

The Question of Bending of the Alkaline Earth Dihalides MX_2 (M = Be, Mg, Ca, Sr, Ba; X = F, Cl, Br, I). An ab Initio Pseudopotential Study

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Abstract: The geometries of the monomeric alkaline earth dihalides MX_2 (M = Be, Mg, Ca, Sr, Ba; X = F, Cl, Br, I) have been obtained from ab initio pseudopotential calculations at the HF and (for M = Ca, Sr, Ba) SDCI levels. In most cases the calculated MX distances agree well with experimental data. The angles agree with experimentally observed trends and give the first reliable values for several of these molecules. Relatively large bending energies indicate BaF_2 , BaCl_2 , BaBr_2 , and SrF_2 definitely to be nonlinear. At higher computational levels, BaI_2 , SrCl_2 , and CaF_2 also are found to favor bent minima but have very flat potential energy surfaces with regard to the bending motions. SrBr_2 is borderline, while CaCl_2 , CaBr_2 , CaI_2 , and SrI_2 as well as the magnesium and beryllium dihalides are linear. The calculated harmonic vibrational frequencies and force constants confirm these trends and are compared critically to experimental IR and Raman data, where available. Previously uncertain or unknown values are predicted. Bending force constants obtained from a polarized ion model correlate to some extent with the ab initio bending force constants, but there are systematic deviations. These point to covalent bonding contributions, i.e. some p-orbital occupancy for Be and Mg and some d-orbital involvement for Ca, Sr, and Ba. Walsh-type diagrams employing Davidson's "internally consistent" MOs indicate the stabilization of the HOMO upon bending to varying degrees to be an inherent feature of ionic Ca, Sr, and Ba MX_2 compounds. It is concluded that both d-orbital participation and core-polarization make major contributions to the bending.

I. Introduction

Exceptions to well-accepted rules in science frequently stimulate attempts to improve and extend existing models or to create new ones. The bent structures of some monomeric alkaline earth dihalides are unexpected. The rationalization of this behavior poses one of the most intriguing problems in modern inorganic chemistry, as all basic models commonly employed for main group structural chemistry (VSEPR model, Walsh diagrams, as well as simple ionic, MO, and valence-bond models) predict these 16-valence-electron triatomics to be linear.¹

Due to experimental difficulties with the techniques used to study these molecules, the evidence for bent or linear structures can be rather indirect. Exact bending angles and bending energies of the equilibrium structures are hard to obtain. Some of the studies came to conflicting conclusions and confusion about which species actually are linear and which ones are bent.²

The early gas-phase electron-diffraction study by Akishin and Spiridonov³ indicated linear structures for all alkaline earth dihalides (with large error margins for the angles), while subsequent studies disagreed. The M-halogen distances of the Soviet group are still used as the most accurate reference in many cases. The gas-phase electric-deflection work of Klemperer et al.⁴ initiated the discussion. The presence or absence of a permanent dipole moment provided evidence for bent or linear structures: CaF_2 , SrF_2 , SrCl_2 , and the Ba dihalides were indicated to be bent in contrast to all other alkaline earth dihalides studied, which had no dipole moments. However, no well-defined bending angles were obtainable. Moreover, these data pertain to temperatures above 1000 K, where significant populations of excited vibrational levels might give rise to geometries different from the equilibrium structures.^{2c}

Most IR and Raman data for these molecules have been obtained by matrix isolation techniques.^{2,5} The shifts of spectral bands observed in different matrices—even for the magnesium dihalides—indicate that the structure of the molecules in matrix environments may well differ from those of the free molecules. Much of these data do not pertain to free gas-phase species.

Earlier quantum chemical calculations have concentrated on the MX_2 species containing lighter atoms,⁶ as high-quality all-

electron calculations involving the heavier species are much more demanding. Numerous studies of the weakly bent CaF_2 ⁶ and some work on CaCl_2 ^{6f,g} have been published. But we could find no ab initio investigation on any Sr or Ba dihalide in the literature (however, see ref 7). Unfortunately, the extremely shallow bending potential of CaF_2 complicates the calculation of an ac-

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Table I. Valence Basis Set Parameters for F, Cl, Br, and I^a

	F		Cl	
	exponent	coefficient	exponent	coefficient
s	7.176 439	-0.239 883	13.332 405	-0.021 349
	3.815 484	0.152 026	2.333 630	0.293 985
	1.027 882	0.613 709	0.526 463	-0.653 428
	0.336 128	0.444 081	0.190 949	-0.535 193
	0.090	1.0	0.059	1.0
p	22.095 207	0.052 266	2.750 936	-0.071 059
	4.968 093	0.234 517	1.135 974	0.221 671
	1.362 114	0.502 265	0.425 235	0.557 456
	0.353 321	0.461 409	0.142 449	0.390 807
	0.090	1.0	0.044	1.0
	Br		I	
	exponent	coefficient	exponent	coefficient
s	4.473 180	0.149 091	2.996 122	0.198 187
	2.299 839	-0.502 322	1.530 043	-0.616 536
	0.411 717	0.727 144	0.304 979	0.730 627
	0.159 334	0.480 406	0.129 969	0.513 428
	0.051	1.0	0.052	1.0
p	1.991 084	-0.165 882	1.034 919	-0.340 155
	0.974 751	0.204 327	0.573 833	0.441 884
	0.352 023	0.601 563	0.203 063	0.604 344
	0.116 653	0.404 562	0.079 099	0.288 949
	0.038	1.0	0.029	1.0

^aOptimized for the quasirelativistic 7-valence-electron pseudopotentials of ref 12.

curate geometry. Even the highest levels of theory employed to date disagree concerning the equilibrium structure of CaF_2 .^{6e-h} In contrast, some Sr and Ba halides should be bent to a greater extent. This should allow the determination of accurate bending angles and bending energies.

We have recently employed a quasirelativistic pseudopotential approach for compounds of Ca, Sr, and Ba that treats the outermost 10 electrons of the alkaline earth atom explicitly.⁸ Such calculations should be of comparable accuracy or, due to the inclusion of major relativistic effects in the pseudopotentials, perhaps even of higher accuracy than high-level all-electron calculations. Our application to CaH_2 , SrH_2 , and BaH_2 confirmed that the bending effects increase when the heavier alkaline earth elements are involved.⁸ While CaH_2 is found to be linear with a flat bending potential, SrH_2 and particularly BaH_2 are significantly bent. The analysis of results using polarized-core 2-valence-electron pseudopotentials indicated that both core-polarization effects and the participation of metal d-orbitals in small (but important) covalent bonding contributions are responsible for the bent geometries.⁸

We now apply the 10-valence-electron pseudopotential approach to calculate the geometries, energy changes upon bending, and vibrational frequencies of the Ca, Sr, and Ba dihalides. The use of quasirelativistic 7-valence-electron pseudopotentials for F, Cl, Br, and I allows the treatment of all molecules as 24-electron systems. For comparison, calculations have also been performed on the dihalides of Be and Mg. We intend to provide a comprehensive set of ab initio geometries and vibrational frequencies of all the alkaline earth dihalides for the first time (except for Ra and At compounds). A major additional aim is the study of the electronic structure of the dihalides and the elucidation of the factors associated with the bending tendencies.

