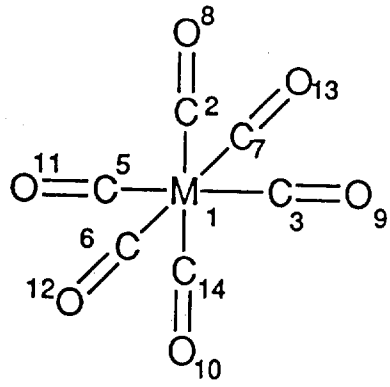
TABLE S1: Symmetry Coordinates for $M(CO)_6$ (O_h symmetry)

A_{1g} $S_1 = 6^{-1/2} (D_1 + D_2 + D_3 + D_4 + D_5 + D_6)$
$S_2 = 6^{-1/2} (R_1 + R_2 + R_3 + R_4 + R_5 + R_6)$

E_g $S_{3a} = 12^{-1/2} (2D_1 - D_2 - D_3 - D_4 - D_5 + 2D_6)$
$S_{3b} = ½ (D_2 + D_4 - D_3 - D_5)$

$S_{4a} = 12^{-1/2} (2R_1 - R_2 - R_3 - R_4 - R_5 + 2R_6)$
$S_{4b} = ½ (R_2 + R_4 - R_3 - R_5)$

T_{1g} $S_{5a} = ½ (ß_{23} - ß_{32} - ß_{43} + ß_{52})$
$S_{5b} = ½ (ß_{36} - ß_{63} - ß_{56} + ß_{13})$
$S_{5c} = ½ (ß_{62} - ß_{26} - ß_{12} + ß_{46})$



T_{1u} $S_{6a} = 2^{-1/2} (D_1 - D_6)$
$S_{6b} = 2^{-1/2} (D_3 - D_5)$
$S_{6c} = 2^{-1/2} (D_4 - D_2)$

$S_{7a} = 2^{-1/2} (R_1 - R_6)$
$S_{7b} = 2^{-1/2} (R_3 - R_5)$
$S_{7c} = 2^{-1/2} (R_4 - R_2)$

$S_{8a} = ½ (ß_{21} + ß_{31} + ß_{41} + ß_{51})$
$S_{8b} = ½ (ß_{63} + ß_{23} + ß_{13} + ß_{43})$
$S_{8c} = ½ (ß_{34} + ß_{64} + ß_{54} + ß_{14})$

$S_{9a} = 8^{-1/2} (\alpha_{12} + \alpha_{13} + \alpha_{14} + \alpha_{15} - \alpha_{26} - \alpha_{36} - \alpha_{46} - \alpha_{56})$
$S_{9b} = 8^{-1/2} (\alpha_{32} + \alpha_{36} + \alpha_{34} + \alpha_{31} - \alpha_{25} - \alpha_{65} - \alpha_{45} - \alpha_{15})$
$S_{9c} = 8^{-1/2} (\alpha_{43} + \alpha_{46} + \alpha_{45} + \alpha_{41} - \alpha_{32} - \alpha_{62} - \alpha_{52} - \alpha_{12})$

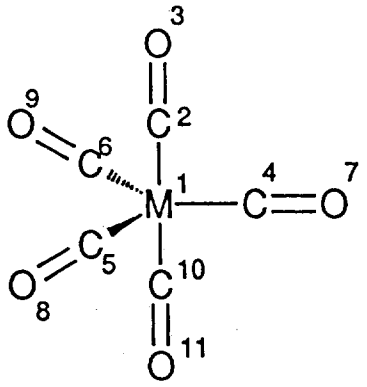
T_{2g} $S_{10a} = ½ (ß_{23} + ß_{32} - ß_{43} - ß_{52})$
$S_{10b} = ½ (ß_{36} + ß_{63} - ß_{56} - ß_{13})$
$S_{10c} = ½ (ß_{62} + ß_{26} - ß_{12} - ß_{46})$

$S_{11a} = ½ (\alpha_{23} + \alpha_{45} - \alpha_{25} - \alpha_{34})$
$S_{11b} = ½ (\alpha_{26} + \alpha_{41} - \alpha_{21} - \alpha_{64})$
$S_{11c} = ½ (\alpha_{36} + \alpha_{51} - \alpha_{31} - \alpha_{65})$

T_{2u} $S_{12a} = ½ (ß_{21} + ß_{41} - ß_{51} - ß_{31})$
$S_{12b} = ½ (ß_{23} + ß_{43} - ß_{63} - ß_{13})$
$S_{12c} = ½ (ß_{34} + ß_{54} - ß_{64} - ß_{14})$

$S_{13a} = 8^{-1/2} (\alpha_{12} + \alpha_{14} + \alpha_{36} + \alpha_{56} - \alpha_{26} - \alpha_{46} - \alpha_{13} - \alpha_{15})$
$S_{13b} = 8^{-1/2} (\alpha_{32} + \alpha_{34} + \alpha_{65} + \alpha_{15} - \alpha_{25} - \alpha_{45} - \alpha_{36} - \alpha_{31})$
$S_{13c} = 8^{-1/2} (\alpha_{43} + \alpha_{45} + \alpha_{62} + \alpha_{12} - \alpha_{32} - \alpha_{52} - \alpha_{46} - \alpha_{41})$

TABLE S2: Symmetry Coordinates for $M(CO)_5$ (D_{3h} symmetry)



A_1' $S_1 = 3^{-1/2} (r_1 + r_2 + r_3)$

$S_2 = 2^{-1/2} (d_4 + d_5)$

$S_3 = 3^{-1/2} (R_1 + R_2 + R_3)$

$S_4 = 2^{-1/2} (D_4 + D_5)$

A_2' $S_5 = 3^{-1/2} (\beta_{13} + \beta_{32} + \beta_{21})$

A_2'' $S_6 = 2^{-1/2} (d_4 - d_5)$

$S_7 = 3^{-1/2} (\gamma_{14} + \gamma_{24} + \gamma_{34})$

$S_8 = 2^{-1/2} (D_4 - D_5)$

$S_9 = 6^{-1/2} (\varepsilon_{14} + \varepsilon_{24} + \varepsilon_{34} - \varepsilon_{15} - \varepsilon_{25} - \varepsilon_{35})$

E' $S_{10a} = 6^{-1/2} (2r_1 - r_2 - r_3)$

$S_{11a} = 2^{-1/2} (\delta_{41} + \delta_{51})$

$S_{12a} = 2^{-1/2} (\beta_{21} - \beta_{32})$

$S_{13a} = 6^{-1/2} (2R_1 - R_2 - R_3)$

$S_{14a} = 12^{-1/2} (2\varepsilon_{14} - \varepsilon_{24} - \varepsilon_{34} + 2\varepsilon_{15} - \varepsilon_{25} - \varepsilon_{35})$

$S_{15a} = 6^{-1/2} (2\alpha_{23} - \alpha_{12} - \alpha_{31})$

$S_{10b} = 2^{-1/2} (r_2 - r_3)$

$S_{11b} = 2^{-1/2} (\delta_{41}' + \delta_{51}')$

$S_{12b} = 6^{-1/2} (-2\beta_{13} + \beta_{21} + \beta_{32})$

$S_{13b} = 2^{-1/2} (R_2 - R_3)$

$S_{14b} = \frac{1}{2} (\varepsilon_{24} - \varepsilon_{34} + \varepsilon_{25} - \varepsilon_{35})$

$S_{15b} = 2^{-1/2} (\alpha_{31} - \alpha_{12})$

E'' $S_{16a} = 2^{-1/2} (\delta_{41} - \delta_{51})$

$S_{17a} = 6^{-1/2} (2\gamma_{14} - \gamma_{24} - \gamma_{34})$

$S_{18a} = 12^{-1/2} (2\varepsilon_{14} - \varepsilon_{24} - \varepsilon_{34} - 2\varepsilon_{15} + \varepsilon_{25} + \varepsilon_{35})$

$S_{16b} = 2^{-1/2} (\delta_{41}' - \delta_{51}')$

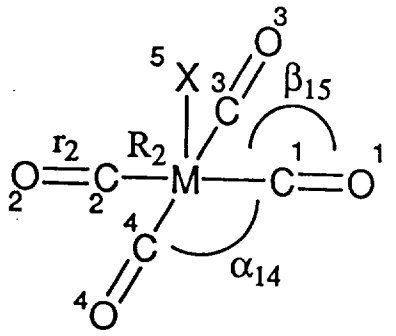
$S_{17b} = 2^{-1/2} (\gamma_{24} - \gamma_{34})$

$S_{18b} = \frac{1}{2} (\varepsilon_{24} - \varepsilon_{34} - \varepsilon_{25} + \varepsilon_{35})$

δ_{41} and δ_{51} are in xz plane; δ_{41}' and δ_{51}' are in yz plane.

