Supporting Information

Central-metal effect on intramolecular vibrational energy transfer of $M(CO)_5Br$ (M = Mn, Re) probed by two-dimensional infrared spectroscopy

Fan Yang[†], Xueqian Dong[†‡], Minjun Feng[†‡], Juan Zhao[†‡*], Jianping Wang[†‡]*

[†] *Beijing National Laboratory for Molecular Sciences; Molecular Reaction Dynamics Laboratory, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China*

[‡] *University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

[*]Author to whom correspondences should be addressed.

Tel: (+86)-010-62563565; Fax: (+86)-010-62563167; E-mail: yangfan@iccas.ac.cn, zhaojuan@iccas.ac.cn

Table S1. Calculated harmonic frequencies (ω, in cm^{-1}), anharmonic frequencies (ν, in cm^{-1}) and transition intensities (I, in KM/mole) of the C≡O stretching modes in $Mn(CO)_5$ Br and $Re(CO)_5Br$ in gas phase.

mode	$Mn(CO)_5Br$					$Re(CO)_5Br$				
	ω	ν	$\Delta\omega_{A1-E}$	$\Delta\nu_{A1-E}$	I	ω	ν	$\Delta\omega_{A1-E}$	$\Delta\nu_{A1-E}$	I
A_1	2090.8	2064.9	39.0	39.3	817.4	2060.2	2032.1	52.1	54.5	1034.7
E	2129.8	2104.2			1275.9	2112.3	2086.6			1614.0
E	2129.8	2104.2			1275.9	2112.3	2086.6			1614.0
B_2	2144.6	2117.8			0	2142.3	2115.3			0
$A_1^{(2)}$	2198.0	2169.8			87.9	2212.2	2182.6			38.7

Table S2. Calculated harmonic frequencies (ω, cm^{-1}) and transition intensities (I, in KM/mole) of all vibrations of $Mn(CO)_5Br$ in gas phase and in two implicit solvents using PCM solvent model.

mode	gas		CCl_4		DMSO	
	ω	I	ω	I	ω	I
B_2	71.2	0.00	61.5	0.00	64.0	0.00
E	71.2	0.38	67.8	0.60	68.1	1.00
E	71.2	0.38	67.8	0.60	68.1	1.00
E	96.1	0.00	93.4	0.04	93.9	0.18
E	96.1	0.00	93.4	0.04	93.9	0.18
B1	100.2	0.00	100.3	0.00	101.1	0.00
A_1	113.4	1.14	112.0	1.8	109.4	3.02
E	116.3	1.67	116.3	2.17	117.5	2.92
E	116.3	1.67	116.3	2.17	117.5	2.92
A_1	220.5	8.78	215.2	13.6	206.1	22.38
A_2	368.9	0.00	363.5	0.00	362.7	0.00
A_1	374.9	0.59	373.3	0.76	372.1	0.89
B_2	381.9	0.00	377.7	0.00	375.1	0.00
E	412.7	17.96	406.6	21.26	403.8	41.65
E	412.7	17.96	406.6	21.26	403.8	41.65
E	424.5	14.67	419.6	24.59	417.2	29.60
E	424.5	14.67	419.6	24.59	417.2	29.60
A_1	475.9	0.43	470.4	1.17	463.5	2.08
B_2	513.8	0.00	507.9	0.00	513.3	0.00
B_1	563.3	0.00	560.1	0.00	513.3	0.00
E	566.8	1.31	560.1	1.88	558.4	4.02
E	566.8	1.31	560.1	1.88	558.4	4.02
E	664.7	127.41	659.7	166.07	652.1	240.42
E	664.7	127.41	659.7	166.07	652.1	240.42
A_1	669.7	188.30	664.8	245.01	658.3	338.84
A_1	2090.8	817.32	2081.3	1053.72	2076.0	1367.92
E	2129.8	1275.89	2119.4	1657.43	2104.8	2315.25
E	2129.8	1275.89	2119.4	1657.43	2104.8	2315.25
B_2	2144.7	0.00	2137.7	0.00	2129.9	0.00
$A_1^{(2)}$	2198.0	87.92	2197.3	125.29	2196.7	181.53

Table S3. Calculated harmonic frequencies (ω, cm^{-1}) and transition intensities (I, in KM/mole) of all vibrations of $Re(CO)_5Br$ in gas phase and in two implicit solvents using PCM solvent model.