Bending force constants obtained from a simple polarized ion model are compared to the ab initio results. Walsh diagrams constructed from MOs that satisfy the "internally consistent SCF equations" formulated by Davidson et al.⁹ and natural bond orbital population analyses¹⁰ are employed to investigate the electronic

Table II. CaX Distances (Å), XCax Bending Angles (deg), Bending Energies ΔE_b (kcal/mol), and Bond Contraction upon Bending ΔR_b (Å) of the Ca Dihalides at different Levels of Theory^a and Comparison to Experimental Data

	SDCI+Q/			exp
	SCF/2d	SCF/5d	5d1f	
CaF_2				
R-CaF	2.037	2.029	2.010	2.10 (3) ^b
angle	linear	162.3	157.5	142 (1) ^c
ΔE_b		0.06	0.19	
ΔR_b		0.004	0.004	
$CaCl_2$				
R-CaCl	2.507	2.506	2.482	2.51 (3), ^b 2.483 (7) ^d
angle	linear	linear	linear	linear
$CaBr_2$				
R-CaBr	2.663	2.660	2.638	2.67 (3), ^b 2.616 (16) ^d
angle	linear	linear	linear	linear
CaI_2				
R-CaI	2.895	2.894	2.865	2.88 (3), ^b 2.840 (10) ^d
angle	linear	linear	linear	linear

^aThe 10-valence-electron pseudopotential for Ca has been employed with a 6s6p5d basis set either contracted to 6s6p2d (SCF/2d) or uncontracted (SCF/5d). For the SDCI calculations one set of f functions was added (SDCI+Q/5d1f). ^bCf. ref 3. ^cThe bending angle for CaF_2 has been obtained by Ramondo et al. (ref 5e,f) from IR spectra in an argon matrix. ^dCf. ref 30 (a more recent study).

structure of the alkaline earth dihalides. Schwerdtfeger and Szentpály recently^{6e} employed the difference between chemical softness values for metal and halide to separate bent from linear structures. This measure also is examined in light of the present data.

II. Computational Details

The quasirelativistic 10-valence-electron pseudopotentials and 6s6p5d-basis sets used for Ca, Sr and Ba have been published recently.⁸ Quasirelativistic MEFIT¹¹ pseudopotentials for the halogen atoms were adapted from Dolg et al.¹² For these ECPs 5s5p-valence basis sets including diffuse exponents have been optimized for the atomic ground state (cf. Table I) and one d-polarization function^{13d} has been added. For Be and Mg both an all-electron and a 2-valence-electron pseudopotential treatment were employed. The all-electron basis sets were 6-311+G* for Be^{13a,b} and McLean and Chandler's [12s6p]/(6s4p) basis set for Mg^{13c} augmented by a diffuse sp set and one d function (this basis set is also designated as 6-311+G* in the Gaussian program series¹⁴). Single electron fit (SEFIT) 2-valence-electron pseudopotentials for Be and Mg have been taken from Fuentealba et al.^{15a} [4s2p1d]/(3s2p1d)-valence basis sets were used for these metals.^{15b-d} Hartree-Fock geometry optimizations and frequency calculations (performed with the Gaussian 88 program¹⁴) have employed a 311/311/1 contraction of the halogen basis sets. For a study of the sensitivity to the d basis on Ca, Sr, and Ba the 5 d functions on the metal have been contracted into two groups.⁸

For M = Ca, Sr, and Ba electron correlation was included via a singles + doubles CI with Davidson's correction¹⁶ (SDCI+Q). The SDCI calculations generally employed the uncontracted 6s6p5d basis sets augmented by one f function⁸ for Ca, Sr, and Ba and a more flexibly contracted (2111/2111/1) halogen valence basis set. The complete MO space was correlated. These calculations have been performed with the

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Table III. SrX Distances (Å), XSrX Bending Angles (deg), Bending Energies ΔE_b (kcal/mol), and Bond Contraction upon Bending ΔR_b (Å) of the Sr Dihalides at Different Levels of Theory^a and Comparison to Experimental Data

	SDCI+Q/			exp
	SCF/2d	SCF/5d	5d1f	
SrF ₂				
R–SrF	2.167	2.164	2.161	2.20 (3) ^b
angle	143.3	141.5	138.8	[108] ^c
ΔE_b	0.69	1.23	1.57	
ΔR_b	0.020	0.022	0.026	
SrCl ₂				
R–SrCl	2.678	2.675	2.640	2.67 (3). ^b 2.616 (6) ^d
angle	linear	167.3	159.5	[120 (20)] ^c
ΔE_b		0.02	0.23	
ΔR_b		0.002	0.007	
SrBr ₂				
R–SrBr	2.835	2.834	2.807	2.82 (3) ^b
angle	linear	linear	164.2	linear
ΔE_b			0.03	
ΔR_b			<0.001	
SrI ₂				
R–SrI	3.069	3.068	3.040	3.03 (3). ^b 3.009 (15) ^e
angle	linear	linear	linear	linear

^aThe 10-valence-electron pseudopotential for Sr has been employed with a 6s6p5d basis set either contracted to 6s6p2d (SCF/2d) or uncontracted (SCF/5d). For the SDCI calculations one set of f functions was added (SDCI+Q/5d1f). ^bCf. ref 3. ^cThe angles are estimates taken from the JANAF tables (ref 20). ^dCf. ref 31a. ^eCf. ref 32a.

MOLPRO program package¹⁷ on the Cray 2 in Stuttgart. The CI geometries have been obtained from a set of single-point calculations. To see whether the effect of the higher excitations is given adequately by Davidson's size consistency correction,¹⁶ we have calculated the geometry for CaF₂ using the CEPA 1 method.¹⁸ Identical geometries for CEPA 1 and SDCI+Q optimizations were obtained.

The theory of Davidson's "internally consistent SCF equations"^{9a} has been applied to many triatomic molecules.^{9b} ICSCF orbitals have been calculated with the MELD program.¹⁹ The natural bond orbital analysis¹⁰ employed the Gaussian 88 adaptation of the NBO program.

III. Results

A. Geometries. Tables II–IV summarize the calculated MX distances and bending angles as well as energy changes and bond contractions upon bending for the Ca, Sr, and Ba dihalides at various levels of theory. Experimental information is included where available. Many of the experimental MX distances are taken from Akishin and Spiridonov,³ but in some cases, more recent available data also are given. Most of the angles are those given in the JANAF tables.²⁰ The experimental angle given for CaF₂ was obtained in a recent FTIR study by Ramondo et al.^{5e}

BaF₂, BaCl₂, SrF₂, and BaBr₂ are bent even when the contracted d basis sets are used. The latter three molecules exhibit moderate angle decreases when the uncontracted d basis is employed, but BaF₂ shows no effect. In view of our previous experience with CaH₂, SrH₂, and BaH₂⁸ this relative insensitivity of the bending angle to contraction of the 5 d functions into two sets indicates the molecules to be genuinely bent. However, the bending energy increases significantly when the d basis is decontracted. Correlation only changes the angle by less than 4° for these four molecules but raises the energies necessary to give linear structures by about 0.2 to 0.6 kcal/mol. The difference in MX bond lengths between the bent molecules and the calculated lengths when linear geometries are enforced is relatively insensitive to correlation. The largest bond contraction upon bending is found for BaF₂. The

Table IV. BaX Distances (Å), XBaX Bending Angles (deg), Bending Energies ΔE_b (kcal/mol), and Bond Contraction upon Bending ΔR_b (Å) of the Ba Dihalides at Different Levels of Theory^a and Comparison to Experimental Data

	SDCI+Q/			exp
	SCF/2d	SCF/5d	5d1f	
BaF ₂				
R–BaF	2.300	2.299	2.254	2.32 (3) ^b
angle	125.3	125.6	123.0	[95] ^c
ΔE_b	3.93	4.30	4.99	
ΔR_b	0.052	0.051	0.050	
BaCl ₂				
R–BaCl	2.846	2.841	2.791	2.82 (3). ^b 2.768 (9) ^d
angle	144.9	141.5	141.4	[100 (20)] ^c
ΔE_b	0.02	0.96	1.63	
ΔR_b	0.023	0.028	0.030	
BaBr ₂				
R–BaBr	3.016	3.009	2.959	2.99 (3) ^b
angle	153.2	146.6	142.9	[150 (30)] ^c
ΔE_b	0.01	0.51	1.08	
ΔR_b	0.013	0.020	0.027	
BaI ₂				
R–BaI	3.265	3.256	3.209	3.20 (3). ^b 3.150 (4) ^e
angle	linear	155.5	152.0	[170] ^c
ΔE_b		0.14	0.38	
ΔR_b		0.009	0.016	

^aThe 10-valence-electron pseudopotential for Ba has been employed with a 6s6p5d basis set either contracted to 6s6p2d (SCF/2d) or uncontracted (SCF/5d). For the SDCI calculations one set of f functions was added (SDCI+Q/5d1f). ^bCf. ref 3. ^cThe angles are estimates taken from the JANAF tables (ref 20). ^dCf. ref 31a. ^eCf. ref 31b.