TABLE S3: Symmetry Coordinates for $M(CO)_4$ (D_{4h} symmetry)

A_{1g}	$S_1 = ½ (r_3 + r_1 + r_4 + r_2)$
	$S_2 = ½ (R_3 + R_1 + R_4 + R_2)$
A_{2g}	$S_3 = ½ (ß_{31} + ß_{14} + ß_{42} + ß_{23})$
A_{2u}	$S_4 = ½ (ß_{35} + ß_{15} + ß_{45} + ß_{25})$
	$S5 = ½ (α'_{31} + α'_{14} + α'_{42} + α'_{23})$
B_{1g}	$S_6 = ½ (r_3 - r_1 + r_4 - r_2)$
	$S_7 = ½ (R_3 - R_1 + R_4 - R_2)$
B_{2g}	$S_8 = ½ (ß_{31} - ß_{14} + ß_{42} - ß_{23})$
	$S_9 = ½ (α_{31} - α_{14} + α_{42} - α_{23})$
B_{2u}	$S_{10} = ½ (ß_{35} - ß_{15} + ß_{45} - ß_{25})$
	$S_{11} = ½ (α'_{31} - α'_{14} + α'_{42} - α'_{23})$
E_g	$S_{12a} = 2^{-1/2} (ß_{35} - ß_{45})$
	$S_{12b} = 2^{-1/2} (ß_{15} - ß_{25})$
E_u	$S_{13a} = 2^{-1/2} (r_3 - r_4)$
	$S_{13a} = 2^{-1/2} (r_1 - r_2)$
	$S_{14a} = 2^{-1/2} (R_3 - R_4)$
	$S_{14a} = 2^{-1/2} (R_1 - R_2)$
	$S_{15a} = 2^{-1/2} (ß_{23} - ß_{14})$
	$S_{15a} = 2^{-1/2} (ß_{31} - ß_{42})$
	$S_{16a} = ½ (α_{31} - α_{14} - α_{42} + α_{23})$
	$S_{16a} = ½ (α_{31} + α_{14} - α_{42} - α_{23})$



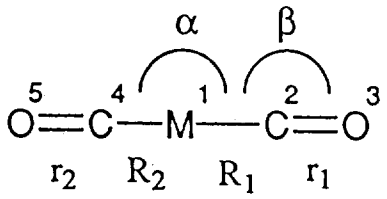
$β_{13}$ = MCO bend in xy plane
$β_{15}$ = MCO bend perpendicular to xy plane
$α_{14}$ = CMC bend in xy plane
$α'_{14}$ = CMC bend perpendicular to xy plane

$ß_{31}$ = MCO bend in xy plane; $ß_{35}$ = MCO bend perpendicular to xy plane.

$α_{14}$ = CMC bend in xy plane; $α'_{14}$ = CMC bend perpendicular to xy plane (out-of-plane-bend).

TABLE S4: Symmetry Coordinates for $M(CO)_2$ ($D_{\infty h}$ symmetry)

Σ_g^+	$S_1 = 2^{-1/2}(r_1 + r_2)$
	$S_2 = 2^{-1/2}(R_1 + R_2)$
Σ_u^-	$S_3 = 2^{-1/2}(r_1 - r_2)$
	$S_4 = 2^{-1/2}(R_1 - R_2)$
Π_g	$S_{5a} = 2^{-1/2}(\beta_{13} + \beta_{23})$
	$S_{5b} = 2^{-1/2}(\beta'_{13} + \beta'_{23})$
Π_u	$S_{6a} = 2^{-1/2}(\beta_{13} - \beta_{23})$
	$S_{6b} = 2^{-1/2}(\beta'_{13} - \beta'_{23})$
	$S_{7a} = \alpha_{12}$
	$S_{7b} = \alpha'_{12}$



α, β in xz plane
α', β' in yz plane

α_{12} and β_{13} in xz plane, α'_{12} and β'_{13} in yz plane.

TABLE S5: (a) Metal-ligand bond lengths (in Å) for $[V(CO)_6]^-$, $[Mn(CO)_6]^+$, and $[Fe(CO)_6]^{2+}$

	V-C	C-O	Mn-C	C-O	Fe-C	C-O
BP86/AE1	1.9632	1.1796	1.8967	1.1509	1.9061	1.1410
BP86/AE2	1.9637	1.1701	1.8926	1.1401	1.9027	1.1299

TABLE S5: (b) Vibrational frequencies (in cm^{-1}) for $[V(CO)_6]^-$, $[Mn(CO)_6]^+$, and $[Fe(CO)_6]^{2+}$

			$[V(CO)_6]^-$		$[Mn(CO)_6]^+$		$[Fe(CO)_6]^{2+}$	
			BP86 AE1	BP86 AE2	BP86 AE1	BP86 AE2	BP86 AE1	BP86 AE2
A_{1g}	ν_1	[CO]	2007	1994	2168	2169	2217	2222
A_{1g}	ν_2	[MC]	382	383	392	394	370	371
E_g	ν_3	[CO]	1913	1888	2108	2105	2182	2187
E_g	ν_4	[MC]	393	394	390	394	361	364
T_{1g}	ν_5	[δMCO]	358	363	352	357	339	341
T_{1u}	ν_6	[CO]	1898	1870	2090	2086	2167	2171
T_{1u}	ν_7	[δMCO]	666	669	660	666	614	617
T_{1u}	ν_8	[MC]	464	463	428	432	391	392
T_{1u}	ν_9	[δCMC]	86	80	113	110	120	117
T_{2g}	ν_{10}	[δMCO]	505	510	526	534	504	509
T_{2g}	ν_{11}	[δCMC]	83	78	97	95	99	98
T_{2u}	ν_{12}	[δMCO]	496	504	502	510	475	479
T_{2u}	ν_{13}	[δCMC]	53	48	73	71	78	77

TABLE S5: (c) Infrared Intensities (in km/mol) for $[V(CO)_6]^-$, $[Mn(CO)_6]^+$, and $[Fe(CO)_6]^{2+}$

			$[V(CO)_6]^-$		$[Mn(CO)_6]^+$		$[Fe(CO)_6]^{2+}$	
			BP86 AE1	BP86 AE2	BP86 AE1	BP86 AE2	BP86 AE1	BP86 AE2
T_{1u}	ν_6	[CO]	5909	6953	2585	2786	1045	1093
T_{1u}	ν_7	[δMCO]	378	367	492	462	356	330
T_{1u}	ν_8	[MC]	11	18	57	58	27	26
T_{1u}	ν_9	[δCMC]	1	1	2	4	2	3

TABLE S6: Harmonic Symmetry. Force Constants F_{ij} and Internal Force Constants F_{int} for $M(CO)_6$ (M = Cr, Mo, W) [a]