mode	gas		CCl_4		DMSO	
	ω	I	ω	I	ω	I
B_2	65.6	0.00	63.8	0.00	64.1	0.00
E	65.8	0.03	64.9	0.08	64.5	0.27
E	65.8	0.03	64.9	0.08	64.5	0.27
E	88.8	0.01	89.1	0.00	89.1	0.00
E	88.8	0.01	89.1	0.00	89.1	0.00
A_1	94.1	0.35	94.2	0.58	93.0	0.88
B_1	95.9	0.00	97.9	0.00	98.2	0.00
E	101.9	0.71	103.3	0.90	104.5	1.12
E	101.9	0.71	103.3	0.90	104.5	1.12
A_1	201.1	7.50	196.1	11.3	188.3	18.3
E	361.9	63.11	357.2	89.6	351.1	139.00
E	361.9	63.11	357.2	89.6	351.1	139.00
A_2	376.0	0.00	372.7	0.00	373.2	0.00
E	427.6	0.30	424.6	0.49	422.66	0.89
E	427.6	0.30	424.6	0.49	422.66	0.89
B_2	434.9	0.00	431.7	0.00	430.3	0.00
A_1	448.3	1.96	447.3	3.14	445.6	5.59
A_1	490.3	3.83	491.3	5.72	490.1	7.93
B_1	518.8	0.00	519.3	0.00	516.3	0.00
B_2	546.6	0.00	546.3	0.00	548.7	0.00
E	570.8	0.05	570.5	0.34	569.9	1.47
E	570.8	0.05	570.5	0.34	569.9	1.47
E	613.2	68.66	611.6	89.3	607.6	135.6
E	613.2	68.66	611.6	89.3	607.6	135.6
A_1	620.7	116.29	619.2	154.7	616.2	227.69
A_1	2060.2	817.32	2044.8	1389.36	2030.2	1927.46
E	2112.3	1614.03	2099.0	2169.51	2079.2	3165.58
E	2112.3	1614.03	2099.0	2169.51	2079.2	3165.58
B_2	2142.3	0.00	2134.0	0.00	2124.2	0.00
$A_1^{(2)}$	2212.1	38.66	2211.8	57.65	2210.2	83.84

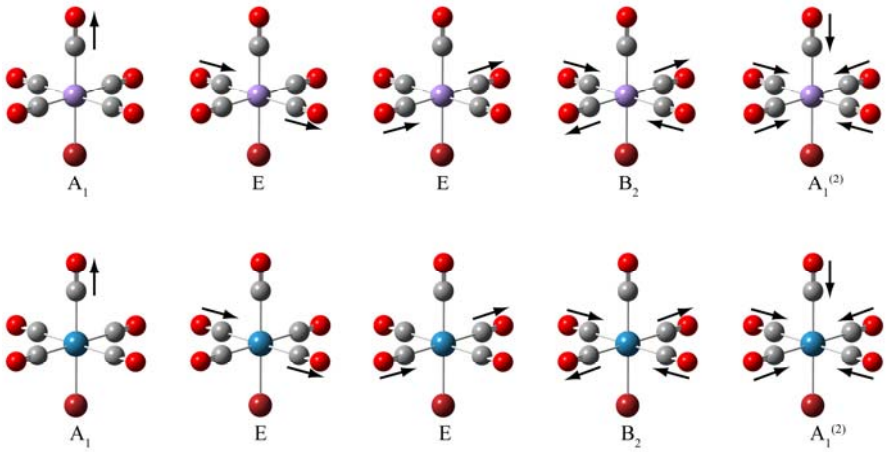

Figure S1. The C≡O stretching normal modes of $Mn(CO)_5Br$ (Top) and $Re(CO)_5Br$ (Bottom) for comparison and are arranged from low- to high-frequency in vibration (from left to right). Their vibrational frequencies are listed in Table S1.