"experimental" angles for SrF₂, BaCl₂, and BaF₂ estimated from IR and Raman spectra^{5b,c,20} are smaller than those obtained in our best calculations. As has been pointed out before,^{6b,2e} this discrepancy may be caused by several effects: The influence of the matrix environment, the population of excited vibrational levels, or the neglect of anharmonicity effects in the experimental angle determination could lead to an underestimation of the angle for the equilibrium structures. Moreover, as Snelson^{2a} has pointed out, the magnitude of the isotopic frequency shifts employed for the angle determination is "not a very sensitive function of the apex angle".^{2a}

BaI₂, SrCl₂, and CaF₂ are calculated to be linear with the contracted d basis but bent when the larger basis sets are employed. The MX₂ distances decrease when the basis is decontracted. This sensitivity to the d basis and the small bending energies at the higher levels of theory indicate a very shallow potential energy surface for the bending motion.⁸ Therefore the bending angles for these molecules—even at the CI level—are not very exact and may well change when even more accurate calculations or experiments are carried out. The small bond contractions upon bending also confirm the differences between bent and linear structures to be small. This situation, already known for CaF₂,⁶ can be extended to BaI₂ and SrCl₂, which exhibit similar behavior. The bending angle and bending energy calculated for CaF₂ with the uncontracted basis set are in good agreement with the best all-electron calculations available in the literature.^{6c–h} This confirms the ability of the 10-valence-electron pseudopotentials to reproduce high-level all-electron calculations. At least to some extent comparable accuracy can be anticipated for the heavier species where no all-electron results are available.

While the calculated angles for CaF₂, SrCl₂, and BaI₂ even at the SDCI+Q level may not be very precise, we consider the calculated angles for the genuinely bent species (particularly BaF₂) to be quite accurate. Our calculated bending energies are generally expected to have errors no larger than ca. 0.5 kcal/mol. While a relative error of this magnitude is very large for the molecules with shallow bending potentials, the energy for BaF₂ appears to be correct within 10%.

The seven molecules discussed above are those Klemperer et al.⁴ found to be bent in the electric quadrupole deflection experiments. The data in Table III indicate SrBr₂ to have an extremely flat potential energy surface. It is linear at the HF level,

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Table V. MX Distances (Å), Vibrational Frequencies ω (cm⁻¹), and Force Constants k (mdyne/Å) for the Be Dihalides

	F	Cl	Br	I
R-BeX				
all-el ^a	1.373	1.806	1.958	2.193
2-ve-ECP ^b	1.390	1.818	1.968	2.197
exp ^c	1.40 (3)	1.75 (3)	1.91 (2)	2.18 (2)
$\omega(\delta_s)$				
all-el ^a	371	258	223	185
2-ve-ECP ^b	384	248	219	186
exp ^c	345	[230]	220	[175]
$\omega(\nu_s)$				
all-el ^a	740	407	245	169
2-ve-ECP ^b	750	405	245	171
exp ^c	[670]	[375]	[227]	[160]
$\omega(\nu_{as})$				
all-el ^a	1601	1153	1014	880
2-ve-ECP ^b	1659	1152	1013	890
exp ^c	1530	1113	1010	873
$k(\delta_s)$				
all-el ^a	0.814	0.386	0.278	0.188
2-ve-ECP ^b	0.872	0.355	0.268	0.190
$k(\nu_s)$				
all-el ^a	6.135	3.407	2.796	2.133
2-ve-ECP ^b	6.293	3.382	2.794	2.197
$k(\nu_{as})$				
all-el ^a	15.134	7.713	5.731	4.243
2-ve-ECP ^b	16.242	7.695	5.728	4.346

^a6-311+G* basis set on Be employed. ^b2-valence-electron pseudopotential and [4s2p1d]/(3s2p1d)-valence basis set on Be employed. ^cThe experimental data are taken from the JANAF tables (ref 20) and references cited therein. The BeX distances are generally those measured by Akishin and Spiridonov (ref 3). Numbers in square brackets are estimated values.

even with the uncontracted basis set, but small correlation contributions suffice to produce some deviations from linearity. As the energy changes and bond contractions upon bending are very small we do not attach much significance to the angle (SrBr₂ was found to be linear by Klemperer et al.^{4a}). These data may still offer some guidelines for the use of this type of calculation to predict properties of compounds of the heavier group 2 elements at higher temperatures: A preference for the bent structures of ca. 0.1 kcal/mol at the HF level (e.g. 6s6p5d basis sets and 10-valence-electron pseudopotentials or comparable all-electron basis sets assumed) or ca. 0.2 kcal/mol at the SDCI+Q level (with one f function added) already seems to indicate an experimentally bent structure. If a significantly bent structure is already found with the contracted d basis, the bending energy at higher levels may be expected to be more than 1 kcal/mol. This kind of rule-of-thumb may help us to use these methods sensibly for the prediction of geometries and other properties of unknown compounds of the heavy alkaline earth elements.

CaCl₂, CaBr₂, CaI₂, and SrI₂ are linear at all levels of theory we employed. The same is true for all Be and Mg dihalides studied. These conclusions are in agreement with the quadrupole deflection data.⁴

The calculated MX distances for the Ca, Sr, and Ba dihalides (cf. Tables II-IV) agree with the experimental values within the given error limits except for the fluorides. In view of our experience with the hydrides of Ca, Sr, and Ba,⁸ we estimate our calculated MX distances (at the SDCI+Q level) to be too large by ca. 1-3 pm for M = Ca, Sr and by ca. 2-4 pm for M = Ba due to the incomplete inclusion of core-valence correlation. With the notable exception of the difluorides this correction would still leave most of the calculated distances in good agreement with the gas-phase electron-diffraction data. As an improvement in the calculations should lead to smaller distances, the direction of the discrepancy for the difluorides is surprising. The calculated CaF distance in CaF₂, for example, is in good agreement with the best all-electron calculations available^{6e-h} but lies ca. 9 pm below the experimental value.³ While this disagreement has been found in all recent studies of this molecule,^{6e-g} the problem has not been addressed before. Possibly the errors arising from thermal av-

Table VI. MX Distances (Å), Vibrational Frequencies ω (cm⁻¹), and Force Constants K (mdyn/Å) for the Mg Dihalides

	F	Cl	Br	I
R-MgX				
all-el ^a	1.753	2.183	2.332	2.560
2-ve-ECP ^b	1.734	2.171	2.324	2.557
exp ^c	1.77 (2)	2.18 (2)	2.34 (3)	[2.54]
$\omega(\delta_s)$				
all-el ^a	155	123	104	86
2-ve-ECP ^b	157	122	102	85
exp ^c	249	93	82	56
$\omega(\nu_s)$				
all-el ^a	580	328	196	133
2-ve-ECP ^b	569	324	198	141
exp ^c	550	327	198	148
$\omega(\nu_{as})$				
all-el ^a	912	631	537	470
2-ve-ECP ^b	894	625	532	464
exp ^c	842	601	497	445
$k(\delta_s)$				
all-el ^a	0.309	0.234	0.168	0.112
2-ve-ECP ^b	0.317	0.227	0.162	0.112
$k(\nu_s)$				
all-el ^a	3.760	2.218	1.779	1.332
2-ve-ECP ^b	3.620	2.160	1.832	1.477
$k(\nu_{as})$				
all-el ^a	10.667	6.110	4.492	3.350
2-ve-ECP ^b	10.248	5.996	4.400	3.265

^aBasis set of McLean and Chandler (ref 13b) for Mg augmented by a diffuse sp set (ref 13a) and one d function (ref 15d). ^b2-valence-electron pseudopotential and [4s2p1d]/(3s2p1d)-valence basis set on Mg employed. ^cThe experimental MgX distances are taken from Akishin and Spiridonov (ref 3). More recent studies give 1.77 (1) Å for MgF₂ (ref 32b) and 2.185 (6) Å for MgCl₂ (ref 32c). The distance in MgI₂ is only estimated (square brackets). The vibrational frequencies are those obtained by Lesiecki and Nibler (ref 2c) from matrix isolation IR and Raman experiments.

eraging and shrinkage effects, and particularly from the presence of dimers in the gas-phase electron-diffraction study, are larger for these three fluorides than those estimated by the authors.³ The corrected values for CaBr₂, SrCl₂, and BaCl₂ would also be slightly below the experimental lower bound of the early studies.³ However, the more recent experimental data given in Tables II-IV agree significantly better with our results.