	M = Cr			M = Mo		M = W	
	BP86 AE1	BP86 AE2	BP86 ECP1	BP86 ECP1	MP2 ECP1	BP86 ECP1	MP2 ECP1
$F_{1,1}$	17.18	17.09	17.20	17.12	16.90	17.04	16.82
$F_{1,2}$	0.27	0.27	0.27	0.25	0.32	0.26	0.32
$F_{2,2}$	2.68	2.73	2.75	2.98	3.12	3.26	3.42
$F_{3,3}$	16.28	16.09	16.27	16.26	16.13	16.16	15.98
$F_{3,4}$	0.65	0.69	0.67	0.68	0.84	0.71	0.88
$F_{4,4}$	2.74	2.78	2.79	2.72	2.81	2.96	3.00
$F_{5,5}$	0.37	0.38	0.37	0.35	0.39	0.37	0.41
$F_{6,6}$	16.34	16.14	16.33	16.34	16.15	16.24	16.08
$F_{6,7}$	0.76	0.80	0.75	0.76	0.98	0.78	0.96
$F_{6,8}$	0.02	0.02	0.03	0.01	0.02	0.01	0.02
$F_{6,9}$	0.03	0.02	0.02	0.00	0.09	0.00	0.08
$F_{7,7}$	2.04	2.04	2.02	1.75	1.72	1.94	1.95
$F_{7,8}$	-0.09	-0.09	-0.08	-0.04	-0.05	-0.05	-0.06
$F_{7,9}$	0.02	-0.03	0.01	-0.01	-0.07	0.03	-0.02
$F_{8,8}$	0.48	0.49	0.50	0.49	0.51	0.51	0.55
$F_{8,9}$	-0.32	-0.33	-0.32	-0.37	-0.33	-0.37	-0.35
$F_{9,9}$	0.89	0.84	0.89	0.90	0.48	0.90	0.52
$F_{10,10}$	0.40	0.41	0.40	0.38	0.41	0.39	0.42
$F_{10,11}$	-0.15	-0.17	-0.16	-0.13	-0.15	-0.12	-0.13
$F_{11,11}$	0.53	0.51	0.54	0.45	0.37	0.45	0.35
$F_{12,12}$	0.46	0.48	0.48	0.47	0.50	0.49	0.53
$F_{12,13}$	-0.22	-0.24	-0.24	-0.29	-0.25	-0.29	-0.28
$F_{13,13}$	0.47	0.46	0.47	0.57	0.30	0.58	0.46
F_{CO}	16.46	16.28	16.46	16.44	16.27	16.35	16.17
F_{MC}	2.38	2.40	2.40	2.28	2.31	2.50	2.54
F_{MCO}	0.43	0.44	0.44	0.42	0.45	0.44	0.48
$F_{CO,CO,cis}$	0.15	0.17	0.15	0.14	0.13	0.15	0.14
$F_{CO,CO,trans}$	0.12	0.14	0.12	0.10	0.12	0.10	0.09

[a] See text for units.

TABLE S7: Harmonic Symmetry Force Constants F_{ij} and Internal Force Constants F_{int} for $M(CO)_5$ (M = Fe, Ru, Os) [a]

	M = Fe			M = Ru		M = Os	
	BP86 AE1	BP86 AE2	BP86 ECP1	BP86 ECP1	MP2 ECP1	BP86 ECP1	MP2 ECP1
$F_{1,1}$	16.58	16.45	16.63	16.49	16.50	16.31	16.34
$F_{1,2}$	0.43	0.47	0.44	0.39	0.32	0.40	0.33
$F_{1,3}$	0.47	0.50	0.48	0.55	0.60	0.59	0.64
$F_{1,4}$	-0.19	-0.21	-0.19	-0.21	-0.22	-0.21	-0.24
$F_{2,2}$	16.70	16.58	16.76	16.83	16.69	16.78	16.71
$F_{2,3}$	-0.15	-0.17	-0.15	-0.14	-0.18	-0.15	-0.22
$F_{2,4}$	0.53	0.57	0.53	0.53	0.69	0.55	0.67
$F_{3,3}$	3.24	3.25	3.23	3.15	3.58	3.67	4.01
$F_{3,4}$	-0.12	-0.12	-0.12	0.12	0.11	0.15	0.15
$F_{4,4}$	3.48	3.52	3.44	3.60	4.24	3.99	4.36
$F_{5,5}$	0.35	0.35	0.36	0.31	0.42	0.37	0.46
$F_{6,6}$	16.54	16.39	16.59	16.71	16.59	16.67	16.63
$F_{6,7}$	0.03	0.03	0.03	0.05	0.08	0.06	0.07
$F_{6,8}$	0.71	0.75	0.71	0.70	0.95	0.72	0.93
$F_{6,9}$	0.02	0.03	0.01	0.11	0.07	0.14	0.09
$F_{7,7}$	0.39	0.40	0.39	0.33	0.40	0.37	0.44
$F_{7,8}$	-0.10	-0.10	-0.09	-0.08	-0.11	-0.10	-0.12
$F_{7,9}$	0.20	0.22	0.20	0.25	0.28	0.28	0.31
$F_{8,8}$	2.46	2.50	2.38	2.05	2.09	2.28	2.29
$F_{8,9}$	-0.07	-0.05	-0.07	-0.12	-0.03	-0.19	-0.11
$F_{9,9}$	0.85	0.83	0.86	0.96	0.98	1.04	0.98
$F_{10,10}$	16.18	16.00	16.21	16.13	16.27	15.96	16.11
$F_{10,11}$	0.00	0.00	0.00	0.00	0.02	0.00	0.01
$F_{10,12}$	0.06	0.06	0.06	0.08	0.09	0.09	0.09
$F_{10,13}$	0.68	0.73	0.69	0.67	0.85	0.71	0.86
$F_{10,14}$	0.02	0.02	0.03	-0.01	-0.02	-0.03	-0.01
$F_{10,15}$	0.07	0.07	0.06	0.11	0.05	0.12	0.06
$F_{11,11}$	0.49	0.51	0.50	0.49	0.55	0.52	0.58
$F_{11,12}$	0.03	0.03	0.03	0.03	0.03	0.02	0.02
$F_{11,13}$	-0.01	-0.01	-0.01	0.03	0.02	0.00	-0.01

TABLE S7: Harmonic Symmetry Force Constants F_{ij} and Internal Force Constants F_{int} for $M(CO)_5$ (M = Fe, Ru, Os) [a] (Continued)

