Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Low-lying states of MX_2 (M=Ag, Au; X=Cl, Br and I) with coupled-cluster approaches: effect of basis set, high level correlation and spin-orbit coupling

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Table S1 Vertical excitation energies in scalar-relativistic calculations (in eV) at the equilibrium structure of the $^1\Sigma_g^+$ state of MX_2^-

State	CCSD	CCSD(T)	EOMIP	Calc.[1]	State	CCSD	CCSD(T)	EOMIP	Calc.[2]
		$AgCl_2$					$AuCl_2$		
$^2\Pi_g$					$^2\Pi_g$				
$^2\Sigma_g^+$	0.009	0.156	0.136	-0.124	$^2\Sigma_g^+$	0.360	0.537	0.565	0.489
$^2\Pi_u$	0.846	0.862	0.890	1.017	$^2\Pi_u$	1.602	1.514	1.611	1.445
$^2\Sigma_u^+$	0.996	1.099	1.140	1.245	$^2\Delta_g$	1.408	1.604	1.727	
$^2\Delta_g$	1.918	2.163	2.315	2.144	$^2\Sigma_u^+$	1.736	1.794	1.875	1.763
		$AgBr_2$					$AuBr_2$		
$^2\Pi_g$					$^2\Pi_g$				
$^2\Sigma_g^+$	0.331	0.436	0.424	0.263	$^2\Sigma_g^+$	0.574	0.761	0.798	0.718
$^2\Pi_u$	0.652	0.663	0.682	0.654	$^2\Pi_u$	1.206	1.166	1.244	1.108
$^2\Sigma_u^+$	0.815	0.909	0.943	0.875	$^2\Sigma_u^+$	1.352	1.450	1.512	1.414
$^2\Delta_g$	2.243	2.455	2.651	2.641	$^2\Delta_g$	1.551	1.764	1.910	
		AgI_2					AuI_2		
$^2\Pi_g$					$^2\Pi_g$				
$^2\Pi_u$	0.501	0.501	0.516	0.486	$^2\Pi_u$	0.880	0.861	0.908	0.823
$^2\Sigma_u^+$	0.648	0.730	0.757	0.697	$^2\Sigma_u^+$	0.996	1.112	1.139	1.099
$^2\Sigma_g^+$	0.719	0.775	0.762	0.642	$^2\Sigma_g^+$	0.969	1.148	1.145	1.120
$^2\Delta_g$	2.717	2.903	3.129	3.190	$^2\Delta_g$	1.895	2.114	2.242	

Table S2 Vertical excitation energies in scalar-relativistic calculations (in eV) at the equilibrium structure of the $^2\Pi_g$ state of MX_2

State	CCSD	CCSD(T)	EOMIP	Calc.[3,4]	State	CCSD	CCSD(T)	EOMIP
			$AgCl_2$				$AuCl_2$	
$^2\Pi_g$					$^2\Pi_g$			
$^2\Sigma_g^+$	0.011	0.160	0.154	0.204	$^2\Sigma_g^+$	0.578	0.747	0.752
$^2\Pi_u$	1.170	1.155	1.224		$^2\Pi_u$	1.675	1.862	1.949
$^2\Sigma_u^+$	1.306	1.376	1.446		$^2\Delta_g$	1.988	1.879	1.983
$^2\Delta_g$	2.013	2.249	2.388	2.265	$^2\Sigma_u^+$	2.115	2.143	2.221
			$AgBr_2$				$AuBr_2$	
$^2\Pi_g$					$^2\Pi_g$			
$^2\Sigma_g^+$	0.343	0.466	0.445		$^2\Sigma_g^+$	0.767	0.945	0.958
$^2\Pi_u$	0.856	0.863	0.888		$^2\Pi_u$	1.501	1.442	1.521
$^2\Sigma_u^+$	1.013	1.101	1.131		$^2\Sigma_u^+$	1.646	1.717	1.772
$^2\Delta_g$	2.295	2.517	2.675		$^2\Delta_g$	1.776	1.978	2.086
			AgI_2				AuI_2	
$^2\Pi_g$					$^2\Pi_g$			
$^2\Pi_u$	0.611	0.609	0.627		$^2\Pi_u$	1.042	1.013	1.067
$^2\Sigma_u^+$	0.752	0.830	0.854		$^2\Sigma_u^+$	1.111	1.284	1.270
$^2\Sigma_g^+$	0.755	0.823	0.800	0.926	$^2\Sigma_g^+$	1.156	1.255	1.284
$^2\Delta_g$	2.757	2.951	3.144	3.244	$^2\Delta_g$	2.053	2.267	2.370

Table S3 Vertical excitation energies and composition of the SO eigenstates in terms of SO-free states for MX_2 at the equilibrium structure of the $^2\Pi_g$ state. All energies are in eV.