The MX distances for the beryllium and magnesium dihalides are given in Tables V and VI. The agreement between the results of our all-electron and 2-valence-electron pseudopotential treatments for the metal is good. For Be the pseudopotential values are ca. 1 pm larger, whereas for Mg the all-electron values are slightly larger. The calculated distances for all species are within the experimental error limits except for BeCl₂ and BeBr₂, where they are ca. 5 pm above the experimental values.³ As valence correlation may be expected to increase the calculated distances by ca. 1-2 pm,^{6b,h,15b} this disagreement would probably even be slightly larger for calculations that consider electron correlation. Thus, as in the case of CaF₂, SrF₂, and BaF₂, the experimental error margins may be greater than those given by the authors (but in this case in the other direction). Note that the calculated stretching frequencies for BeCl₂ and BeBr₂ (as well as for CaF₂, SrF₂, and BaF₂) are in good agreement with the available experimental data (vide infra).

B. Frequency Analysis. The harmonic vibrational frequencies and force constants of the Ca, Sr, and Ba dihalides have been calculated at the HF level with use of the 6s6p5d basis sets on the metals. The results are compiled in Tables VII-IX. Generally, the calculated stretching frequencies are within ca. 10% of the experimental values in cases where presumably reliable experimental data are available. The largest discrepancies between calculated and estimated²⁰ stretching frequencies are found for the symmetric mode in CaCl₂ and CaBr₂ as well as for the asymmetric mode in BaBr₂ and BaI₂. In those cases we expect our calculations to give better values for these frequencies than the estimates given in the JANAF tables.²⁰ The nonmonotonous trend for the asymmetric stretching force constants in the series

Table VII. Vibrational Frequencies (cm^{-1}) and Force Constants ($\text{mdyn}/\text{\AA}$) of the Ca Dihalides Calculated at the SCF Level with 6s6p5d Basis Set on Ca and [5s5p1d]/(3s3p1d) Halogen Valence Basis Sets and Comparison to Experimental Data^a

mode ^b	F	Cl	Br	I
$\omega(\delta_s)$ calc	65	48	44	42
$\omega(\delta_s)$ exp	166	71.5	67	[50]
$\omega(\nu_s)$ calc	494	275	170	121
$\omega(\nu_s)$ exp	484	[217]	[148]	[117]
$\omega(\nu_{as})$ calc	609	420	350	308
$\omega(\nu_{as})$ exp	560	395	335	299
$k(\delta_s)$ calc	<u>0.063</u> ^c	0.051	0.051	0.045
$k(\nu_s)$ calc	2.778	1.560	1.336	1.095
$k(\nu_{as})$ calc	5.515	3.953	3.203	2.464

^aThe experimental δ_s and ν_{as} frequencies have been obtained by Ramondo et al. in an argon matrix (ref 5f). The ν_s values have been taken from the JANAF tables (ref 20) and references cited therein. Numbers in square brackets are estimated values. ^b δ_s is the bending mode, ν_s and ν_{as} are the symmetric and antisymmetric stretching mode, respectively. ^cUnderlined bending force constants pertain to bent equilibrium geometries.

Table VIII. Vibrational Frequencies (cm^{-1}) and Force Constants ($\text{mdyn}/\text{\AA}$) of the Sr Dihalides Calculated at the SCF Level with 6s6p5d Basis Set on Sr and [5s5p1d]/(3s3p1d) Halogen Valence Basis Sets and Comparison to Experimental Data^a

mode ^b	F	Cl	Br	I
$\omega(\delta_{as})$ calc	77	20	11	17
$\omega(\delta_{as})$ exp	82	44	[37]	[31]
$\omega(\nu_s)$ calc	465	256	152	113
$\omega(\nu_s)$ exp	442	270	[157]	[111]
$\omega(\nu_{as})$ calc	480	307	242	205
$\omega(\nu_{as})$ exp	443	300	[263]	[219]
$k(\delta_s)$ calc	<u>0.082</u> ^c	<u>0.012</u> ^c	0.006	0.016
$k(\nu_s)$ calc	2.533	1.359	1.072	0.949
$k(\nu_{as})$ calc	3.304	2.649	2.925	2.370

^aThe experimental frequencies are taken from the JANAF tables (ref 20) and references cited therein. Numbers in square brackets are estimated values. ^b δ_s is the bending mode, ν_s and ν_{as} are the symmetric and antisymmetric stretching mode, respectively. ^cUnderlined bending force constants pertain to bent equilibrium geometries.

MCl_2 , MBr_2 , MI_2 ($M = \text{Sr}, \text{Ba}$) is peculiar and needs further investigation.

The agreement between calculated and experimental bending frequencies is less satisfactory than that for the stretching modes. The discrepancies are particularly obvious for CaF_2 and SrCl_2 , species that are found to have a shallow bending potential. For CaCl_2 and CaBr_2 the disagreement also is large. Generally the calculated bending frequencies are smaller than the experimental values. Except for BaF_2 this is also true for cases where only experimental estimates are available. Apart from the errors in the calculations, the matrix environment may affect the measured bending frequencies. This possibility is supported by the frequency shifts observed in different matrices.^{2,5}

The frequencies for the Be and Mg dihalides are summarized in Tables V and VI. The agreement between all-electron and pseudopotential treatment for the metal is good, as was observed for the MX distances. The largest deviation from the experimental frequencies for the Be dihalides is below 10% with the calculated frequency usually being slightly higher than the experimental value. This already satisfactory agreement with the experiment probably would be improved further by inclusion of valence correlation. For the Mg dihalides the agreement is comparably good for the stretching frequencies. The calculated bending frequencies, however, differ significantly from experiment; the value for MgF_2 is low but the others high. The bending frequency for MgF_2 is in excellent agreement with good all-electron calculations^{6a,b,h} and with a gas-phase value of 160 (3) cm^{-1} measured by Baikov.²¹ Hence, the matrix environment may have a strong

Table IX. Vibrational Frequencies (cm^{-1}) and Force Constants ($\text{mdyn}/\text{\AA}$) of the Ba Dihalides Calculated at the SCF Level with 6s6p5d Basis Set on Ba and [5s5p1d]/(3s3p1d) Halogen Valence Basis Sets and Comparison to Experimental Data^a

mode ^b	F	Cl	Br	I
$\omega(\delta_s)$ calc	87	38	24	15
$\omega(\delta_s)$ exp	[64]	[36]	[28]	[26]
$\omega(\nu_s)$ calc	421	245	154	110
$\omega(\nu_s)$ exp	390	255	[160]	[111]
$\omega(\nu_{as})$ calc	432	258	189	158
$\omega(\nu_{as})$ exp	413	265	[223]	[185]
$k(\delta_s)$ calc ^c	<u>0.096</u>	<u>0.037</u>	<u>0.032</u>	<u>0.018</u>
$k(\nu_s)$ calc	2.342	1.297	1.162	0.908
$k(\nu_{as})$ calc	2.211	1.787	2.132	1.957

^aThe experimental frequencies are taken from the JANAF tables (ref 20) and references cited therein. Numbers in square brackets are estimated values. ^b ν_s is the bending mode, ν_s and ν_{as} are the symmetric and antisymmetric stretching mode, respectively. ^cAll bending force constants pertain to bent equilibrium geometries.

influence on the bending frequency.²

C. Electronic Structure and Bending Effects. The large number of ab initio data given in the two preceding sections allows the examination of the models commonly employed to explain the bent geometries, particularly the polarized ion model^{4,6e,i,22} and the "d-orbital participation model".²³ Let us turn to the simple ionic model first. We will focus on the bending force constants for the linear molecules. Negative values indicate a bent equilibrium structure and pertain to the two imaginary frequencies found for a forced linear geometry. The force constants allow us to compare the bending tendency for the complete set of molecules studied in this work whereas the bending angle is less informative.