	M = Fe			M = Ru		M = Os	
	BP86 AE1	BP86 AE2	BP86 ECP1	BP86 ECP1	MP2 ECP1	BP86 ECP1	MP2 ECP1
$F_{11,14}$	-0.24	-0.25	-0.24	-0.31	-0.29	-0.32	-0.32
$F_{11,15}$	0.06	0.06	0.06	0.06	0.06	0.05	0.05
$F_{12,12}$	0.42	0.42	0.42	0.39	0.48	0.44	0.52
$F_{12,13}$	-0.16	-0.16	-0.16	-0.21	-0.23	-0.20	-0.21
$F_{12,14}$	-0.13	-0.13	-0.13	-0.16	-0.17	-0.16	-0.16
$F_{12,15}$	0.12	0.12	0.12	0.12	0.12	0.09	0.10
$F_{13,13}$	2.66	2.65	2.58	2.30	2.50	2.69	2.88
$F_{13,14}$	0.00	-0.01	0.01	0.01	-0.07	0.09	0.04
$F_{13,15}$	-0.03	-0.03	-0.03	-0.01	-0.04	0.03	0.01
$F_{14,14}$	0.76	0.75	0.75	0.93	0.81	0.99	0.90
$F_{14,15}$	-0.23	-0.23	-0.24	-0.26	-0.26	-0.26	-0.26
$F_{15,15}$	0.24	0.23	0.24	0.20	0.21	0.18	0.19
$F_{16,16}$	0.46	0.48	0.47	0.45	0.51	0.47	0.53
$F_{16,17}$	-0.03	-0.03	-0.03	-0.03	-0.02	-0.02	-0.02
$F_{16,18}$	-0.13	-0.14	-0.13	-0.12	-0.13	-0.11	-0.12
$F_{17,17}$	0.36	0.37	0.36	0.27	0.34	0.30	0.36
$F_{17,18}$	0.08	0.09	0.09	0.06	0.09	0.05	0.08
$F_{18,18}$	0.54	0.53	0.56	0.50	0.56	0.51	0.54
$F_{CO,ax}$	16.62	16.49	16.67	16.77	16.64	16.72	16.67
$F_{CO,eq}$	16.32	16.15	16.35	16.25	16.35	16.08	16.19
$F_{MC,ax}$	2.97	3.01	2.91	2.82	3.17	3.14	3.32
$F_{MC,eq}$	2.85	2.85	2.80	2.58	2.86	3.02	3.26
$F_{MCO,ax-eq}$	0.48	0.49	0.49	0.47	0.53	0.49	0.55
$F_{MCO,eq-ax}$	0.37	0.38	0.37	0.29	0.36	0.32	0.39
$F_{MCO,eq-eq}$	0.39	0.40	0.40	0.37	0.46	0.41	0.50
$F_{CO,CO,ax-eq}$	0.17	0.19	0.18	0.16	0.13	0.16	0.14
$F_{CO,CO,ax-ax}$	0.08	0.09	0.08	0.06	0.05	0.05	0.04
$F_{CO,CO,eq-eq}$	0.13	0.15	0.14	0.12	0.08	0.11	0.08

[a] See text for units.

TABLE S8: Harmonic Symmetry Force Constants F_{ij} and Internal Force Constants F_{int} for $M(CO)_4$ (M = Ni, Pd, Pt) [a]

	M = Ni			M = Pd		M = Pt	
	BP86 AE1	BP86 AE2	BP86 ECP1	BP86 ECP1	MP2 ECP1	BP86 ECP1	MP2 ECP1
$F_{1,1}$	17.30	17.22	17.37	17.34	17.44	17.09	17.17
$F_{1,2}$	0.29	0.30	0.26	0.35	0.38	0.46	0.50
$F_{2,2}$	2.59	2.57	2.54	2.05	2.16	2.86	3.19
$F_{3,3}$	0.34	0.34	0.34	0.23	0.30	0.32	0.40
$F_{3,4}$	0.16	0.16	0.17	0.14	0.15	0.13	0.14
$F_{4,4}$	0.32	0.31	0.33	0.25	0.28	0.25	0.29
$F_{5,5}$	16.70	16.55	16.74	16.83	17.06	16.57	16.77
$F_{5,6}$	0.55	0.58	0.54	0.51	0.63	0.58	0.74
$F_{5,7}$	-0.04	-0.04	-0.04	-0.04	-0.05	-0.06	-0.07
$F_{5,8}$	-0.05	-0.05	-0.04	-0.08	-0.06	-0.12	-0.11
$F_{6,6}$	2.29	2.26	2.18	1.67	1.76	2.23	2.45
$F_{6,7}$	0.21	0.21	0.21	0.24	0.24	0.30	0.32
$F_{6,8}$	0.26	0.25	0.27	0.33	0.33	0.41	0.42
$F_{7,7}$	0.29	0.29	0.28	0.18	0.25	0.26	0.35
$F_{7,8}$	0.18	0.17	0.17	0.17	0.18	0.19	0.20
$F_{8,8}$	0.47	0.46	0.48	0.48	0.49	0.57	0.60
$F_{9,9}$	0.22	0.22	0.22	0.12	0.20	0.19	0.29
F_{CO}	16.85	16.72	16.90	16.96	17.15	16.70	16.87
F_{MC}	2.36	2.34	2.27	1.76	1.86	2.39	2.64
F_{MCO}	0.27	0.28	0.27	0.17	0.24	0.25	0.34
$F_{CO,CO}$	0.15	0.17	0.16	0.13	0.10	0.13	0.10

[a] See text for units.

TABLE S9: Harmonic Symmetry Force Constants F_{ij} and Internal Force Constants F_{int} for the 3d complexes $[M(CO)_6]^n$ (M = V, Mn, Fe; n = -1, 1, 2, respectively) [a]

	M = V			M = Mn			M = Fe		
	BP86 AE1	BP86 AE2	BP86 ECP1	BP86 AE1	BP86 AE2	BP86 ECP1	BP86 AE1	BP86 AE2	BP86 ECP1
$F_{1,1}$	15.79	15.56	15.76	18.38	18.40	18.44	19.28	19.39	19.37
$F_{1,2}$	0.31	0.29	0.29	0.23	0.24	0.23	0.18	0.19	0.18
$F_{2,2}$	2.49	2.50	2.57	2.62	2.66	2.59	2.33	2.34	2.21
$F_{3,3}$	14.59	14.22	14.53	17.81	17.77	17.86	19.03	19.11	19.11
$F_{3,4}$	0.59	0.61	0.60	0.61	0.64	0.61	0.45	0.46	0.43
$F_{4,4}$	2.61	2.62	2.68	2.55	2.60	2.51	2.18	2.22	2.08
$F_{5,5}$	0.38	0.39	0.38	0.35	0.35	0.34	0.32	0.32	0.31
$F_{6,6}$	14.68	14.30	14.61	17.84	17.81	17.89	19.05	19.13	19.13
$F_{6,7}$	0.71	0.74	0.70	0.68	0.72	0.67	0.49	0.51	0.46
$F_{6,8}$	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02
$F_{6,9}$	0.02	0.01	0.01	0.03	0.02	0.02	0.03	0.03	0.03
$F_{7,7}$	2.07	2.04	2.06	1.78	1.81	1.70	1.49	1.51	1.40
$F_{7,8}$	-0.10	-0.10	-0.09	-0.07	-0.07	-0.06	-0.04	-0.04	-0.03
$F_{7,9}$	-0.03	-0.07	-0.02	0.09	0.04	0.07	0.14	0.09	0.13
$F_{8,8}$	0.52	0.52	0.54	0.43	0.44	0.43	0.37	0.37	0.36
$F_{8,9}$	-0.32	-0.34	-0.33	-0.28	-0.29	-0.27	-0.21	-0.21	-0.19
$F_{9,9}$	0.67	0.62	0.67	1.05	0.99	1.04	1.11	1.04	1.08
$F_{10,10}$	0.41	0.41	0.41	0.38	0.39	0.38	0.35	0.35	0.34
$F_{10,11}$	-0.15	-0.17	-0.17	-0.14	-0.15	-0.15	-0.11	-0.12	-0.11
$F_{11,11}$	0.44	0.41	0.44	0.59	0.57	0.61	0.60	0.59	0.63
$F_{12,12}$	0.49	0.50	0.51	0.42	0.43	0.43	0.37	0.37	0.36
$F_{12,13}$	-0.21	-0.23	-0.23	-0.20	-0.22	-0.22	-0.16	-0.17	-0.17
$F_{13,13}$	0.34	0.31	0.32	0.60	0.58	0.60	0.67	0.64	0.67
F_{CO}	14.84	14.49	14.78	17.92	17.89	17.97	19.08	19.17	19.16
F_{MC}	2.32	2.31	2.35	2.17	2.22	2.12	1.86	1.88	1.76
F_{MCO}	0.45	0.45	0.46	0.40	0.40	0.39	0.35	0.35	0.34
$F_{CO,CO,cis}$	0.20	0.22	0.21	0.10	0.10	0.10	0.04	0.05	0.04
$F_{CO,CO,trans}$	0.15	0.18	0.16	0.08	0.09	0.08	0.03	0.04	0.03

[a] See text for units.