State	Composition	Calc.	Calc.[3-5]	State	Composition	Calc.	Expt.[6]
$AgCl_2$				$AuCl_2$			
3/2g	$^2\Pi_{g(0.93)}$			3/2g	$^2\Pi_{g(0.91)}\,^2\Delta_{g(0.02)}$		
1/2g	$^2\Pi_{g(0.73)}\,^2\Sigma_g^{+}{}_{(0.21)}$	0.02	0.06	1/2g	$^2\Pi_{g(0.78)}\,^2\Sigma_g^{+}{}_{(0.16)}$	0.20	0.23
1/2g	$^2\Sigma_g^{+}{}_{(0.73)}\,^2\Pi_{g(0.21)}$	0.23	0.47	1/2g	$^2\Sigma_g^{+}{}_{(0.77)}\,^2\Pi_{g(0.18)}$	1.09	0.99
3/2u	$^2\Pi_{u(0.94)}$	1.25		5/2g	$^2\Delta_{g(0.93)}$	1.57	1.44
1/2u	$^2\Pi_{u(0.93)}$	1.26		3/2u	$^2\Pi_{u(0.93)}$	2.18	1.57
1/2u	$^2\Sigma_u^{+}{}_{(0.93)}$	1.48		1/2u	$^2\Pi_{u(0.87)}\,^2\Sigma_u^{+}{}_{(0.06)}$	2.19	
5/2g	$^2\Delta_{g(0.93)}$	2.23	2.15	1/2u	$^2\Sigma_u^{+}{}_{(0.85)}\,^2\Pi_{u(0.08)}$	2.47	
3/2g	$^2\Delta_{g(0.87)}\,^2\Pi_{g(0.06)}$	2.61	2.51	3/2g	$^2\Delta_{g(0.80)}\,^2\Pi_{g(0.13)}$	2.71	
3/2g	$^2\Pi_{g(0.87)}\,^2\Delta_{g(0.06)}$	3.33		3/2g	$^2\Pi_{g(0.82)}\,^2\Delta_{g(0.10)}$	4.02	
$AgBr_2$				$AuBr_2$			
3/2g	$^2\Pi_{g(0.94)}$			3/2g	$^2\Pi_{g(0.92)}\,^2\Delta_{g(0.02)}$		
1/2g	$^2\Pi_{g(0.91)}\,^2\Sigma_g^{+}{}_{(0.03)}$	0.29	0.29	1/2g	$^2\Pi_{g(0.85)}\,^2\Sigma_g^{+}{}_{(0.09)}$	0.40	0.35
1/2g	$^2\Sigma_g^{+}{}_{(0.91)}\,^2\Pi_{g(0.03)}$	0.60	0.66	1/2g	$^2\Sigma_g^{+}{}_{(0.84)}\,^2\Pi_{g(0.10)}$	1.25	1.03
3/2u	$^2\Pi_{u(0.94)}$	0.89	0.46	3/2u	$^2\Pi_{u(0.94)}$	1.64	1.26
1/2u	$^2\Pi_{u(0.58)}\,^2\Sigma_u^{+}{}_{(0.37)}$	1.03	0.60	1/2u	$^2\Pi_{u(0.61)}\,^2\Sigma_u^{+}{}_{(0.33)}$	1.85	1.50
1/2u	$^2\Sigma_u^{+}{}_{(0.57)}\,^2\Pi_{u(0.38)}$	1.45	1.03	5/2g	$^2\Delta_{g(0.93)}$	1.77	
5/2g	$^2\Delta_{g(0.92)}$	2.63	2.42	1/2u	$^2\Sigma_u^{+}{}_{(0.62)}\,^2\Pi_{u(0.33)}$	2.18	
3/2g	$^2\Delta_{g(0.76)}\,^2\Pi_{g(0.16)}$	2.97	2.85	3/2g	$^2\Delta_{g(0.69)}\,^2\Pi_{g(0.24)}$	2.77	
3/2g	$^2\Pi_{g(0.76)}\,^2\Delta_{g(0.16)}$	3.46		3/2g	$^2\Pi_{g(0.70)}\,^2\Delta_{g(0.22)}$	3.85	
AgI_2				AuI_2			
3/2g	$^2\Pi_{g(0.94)}$			3/2g	$^2\Pi_{g(0.93)}\,^2\Delta_{g(0.01)}$		
1/2g	$^2\Pi_{g(0.81)}\,^2\Sigma_g^{+}{}_{(0.13)}$	0.51	0.53	1/2g	$^2\Pi_{g(0.91)}\,^2\Sigma_g^{+}{}_{(0.04)}$	0.64	0.62
3/2u	$^2\Pi_{u(0.95)}$	0.63		3/2u	$^2\Pi_{u(0.94)}$	1.12	0.90
1/2u	$^2\Sigma_u^{+}{}_{(0.51)}\,^2\Pi_{u(0.44)}$	0.76		1/2u	$^2\Sigma_u^{+}{}_{(0.51)}\,^2\Pi_{u(0.43)}$	1.32	1.13
1/2g	$^2\Sigma_g^{+}{}_{(0.80)}\,^2\Pi_{g(0.14)}$	1.18	1.40	1/2g	$^2\Sigma_g^{+}{}_{(0.90)}\,^2\Pi_{g(0.04)}$	1.55	1.44
1/2u	$^2\Pi_{u(0.52)}\,^2\Sigma_u^{+}{}_{(0.42)}$	1.65		1/2u	$^2\Pi_{u(0.53)}\,^2\Sigma_u^{+}{}_{(0.41)}$	2.13	1.98
5/2g	$^2\Delta_{g(0.91)}$	3.24	3.37	5/2g	$^2\Delta_{g(0.92)}$	2.13	
3/2g	$^2\Pi_{g(0.58)}\,^2\Delta_{g(0.33)}$	3.92		3/2g	$^2\Pi_{g(0.52)}\,^2\Delta_{g(0.39)}$	3.96	
3/2g	$^2\Delta_{g(0.58)}\,^2\Pi_{g(0.33)}$	3.51	3.78	3/2g	$^2\Delta_{g(0.52)}\,^2\Pi_{g(0.40)}$	2.92	

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