with thallium atoms. *J. Phys. Chem.*, 84(9), 951.

211. Kelsall, B.J., Andrews, L., 1983. FTIR spectroscopic studies of the matrix photoionization and photolysis products of methylene halides. *J. Mol. Spectrosc.*, 97(2), 362.

212. Wu, Y.-J., Lin, M.-Y., Hsu, S.-C., Cheng, B.-M., 2009. Infrared Absorption Spectra of t-HNOH Radicals Generated on VUV Irradiation of NO in Solid Hydrogen. *Chem. Phys. Chem.*, 10(6), 901.
213. Wang, X., Andrews, L., 2003. Matrix Infrared Spectra and Density Functional Theory Calculations of Manganese and Rhenium Hydrides. *J. Phys. Chem. A*, 107(20), 4081.
214. Hawkins, M., Andrews, L., 1985. Photochemistry of an ozone complex with iodomethane in solid argon at 17 K. Infrared spectra of iodosomethane (CH₃IO) and the hydrogen-bonded CH₂O--HI complex. *Inorg. Chem.*, 24(20), 3285.
215. Chu, L.-K., Lee, Y.-P., 2010. Transient infrared spectra of CH₃SOO and CH₃SO observed with a step-scan Fourier-transform spectrometer. *J. Chem. Phys.*, 133(18), 184303.
216. Bohn, R.B., Brabson, G.D., Andrews, L., 1992. Reaction of atomic hydrogen and carbon disulfide: infrared spectra of HSCS and HSHCS in solid argon. *J. Phys. Chem.*, 96(4), 1582.
217. Mielke, Z., Hawins, M., Andrews, L., 1989. Matrix reactions of oxygen atoms with methyl cyanide: infrared spectra of hydroxyacetonitrile and acetonitrile-N-oxide. *J. Phys. Chem.*, 93(2), 558.
218. Kauffman, J.W., Hauge, R.H., Margrave, J.L., 1984b. Infrared matrix isolation studies of the interactions of Mg, Ca, Sr, and Ba atoms and small clusters with water. *High Temp. Sci.*, 18, 97–118.
219. Kuhne, ., Gunthard, H.H., 1976. Spectroscopic study of the ozone-ethylene reaction. Matrix-infrared spectra of three isotopic ethylene ozonides. *J. Phys. Chem.*, 80(11), 1238.
220. Maier, G., Preiss, T., Reisenauer, H.P., Hess, B.A.Jr., Schaad, L.J., 1994. Small Rings. Part 81. Chlorinated Cyclopropenylidenes, Vinylidenecarbenes, and Propargylenes: Identification by Matrix Isolation Spectroscopy. *J. Am. Chem. Soc.*, 116(5), 2014.
