

***Ab initio* model potential study of the equilibrium geometry of alkaline earth dihalides: MX_2 ($\text{M} = \text{Mg, Ca, Sr, Ba}$; $\text{X} = \text{F, Cl, Br, I}$)**

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The ground state equilibrium geometry of alkaline earth dihalides MX_2 ($\text{M} = \text{Mg, Ca, Sr, Ba}$; $\text{X} = \text{F, Cl, Br, I}$) has been optimized at the Hartree–Fock (HF) level using the Cowan–Griffin relativistic *ab initio* model potential method and a uniformly good, extended, *spd* valence basis set. The results show that, according to the method, all magnesium dihalides and CaCl_2 , CaBr_2 , and CaI_2 are linear, SrF_2 and all barium dihalides are bent, and CaF_2 and SrCl_2 , SrBr_2 , and SrI_2 are quasilinear molecules. The alkaline earth $(n - 1)d$ orbitals are shown to be responsible for the bending of the heavier molecules while their $(n - 1)p$ orbitals contribute considerably to the final quantitative prediction of the apex angle and the relative stability of the bent structures. Relativistic effects are shown to be very small on the bond distances and vibrational frequencies; they are important on the size of the bending barrier of the bent molecules. The results obtained are compared to previous theoretical studies and provide some insight in the interpretation of the contradictory experimental conclusions.

I. INTRODUCTION

The molecular geometry and vibrational spectra of alkaline earth dihalides MX_2 ($\text{M} = \text{Mg, Ca, Sr, Ba}$; $\text{X} = \text{F, Cl, Br, I}$) have been the subject of many experimental^{1–13} and theoretical^{14–21} investigations. In spite of this, a systematic and uniformly accurate study of these molecules and properties is missing from both the experimental and theoretical points of view.

Experiments^{1–13} have been conducted to infer the values of the equilibrium metal–ligand distance (r_e) and the bond angle (α_e) as well as the vibrational frequencies (for totally symmetric stretching $\bar{\nu}_1$, bending $\bar{\nu}_2$, and antisymmetric stretching $\bar{\nu}_3$ modes). However, quite often, either the error associated with the measurements or the wide range of values published by different groups, bring about some uncertainty on the experimental description of the bonding, particularly, on the linear or bent nature of these molecules.

From a theoretical point of view, the geometry of only MX_2 ($\text{M} = \text{Mg, Ca, Sr}$; $\text{X} = \text{F, Cl}$), and SrBr_2 and SrI_2 has been calculated (not always completely optimized) at the *ab initio* nonrelativistic Hartree–Fock (HF) level. The quality of the basis sets used varies, ranging from small minimal basis sets to extended ones with polarization and diffuse functions.

It is apparent that a systematic study of the bonding in all these molecules, based on the use of uniformly good basis sets, and reflecting the effects of both relativistic interactions and electron correlation is necessary. Along this line, we present here the results of valence electron calculations on the ground state of the 16 molecules at the HF level, with optimization of the $D_{\infty h}$ and C_{2v} symmetries, using the Cowan–Griffin relativistic *ab initio* model potential (AIMP) method²² and a uniformly good, extended, *spd* basis set. The main goal of this study has been to obtain a

uniformly accurate description of the bonding properties of the MX_2 set trying to clarify their linear/bent nature. In particular, this study should serve to interpret the often inconsistent experimental data. The results are expected to be an adequate reference for the study of other relativistic effects and electron correlation contributions, which have been neglected at this stage due to the high cost of performing the geometry optimization for the whole set of molecules beyond the HF level.

In Secs. II and III we summarize available experimental and theoretical results, respectively, focusing on their accuracy/uncertainty. In Sec. IV we describe the characteristics of the calculations. In Sec. V we compare our results with previous experimental and *ab initio* theoretical works and analyze the effects of the relativistic terms included in the calculations as well as the involvement of the alkaline earth $(n - 1)p$ and $(n - 1)d$ orbitals in the bonding. In Sec. VI we summarize the conclusions of our study.

II. EXPERIMENTS

The comparison of the results of our calculations with the experiments published so far is somewhat difficult because it is not always clear what is the precision of the measurements. The study of the experimental work^{1–13} shows that the analysis of the results produced by different techniques is not easy: Different schemes of analysis of the same experimental data, which produce considerable discrepancies, are available; reinvestigations of some properties have been necessary; measurements corresponding to different techniques are not always consistent. Therefore, in order to facilitate the discussion of our results later on, we summarize here the experimental data focusing on their accuracy/uncertainty.

The molecular geometry and vibrational spectra of the

alkaline earth dihalides have been examined using several experimental techniques: (i) electron diffraction (ED),^{1,11-13} (ii) molecular beam electric deflection (MBED),⁴ (iii) gas phase infrared spectroscopy^{2,3,7} (ir gas) and infrared spectroscopy of vapor isolated in solid matrices^{5,6,8-10} (ir mat), and (iv) Raman spectroscopy (R).¹⁰ The accuracy of the published information, as discussed by the authors,¹⁻¹³ is summarized next. Corresponding experimental results are collected in Table I.

A. Electron diffraction

A very early study of electron diffraction (ED) was conducted by Akishin *et al.*¹ in 1957. In spite of the uncertainty on the X-M-X angle (typically 30°) the authors concluded that *all* alkaline earth dihalides have linear structure. Since then, ED reinvestigations which show that not all of the molecules are linear, have been published in the last decade; they use the same experimental technique, but different structure analysis methods.¹¹⁻¹³ The authors¹¹⁻¹³ are unanimous on the necessity of correcting the thermally averaged structural parameters to account for vibrational effects, but they do not coincide in the procedure actually used to do so. As a matter of fact, Gershikov and Spiridonov¹² have shown that different assumptions for the trajectories of the terminal atoms for the bending mode seriously affect the vibrational corrections and thus the actual value obtained, for instance, for the M-X distance. As a showcase¹² the thermally averaged values r_g , published by Kasparov *et al.*¹¹ for the M-X distance in MgCl₂ and CaI₂, 2.186 and 2.867 Å, are larger than the corrected values, and come to 2.130 and 2.757 Å, respectively if small linearized normal mode displacements are assumed in the vibrational correction procedure,¹² or to 2.179 and 2.859 Å, if a further correction is included that accounts for curvilinearity effects.¹²

B. Molecular beam electric deflection

This technique has been used to determine whether a particular MX₂ molecule is linear and centrosymmetric or, on the contrary, is bent and thus shows a permanent dipole moment. The results are not quantitative in measuring the apex angle. Using MBED experiments to study MX₂ molecules in gas phase, Klemperer *et al.*⁴ concluded that CaF₂, SrF₂, SrCl₂, and all barium dihalides have bent structure in contrast to the conclusions of Akishin *et al.*¹ This early controversy led to a considerable (mainly experimental) effort aimed at consistently determining the equilibrium geometry of the alkaline earth dihalides through ED and ir/R techniques, mainly.