TABLE S10: Harmonic Symmetry Force Constants F_{ij} and Internal Force Constants F_{int} for the complexes $[M(CO)_6]^n$ (M = Nb, Ta; Re; Ru, Os; Co, Rh, Ir; Pt; Au; n = -1 to 5, respectively) [a]

	M = Nb	M = Ta	M = Re	M = Ru	M = Os	M = Co	M = Rh	M = Ir	M = Pt	M = Au
$F_{1,1}$	15.72	15.65	18.28	19.32	19.32	19.81	19.86	19.88	19.96	19.42
$F_{1,2}$	0.27	0.26	0.23	0.14	0.21	0.07	0.04	0.07	-0.05	-0.14
$F_{2,2}$	2.60	2.77	3.40	2.80	3.25	1.80	2.31	2.81	2.16	1.04
$F_{3,3}$	14.56	14.48	17.70	19.06	19.02	19.77	19.79	19.78	19.95	19.37
$F_{3,4}$	0.61	0.60	0.68	0.47	0.57	0.18	0.21	0.28	0.02	-0.22
$F_{4,4}$	2.44	2.58	2.98	2.40	2.78	1.67	1.99	2.36	1.77	0.64
$F_{5,5}$	0.34	0.36	0.36	0.32	0.34	0.28	0.29	0.32	0.30	0.28
$F_{6,6}$	14.68	14.61	17.77	19.10	19.03	19.78	19.82	19.82	19.97	19.38
$F_{6,7}$	0.69	0.69	0.72	0.47	0.54	0.20	0.21	0.28	0.07	-0.07
$F_{6,8}$	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00
$F_{6,9}$	-0.02	-0.02	0.01	0.01	0.01	0.04	0.02	0.02	0.03	0.01
$F_{7,7}$	1.73	1.86	1.78	1.33	1.49	1.22	1.19	1.34	1.25	0.85
$F_{7,8}$	-0.05	-0.06	-0.04	-0.02	-0.04	-0.01	-0.01	-0.02	-0.01	-0.01
$F_{7,9}$	-0.04	-0.01	0.10	0.12	0.16	0.15	0.17	0.21	0.22	0.17
$F_{8,8}$	0.50	0.52	0.47	0.38	0.41	0.31	0.32	0.36	0.32	0.29
$F_{8,9}$	-0.35	-0.34	-0.36	-0.27	-0.30	-0.11	-0.17	-0.21	-0.12	-0.04
$F_{9,9}$	0.63	0.62	1.15	1.25	1.31	0.99	1.20	1.37	1.27	0.99
$F_{10,10}$	0.37	0.36	0.38	0.34	0.36	0.30	0.30	0.33	0.31	0.29
$F_{10,11}$	-0.13	-0.11	-0.11	-0.10	-0.10	-0.07	-0.06	-0.07	-0.04	0.00
$F_{11,11}$	0.35	0.35	0.53	0.56	0.58	0.60	0.53	0.59	0.55	0.45
$F_{12,12}$	0.49	0.50	0.46	0.38	0.41	0.31	0.32	0.36	0.32	0.29
$F_{12,13}$	-0.27	-0.26	-0.29	-0.23	-0.25	-0.10	-0.16	-0.19	-0.13	-0.06
$F_{13,13}$	0.39	0.38	0.76	0.84	0.91	0.63	0.83	0.97	0.90	0.65
F_{CO}	14.81	14.74	17.84	19.12	19.08	19.78	19.82	19.82	19.96	19.38
F_{MC}	2.12	2.25	2.45	1.93	2.21	1.47	1.64	1.93	1.58	0.81
F_{MCO}	0.42	0.43	0.42	0.36	0.38	0.30	0.31	0.34	0.31	0.29
$F_{CO,CO,cis}$	0.19	0.20	0.10	0.04	0.05	0.01	0.01	0.02	0.00	0.01
$F_{CO,CO,trans}$	0.14	0.13	0.06	0.02	0.05	0.00	0.00	0.00	-0.01	0.00

[a] Calculated at BP86/ECP1. See text for units.

TABLE S11: Harmonic Symmetry Force Constants F_{ij} and Internal Force Constants F_{int} for the complexes $[M(CO)_4]^n$ (M = Co, Rh, Ir; Ni, Pd, Pt; Au; Hg; n = 1 to 4, respectively) [a]

	M = Co	M = Rh	M = Ir	M = Ni	M = Pd	M = Pt	M = Au	M = Hg
$F_{1,1}$	18.62	18.70	18.58	19.76	19.79	19.74	20.14	19.48
$F_{1,2}$	0.25	0.22	0.27	0.11	0.08	0.14	-0.05	-0.17
$F_{2,2}$	2.73	3.10	3.80	2.00	2.37	3.08	2.16	0.66
$F_{3,3}$	0.31	0.28	0.33	0.28	0.26	0.30	0.28	0.25
$F_{4,4}$	0.34	0.35	0.42	0.29	0.29	0.35	0.30	0.24
$F_{4,5}$	-0.07	-0.10	-0.15	-0.06	-0.09	-0.13	-0.08	-0.02
$F_{5,5}$	0.04	0.11	0.15	0.17	0.24	0.31	0.34	0.23
$F_{6,6}$	18.22	18.37	18.24	19.67	19.71	19.62	20.14	19.43
$F_{6,7}$	0.53	0.54	0.62	0.25	0.25	0.35	0.03	-0.24
$F_{7,7}$	2.79	2.73	3.40	1.95	2.01	2.65	1.86	0.44
$F_{8,8}$	0.37	0.33	0.37	0.31	0.28	0.33	0.29	0.25
$F_{8,9}$	-0.13	-0.11	-0.11	-0.07	-0.07	-0.08	-0.04	0.02
$F_{9,9}$	0.60	0.55	0.60	0.56	0.50	0.58	0.51	0.37
$F_{10,10}$	0.36	0.36	0.43	0.29	0.30	0.36	0.30	0.24
$F_{10,11}$	-0.10	-0.13	-0.16	-0.08	-0.11	-0.14	-0.10	-0.05
$F_{11,11}$	0.02	0.09	0.07	0.13	0.20	0.21	0.26	0.14
$F_{12,12}$	0.27	0.28	0.33	0.26	0.26	0.30	0.27	0.23
$F_{13,13}$	18.22	18.40	18.27	19.68	19.73	19.65	20.15	19.45
$F_{13,14}$	0.70	0.64	0.72	0.29	0.26	0.37	0.06	-0.11
$F_{13,15}$	0.01	0.01	0.01	0.00	0.01	0.00	0.00	-0.01
$F_{13,16}$	0.09	0.03	0.03	0.05	0.01	0.02	0.02	0.01
$F_{14,14}$	1.59	1.42	1.74	1.30	1.25	1.47	1.44	0.83
$F_{14,15}$	0.01	0.03	0.01	0.01	0.02	0.00	0.00	-0.01
$F_{14,16}$	-0.10	-0.07	0.01	-0.01	0.00	0.08	0.13	0.13
$F_{15,15}$	0.38	0.35	0.41	0.31	0.30	0.35	0.30	0.25
$F_{15,16}$	-0.21	-0.25	-0.30	-0.11	-0.16	-0.21	-0.11	-0.02
$F_{16,16}$	0.81	0.96	1.08	0.80	0.95	1.15	1.04	0.65
F_{CO}	18.32	18.47	18.34	19.70	19.74	19.67	20.15	19.45
F_{MC}	2.18	2.17	2.67	1.64	1.72	2.16	1.72	0.69
F_{MCO}	0.36	0.33	0.38	0.30	0.28	0.33	0.29	0.25
F'_{MCO}	0.31	0.32	0.38	0.27	0.27	0.33	0.28	0.24
$F_{CO,CO,cis}$	0.10	0.08	0.09	0.02	0.02	0.03	0.00	0.01
$F_{CO,CO,trans}$	0.10	0.07	0.07	0.02	0.01	0.01	-0.01	0.00

[a] = Calculated at BP86/ECP1. F_{MCO} = in molecular plane; F'_{MCO} = perpendicular to molecular plane. See text for units.