The terms we consider for the model are the anion-anion repulsion (k_1), the polarization of the cation by the anions (k_2), the polarization of each anion by both the cation and the second anion (k_3), and the dipole-dipole contributions (k_4). While Guido and Gigli found dipole-dipole interactions to be of minor importance for the bending,^{22a} the results of DeKock and co-workers⁶ⁱ indicated a significant contribution. We cannot exclude that even higher order terms of the multipole expansion are important. However, at present, we do not want to overburden the model. The significance of, for example, charge-quadrupole terms may be examined in future studies. Earlier investigations showed that the results strongly depend on the values of the anion and cation polarizabilities.^{6e,i,22a} We chose a presumably very accurate set of values obtained from high-level ab initio calculations.²⁴ Of course, it would be highly desirable to employ dipole polarizabilities for partially charged ions, but to date there exists no theoretically sound way to obtain such values. The lack of ionic quadrupole polarizabilities of comparable accuracy to the dipole polarizabilities employed is another reason for our neglect of higher order terms in the multipole expansion.

Table X provides the data obtained for k_1 - k_4 and compares them with the ab initio values. As indicated in Figure 1a the polarized ion model bending force constants for the Be and Mg dihalides are lower than the ab initio values (except for MgF_2). This may indicate some covalent bonding contributions with metal p-orbital participation.

For the Ca, Sr, and Ba dihalides the polarized ion model gives values that are larger than the ab initio results (except for CaI_2). The deviations are particularly obvious for CaF_2 , SrF_2 , and BaF_2 , whereas the smallest deviations are observed for the diiodides. For CaI_2 the agreement between polarized ion model and ab initio calculations is excellent. The contribution from cation polarization (k_2) and the dipole-dipole term (k_4) certainly favor a bent geometry (cf. Table X) and show the "correct" trend for the heavier metals. The dipole-dipole term indeed appears to be important, particularly for all difluorides, and for the dihalides of the heavier

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(21) (a) Baikov, V. I. *Opt. Spektrosk.* **1968**, *25*, 356. (b) Baikov, V. I. *Opt. Spektrosk.* **1968**, *27*, 923.

Table X. Polarized Ion Model Bending Force Constants for Linear Group 2 Dihalides and Comparison to ab Initio Bending Force Constants

	R^a	Q^a	k_1^b	k_2^b	k_3^b	k_4^b	k_{POL}^b	k_{ECP}^a
BeF ₂	1.390	0.894	0.473	-0.011	0.407	-0.040	0.828	0.872
BeCl ₂	1.818	0.749	0.133	-0.001	0.139	-0.006	0.265	0.355
BeBr ₂	1.968	0.701	0.083	-0.001	0.093	-0.003	0.172	0.278
BeI ₂	2.197	0.628	0.046	-0.000	0.054	-0.001	0.099	0.188
MgF ₂	1.734	0.958	0.301	-0.033	0.133	-0.062	0.339	0.309
MgCl ₂	2.171	0.869	0.124	-0.017	0.076	-0.018	0.176	0.234
MgBr ₂	2.324	0.831	0.081	-0.004	0.055	-0.011	0.121	0.168
MgI ₂	2.557	0.770	0.048	-0.002	0.036	-0.005	0.077	0.112
CaF ₂	2.033	0.963	0.160	-0.070	0.044	-0.083	0.053	-0.024
CaCl ₂	2.562	0.925	0.088	-0.019	0.032	-0.031	0.071	0.051
CaBr ₂	2.661	0.904	0.070	-0.014	0.032	-0.026	0.062	0.051
CaI ₂	2.894	0.860	0.045	-0.007	0.023	-0.015	0.046	0.045
SrF ₂	2.186	0.969	0.097	-0.061	0.022	-0.058	0.000	-0.071
SrCl ₂	2.677	0.940	0.065	-0.022	0.021	-0.032	0.033	-0.007
SrBr ₂	2.834	0.924	0.065	-0.019	0.024	-0.030	0.040	0.006
SrI ₂	3.068	0.895	0.047	-0.011	0.020	-0.020	0.037	0.016
BaF ₂	2.352	0.970	0.065	-0.061	0.012	-0.047	-0.030	-0.098
BaCl ₂	2.869	0.950	0.044	-0.023	0.012	-0.026	0.007	-0.036
BaBr ₂	3.029	0.938	0.049	-0.021	0.015	-0.029	0.015	-0.030
BaI ₂	3.265	0.916	0.042	-0.014	0.015	-0.020	0.004	-0.014

^aSCF values for M-halogen distances (R), halogen NBO charges (Q), and bending force constants (k_{ECP}) are those obtained with 2-valence-electron pseudopotentials for Be and Mg and 10-valence-electron pseudopotentials with uncontracted 6s6p5d basis sets for Ca, Sr, and Ba. ^bThe polarized ion model force constant $k_{POL} = k_1 + k_2 + k_3 + k_4$ consists of the following: $k_1 = Q^2/8R$, anion-anion repulsion; $k_2 = -\alpha_k Q^2/R^4$, polarization of cation by anions; $k_3 = {}^3/_{16}\alpha_1 Q^2/R^4$, polarization of anions by cation and another anion; $k_4 = {}^{13}/_2\alpha_1\alpha_k Q^2/R^7$, interaction between charge-induced metal dipole with charge-induced anion dipoles. α_k, α_1 : self-consistency-corrected free cation and anion dipole polarizabilities (ref 24). k_1, k_2, k_3 , and k_4 pertain to the internal MX_2 angle coordinate and have been converted to the normal bending coordinate obtained from the ab initio calculations.

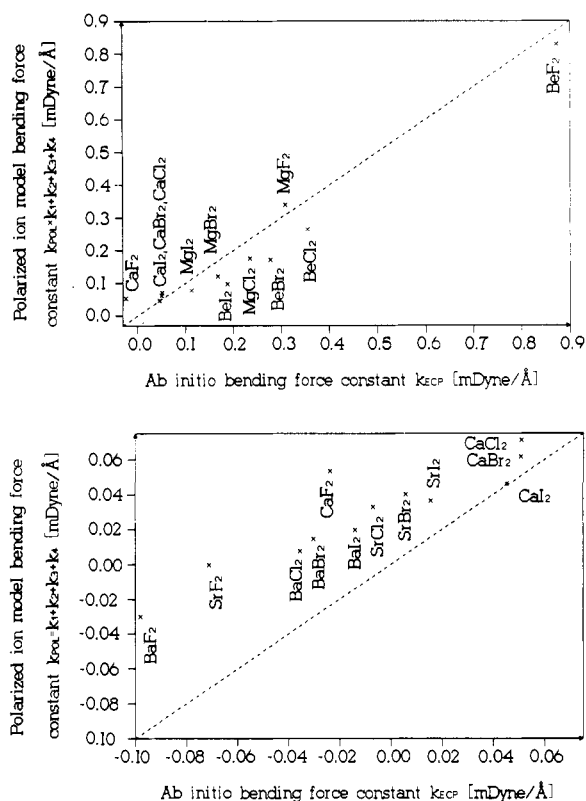


Figure 1. Comparison of bending force constants obtained from a polarized ion model with ab initio bending force constants (---, line expected for ideal 1:1 correspondence between polarized ion model and ab initio values): (a) M = Be, Mg, and Ca; (b) M = Ca, Sr, and Ba.

metals. However, only for BaF₂ the sum $k_2 + k_4$ overcompensates the repulsive terms $k_1 + k_3$, with a resulting bent geometry. Table X also allows the relative importance of the factors that oppose bending to be estimated. While the anion-anion repulsion (k_1) and the anion polarization (k_3) contribute about equally to the polarized ion model bending force constant of the Be dihalides, the importance of k_3 decreases for the heavier metals.