It is worth stressing that the sensitivity to the bond angle of electric deflection experiments may be limited depending on the size of the bending barrier and the electronic polarizability. Tunnel effects and induced dipole moments are the origin of these uncertainties.⁴

C. Infrared spectroscopy

Infrared spectra of gas phase MX₂ (ir gas)^{2,3,7} and of MX₂ vapor trapped in solid matrices^{5,6,8-10} (ir mat) have been reported. These experiments have been performed not

only to measure the vibrational frequencies, but also to distinguish the linearity or nonlinearity, and furthermore, to infer the apex angle, of the MX₂ molecules through two complementary criteria: (i) the number of ir-active bands, and (ii) the measurement of the frequency shift produced by isotopic substitution of the central atom.

Snelson⁵ and Hauge *et al.*⁸ have pointed out the shortcomings of the use of the matrix isotopic shift technique to determine the apex angle because of the very small dependence of the isotopic shift on the bond angle in the range 150°–180°. Another difficulty associated with these experiments is the formation of polymeric species^{5,8} and/or of complexes of the matrix trapped MX₂ molecules with impurities¹⁰ that can lead to erroneous/uncertain assignments of the vibrational bands. Actually, in the case of MgF₂, these difficulties led to some controversy: Contradicting previous results,^{1,4} Mann *et al.*⁶ deduced a bent structure with an apex angle of 158° for MgF₂ based on the isotopic frequency shift measurements and cited, in support of this conclusion, the assignment of a band at 478 cm⁻¹ to the symmetric stretch ($\bar{\nu}_1$), ir active only for bent configuration. This band was shown to be ascribable to dimeric MgF₂,^{5,8} and MgF₂ was shown to be linear.^{1,4,5,8,10,11}

Also, it is timely to comment on what has been called *matrix effects*,⁵ associated to the matrix isolation technique. These effects bring about some discrepancies between the results of gas-phase ir spectra and matrix isolation ir spectra: Most of the absorption bands exhibit a multiplet structure that is present under all conditions of matrix dilution and, therefore, is not ascribable to polymeric compounds, but to the trapped species occupying more than one site in the matrix lattice (see data corresponding to Ref. 9 in Table I as an example). More troublesome than this splitting is the effect of the matrix environment on the band center which is shifted from the *true gas-phase value* to some other frequency. It has been suggested⁵ that the matrix values of the frequencies be corrected to estimate *gas phase* frequencies through some empirical approach using accurately known frequency shift values corresponding to chemically similar compounds.⁵ This correction has been actually estimated as 15 cm⁻¹ to be added to the neon matrix frequencies of MX₂ compounds⁵ in order to give a more realistic gas-phase frequency assignment.

III. PREVIOUS CALCULATIONS

The calculation of the equilibrium geometry and vibrational frequencies of alkaline earth dihalides is also a difficult task for two reasons. First, the number of electrons to be treated grows very rapidly as the size of the central metal and/or the halogens grows. This means not only higher computing time requirements, but also the need for the inclusion of relativistic terms. Second, the basis set to be used both at the HF level or beyond must be very flexible, if the errors associated to truncation are to be small in order to get reliable predictions of the chemical bond. This second circumstance is a consequence of the chemical nature of the elements involved, alkaline earths and halogens, and of the chemical bonds they form in the MX₂ molecules. It is well known that alkaline earth polarizability varies along the IIA

TABLE I. Experimental and calculated values of bond length, bond angle, and vibrational frequencies of MX_2 molecules.

	Method	Ref.	$r_e/\text{\AA}$	α_c/deg	$\bar{\nu}_1/\text{cm}^{-1}$	$\bar{\nu}_2/\text{cm}^{-1}$	$\bar{\nu}_3/\text{cm}^{-1}$	
MgF_2	ED	1	1.77 (1)	180(30)				
		11	1.770(9)	180	540(20)	165(10)	825(20)	
	IR gas	7					825(10)	
		5				270(10)	875(10)	
	IR mat	6		158	478	242	837	
		8		180	552 ^a	247	851	
	IR/R mat	10		180	550	249	842	
		This work		1.758	180	579	151	927
	MgCl_2	ED	1	2.18 (2)	180(10)			
			11	2.185(6)	180		105(5)	
12			2.130,2.179					
IR gas		2				295	597	
		3					588	
		7			297 ^b			
IR mat		6		180	298 ^b	88	590	
		9					585,603	
		10		180	326	93	601	
IR/R mat		This work		180	292	105	577	
	ED	1	2.206	180(10)				
MgBr_2	ED	1	2.34 (3)	180(10)				
		3					490	
	IR gas	7			178 ^b			
		9					502,509,520	
	IR/R mat	10		180	198	82	497	
		This work		2.349	180	190	80	522
	IR/R mat	10		180	148	56	445	
		This work		2.580	180	132	78	447
	CaF_2	ED	1	2.10 (3)	180			
			4		bent			
IR gas		7			412 ^b		575(10)	
		5		145(30)	520(10)		595(10)	
IR mat		6		140	485	140	554	
		This work		2.053	180	456	17	637
CaCl_2	ED	1	2.51 (3)	180(30)				
		12	2.451(3)					
		13	2.483(7)	180		69		
	MBED	4		linear				
		7			238 ^b		395(7)	
	IR mat	6		180	243 ^b	64	402	
		This work		2.540	180	265	50	442
	CaBr_2	ED	1	2.67 (3)	180(10)			
			13	2.616(16)			72	
		MBED	4		linear			
7					148 ^b		330(5)	
CaI_2	ED	1	2.680	180	171	33	382	
		11	2.88 (3)	180(10)				
	IR gas	12	2.866(9)	180	115(10)	50(10)	295(30)	
		13	2.757,2.859					
	IR mat	7			107 ^b		290(5)	
		This work		2.903	180	117	34	316
SrF_2	ED	1	2.20 (3)	180				
		4		bent				
	IR gas	7			380 ^b		455(7)	
		5		bent	485(10)		490(10)	
	IR mat	6		108	442	82	443	
		This work		2.191	144	440	76	509
SrCl_2	ED	1	2.67 (3)	180(30)				
		4		bent				
	IR gas	7			223 ^b		300(7)	
		6		120	269	44	300	
	IR mat	This work		2.700	180	251	19	337
		ED	1	2.82 (3)	180(10)			
SrBr_2	MBED	4		linear				
		7			137 ^b		231 ^b	
	IR gas	This work		2.830	172	160	13	267
		ED	1	3.03 (3)	180(10)			
SrI_2	ED	11	3.009	180	105(10)	30(5)	190(20)	

TABLE I. (continued).