221. Sander, W.W., 1987. Chemiluminescence from arylcarbene oxidation: Phenylchlorocarbene and (2-chlorophenyl) carbene. *Spectrochim. Acta Part A Molec. Spectr.*, 43(5), 637–646.
222. Downs, A.J., Greene, T.M., Johnsen, E., Brain, P.T., Morrison, C.A., Parsons, S., Pulham, C.R., Rankin, D.W.H., Aarsent, K., Mills, I.M., Page, E.M., Rice, D.A., 2001. Preparation and Properties of Gallaborane, GaBH₆: Structure of the Gaseous Molecule H₂Ga(μ-H)2BH₂ As Determined by Vibrational, Electron Diffraction, and ab Initio Studies, and Structure of the Crystalline Solid at 110 K As Determined by X-ray Diffraction. *Inorg. Chem.*, 40(14), 3484–3497.
223. Niki, H., Maker, P.D., Savage, C.M., Breitenbach, L.P., 1981. A FT IR study of a transitory product in the gas-phase ozone-ethylene reaction. *J. Phys. Chem.*, 85(8), 1024.
224. von Ahsen, S., Francisco, J.S., 2005. Spectroscopic Evidence of the Existence of the CF₃OSO₃ Radical. *J. Phys. Chem. A*, 109(41), 9193–9195.
225. Akai, N., Wakamatsu, D., Yoshinobu, T., Kawai, A., Shibuya, K., 2010. Matrix-isolation infrared spectra of HOObR and HOBrO produced upon VUV light irradiation of HBr/O₂/Ne system. *Chem. Phys. Lett.*, 499(1-3), 117.
226. Zhou, H., Gong, Y., Zhou, M., 2007. Infrared Spectra of Chlorinated Ethylene Cations: C₂Cl₄⁺, C₂HCl₃⁺, 1,1-C₂H₂Cl₂⁺, and trans-C₂H₂Cl₂⁺ in Solid Argon. *J. Phys. Chem. A*, 111(4), 603–609.
227. Chang, S.-C., Kafafi, Z.H., Hauge, R.H., Billups, W.E., Margrave, J.L., 1987. Isolation and characterization of copper methylene (CuCH₂) via FTIR matrix isolation spectroscopy. *J. Am. Chem. Soc.*, 109(15), 4508.
228. Han, D.S., Rittby, C.M.L., Graham, W.R.M., 1998. Fourier transform infrared observation of the ν₁(σ) mode of linear SiCH in Ar at 10 K. *J. Chem. Phys.*, 108, 3504.
229. Brom, J.M.Jr., Weltner, W.Jr., 1973. Absorption spectrum of BS₂ at 40K. *J. Mol. Spectrosc.*, 45(1), 82.
230. Andrews, L., Grzybowski, J.M., Allen, R.O., 1975. Infrared spectra of the molecular ions and radicals produced by proton radiolysis of carbon tetrachloride in argon during condensation at 15.deg.K. *J. Phys. Chem.*, 79(9), 904.

