Bending Ternary Dihalides
A Single Functional Form For Linearization Energies

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Introduction

Although the bonding in the symmetric groups 2 and 12 dihalides (MX_2) has been studied extensively[1,2], remarkably little work – experimental or theoretical – has been done on the mixed (ternary) dihalides, MXY.

Previously, a criterion[3,4] based on atomic softness (σ) was proposed for the bending of MX_2 and MXY molecules. We extend this softness criterion on the slate of the mixed dihalides and the predicted separation is achieved between the bent and linear structures with almost the same cutoff, and with quasilinear species straddling the boundary.

In this work, we report a complete assessment of the bonding preferences and vibrational frequencies of the mixed dihalides of the groups 2 and 12 metals MX_2 and MXY.

Computational Methods

The molecular geometries and harmonic vibrational frequency data for all systems considered in this work been examined at the B3PW91, MP2(full), and CCSD(t) levels using Gaussian 09. cc-pV5Z[5] basis sets were employed for all elements preceding Br. Small core MDF pseudopotentials were used for heavier elements, along with the corresponding quintuple zeta basis sets for valence electrons. The barrier to linearization has been computed as:

$$E_{barrier} = E_{linear} - E_{bent}$$

References

1. Hargittai, M. The molecular geometry of gas phase metal-halides *Coord. Chem. Rev.* **1988**, *91*, 35-88.
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3. von Szentpály, L.; Schwerdtfeger, P. Which double-octet ABC molecules are bent? *Chem. Phys. Lett.* **1990**, *170*, 555-560.
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Key Observations

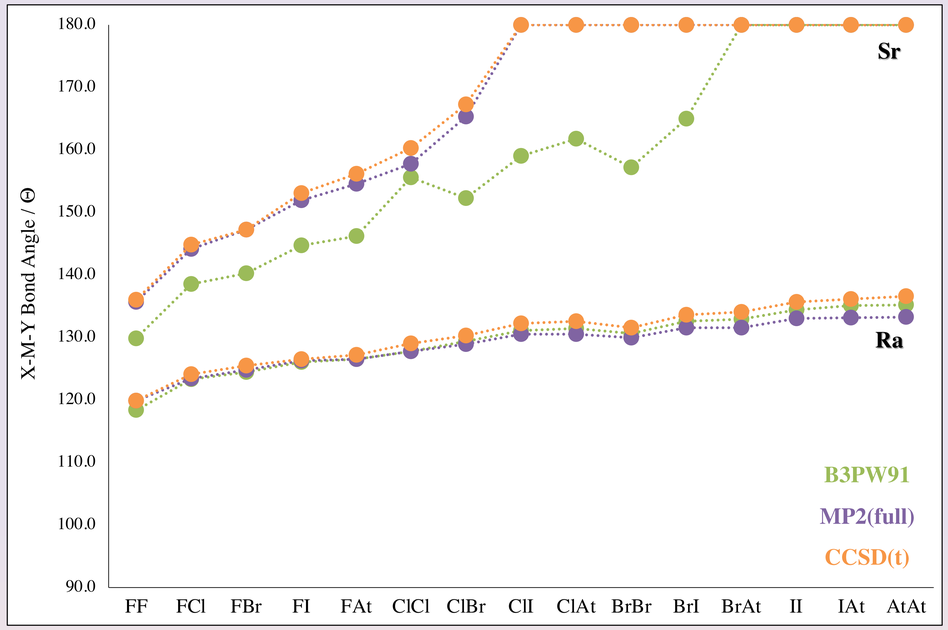

Figure 1. Computed bond angles at the B3PW91, MP2(full), and CCSD(T) levels for M = Sr, and Ra. All M = Be, Mg, Zn, Cd and Hg systems are linear. For M = Ca, only the difluoride is bent for the ab initio methods. At the B3PW91 level, CaFCl and CaFBr are also bent with very shallow minima. The data tracks closely for all methods for M = Ba as they do for M = Ra.