	Method	Ref.	$r_e/\text{Å}$	α_e/deg	$\bar{\nu}_1/\text{cm}^{-1}$	$\bar{\nu}_2/\text{cm}^{-1}$	$\bar{\nu}_3/\text{cm}^{-1}$
	MBED	4		linear			
	IR gas	7			100 ^b		197 ^b
BaF ₂	This work		3.061	180	110	9	217
	ED	1	2.32 (3)	180			
	MBED	4		bent			
	IR gas	7			367 ^b		415(7)
	IR mat	5		bent	450(10)		430(10)
		6		100 ^b	390	64	413
BaCl ₂	This work		2.331	126	406	77	436
	ED	1	2.82 (3)	180(40)			
	MBED	4		bent			
	IR gas	7			215 ^b		265(5)
	IR mat	6		100 ^b	255	36	260
	This work		2.898	143	233	36	275
BaBr ₂	ED	1	2.99 (3)	180(30)			
	MBED	4		bent			
	IR gas	7			128 ^b		188 ^b
	This work		3.026	146	154	25	211
	ED	1	3.20 (3)	180(20)			
BaI ₂		12	3.150(7)	148(9)	106(12)	16	145(21)
	MBED	4		bent			
	IR gas	7			93 ^b		157 ^b
	This work		3.274	157	105	18	169

^a MgF₂ is complexed with other molecules in an argon matrix, thereby causing the $\bar{\nu}_1$ to be IR active.

^b Approximately estimated value.

group²³ and also that their unoccupied *d* shells lay quite low in energy and tend to adopt an active role in molecular environments.^{24,25} Halogens, on their turn, have very high (though variable along the VIIA group) electronegativity and therefore easily form anions in the molecular environment. These chemical behaviors must influence the basis set design to study the equilibrium geometry of the MX₂ molecules. Consequently, double zeta plus polarization quality

must be consistently used for all atoms, at least for the valence shells. *d*-type functions that allow for the participation of unoccupied *d* orbitals (especially for Ca, Sr, and Ba) are also necessary,^{24,25} and diffuse functions added to the halogen basis sets for a better representation of the anions diffuse electronic densities are also known to be very important.²⁶

In Table II we collect most of the *ab initio* calculations reported so far and summarize some details of the calcula-

TABLE II. Previous *ab initio* calculations on MX₂ molecules: characteristics and results.

Molecule	Ref.	Basis set	Extra functions			Method	Optimization		Results	
			Polar.	Diff. on X	Unocc. orb. M		$r(\text{M-X})$	(X-M-X)	$r_e(\text{Å})$	$\alpha_e(\text{deg})$
MgF ₂	14	double zeta	...	1s1p	1d	HF	opt. ^a	180	1.77	...
						beyond HF	opt.	opt.	1.77	180
	15	minimal	1p1d	HF	opt.	opt.	1.762	180
	17	small minimal	none/1d	UHF	opt.	180	1.665/1.643	...
	18	double zeta	1d	HF	opt.	partly opt.	1.77	...
	20	double zeta	HF	opt.	180	1.76	...
21	double zeta	1d ^M 1d ^X	1s1p	1d	HF	opt.	180	1.770	...	
MgCl ₂	21	double zeta	1d ^M 1d ^X	1s1p	1d	HF	opt.	180	2.207	...
	CaF ₂	15	minimal	...	none/1d	HF	2.10	opt.	...	180/145
CaF ₂	16	double zeta	2d/3d	HF	2.148	opt.	...	180
	19	small minimal	HF	opt.	180	2.209	...
	16	double zeta	2p ^M 1d ^X	1p	1p3d	HF; ECP on Cl	opt.	opt.	2.527	180
SrF ₂	19	small minimal	HF	opt.	180	2.321	...
SrCl ₂	19	small minimal	HF	opt.	180	2.701	...
SrBr ₂	19	small minimal	HF	opt.	180	2.832	...
SrI ₂	19	small minimal	HF	opt.	180	3.059	...

^aThe abbreviation opt. means that the geometry parameter has been optimized; otherwise the quoted constant value has been used.

tions as well as the characteristics of the basis sets used. It can be seen that only MgF_2 , MgCl_2 , CaF_2 , and CaCl_2 have been studied beyond the small minimal basis set HF level.

The comparison of those results collected in Table II corresponding to the more extensive basis sets, with the experimental data of Table I, shows a very good agreement for MgF_2 , MgCl_2 , and CaCl_2 , and disagreement in CaF_2 which is shown to be linear in Ref. 16 while it is described as bent by MBED⁴ and ir mat.^{5,6}

IV. DETAILS OF THE CALCULATIONS

Due to the growing number of electrons going down the IIA and VIIA groups (MgF_2 :30; BaI_2 :162) we decided to study the electronic structure of the ground state of MX_2 molecules through valence-electron calculations. In this way, all 4 alkaline earth are 8-electron atoms and all 4 halogens are 7-electron atoms, the number of occupied molecular orbitals for the 16 molecules being only 11. As valence-electron method we have used the *ab initio model potential* method (AIMP)²² at the HF level. The atomic valence basis sets are very flexible; they are considerably splitted and extended by the use of polarization, diffuse, and extra *d*-type functions according to the comments in Sec. III. The details of both model potentials and valence basis sets are described next. All of them are available from the authors upon request.

A. Nonrelativistic model potentials and basis sets

With respect to their valence properties, main group elements are usually considered to be ns^x elements (IA and IIA groups) and ns^2np^x elements (IIIA to VIIIA groups). However, the core character of the outermost $(n-1)p$ orbitals of alkaline earths is questionable. As a matter of fact, it can be shown (see Sec. V) that $(n-1)p$ orbitals do influence the bonding properties of the ground state of most MX_2 molecules considered here. Consequently, we have prepared core model potentials and valence basis sets for Mg, Ca, Sr, and Ba including $(n-1)pns$ orbitals in the valence that we refer to as core-2s (Be-like), core-3s (Mg-like), core-3d (Zn-like), and core-4d (Cd-like), respectively, so indicating what the outermost core orbital is. These model potentials and basis sets have been prepared following the same procedure as in Ref. 22(a). In order to study the effects of the $(n-1)p$ orbitals on the equilibrium geometry, we performed nonrelativistic calculations with the alkaline earth atomic core including up to the $(n-1)p$ orbitals; the corresponding nonrelativistic core $(n-1)p$ model potentials and basis sets have been taken from Ref. 22(a). For the halogens we have used the nonrelativistic model potentials and basis sets presented in Ref. 22(a): in all cases the valence is $nsnp$.

The ability of the AIMP valence basis sets to mimic the behavior of all electron (AE) basis sets with the same quality in the valence part has been shown in a number of atomic and molecular test calculations.²² This means that all the experience already gathered on the design of molecular basis sets can be used for model potential calculations: first, analogous splitting pattern for the outermost orbitals can be used and second, the atomic AIMP valence basis sets can be extended with the same extra functions that have been obtained for

AE basis sets (in order to make them flexible enough to meet the molecular environment demands). In Table III we show the molecular basis sets used in the calculations. At least single splitting (corresponding to double-zeta quality for the valence) is used, and double or triple splitting is considered going down the IIA and VIIA groups.