231. Chertihin, G.V., Saffel, W., Yustein, J.T., Andrews, L., Neurock, M., Ricca, A., Bauschlicher, C.W.Jr., 1996. Reactions of Laser-Ablated Iron Atoms with Oxygen Molecules in Condensing Argon. Infrared Spectra and Density Functional Calculations of Iron Oxide Product Molecules. *J. Phys. Chem.*, 100(13), 5261.
232. Hauge, R.H., Kafafi, Z.H., Margrave, J.L., 1987. In: Jena, P., Rao, B.K., Khanna, S.N. (eds.), *Physics and Chemistry of Small Clusters*, p. 787.
233. Johnsson, K., Engdahl, A., Kolm, J., Nieminen, J., Nelander, B., 1995. The ClOClO, BrOClO, and IOClO Molecules and Their Photoisomerization. A Matrix Isolation Study. *J. Phys. Chem.*, 99(12), 3902.
234. Maier, G., Schmidt, C., Reisenauer, H.P., Endlein, E., Becker, D., Eckwert, J., Hess, B.A.Jr., Schaad, L.J., 1993. Blausäure-N-methylid: Darstellung, spektroskopische Eigenschaften und seine Beziehung zu anderen C₂H₃N-Isomeren. *Chem. Ber.*, 126(10), 2337.
235. Brabson, G.D., Andrews, L., Marsden, C.J., 1996. Reactions of Selenium and Oxygen. Matrix Infrared Spectra and Density Functional Calculations of Novel SexO_y Molecules. *J. Phys. Chem.*, 100(41), 16487–16494.
236. Miller, J.H., Andrews, L., 1980. Matrix photoionization and radiolysis of boron trihalides. Infrared and ultraviolet spectra of boron trichloride(1+) and boron tribromide(1+) and infrared spectra of boron dichloride and boron dibromide. *J. Am. Chem. Soc.*, 102(15), 4900.
237. Burkholder, T.R., Yustein, J.T., Andrews, L., 1992. Reactions of pulsed laser evaporated gallium and indium atoms with molecular oxygen: matrix infrared spectra of new gallium dioxide and indium dioxide species. *J. Phys. Chem.*, 96(25), 10189.
238. Wang, X., Andrews, L., 2009. Infrared Spectra and Density Functional Calculations for SMO₂ Molecules (M = Cr, Mo, W). *J. Phys. Chem. A*, 113(31), 8934–8941.
239. Lannon, J.A., Verderame, F.D., Anderson, R.W.Jr., 1971. Infrared Spectrum of Solid and Matrix-Isolated H₂O₂ and D₂O₂. *J. Chem. Phys.*, 54(5), 2212.
240. Withnall, R., Andrews, L., 1988. Matrix reactions of methylsilanes and oxygen atoms. *J. Phys. Chem.*, 92(3), 594.
241. Withnall, R., Andrews, L., 1990. Matrix reactions of germane and oxygen atoms: infrared spectroscopic evidence of germylene-water complex, germanone, germanol, hydroxygermylene, and germanic acid. *J. Phys. Chem.*, 94(6), 2351.
242. Prochaska, F.T., Andrews, L., 1977. Matrix photodissociation and photoionization of carbon tetrahalides with noble gas resonance radiation. *J. Chem. Phys.*, 67(3), 1091.
243. Wang, X., Andrews, L., Tam, S., DeRose, M.E., Fajardo, M.E., 2003. Infrared Spectra of Aluminum Hydrides in Solid Hydrogen: Al₂H₄ and Al₂H₆. *J. Am. Chem. Soc.*, 125(30), 9218–9228.
244. Manceron, L., Andrews, L., 1988. Infrared spectra and structures of lithium-benzene and lithium-dibenzene complexes in solid argon. *J. Am. Chem. Soc.*, 110(12), 3840.
245. Burdett, J.K., Hodges, L., Dunning, V., Current, J.H., 1970. Infrared studies of the matrix isolated photolysis products of PF₂H and P₂F₄ and the thermal decomposition products of P₂F₄. *J. Phys. Chem.*, 74(23), 4053.
246. Niki, H., Maker, P.D., Savage, C.M., Breitenbach, L.P., Hurley, M.D., 1985. FTIR study of the kinetics and mechanism for the chlorine-atom-initiated reactions of trichlorosilane. *J. Phys. Chem.*, 89(17), 3725.
247. Pernice, H., Garcia, P., Willner, H., Francisco, J.S., Mills, F.P., Allen, M., Yung, y.L., 2004. Laboratory evidence for a key intermediate in the Venus atmosphere: Peroxychloroformyl radical. *Proc. Nat. Acad. Sci.*, 101(39), 14007.
248. Andrews, L., Wang, X., 2002c. Infrared Spectra of the Novel Si₂H₂ and Si₂H₄ Species and the SiH_{1,2,3} Intermediated in Solid Neon, Argon, and Deuterium. *J. Phys. Chem. A*, 106(34), 7696–7702.
249. Maier, G., Endres, J., 2000. Photochemistry of Matrix-Isolated 4-Diazo-4H-imidazole: IR-Spectroscopic