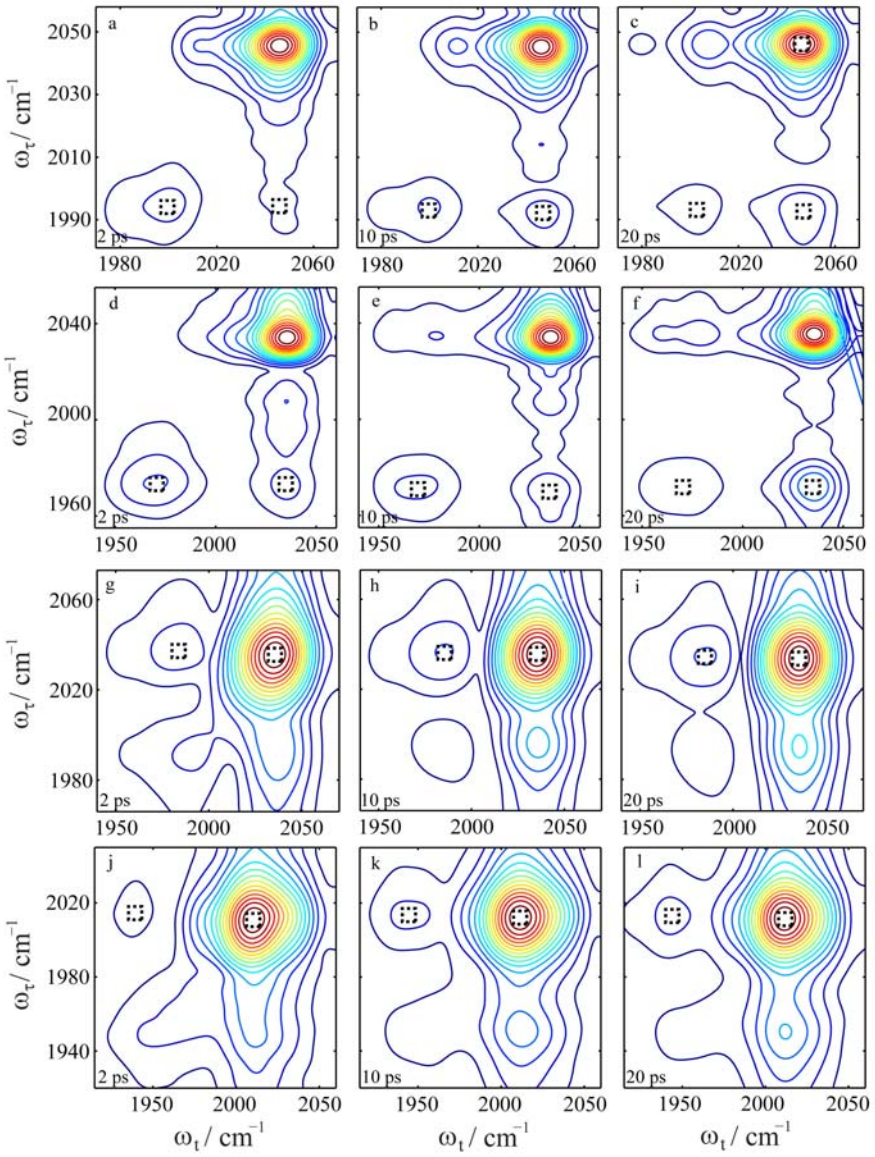

Figure S2. Representative waiting time-dependent absolute non-rephasing 2D IR spectra of $Mn(CO)_5Br$ in CCl_4 (a-c), $Re(CO)_5Br$ in CCl_4 (d-f), $Mn(CO)_5Br$ in DMSO (g-i) and $Re(CO)_5Br$ in DMSO (j-l) in the frequency region of the CO stretching. T_w (2 ps, 10 ps and 20 ps) from left to right are marked in each case.

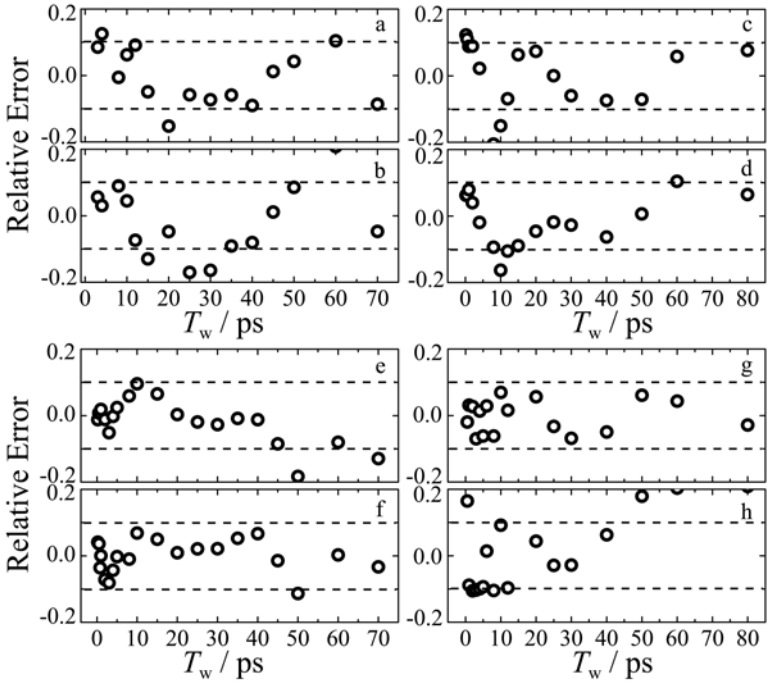

Figure S3. Ratio of residual and peak amplitude obtained in Fig. 3 as a function of the waiting time. Dashed lines indicate ±10 % limit.