As to functions to extend the atomic sets (Table III), *orthogonalization functions* have been proven to be necessary in model potential calculations²² when a particular symmetry does not include occupied valence atomic orbitals but only core orbitals; the role of these functions is not to represent any valence orbitals, but to enable the molecular orbitals to reach high orthogonality with the cores. These functions have been taken from Ref. 27 and correspond to that contracted Gaussian type function (CGTF) that contributes most to the outermost core orbital of the symmetry been considered. *Polarization functions* have been added to all atomic basis sets. One *d*-type polarization function for the halogens and one *p*-type for the alkaline earths;²⁷ for magnesium, one *d*-type polarization function generated to be used with Mg^{2+27} is also included (see below for *d*-type polarization functions for Ca, Sr, and Ba). *Diffuse functions* for anions have been taken from Ref. 26 for F and Cl. For Br and I one *p*-type Gaussian-type function (GTF) with exponent 0.043 and 0.039, respectively, leads to electron affinity values different from the numerical HF ones by 0.05 and 0.03 eV, respectively, when added to the basis sets of Ref. 27 Br (43321|4321|31) and I (433321|43321|421). Finally, an important set of *extra d-type functions* have been used in the basis sets of Ca, Sr, and Ba. These functions pursue two objectives: (i) they act as polarization and orthogonalization functions (particularly the innermost contracted) and (ii) they enable the participation of unoccupied $(n-1)d$ orbitals. The set (311) used for Ca has been taken from Ref. 24, the sets (421)-Sr and (3221)-Ba have been optimized in atomic calculations on Sr^+ ($4d^{1-2}D$) and Ba^+ ($4d^{1-2}D$).

B. Cowan-Griffin relativistic model potentials and basis sets

The major relativistic effects may be straightforwardly included in the AIMP^{22(c),28} along the Cowan-Griffin ap-

TABLE III. Basis sets used in the molecular calculations on MX_2 molecules.^a

Element		Valence basis set
Mg	core-2p	(61 3 ^o * 1*)
	core-2s	(61 411* 1*)
Ca	core-3p	(81 3 ^o * 311)
	core-3s	(81 511* 311)
Sr	core-4p	(10,1 3 ^o * 421)
	core-3d	(10,1 711* 421)
Ba	core-5p	(11,11 3 ^o * 3221)
	core-4d	(11,11 911* 3221)
F	core-1s	(41 3111 [^] 1*)
Cl	core-2p	(61 4111 [^] 1*)
Br	core-3d	(711 51111 [^] 3 ^o *1*)
I	core-4d	(911 71111 [^] 3 ^o *1*)

^aSuperscripts o, *, and A denote orthogonalization, polarization, and diffuse for anion-type functions, respectively.

proximation.²⁹ The atomic one-electron operators that constitute the Cowan–Griffin relativistic AIMP are constructed as follows. The numerical Cowan–Griffin (CG) solution is obtained for each atom for which relativistic effects are to be considered. The atomic relativistic (CG) core orbitals are expressed analytically and used to construct the usual core potentials:²² Coulomb, exchange, and projector operators. Thereby these operators bring indirect relativistic effects to the molecular valence due to relativistic core orbital change. The valence mass velocity (MV) and Darwin (DW) potentials, which correspond to orbital-dependent local one-electron operators, are also obtained along the atomic numerical CG calculation. These operators are represented through nonlocal spectral expansion^{22(c)} which, carried to the molecular calculation, ensure that one center valence mass velocity and Darwin integrals are exactly evaluated. This *explicit* representation of atomic MV and DW potentials in the molecular calculation is characteristic of the AIMP method and is in clear contrast with what is usually done in pseudo-, effective, and model potential methods³⁰ which include valence MV and DW potentials *indirectly* through the parametrization of their potentials so as to reproduce CG (reference) all electron results.³⁰

We would like to stress now that, according to the *ab initio* philosophy on which the AIMP method is based, no attempt is ever done to reproduce any reference all electron CG results through parametrization: neither in the construction of model potential operators with relativistic orbitals, nor in the construction of explicit valence MV and DW operators. The only parameters of the method are those in the valence basis set which is optimized through the application of the variational principle to the valence energy.

Cowan–Griffin relativistic core model potentials and valence basis sets have been obtained for Sr (core–4*p* and core–3*d*), Ba (core–5*p* and core–4*d*), Br (core–3*d*), and I (core–4*d*). The basis set patterns used for the molecular cal-

culations are the same as in Table III with the only exception of Sr *d*-type functions that are now (321). Polarization functions and diffuse functions for anions have been taken from the nonrelativistic sets (test calculations have shown that they are transferable from the nonrelativistic to the Cowan–Griffin relativistic calculations); orthogonalization functions and *d*-type functions for unoccupied ($n - 1$)*d* orbitals have been obtained along atomic Cowan–Griffin relativistic AIMP calculations using the same criteria as the ones used in their nonrelativistic preparation.

V. RESULTS

In this section we analyze the bonding properties of the ground state of MX₂ molecules emphasizing on the equilibrium geometry. Since the quality of the results for the 16 molecules is uniform, overall descriptions of the properties and of their variations along the IIA and VIIA groups are expected to be meaningful. We compare our results with those of previous experimental and theoretical investigations, and analyze them so as to point out (i) the role of different atomic orbitals and (ii) the relativistic effects on the bonding properties.

The results to be discussed (Table IV) are those corresponding to the most accurate calculations of the ones performed along this study, where (i) a Cowan–Griffin relativistic-type of approximation is used for Sr, Ba, Br, and I, (ii) the valence space is defined as ($n - 1$)*pns*($n - 1$)*d* for the alkaline earths and *nsnp* for the halogens, and (iii) the atomic valence basis sets are considerably splitted and extended with orthogonalization, polarization, and diffuse functions (cf. Sec. IV).

A. Geometry of the MX₂ molecules in their ground state

The results collected in Table IV show that, according to our calculations, there are three groups of molecules in the

TABLE IV. Cowan–Griffin-relativistic *ab initio* model potential results on MX₂ molecules.