Under the assumption that higher order terms of the multipole expansion model need not be considered and the ab initio bending

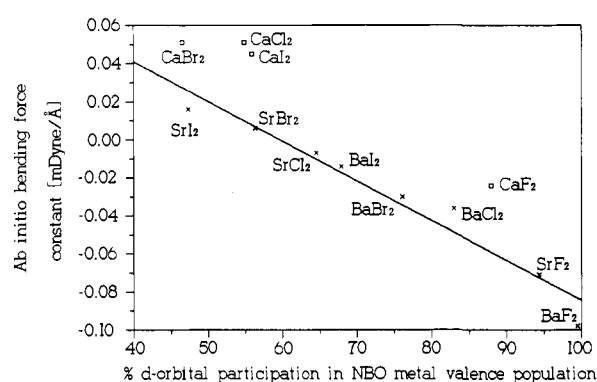


Figure 2. Calculated bending force constants plotted against d-orbital participation in NBO valence populations (100%(valence-d population)/(total valence population)); see Table XI for numerical data). A negative sign for the bending force constant is connected to an imaginary frequency. Both force constants and NBO populations have been obtained from SCF calculations with the uncontracted 6s6p5d-valence basis sets on the metals. The regression line excludes the Ca dihalides.

force constants are accurate, we may analyze the data: Bending force constants for the alkaline earth dihalides obtained from a polarized ion model show only limited correlation with ab initio bending force constants. The model underestimates the bending force constants for most of the Be and Mg dihalides and overestimates the force constants for most dihalides of the heavier metals (particularly for the difluorides). Thus, the nature of the remaining valence population, although quite small, appears to influence the observed bending force constants. Obviously, a major difference between the Be and Mg dihalides on one side and the Ca, Sr, and Ba dihalides on the other side is the availability of low-lying d orbitals for the heavier metals. Figure 2 plots the calculated bending force constants against the magnitude of d-orbital participation in the valence population obtained from a natural bond orbital analysis (cf. Table XI for numerical data). As an increasing positive charge on the metal decreases the s-d gap, it is not surprising that the difluorides exhibit the largest d-orbital participation. The Ba atom in BaF₂, for example, may be viewed as almost completely d hybridized. But note that the valence population on the metal in all cases is small (cf. Tables XI and XIV). For the Ba and Sr dihalides a reasonable correlation between d-orbital participation and bending force constant is

Table XI. Absolute and Relative (%) s-, p-, and d-Valence Populations for Ca, Sr, and Ba Dihalides Obtained from an NBO Population Analysis^a

	s population	p population	d population
CaF ₂	0.0052 (7.1)	0.0037 (5.0)	0.0645 (87.9)
CaCl ₂	0.0512 (34.2)	0.0164 (10.9)	0.0822 (54.9)
CaBr ₂	0.0800 (41.8)	0.0225 (11.7)	0.0891 (46.5)
CaI ₂	0.0962 (34.3)	0.0278 (9.9)	0.1568 (55.8)
SrF ₂	0.0025 (4.0)	0.0010 (1.6)	0.0586 (94.4)
SrCl ₂	0.0328 (27.6)	0.0094 (7.9)	0.0768 (64.5)
SrBr ₂	0.0529 (34.8)	0.0135 (8.9)	0.0858 (56.3)
SrI ₂	0.0896 (42.6)	0.0211 (10.0)	0.0995 (47.4)
BaF ₂	0.0004 (0.7)	0.0000 (0.0)	0.0599 (99.3)
BaCl ₂	0.0131 (13.0)	0.0041 (4.0)	0.0837 (83.0)
BaBr ₂	0.0233 (18.6)	0.0066 (5.3)	0.0951 (76.1)
BaI ₂	0.0434 (25.8)	0.0106 (6.3)	0.1143 (67.9)

^aThe absolute valence s and p populations have been obtained by subtracting two and six electrons from the total (10-valence-electron pseudopotential) NBO s and p populations, respectively (this corresponds to a nominally completely filled ($n-1$) shell). The total NBO p population for BaF₂ was only 5.9992; the valence p population was therefore set to 0. Generally the SCF populations obtained for linear geometries with the 6s6p5d metal basis sets have been employed. The relative populations are given in parentheses.

Table XII. X-X Distances (Å) for Ca, Sr, and Ba MX₂ Compounds from SDCI+Q-Optimized Geometries

X	M =		
	Ca	Sr	Ba
H ^a	4.110	4.131	3.981
F	3.943	4.046	3.962
Cl	4.964	5.196	5.193
Br	5.276	5.561	5.611
I	5.730	6.080	6.227

^aCf. ref 8.

observed. The full line is the regression line obtained when the Ca halides are excluded.

The values for the Ca dihalides lie considerably above this line. Other factors, as the interactions between the anions, seem to contribute more strongly to the observed bending force constants than for the Sr and Ba dihalides. Table XII summarizes the halogen-halogen distances obtained from the SDCI+Q calculations for the Ca, Sr, and Ba dihalides and dihydrides. The values for CaCl₂, CaBr₂, and CaI₂ are up to 0.5 Å smaller than those for the neighboring dihalides. This supports the importance of anion-anion interactions for these ionic molecules.

CaF₂ exhibits the largest deviations from both the simple ionic and the d-hybridization model. The large d-orbital participation (cf. Figure 2, Table XI) should favor a strongly bent structure. This is offset by a significant anion-anion repulsion due to the short CaF distance (cf. k_1 in Table X). The observed shallow bending potential results.

As indicated by Figure 3a the softness criterion introduced recently to discriminate bent and linear structures^{6e} follows the trends of the d-orbital participation for the Ba and Sr dihalides approximately. The correlation with the calculated bending force constants is reasonable for these two elements, in agreement with the heavy-light rule formulated by Klemperer et al.⁴ and Hayes.²³ For the Ca dihalides the situation once again is far less clearcut. The trend of the force constants for the Be and Mg dihalides is completely reversed (cf. Figure 3b). Obviously both the heavy-light rule and the softness criterion cannot be applied to the complete set of the group 2 dihalides. Note that the experimental trends for the bending force constants of the group 12 dihalides for a given metal²⁵ closely parallel those found here for the Be and Mg dihalides.

Walsh diagrams²⁶ have been valuable for the qualitative prediction and rationalization of the geometries of triatomic molecules

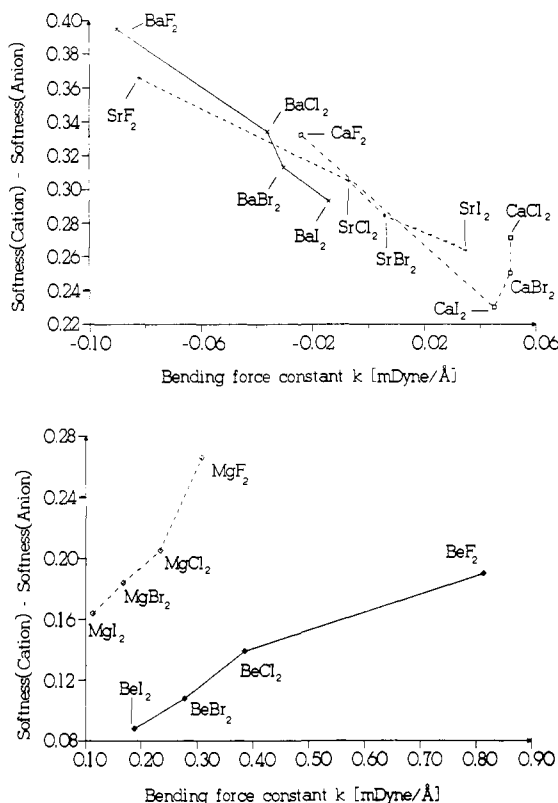


Figure 3. Softness values of cation and anion as a measure of bending tendency. Generally the bending force constants obtained for linear geometries have been employed. The softness values listed in ref 6e have been used. (a) Ca, Sr, and Ba dihalides; (b) Be and Mg dihalides.

and related species. Canonical SCF-MO energies ϵ_i work well in many cases.²⁷ However, for strongly ionic systems such as Li₂O, large discrepancies between the behavior of the sum of the SCF-MO energies ($\sum 2\epsilon_i$) and the Hartree-Fock total energy occur.^{9b,28} The HF energy may be expressed as

$$E_{\text{HF}} = \sum 2\epsilon_i + V_N - V_e \quad (1)$$

with $V_N = \sum_{A \neq B} Z_A Z_B R_{AB}^{-1}$ internuclear repulsion energy and $V_e = \sum_{i=1}^{N/2} (\epsilon_i - h_{ij})$ electron-electron repulsion energy.