TABLE S12: (a) ^{13}CO and $C^{18}O$ Isotopic Shifts (in cm^{-1}) for $Ru(CO)_5$ and $Os(CO)_5$

			$Ru(^{13}CO)_5$		$Ru(C^{18}O)_5$	$Os(^{13}CO)_5$	$Os(C^{18}O)_5$
			exp.[a]	calc.	calc.	calc.	calc.
A_1'	ν_1	[CO]		50.6	44.9	51.2	44.1
A_1'	ν_2	[CO]		47.4	44.5	48.0	43.6
A_1'	ν_3	[MC]		7.2	16.7	7.4	17.8
A_1'	ν_4	[MC]		10.0	15.4	7.3	16.7
A_2'	ν_5	[δMCO]		9.9	4.2	10.6	4.5
A_2''	ν_6	[CO]	45.2	46.1	47.2	46.3	46.7
A_2''	ν_7	[δMCO]		15.1	2.2	18.1	2.5
A_2''	ν_8	[MC]		3.5	9.9	5.5	11.4
A_2''	ν_9	[δCMC]		0.2	3.9	0.2	4.0
E'	ν_{10}	[CO]	45.4	45.8	45.7	46.1	44.8
E'	ν_{11}	[δMCO]		17.6	3.2	19.1	3.4
E'	ν_{12}	[δMCO]		9.1	9.7	8.1	11.5
E'	ν_{13}	[MC]		10.2	5.3	11.1	5.7
E'	ν_{14}	[δCMC]		0.2	3.7	0.4	4.4
E'	ν_{15}	[δCMC]		0.3	2.1	0.3	2.0
E''	ν_{16}	[δMCO]		17.1	3.2	16.9	3.4
E''	ν_{17}	[δMCO]		10.0	3.8	10.5	4.0
E''	ν_{18}	[δCMC]		0.4	4.4	0.2	3.8

TABLE S12: (b) ^{13}CO and $C^{18}O$ isotopic shifts (in cm^{-1}) for $Pd(CO)_4$ and $Pt(CO)_4$

			$Pd(^{13}CO)_4$	$Pd(C^{18}O)_4$		$Pt(^{13}CO)_4$		$Pt(C^{18}O)_4$
			calc.	exp.[b]	calc.	exp.[c]	calc.	calc.
A_1	ν_1	[CO]	48.3		47.5		49.0	46.1
A_1	ν_2	[MC]	5.8		12.3		3.8	14.6
E	ν_3	[δMCO]	13.3		2.4		17.1	3.1
E	ν_4	[δCMC]	0.2		2.4		0.2	2.6
T_2	ν_5	[CO]	46.3	48.3	47.5	46.4	46.7	46.2
T_2	ν_6	[δMCO]	11.8		6.6		13.1	7.9
T_2	ν_7	[MC]	5.3		4.5		6.4	6.0
T_2	ν_8	[δCMC]	0.1		2.6		0.1	3.0
T_1	ν_9	[δMCO]	6.3		2.5		7.7	3.2

TABLE S13: ^{13}CO Isotopic Shifts (in cm^{-1}) for $[M(CO)_6]^n$

			M = Mn	M = Re	M = Fe		M = Ru		M = Os	
			calc.	calc.	exp.[b]	calc.	exp.[b]	calc.	exp.[b]	calc.
A_{1g}	ν_1	[CO]	51.0	52.3	51	51.8	51	52.9	53	53.4
A_{1g}	ν_2	[MC]	6.3	6.9		6.0		6.4		6.8
E_g	ν_3	[CO]	48.7	49.2	51	50.5	50	50.8	52	51.0
E_g	ν_4	[MC]	6.4	6.8		5.9		6.2		6.6
T_{1g}	ν_5	[δMCO]	10.8	10.5		10.3		9.8		10.1
T_{1u}	ν_6	[CO]	47.1	46.9	49	49.1	50	48.9	49	48.9
T_{1u}	ν_7	[δMCO]	14.5	18.8		13.7		16.6		18.5
T_{1u}	ν_8	[MC]	7.5	5.3		6.6		4.9		4.8
T_{1u}	ν_9	[δCMC]	0.4	0.1		0.4		0.2		0.2
T_{2g}	ν_{10}	[δMCO]	19.3	16.9		18.5		16.7		16.7
T_{2g}	ν_{11}	[δCMC]	0.3	0.4		0.3		0.3		0.4
T_{2u}	ν_{12}	[δMCO]	17.7	18.2		16.7		17.2		17.8
T_{2u}	ν_{13}	[δCMC]	0.3	0.3		0.3		0.3		0.3

			M = Co	M = Rh	M = Ir		M = Pt	M = Au
			calc.	calc.	exp.[c]	calc.	calc.	calc.
A_{1g}	ν_1	[CO]	52.1	53.1	54	53.8	53.3	51.3
A_{1g}	ν_2	[MC]	5.5	6.0		6.5	5.8	4.3
E_g	ν_3	[CO]	51.5	51.9	54	52.3	52.5	50.9
E_g	ν_4	[MC]	5.4	5.7		6.1	5.4	3.5
T_{1g}	ν_5	[δMCO]	9.7	9.3		9.7	9.2	8.6
T_{1u}	ν_6	[CO]	50.7	50.6	51	50.7	51.5	50.7
T_{1u}	ν_7	[δMCO]	12.2	15.0	18	17.3	15.5	13.2
T_{1u}	ν_8	[MC]	6.2	4.6		4.4	4.3	3.5
T_{1u}	ν_9	[δCMC]	0.4	0.3		0.2	0.1	0.2
T_{2g}	ν_{10}	[δMCO]	16.9	15.4		16.0	14.7	12.6
T_{2g}	ν_{11}	[δCMC]	0.3	0.4		0.4	0.4	0.4
T_{2u}	ν_{12}	[δMCO]	14.9	15.7		16.8	15.2	12.5
T_{2u}	ν_{13}	[δCMC]	0.4	0.3		0.4	0.4	0.4

[a] Calculated values at BP86/ECP2. [b] Reference 54. [c] Reference 52.

Figure Captions for Supplementary Material

Figure S1. BP86/ECP1 and BP86/ECP2 versus BP86/AE1 and BP86/AE2 force constants for the 3d complexes $[M(CO)_6]^n$ (M = V, Cr, Mn, Fe; n = -1 to 2, respectively), $M(CO)_5$, and $Ni(CO)_4$, in the region between 14.0 and 20.0 mdyn/Å (C-O stretches). The correlation line with unit slope is shown. See text for units.

Figure S2. BP86/ECP1 and BP86/ECP2 versus BP86/AE1 and BP86/AE2 force constants for the 3d complexes $[M(CO)_6]^n$ (M = V, Cr, Mn, Fe; n = -1 to 2, respectively), $M(CO)_5$, and $Ni(CO)_4$, in the region between -0.5 and 4.0 mdyn/Å (M-C stretches, all bends and coupling constants). The correlation line with unit slope is shown. See text for units.

Figure S3. BP86/ECP1 versus MP2/ECP1 force constants for all neutral 4d and 5d carbonyls, in the region between 15.5 and 17.5 mdyn/Å (C-O stretches). The correlation line with unit slope is shown. See text for units.

Figure S4. BP86/ECP1 versus MP2/ECP1 force constants for all neutral 4d and 5d carbonyls, in the region between -0.5 and 4.5 mdyn/Å (M-C stretches, all bends and coupling constants). The correlation line with unit slope is shown. See text for units.