	$r_e/(\text{Å})$	$\alpha_e/(\text{deg})$	$\bar{v}_1/(\text{cm}^{-1})$	$\bar{v}_2/(\text{cm}^{-1})$	$\bar{v}_3/(\text{cm}^{-1})$	$V_0/(\text{cm}^{-1})$
MgF ₂	1.758	180	579	151	927	
MgCl ₂	2.206	180	292	105	577	
MgBr ₂	2.349	180	190	80	522	
MgI ₂	2.580	180	132	78	447	
CaF ₂	2.053	180	456	17	637	
CaCl ₂	2.540	180	265	50	442	
CaBr ₂	2.680	180	171	33	382	
CaI ₂	2.903	180	117	34	316	
SrF ₂	2.191	144	440	76	509	167
SrCl ₂	2.700	180	251	19	337	
SrBr ₂	2.830	172	160	13	267	6
SrI ₂	3.061	180	110	9	217	
BaF ₂	2.331	126	406	77	436	1086
BaCl ₂	2.898	143	233	36	275	170
BaBr ₂	3.026	146	154	25	211	215
BaI ₂	3.275	157	105	18	169	89

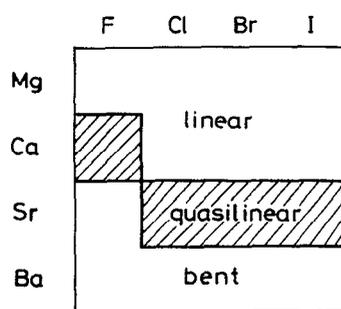


FIG. 1. Classification of the MX_2 molecules according to the results of Cowan-Griffin relativistic calculation.

MX_2 set in what respects to their equilibrium geometry. These groups are illustrated in Fig. 1. Group 1 is formed by linear molecules: MgX_2 , CaCl_2 , CaBr_2 , and CaI_2 . Group 2 includes all clearly bent molecules: SrF_2 and BaX_2 . Finally, group 3 contains what may be called quasilinear molecules: CaF_2 , SrCl_2 , SrBr_2 , and SrI_2 , meaning that their nuclear potential is very flat along the bending coordinate. As a matter of fact, the variation of the energy with the bond angle, in these molecules, is so small that the precision of the method only allows us to stress on the flatness of the potential, whereas the particular values of α_e , $\bar{\nu}_2$, and V_0 (bending barrier) become quite irrelevant. As a consequence of this flatness, external perturbations might strongly affect the angle of these molecules, and, in consequence, experimental results based on techniques in which the external perturbations are significant, such as molecular beam electric deflec-

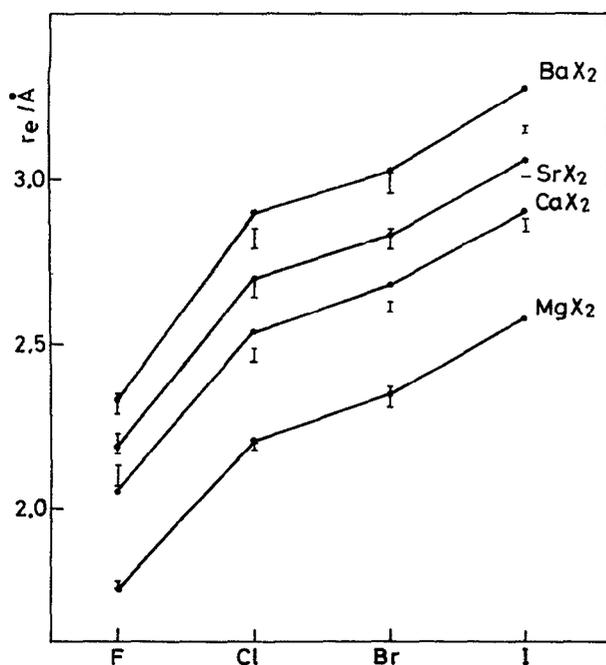


FIG. 2. Ground state bond length of MX_2 molecules: Cowan-Griffin relativistic AIMP results (solid lines) and most recent electron diffraction measurements (vertical bars).

tion and matrix isolation techniques, should be analyzed with caution.

The comparison of our results with the experimental data can be seen in Table I and Figs. 2 to 5. Given the flexibility of the valence *spd* basis set used, the discrepancies are expected to be ascribable to relativistic effects beyond the Cowan-Griffin level considered here and to electron correlation corrections. CaH results by Pettersson *et al.*²⁴ suggest that *f* functions on the alkaline earths might also be necessary beyond the HF level. However, the accuracy of available experimental data as discussed in Sec. II should be kept in mind.

The bigger discrepancies between our r_e values and the thermally averaged M-X distance corresponding to the more recent ED data available, amount to 0.02 for MgX_2 , 0.06 for CaX_2 , 0.05 for SrX_2 , and 0.08 Å for BaX_2 compounds. Of these, only Mg, Ca, and Sr difluorides show shorter r_e than the experimental values. Correction of the thermally averaged ED values for vibrational effects¹² could lead to slightly shorter M-X distances; then, the discrepancies rise to 0.09 for CaCl_2 ¹² and 0.1 Å for BaI_2 .¹² The overall tendencies are correct, suggesting that the unmeasured Mg-I distance might be slightly lower than 2.58 Å. As mentioned before, a central goal of our work has been to estab-

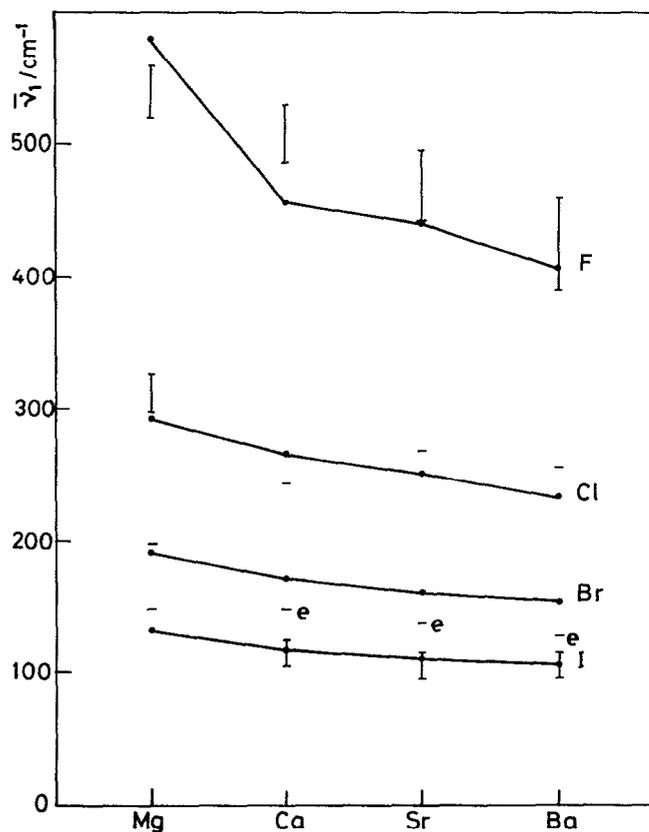


FIG. 3. Vibrational frequency for the symmetric stretching of MX_2 molecules. Cowan-Griffin relativistic AIMP results (solid lines), experimental results (vertical bars), and approximately estimated values (e).