The observed discrepancy is due to the fact that for ionic systems the term $(V_N - V_e)$ in eq 1 changes much more strongly with variation of the bending angle than for nonionic systems.^{9b}

Diagrams a, c, and d in Figure 4 demonstrate the complete failure of the canonical SCF-MO energies to predict the bent geometry for BaH₂. While the HOMO ($2b_2$) favors a bent geometry, this influence (which also occurs for the corresponding ICSCF orbital, see Figure 4b and text below) is by far overcompensated by the other MOs. Hence, the canonical MOs may not be employed to rationalize the structures of ionic MX₂ compounds of the heavy alkaline earth elements. On the other hand, the sum of the "internally consistent SCF orbitals" (ICSCF orbitals) introduced by Davidson,^{9a} by definition, behaves like the total energy. Moreover, the ICSCF orbitals have been thoroughly tested for the construction of Walsh diagrams.^{9b}

As the great number of orbitals involved for the dihalides complicates the discussion, we will focus first on Walsh diagrams constructed for CaH₂, SrH₂, and BaH₂ (the wave functions are those obtained in ref 8). The situation for the difluorides will be discussed below. The subvalence shell on the metal is explicitly included for both the dihydrides and the difluorides.

The behavior of the HOMO ($2b_2$) is the most prominent feature in the ICSCF-Walsh diagrams for BaH₂, SrH₂, and CaH₂ (cf. Figure 4, b,e,f). In all three cases it exhibits a minimum at a

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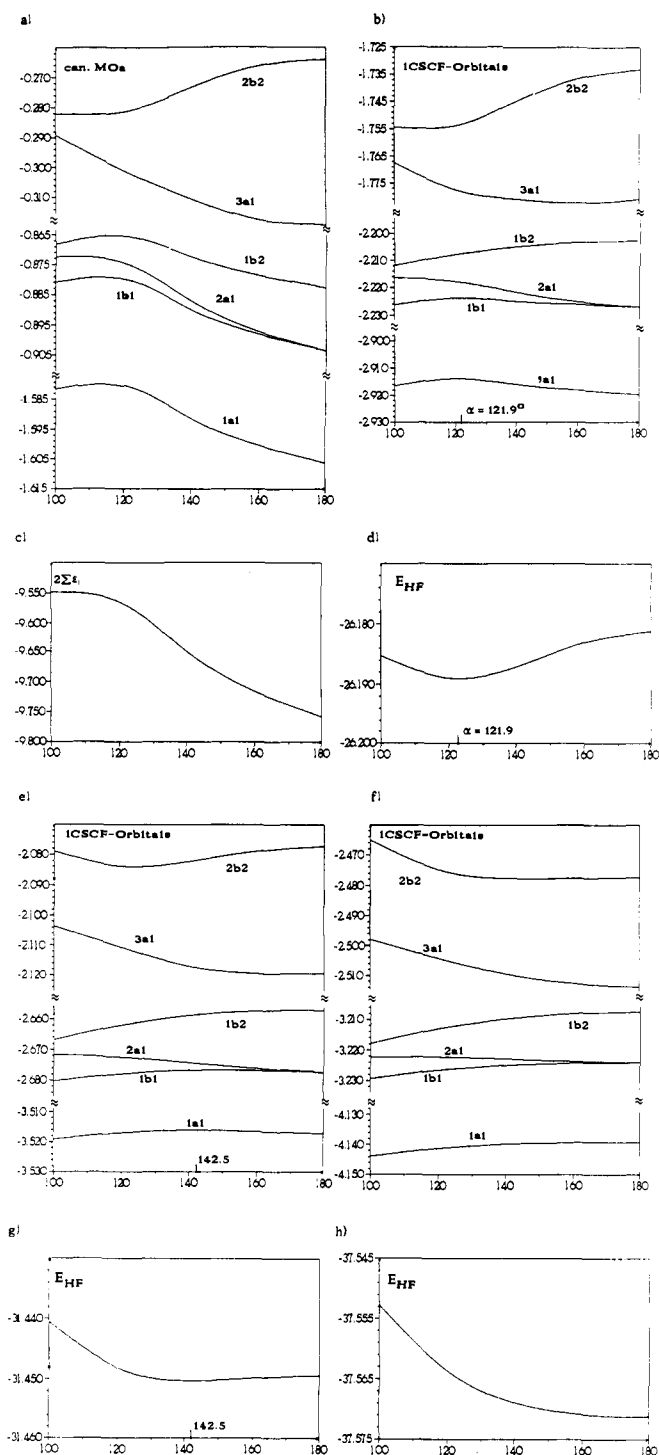


Figure 4. Walsh diagrams for MH_2 ($M = Ca, Sr, Ba$) with energy in au: (a) BaH_2 , canonical MOs; (b) BaH_2 , ICSCF MOs; (c) BaH_2 , sum of canonical MO energies (energy scale compressed by a factor of 0.5); (d) BaH_2 , total energy; (e) SrH_2 , ICSCF-MOs; (f) CaH_2 , ICSCF-MOs; (g) SrH_2 , total energy; (h) CaH_2 , total energy.

nonlinear geometry. The heights and positions of the well, however, differ strongly among the three molecules. While the slope of the curve is quite steep with a minimum below 120° for BaH_2 , for SrH_2 and CaH_2 the minimum shifts successively to larger angles and becomes increasingly shallow. This behavior of the HOMO is reflected in the total energy (cf. Figure 4, d,g,h) which shows a relatively steep minimum (bending energy $\Delta E_b = 4.9$ kcal/mol) at 121.9° for BaH_2 , a much more shallow minimum ($\Delta E_b = 0.60$ kcal/mol) at 142.5° for SrH_2 , and a preference for a linear geometry for CaH_2 .⁸ Thus, while there are also small changes for the other orbitals when going from BaH_2 to CaH_2 ,

the HOMO ($2b_2$) yields the dominant contribution to the differences in the geometries of the three molecules. Inspection of the ICSCF eigenvectors shows a strong participation of the metal d_{yz} functions in the HOMO (the importance of the HOMO has already been discussed in earlier studies^{6i,7b,23}). As was demonstrated for the dihydrides,⁸ and as is emphasized by the bending force constants obtained from the polarized ion model (cf. Table X), the polarization of the subvalence shell on the metal also is important for the bending. Thus, while the dominance of the HOMO in the Walsh diagrams is consistent with the qualitative Walsh diagrams of Hayes,²³ which include metal d orbitals in the valence shell, the influence of the penultimate shell may not be disregarded (the HOMO energy may be expected to reflect core-polarization as well).

For CaF_2 , SrF_2 , and BaF_2 , Table XIII summarizes the ICSCF orbital energies for both the optimized bent and the restricted linear geometries. The orbital energy changes again indicate a large contribution from the HOMO ($4b_2$) to bending. However, the low-lying $1b_2$ and $2a_1$ MOs, which are mostly localized on the fluorine atoms, also have sizable influences. This is understandable in view of the charge transfer from halide to metal (primarily into the $(n-1)d_{yz}$ orbital) which is generally observed upon bending (see Table XIV for the NBO charges). Thus, MOs mostly localized on the fluorine atoms are stabilized, whereas occupied core orbitals (particularly the $3a_1$ and $4a_1$ MOs) on the metal are destabilized. The charge transfer upon bending is manifest in the NBO atomic net charges for CaF_2 , SrF_2 , and BaF_2 . These are almost identical in the optimized bent geometries, but the expected slight increase along this series is observed for the linear structures (see Table XIV). The bending energy is a composite of different, rather large effects which point in opposite directions. Hence, the dihydrides are useful as the simplest model for the dihalides and other compounds of Ca, Sr, and Ba.