Identification of 4H-Imidazol-4-ylidene. *Eur. J. Org. Chem.*, 14, 2535–2539.

250. Zhou, M., Andrews, L., 1999. Infrared Spectra of CNbO, CMO-, OMCCO, (C2)MO2, and M(CO)_x (x = 1-6) (M = Nb, Ta) in Solid Neon. *J. Phys. Chem. A*, 103(39), 7785–7794.

251. Wang, X., Andrews, L., 2004d. Infrared Spectra of Thallium Hydrides in Solid Neon, Hydrogen, and Argon. *J. Phys. Chem. A*, 108(16), 3396.

252. Green, D.W., Erwin, K.M., 1981. Infrared spectra of matrix-isolated tungsten oxides. *J. Mol. Spectrosc.*, 89(1), 145.

253. Downs, A.J., Goode, M.J., Pulham, C.R., 1989. Gallane at last! Synthesis and properties of binary gallium hydride. *J. Am. Chem. Soc.*, 111(5), 1936.

254. Coates, J., Meyers, R.A., 2000. Interpretation of infrared spectra, a practical approach. In: Meyers, R.A. (ed.), *Encyclopedia of Analytical Chemistry*. John Wiley & Sons Ltd, Chichester, UK, 10815 – 10837.

255. Holland, H.D., Turekian, K.K., 2014. *Treatise on Geochemistry, Reference Work*, 2nd ed. Elsevier Science, Oxford, UK, ISBN 978-0-08-098300-4

256. Yoffe, D., Frim, R., Ukeles, S.D., Dagani, M.J., Barda, H.J., Benya, T., Sanders, D.C., 2013. Bromine Compounds. In: *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, Germany, doi:10.1002/14356007.a04_405

257. ATSDR (Agency for Toxic Substances and Disease Registry), 1992. Toxicological Profile for Bromomethane. U.S. Public Health Service, 129 pp., retrieved 23.04.2021

258. Howle, C.R., Collins, D.J., Tuckett, R.P., Malins, A.E.R., 2005. Threshold photoelectron–photoion coincidence spectroscopy study of CHCl₂F⁺, CHClF₂⁺, and CH₂ClF⁺: Steric influence of the chlorine, fluorine and hydrogen atoms. *Phys. Chem. Chem. Phys.*, 7, 2287–2297.

259. Melosso, M., Melli, A., Puzzarini, C., Codella, C., Spada, L., Dore, L., Degli Esposti, C., Lefloch, B., Bachiller, R., Ceccarelli, C., Cernicharo, J., Barone, V., 2018. Laboratory measurements and astronomical search for cyanomethanimine. *A&A*, 609, A121, 8 pp.

260. Evans, R.A., Lorencak, P., Ha, T.K., Wentrup, C., 1991. HCN dimers: iminoacetonitrile and N-cyanomethanimine. *J. Am. Chem. Soc.*, 113(19), 7261–7276.

261. Bock, H., Mohmand, S., Hirabayashi, T., Maier, G., Reisenauer, H.P., 1983. Photoelektronen-spektroskopischer Nachweis und Matrix-Isolierung von Thio-para-benzochinonen. *Chem. Ber.*, 116, 273–281 (in German).

262. Andrews, D.U., Heazlewood, B.R., Maccarone, A.T., Conroy, T., Payne, R.J., Jordan, M.J.T., Kable, S. H. (2012). Photo-tautomerization of acetaldehyde to vinyl alcohol: A potential route to tropospheric acids". *Science*, 337, 1203–1206.

263. Clayden, J., Greeves, N., Warren, S., 2012. *Organic Chemistry*, 2nd ed. Oxford University Press, Oxford, UK, 1264 p.

264. Jolad, S.D., Rajagopalan, S., 1966. 2-Bromo-4-methylbenzaldehyde. *Org. Synth.*, 46, 13.

265. Millar, T.J., Parquhar, P.R.A., Willacy, K., 1997. The UMIST Database for Astrochemistry 1995. *Astron. Astrophys. Suppl. Ser.*, 1221, 139–185.

266. Glarborg, P., Marshall, P., 2016. Importance of the Hydrogen Isocyanide Isomer in Modeling Hydrogen Cyanide Oxidation in Combustion. *En. Fuels*, 31, 2156–2163.

267. Wang, X., Creek, D.J., Schiaffo, C.E., Yuxiang, D., Chollet, J. Scheurer, C., Wittlin, S., Charman, S.A., Dussault, P.H., Wood, J.K., Vennerstrom, J.L., 2009. Spiroadamantyl 1,2,4-trioxolane, 1,2,4-trioxane, 1,2,4-trioxepane pairs: Relationship between peroxide bond iron(II) reactivity, heme alkylation efficiency, and antimalarial activity. *Bioorg. Med. Chem. Lett.*, 19, 4542–4545.