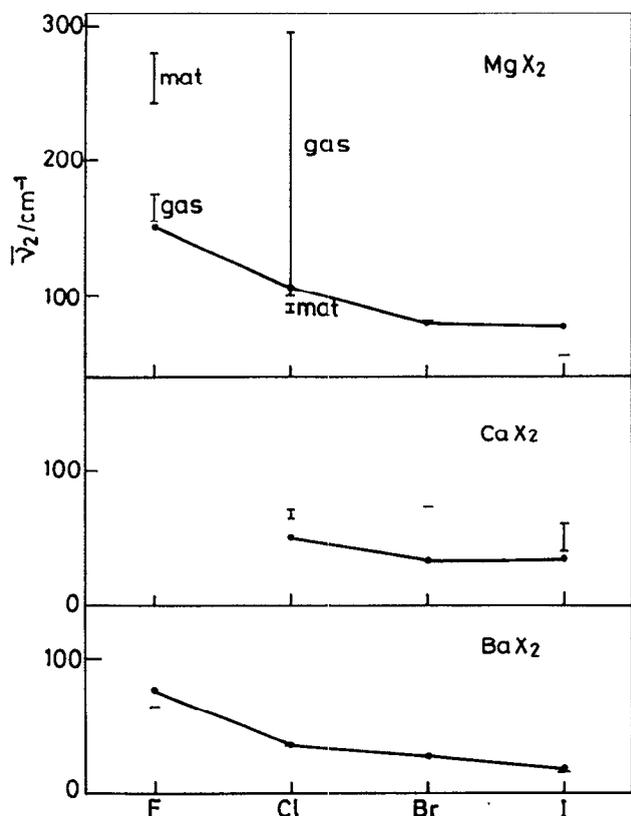


FIG. 4. Vibrational frequency for the bending of MX_2 molecules. Cowan-Griffin relativistic AIMP results (solid lines) and experimental results (vertical bars). Only linear and bent molecules (except SrF_2) are shown.

lish, in the framework of a *uniform* theoretical treatment, the variation of the equilibrium geometry from linear to bent along the IIA and VIIA groups. In this way, our results can help to interpret the experimental data, which, in this respect, are particularly contradictory and of irregular accuracy. All molecules of group 1 are found to be linear experimentally in agreement with our results. For molecules of group 2, the experimental picture is not consistent: while Akishin *et al.*¹ conclude that all of them are linear, MBED experiments,⁴ ir mat^{5,6} (except for BaBr_2 and BaI_2 , not studied through this technique) and the recent ED study of BaI_2 by Gershikov *et al.*¹² describe them as bent molecules. The results of our work support the conclusions of the latter. However, the apex angle is usually found to be smaller than the calculated one when determined by ir mat through the isotopic shift technique. More accurate measurements of the apex angle for this group of molecules are only available for BaI_2 ,¹² where it has been inferred from gas phase ED experiments (including vibrational corrections) and come to $148(9)^\circ$ in good agreement with our calculated 157° . For group 3 of quasilinear molecules, the only available gas phase ED experiments are those of Ref. 1, covering the four molecules, and those of Ref. 11 for SrI_2 . (The ir-gas study of Ref. 7, on the vibrational stretching spectral region, assigns

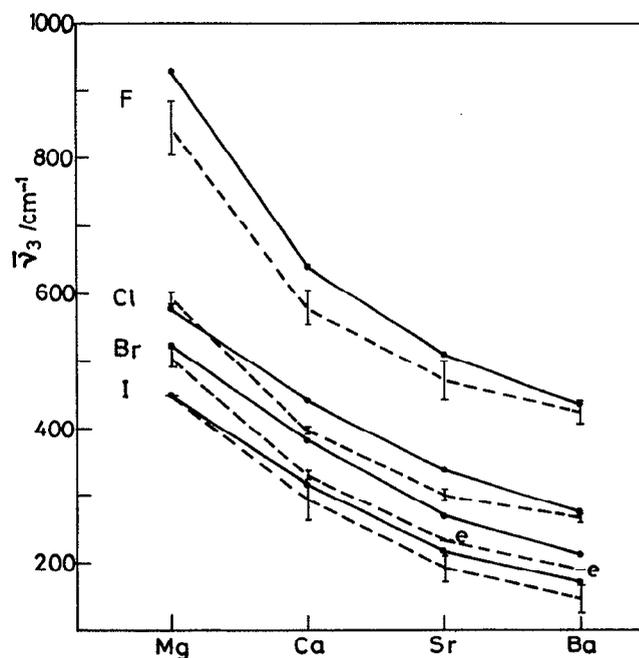


FIG. 5. Vibrational frequency for the antisymmetric stretching of MX_2 molecules. Cowan-Griffin relativistic AIMP results (solid lines), experimental results (vertical bars), and approximately estimated values (e).

only the antisymmetric one; the values of $\bar{\nu}_1$ that appear in Table I and Fig. 3 correspond to estimations based on vapor entropy calculations.) All these experiments describe them as linear molecules. However, CaF_2 and SrCl_2 are found to be bent both through MBED and ir-mat experiments, with bond angles of 145° (ir mat) and 120° (ir mat), respectively. The flatness of the nuclear potentials calculated in this work suggests that, in these cases, both matrix effects and induced dipole moment interactions along ir mat and MBED experiments could easily induce a bent structure or, at least, lower the angle of an already bent structure. To illustrate this, the calculated minimum energies at $\alpha = 150^\circ$, taking the linear minimum as the reference, are 86 cm^{-1} for CaF_2 and 162 cm^{-1} for SrCl_2 . This value for SrCl_2 at $\alpha = 120^\circ$ is, however, 1217 cm^{-1} , suggesting that 120° for SrCl_2 might be too low. Due to the uncertainty that may be expected from both ir mat and MBED experiments when applied to flat potential molecules, we would like to stress on the classification of CaF_2 and SrCl_2 as, simply, quasilinear molecules.

As to the vibrational frequencies, a close look to the experimental data (Table I, Figs. 3 to 5) reflects so wide a discrepancy between the results of different techniques or from gas phase vs matrix isolation experiments, that there is no easy way to make an overall comparison. Nevertheless, excluding the quasilinear molecules where particularly our $\bar{\nu}_2$ becomes considerably inaccurate and simply reflects the flatness of the potential, the variations of the $\bar{\nu}_i$ along the IIA and VIIA groups coincide qualitatively, and the overall quantitative agreement is satisfactory. Note that the vibra-

tional frequencies have been calculated using the valence force field approximation,³¹ which may affect especially the quality of $\bar{\nu}_3$.

We would like to compare now our results with those of previous *ab initio* calculations. Since it has been shown, through basis set effect studies, the importance of a proper representation of $(n-1)d$ orbitals in the alkaline earth basis sets,^{22(a),24,25} of diffuse functions for halogens,²⁶ and of the use of split valence and polarization functions in molecular calculations, we will only compare our results to the ones of previous calculations which use basis sets of similar quality as those in Table III. In this way we will be able to avoid the consideration of uncontrolled basis set truncation effects along the discussion.