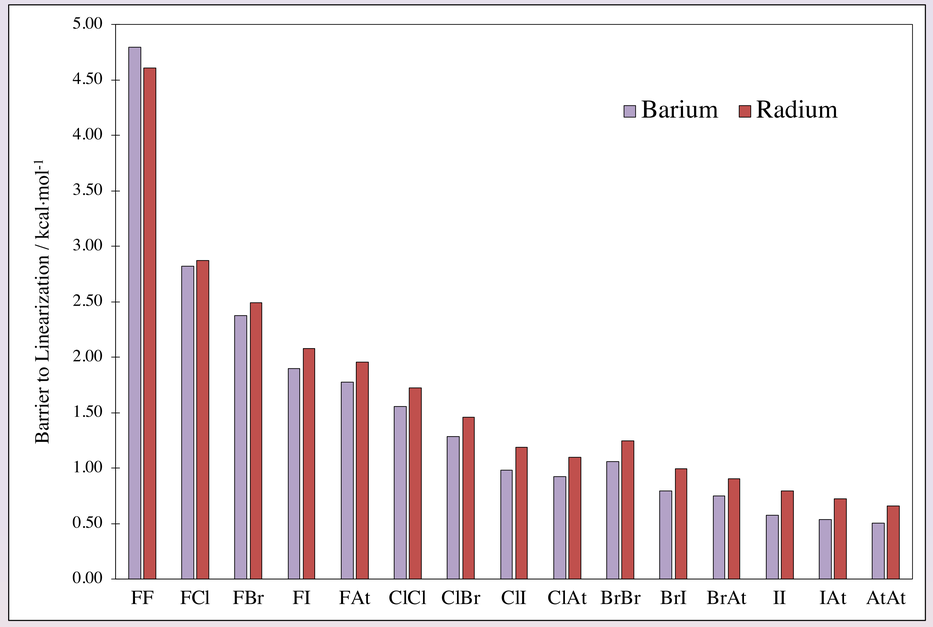

Figure 2. Barriers to linearization at the CCSD(T) level for the Ba and Ra dihalides. For the Sr and Ca systems that are bent the well depths in kcal·mol^{-1} units are as follows: for SrFY: 1.54, 0.50, 0.31, 0.15, and 0.09, for Y = F, Cl, Br, I, and At, with 0.04 for $SrCl_2$, and 0.00 for SrClBr. For CaF_2, we obtained a barrier of 0.07 kcal·mol^{-1}.

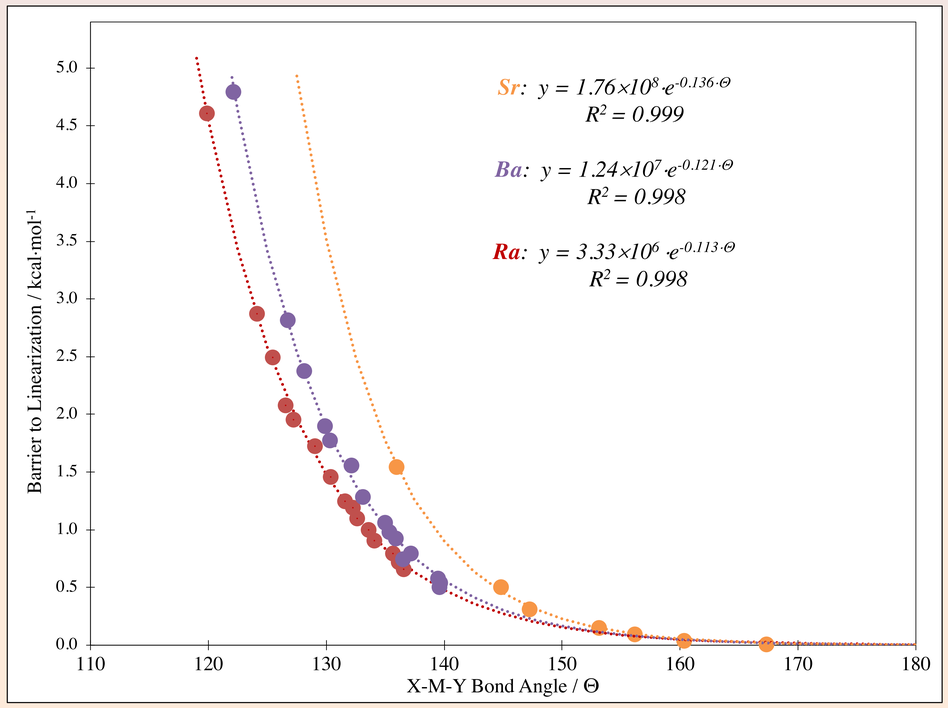

Figure 3. A representation of the relationship between bond angle and the energy barriers to linearization, $E_{barrier}$, for the bent group 2 binary and ternary dihalides of Sr, Ba, and Ra at the CCSD(T) level of theory.

MXY	Be	Mg	Ca	Sr	Ba	Ra	Zn	Cd	Hg
F_2	0.190	0.266	0.332	0.366	0.395	0.429	0.224	0.224	0.230
FCl	0.160	0.236	0.302	0.336	0.365	0.399	0.194	0.194	0.200
FBr	0.149	0.225	0.291	0.325	0.354	0.388	0.183	0.183	0.189
FI	0.139	0.215	0.281	0.315	0.344	0.378	0.173	0.173	0.179
FAt	0.147	0.223	0.289	0.323	0.352	0.386	0.181	0.181	0.187
Cl_2	0.129	0.205	0.271	0.305	0.334	0.368	0.163	0.163	0.169
ClBr	0.119	0.195	0.261	0.295	0.324	0.358	0.153	0.153	0.159
ClI	0.109	0.185	0.251	0.285	0.314	0.348	0.143	0.143	0.149
ClAt	0.117	0.193	0.259	0.293	0.322	0.356	0.151	0.151	0.157
Br_2	0.108	0.184	0.250	0.284	0.313	0.347	0.142	0.142	0.148
BrI	0.098	0.174	0.240	0.274	0.303	0.337	0.132	0.132	0.138
BrAt	0.106	0.182	0.248	0.282	0.311	0.345	0.140	0.140	0.146
I_2	0.088	0.164	0.230	0.264	0.293	0.327	0.122	0.122	0.128
IAt	0.096	0.172	0.238	0.272	0.301	0.335	0.130	0.130	0.136
At_2	0.104	0.180	0.246	0.280	0.309	0.343	0.138	0.138	0.144

Table 1. Softness differences for MXY molecules, where Δσ is the difference between σ_M and the arithmetic mean of σ_X and σ_Y. Orange and white cells indicate systems with bent and linear geometries respectively.