268. Lee, R., Coote, M.L., 2013. New insights into 1,2,4-trioxolane stability and the crucial role of ozone in promoting polymer degradation. *Phys. Chem. Chem. Phys.*, 15(39), 16428–16431.
269. Ribeiro, J., Ferreira da Silva, E., Flores, D., 2010. Burning of coal waste piles from Douro coalfield (Portugal): petrological, geochemical and mineralogical characterization. *Int. J. Coal. Geol.*, 81, 359–372.
270. Toukabri, R., Shi, Y.J., 2014. Dominance of Silylene Chemistry in the Decomposition of Monomethylsilane in the Presence of a Heated Metal Filament. *J. Phys. Chem. A*, 118, 3866–3874.
271. Adachi, H., Basco, N., 1979. The reaction of ethylperoxy radicals with NO₂. *Chem. Phys. Lett.*, 67(2-3), 324–328.
272. Wenk, H.H., Sander, W., Leonov, A., de Meijere, A., 1999. Matrix Isolation and Photochemistry of Tetrafluoro-p-xylylene. *Eur. J. Org. Chem.*, 1999(12), 3287–3290.
273. Kroto, H.W., Landsberg, B.M., Suffolk, R.J., Vodden, A., 1974. The photoelectron and microwave spectra of the unstable species thioacetaldehyde, CH₃CHS, and thioacetone, (CH₃)₂CS. *Chem. Phys. Lett.*, 29(2), 265–269.
274. Maier, G., Flögel, U., Reisenauer, H.P., Hess, B., Andes Jr., Schaad, L.J., 1991. HCl-Abspaltung aus Ethansulfenylchlorid und Chlordimethylsulfid. *Chem. Ber.*, 124(11), 2609–2612.
275. Downs, A.J., 1962. 846. Thiocarbonyl fluoride. *J. Chem. Soc.*, “0”, 4361, doi:10.1039/JR9620004361.
276. Yu, J., Lin, J.-H., Xiao, J.-C., 2017. Reaction of Thiocarbonyl Fluoride Generate from Difluorocarbene with Amines. *Angew. Chem. Int. Ed.*, 56(52), 16669–16673.
277. Middleton, W.J., Howard, E.G., Sharkey, W.H., 1965. Fluorothiocabonyl Compounds. I. Preparation of Thio Ketones, Thioacyl Halides, and Thio Esters. *J. Org. Chem.* 30(5), 1375–1384.
278. Rassadin, V.A., Six, Y., 2014. A study of the reaction of n-BuLi with Ti(OiPr)₄ as a method to generate titanacyclopropane and titanacyclopropene species. *Tetrahedron*, 70(4), 787–794.
279. Morlender-Vais, N., Solodovnikova, N., Marek, I., 2000. Intramolecular carbometalation of functionalized terminal alkynes via low-valent titanium complexes. *Chem. Commun.*, 2000, 1849–1850.
280. Kruszewski Ł., 2018. Geochemical Behavior of Trace Elements in the Upper and Lower Silesian Basin Coal-Fire Gob Piles of Poland. Chapter 19, in: Stracher, G.B. (Ed.), *Coal and Peat Fires: A Global Perspective*, vol. 5 – “Case Studies – Advances in Field and Laboratory Research”, 407–449.
281. Ketris, M.P., Yudovich, Ya.E., 2009. Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. *Int. J. Coal. Geol.*, 78, 135–148.
282. Albani, D., Capdevila-Cortada, M., Vilé, G., Mitchell, S., Martin, O., López, N., Pérez-Ramírez, J., 2017. Semihydrogenation of Acetylene on Indium Oxide: Proposed Single-Ensemble Catalysis. *Angew. Chem. Int. Ed.*, 56, 10755–10760.
283. Mirakov, M.A., Pautov, L.A., Siidra, O.I., Makhmadsharif, S., Karpenko, V.Y., Plechov, P.Y., 2020. Hasanovite, IMA 2020-033. In: *CNMNC Newsletter 57*, *Eur. J. Mineral.*, 32, doi:10.5194/ejm-32-495-2020.
284. Sander, Bucher, G., Wandel, H., Krafka, E., Cremer, D., Sheldrick, W.S., 2010. Photochemistry of p-Benzoquinone Diazide Carboxylic Acids: Formation of 2,4-Didehydrophenols.