High quality basis sets have been used for MgF_2 and MgCl_2 by Jasien and Dykstra²¹ and for CaCl_2 by Yarkony *et al.*¹⁶ leading to r_e values in close agreement with ours, being the discrepancy at most 0.01 Å. Although the angle was not optimized for MgF_2 nor for MgCl_2 in Ref. 1, the corresponding optimization on CaCl_2 was performed¹⁶ leading also to 180°. Yarkony *et al.*¹⁶ used also a good basis set for Ca and F (although no polarization nor diffuse functions were included in the fluorine basis set) in order to study the linear/bent structure of CaF_2 . The authors found a linear equilibrium geometry for this molecule so contradicting the experiments and suggested that a better fluorine basis set might lead to agreement with the MBED and ir mat results. Our results show that a better fluorine basis set describes CaF_2 as a quasilinear molecule with a flatter nuclear potential: The energy necessary to bend the molecule down to 150° is 86 cm^{-1} in our calculation, vs 173 cm^{-1} found by Yarkony *et al.*¹⁶

B. Role of the alkaline earth $(n-1)p$ and $(n-1)d$ orbitals on the bonding

Looking at Fig. 1 and Table IV, it can be seen that the more polarizable the alkaline earth and the smaller the halogen, the more likely is the molecule to be bent, and, within group 2, the smaller is the apex angle predicted. This tendency has been commented by Klemperer *et al.*⁴ as the qualitative prediction corresponding to the simple classical polarizable ion model used by Debye.³² The analysis of the bonding, which follows, shows that this overall behavior is actually shown *only* when flexible basis sets are used to represent $(n-1)p$ and $(n-1)d$ orbitals, so enabling the physical response of the central atom densities to the polarizing power of the ligands. Otherwise, *all* MX_2 molecules are wrongly predicted to be linear.

Let us now study the role of the alkaline earth $(n-1)p$ orbitals in the bonding. It is possible to study very directly the participation of a particular atomic orbital in the molecular bonds by comparing two types of calculations: First, the atomic orbital is frozen and included in the core model potential to restrict its effects on the bonds. Second, the atomic orbital is promoted to the valence and represented by a flexible enough basis set, so that it could eventually contribute to the bonding. The closer the effective core potential method used is to the frozen orbital approximation, the better the

comparison just described illustrates the atomic orbital participation in the bonding.

In Table V we present this kind of study of the bonding for the MX_2 set. The $(n-1)p$ orbitals are included in the core definition in the calculations labeled core $(n-1)p$ and are promoted to the molecular valence otherwise [core $(n-1)s$ or core $(n-2)d$ calculations]. Note that the orthogonalization functions used in core $(n-1)p$ basis sets only serve to the purpose of achieving strong orthogonality, the six p electrons being frozen core electrons.²²

In the magnesium dihalides, the promotion of the Mg $2p$ orbitals to the valence, only produces a small change in r_e , $|\Delta r_e| < 0.02$ Å, and minor effects in the vibrational frequencies, revealing a negligible deformation of them. However, the variation of the molecular properties after promoting the $(n-1)p$ orbitals to the valence is significant in the rest of MX_2 molecules. The changes in r_e , with the only exception of CaF_2 , range from 0.05 to 0.18 Å, big enough to be ascribed to actual $(n-1)p$ participation in the bonding. r_e is extremely affected in BaF_2 , which shows a collapsing nuclear potential when the $(n-1)p$ orbitals are frozen (if an all electron basis set is used, in order to ensure very high core-valence orthogonality, the result is a too short r_e , 2.207 Å.) The $(n-1)p$ orbitals also produce a significant decrease of the apex angle of the bent molecules, as well as a very important effect on their energy barrier at the linear geometry V_0 , which is multiplied by a factor of 2.5 in SrF_2 and goes from a very low, or even null value, to a quite high value for BaX_2 . The vibrational frequencies $\bar{\nu}_1$ and $\bar{\nu}_3$ for SrF_2 and BaF_2 , and $\bar{\nu}_2$ for the bent and quasilinear molecules are also quite affected by the $(n-1)p$ orbitals.

All these results show that the $(n-1)p$ orbitals remain essentially atomic for magnesium dihalides but do participate in the bonding in the rest of the molecules, being particularly active in stabilizing the bent structures according to the polarizable ion model sequence, so suggesting that $(n-1)p$ orbitals contribute to the polarization of the alkaline earth by the ligands.

The involvement of the alkaline earth $(n-1)d$ orbitals in the bonding has been shown in studies of basis set effects on some of their compounds, both in nonrelativistic and relativistic calculations.^{22(a),24,25}

We have picked up the bent molecules, SrF_2 and BaX_2 , to illustrate the role of $(n-1)d$ orbitals in the bonding properties of the dihalides. For this purpose we removed the (21) and (22) outermost d CGTF from the basis sets (10,1|711*|321) of Sr and (11,11|911*|3221) of Ba, respectively. These CGTF are the ones actually representing $(n-1)d$ orbitals while the innermost CGTF (3) serve only for core-valence orthogonality purposes and thus must be kept in the basis set.

The results, to be compared with those of Table IV, are: $r_e = 2.279$ Å for SrF_2 and $r_e = 2.452, 3.045, 3.180$, and 3.422 Å for $\text{BaF}_2, \text{BaCl}_2, \text{BaBr}_2$, and BaI_2 , respectively. In all cases the bond angle turns to be 180°. These results show the chief role of $(n-1)d$ in the bonding of alkaline earth dihalides.

Altogether, the results in this subsection show that the

TABLE V. Nonrelativistic (NR) and Cowan-Griffin relativistic AIMP (QR) results on MX_2 molecules. The alkaline earth $(n-1)p$ orbitals are included in the core in the calculations labeled core $(n-1)p$; they are part of the molecular valence otherwise.

			F	Cl	Br	I
			$r_e/(\text{Å})$			
Mg	core-2p	NR	1.735	2.186	2.339	2.585
		QR			2.368	2.598
	core-2s	NR	1.758	2.206	2.355	2.597
		QR			2.349	2.580
Ca	core-3p	NR	2.071	2.623	2.781	3.046
		QR			2.772	3.031
	core-3s	NR	2.053	2.540	2.683	2.923
		QR			2.680	2.903
Sr	core-4p	NR	2.125	2.802	2.960	3.234
		QR	2.148	2.799	2.945	3.207
	core-3d	NR	2.176	2.701	2.842	3.086
		QR	2.191	2.700	2.830	3.061
Ba	core-5p	NR		3.052	3.203	3.472
		QR		3.053	3.205	3.457
	core-4d	NR	2.326	2.890	3.028	3.290
		QR	2.331	2.898	3.026	3.275
			$\alpha_e/(\text{deg})$			
Sr	core-4p	NR	147			
		QR	155			
	core-3d	NR	138			
		QR	144			
Ba	core-5p	NR		180	164	167
		QR		180	169	170
	core-4d	NR	125	140	142	153
		QR	126	143	146	157
			$V_0/(\text{cm}^{-1})$			
Sr	core-4p	NR	206			
		QR	65			
	core-3d	NR	429			
		QR	167			
Ba	core-5p	NR			21	8
		QR			6	4
	core-4d	NR	1396	292	321	133
		QR	1086	170	215	89
			$\bar{\nu}_1/(\text{cm}^{-1})$			
Mg	core-2p	NR	570	312	195	137
		QR			184	135
	core-2s	NR	579	292	190	135
		QR			190	132
Ca	core-3p	NR	418	246	155	110
		QR			153	108
	core-3s	NR	456	265	167	120
		QR			171	117
Sr	core-4p	NR	298	230	147	104
		QR	296	235	146	102
	core-3d	NR	457	247	152	110
		QR	440	251	160	110
Ba	core-5p	NR		210	137	102
		QR		205	134	99
	core-4d	NR	404	234	156	109
		QR	406	233	154	105
			$\bar{\nu}_2/\text{cm}^{-1}$			
Mg	core 2p	NR	154	106	90	79
		QR			92	79
	core 2s	NR	151	105	90	79
		QR			80	78
Ca	core 3p	NR	51	53	36	30
		QR			37	31
	core 3s	NR	17	50	36	33
		QR			33	34
Sr	core 4p	NR	86	27	22	21