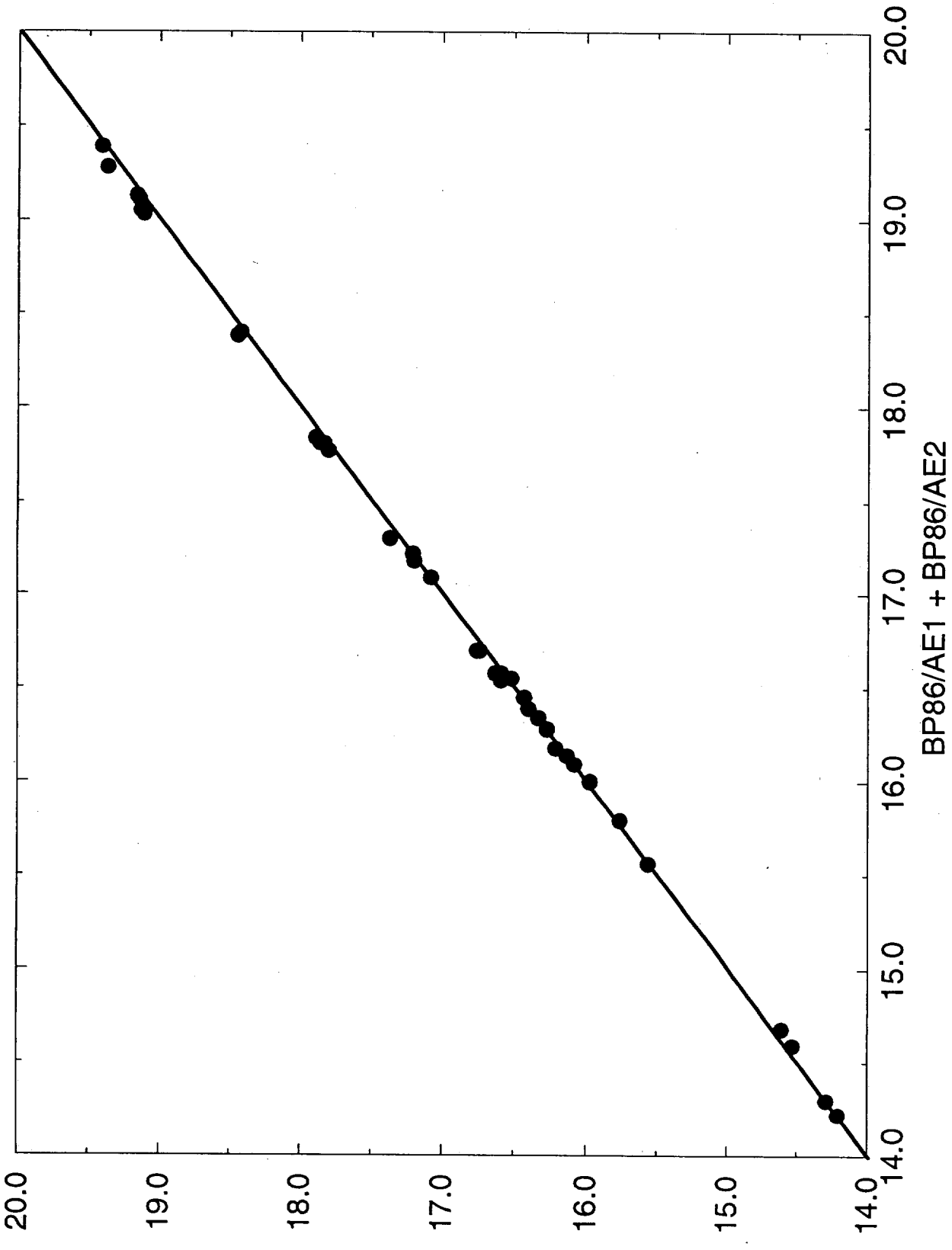


Figure S1

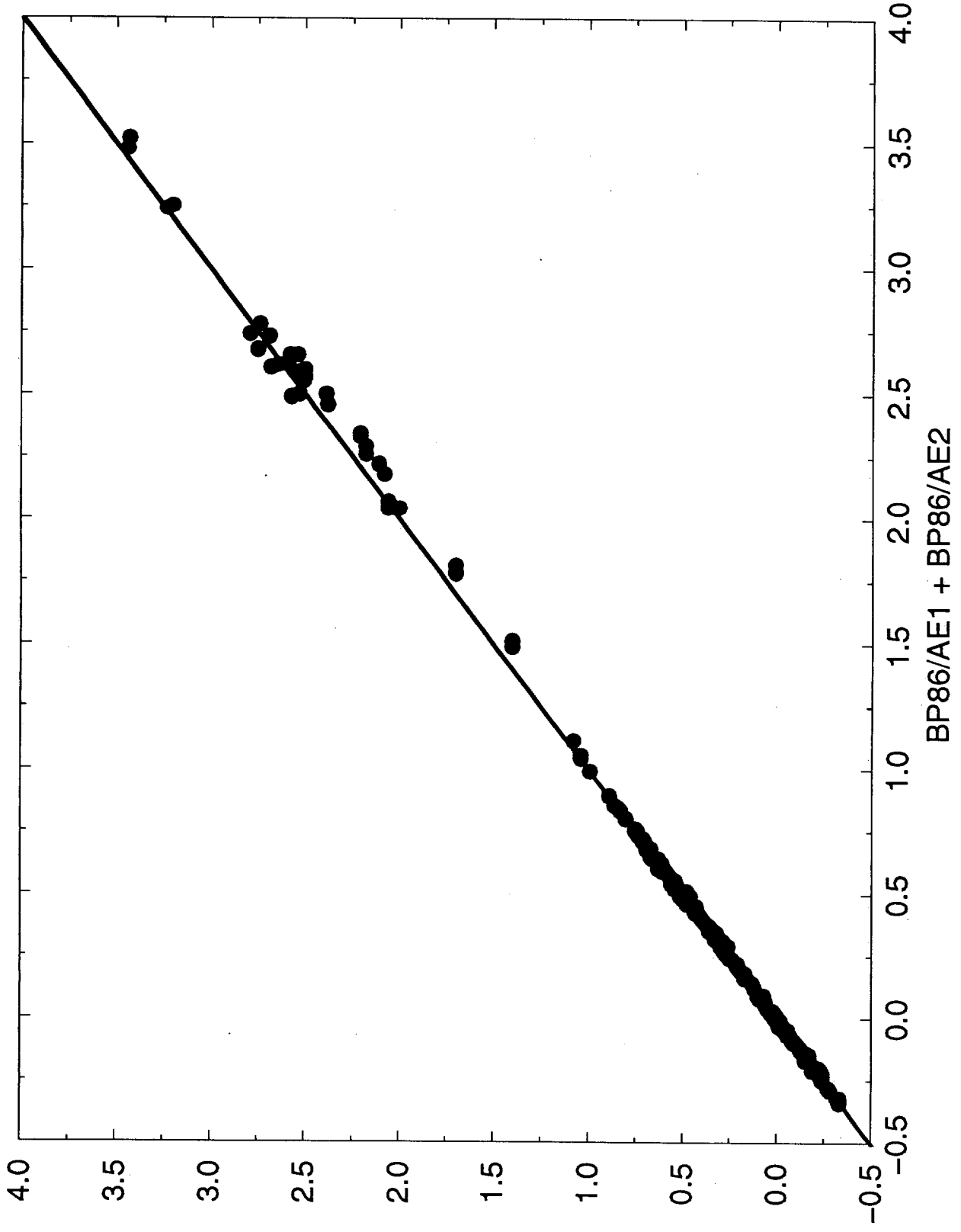

BP86/ECP1 + BP86/ECP2
BP86/AE1 + BP86/AE2
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5