IV. Conclusions

The present work provides a comprehensive set of structural and vibration spectroscopical data for the alkaline earth dihalides obtained from high-quality ab initio calculations. While the agreement with available experimental data is good in most cases, some specific deviations between calculations and experiment are observed. In the case of several metal-halogen distances (e.g. for CaF_2 , SrF_2 , BaF_2 , $BeCl_2$, and $BeBr_2$) a reevaluation or reinterpretation of experimental data would be desirable to locate possible sources of error. Discrepancies between various calculated and experimental bending frequencies point to problems connected to very shallow bending potentials. These render it difficult to obtain accurate bending frequencies for the isolated molecules, both computationally and experimentally. Bending angles estimated from IR and Raman isotopic shift experiments generally appear to be significantly too small. However, several alkaline earth dihalides definitely have bent equilibrium structures.

As we received a preprint of a related work by Seijo, Barandiaran, and Huzinaga^{7a} shortly after this work was completed, we would like to comment briefly on their results and relate them to ours. Seijo et al. employed (8-valence-electron model-potentials) for Ca, Sr, and Ba. This means that the $(n-1)s$ orbital is part of the core, in contrast to our 10-valence-electron pseudopotentials. As the work was restricted to the Hartree-Fock level of theory, the data should be compared to our Hartree-Fock results. The distances obtained by Seijo et al. usually are slightly (1–4 pm) larger than our SCF values. As these small discrepancies are also present for the relatively uncritical Mg dihalides, it is possible that differences in the halogen valence basis sets are responsible for the deviations. The agreement for the stretching frequencies is reasonable in all cases. Bending frequencies and bending angles are in excellent agreement, provided that a relatively steep bending potential is present. However, discrepancies are observed for the critical cases, CaF_2 , $SrCl_2$, $SrBr_2$, and SrI_2 . For CaF_2 and $SrCl_2$ even the contraction of our five d sets into two groups has a significant influence on the bending angles (cf. section III.A.) As the d functions employed by Seijo et al.^{7a} are contracted, this may be the source of the discrepancies. However, as we pointed out

Table XIII. ICSCF-MO Energies (au) for MF₂ (M = Ca, Sr, Ba) (6s6p5d Basis Sets on M Used)

MO	(a) CaF ₂			(b) SrF ₂			(c) BaF ₂		
	$\varphi = 162.3^\circ$	$\varphi = 180.0^\circ$	diff ^a	$\varphi = 141.5$	$\varphi = 180.0$	diff ^a	$\varphi = 125.6$	$\varphi = 180.0$	diff ^a
4b ₂	-3.0147	-3.1034	-0.0013	-2.8274	-2.8198	-0.0076	-2.6699	-2.6517	-0.0182
5a ₁	-3.0306	-3.0302	-0.0004	-2.8453	-2.8436	-0.0017	-2.6852	-2.6849	-0.0003
2b ₁	-3.0307	-3.0302	-0.0005	-2.8461	-2.8436	-0.0025	-2.6906	-2.6849	-0.0057
1a ₂	-3.0392	-3.0392	+0.0000	-2.8546	-2.8538	-0.0008	-2.6992	-2.6962	-0.0030
3b ₂	-3.0393	-3.0392	-0.0001	-2.8547	-2.8538	-0.0009	-2.6997	-2.6962	-0.0035
4a ₁	-3.0600	-3.0610	+0.0010	-2.8708	-2.8755	+0.0047	-2.7093	-2.7174	+0.0081
2b ₂	-3.7684	-3.7679	-0.0005	-3.4101	-3.4086	-0.0015	-3.1107	-3.1081	-0.0026
3a ₁	-3.8251	-3.8275	+0.0024	-3.4471	-3.4560	+0.0089	-3.1363	-3.1551	+0.0188
1b ₁	-3.8271	-3.8275	+0.0004	-3.4533	-3.4560	+0.0027	-3.1480	-3.1551	+0.0071
2a ₁	-3.9412	-3.9399	-0.0013	-3.7559	-3.7527	-0.0032	-3.5971	-3.5919	-0.0052
1b ₂	-3.9709	-3.9706	-0.0003	-3.7684	-3.7662	-0.0022	-3.6087	-3.6029	-0.0058
1a ₁	-4.7381	-4.7385	+0.0004	-4.2923	-4.2953	+0.0030	-3.8418	-3.8488	+0.0070
ΔE_{HF}	-0.00013 au (0.06 kcal/mol)			-0.00200 au (1.23 kcal/mol)			-0.006932 au (4.30 kcal/mol)		

^a Difference $\epsilon_{\text{bent}}^{\text{ICSCF}} - \epsilon_{\text{linear}}^{\text{ICSCF}}$ (a negative sign indicates a preference for a bent structure).

Table XIV. NBO Metal Net Charges for the Alkaline Earth Dihalides^a

M	F	Cl	Br	I
Be	1.788	1.498	1.402	1.256
Mg	1.916	1.738	1.662	1.540
Ca	1.927 (1.924)	1.850	1.808	1.719
Sr	1.938 (1.927)	1.881 (1.879)	1.848	1.790
Ba	1.940 (1.921)	1.899 (1.881)	1.875 (1.861)	1.832 (1.819)

^a For Ca, Sr, and Ba the uncontracted 6s6p5d basis sets were employed. For Be and Mg 2-valence-electron pseudopotential values are given. The numbers pertain to linear geometries. For molecules that are bent at this level of theory, the charges obtained for the optimized geometries are given in parentheses.

above, bending angles and bending frequencies for these extremely floppy molecules should not be taken too seriously (Seijo et al. have employed the term "quasilinear" for these species).

Our large set of data for the group 2 dihalides has been used to analyze the reasons for bending. The bending force constants obtained from a polarized ion model show only limited correlation with the ab initio results. The observed systematic deviations indicate that small covalent contributions to the bonding influence the bending force constants. The involvement of metal p orbitals for Be and Mg appears to increase the bending force constants, while the participation of metal d orbitals in bonding seems to decrease them for the Ca, Sr, and Ba dihalides. As the bending force constants for the latter species are up to 2 orders of magnitude smaller than those for the Be and Mg dihalides (cf. $k(\delta_s)$ in Tables V-IX), the covalent contributions necessarily are much more decisive as to whether bent or linear equilibrium geometries are obtained (particularly for species with an extremely shallow bending potential).

Thus, while Be and Mg behave as expected¹ for 2nd-column main-group metals, Ca, Sr, and Ba extend the three transition-metal rows. In fact, the d-orbital participation in bonding for the heavy alkaline earth metals is more important than that for the group 12 elements, which are frequently considered to be transition metals (note a study of some zinc compounds^{15b}). The need of large metal d-basis sets to describe ionic compounds of Ca, Sr, and Ba underlines the proximity to the early transition metals. These observations may help to explain the similarities²⁹ in the

chemistry of organometallic compounds of Ca, Sr, and Ba and some ionic lanthanoid organometallics.

We conclude that both core-polarization (influence of the subvalence shell) and d-orbital participation in small covalent bonding contributions (influence of the valence shell) to varying extents control the bending in Ca, Sr, and Ba dihalides. This is very similar to the conclusions drawn for the dihydrides of these elements⁸ (although the polarization potential employed in that work did not include dipole-dipole terms). It may be inconvenient for the chemist that no simple model adequately describes this complete group of the periodic table; many different effects have to be taken into account. The change of electronic structure characteristics observed when going from compounds of Be and Mg to those of Ca, Sr, and Ba, provides both challenges and opportunities with regard to computational methodology, interpretations, and the practical consequences for organometallic and bioinorganic alkaline earth chemistry. Ab initio pseudopotential calculations can be used to obtain important information.

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