TABLE V. (continued).

			F	Cl	Br	I
Ba	core 3 <i>d</i>	QR	69	25	9	12
		NR	74	13	13	17
	core 5 <i>p</i>	QR	76	19	13	9
		NR		6	18	9
	core 4 <i>d</i>	QR		8	8	10
		NR	87	36	29	21
		QR	77	36	25	18
$\bar{\nu}_3/\text{cm}^{-1}$						
Mg	core 2 <i>p</i>	NR	912	617	536	465
		QR			508	456
	core 2 <i>s</i>	NR	927	577	523	458
		QR			522	447
Ca	core 3 <i>p</i>	NR	584	409	347	298
		QR			342	291
	core 3 <i>s</i>	NR	637	442	374	326
		QR			382	316
Sr	core 4 <i>p</i>	NR	345	310	247	206
		QR	348	316	246	201
	core 3 <i>d</i>	NR	523	332	256	218
		QR	509	337	267	217
Ba	core 5 <i>p</i>	NR		259	198	169
		QR		252	196	166
	core 4 <i>d</i>	NR	433	274	210	172
		QR	436	275	211	169

alkaline earths are far from being ns^2 elements; instead, they are as demanding in terms of basis set requirements as transition metal elements, being their actual chemical valence $(n-1)pns(n-1)d$. These results are in the line of what has been found for CaH beyond the HF level²⁴ and for alkaline earth hydrides in relativistic calculations²⁵ where both $(n-1)p$ and $(n-1)d$ orbitals have been found to contribute strongly to the accuracy of the calculated equilibrium geometry.

C. Relativistic effects

The relativistic effects introduced according to the approximate method described in Sec. IV for the molecules containing Sr, Ba, Br, and I are also shown in Table V.

The effects in bond length (always below 0.02 Å in absolute value), bond angle, and vibrational frequencies are very small. Magnesium and calcium compounds show a bond length contraction that grows from the dibromide to the diiodide. Strontium and barium diiodide show a relativistic contraction that is progressively canceled and turned to a net expansion towards the difluorides. Previous studies by Pyykkö *et al.*²⁵ have also shown that the participation of $(n-1)d$ orbitals of IIA elements tend to cancel most of the relativistic contraction and sometimes even induce small relativistic bondlength expansions in alkaline earth hydrides. We have done some numerical experimentation to prove that this is also true for the dihalides: The relativistic effect on r_e , $\Delta r_e = r_e(\text{QR}) - r_e(\text{NR})$, for SrF₂ is found to be a contraction if $(n-1)d$ orbitals are removed from the valence, $\Delta r_e = -0.015$ Å. When they are included in the valence

space (see Table V), Δr_e turns to be +0.015 Å. The interplay between the expansion brought about by the $(n-1)d$ orbitals and the contraction due to the $(n-1)pns$ orbitals of Sr and Ba, and to the $nsnp$ orbitals of Br and I, is responsible for the progressive cancellation of the contraction commented above when going from the diiodides towards the difluorides.

The relativistic effect which is more remarkable in the MX₂ molecules is the reduction of the barrier at the linear geometry of the bent molecules V_0 . This means that relativistic terms produce a smaller stabilization of the bent structures relative to the stabilization of the linear arrangement. Again, the smaller the ligand and the more polarizable the alkaline earth, the greater is the relativistic decrease of the barrier V_0 (see Table V). This feature can be explained taking into account that d orbitals are known to be instabilized by relativity³³ and that $(n-1)d$ orbitals have just been shown to be responsible for the bending. In any case, the relativistic decrease of the bending barrier is not so high as to change the description of these molecules from bent to quasilinear.

VI. CONCLUSIONS

The equilibrium geometry of alkaline earth dihalides has been studied at the HF level using the Cowan-Griffin relativistic *ab initio* model potential method and a uniformly good, extended, *spd* valence basis set. According to this method, all magnesium dihalides and CaCl₂, CaBr₂, and CaI₂ are linear, SrF₂ and all barium dihalides are bent, and CaF₂ and SrCl₂, SrBr₂, and SrI₂ are quasilinear molecules.

Calculated bond distances are close to the experimental data available and follow the correct tendency, the magnitude of the discrepancies being ascribable to electron correlation corrections and further improvements in the relativistic treatment and basis set (i.e., use of f functions for the alkaline earths). The major discrepancies with the available experimental data appear in the group of quasilinear molecules: CaF_2 and SrCl_2 are described to be bent in molecular beam electric deflection and infrared of vapor isolated in solid matrix experiments. The very flat potential, with respect to the bending angle, found for these molecules, suggests that the interaction between the applied electric field and the molecules, in the first case, and between the solid matrix and the molecules, in the second case, may be responsible for the experimental detection of bent structures. The apex angle of the bent molecules is calculated higher than the experimental values corresponding to matrix isolation techniques and are in good agreement with more accurate gas phase electron diffraction studies.

A comparable, systematic and *uniformly accurate* experimental study of the geometry and vibrational frequencies of these molecules would be necessary. Particularly, accurate determinations of the apex angle and of the bending barrier would be required to contrast our results and, especially, their evolution along the IIA and VIIA groups.

Of particular interest has been the analysis of the participation of $(n-1)p$ and $(n-1)d$ orbitals of the alkaline earths and of the relativistic effects in the bonding properties. The $(n-1)d$ orbitals are shown to be responsible for the bending of the heavier molecules while $(n-1)p$ contribute considerably to the final quantitative prediction of the apex angle and the relative stability of the bent structures. Relativistic effects are shown to be very small on the bond distances and vibrational frequencies and considerable on the size of the bending barrier of the bent molecules, whose value is considerably decreased, this corresponding to a smaller relative stabilization of the bent configuration related to the $(n-1)d$ involvement in the bending.

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