Figure S2

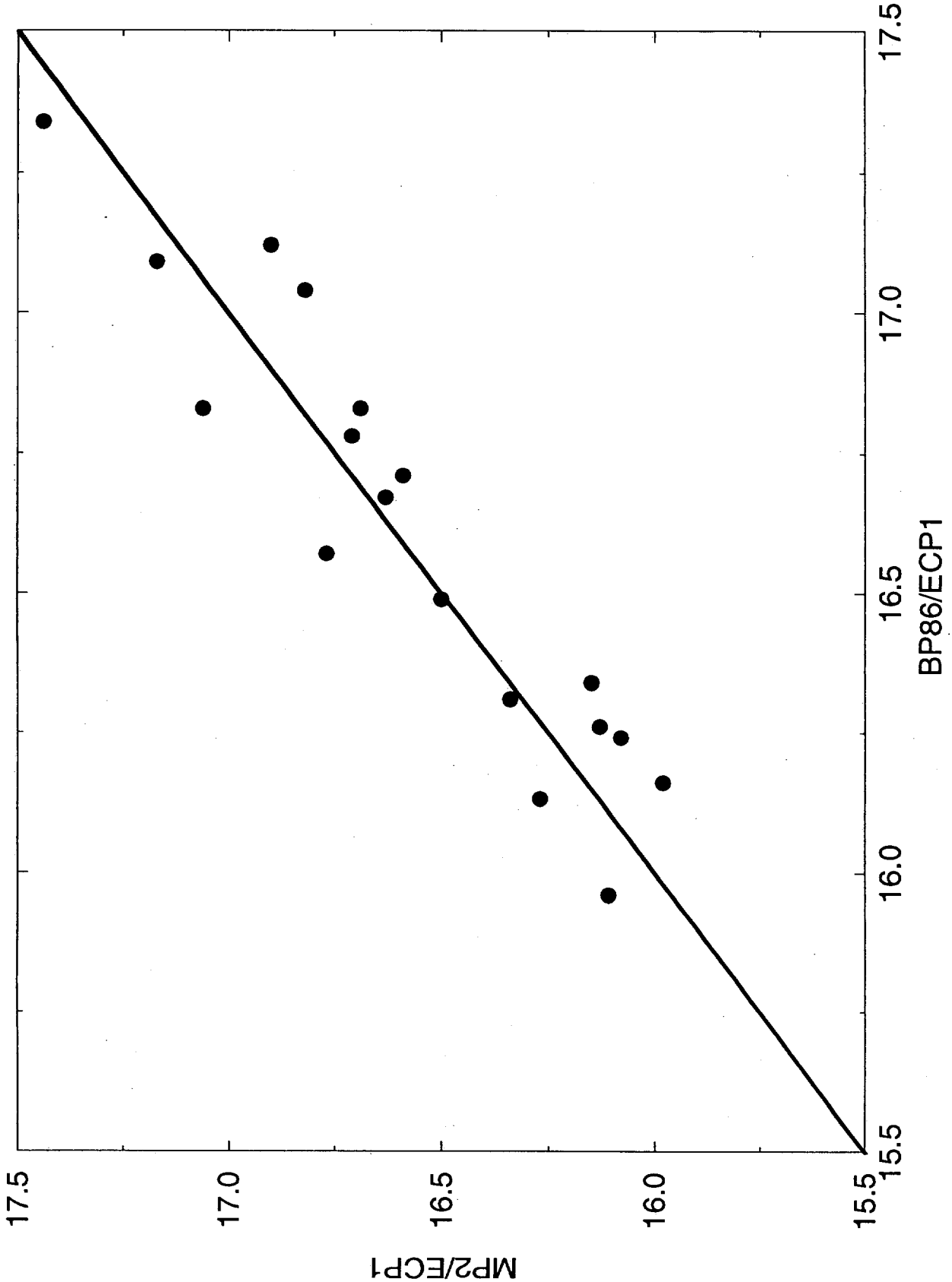


Figure S3

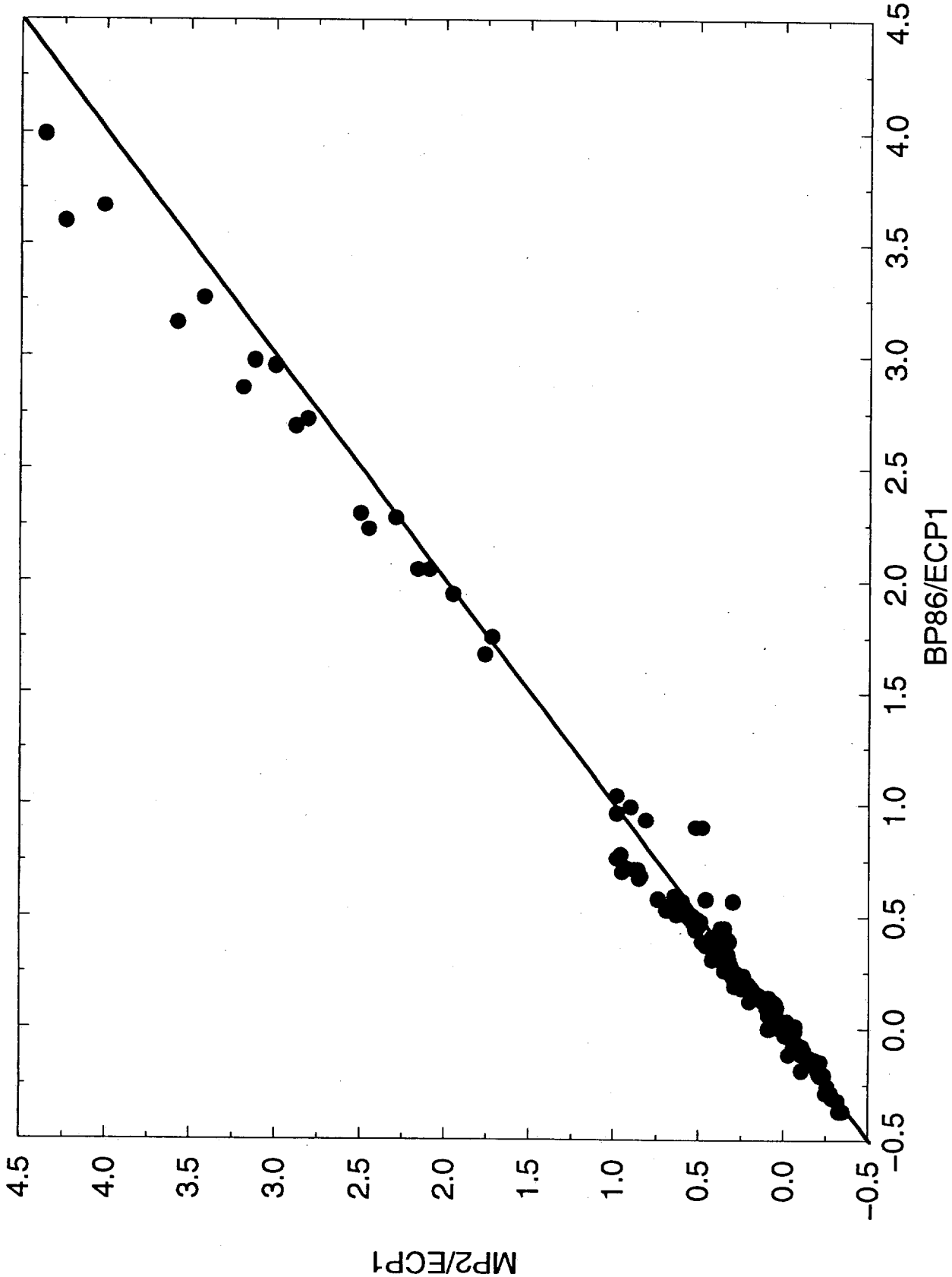


Figure S4