Coordination Chemistry Reviews, 9 (1972/73) 189–200

INFRARED SPECTRA AND GEOMETRY OF GROUP II METAL DIHALIDES

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(Received February 25th, 1972)

CONTENTS

A. INTRODUCTION

The infrared spectra of the Group II dihalides have been subject to many investigations in the gas phase, and in inert gas matrices. The purpose of these is to determine force constants and apex angles of the isolated molecules from vibrational frequencies. Some of the molecules are linear and others are bent. In linear molecules the force constants can easily be determined by assuming the valence force-field model [1a]. The symmetric stretch frequency ν_1, which does not appear in the infrared, is also determined by use of this model. In bent molecules an initial indication of the geometry is deduced from the number of frequencies appearing in the spectrum. An absorption due to ν_1, together with the asymmetric stretch frequency ν_3 and the bending frequency ν_2, indicates non-linearity. The apex angle may be calculated from the three gas-phase frequencies (Herzberg [1a], eqn. II (192)), but it should be noted that this method does not usually give satisfactory results. Another possibility for determining apex angles is to measure the isotope effect. According to the Teller–Redlich product rule, the apex angle is calculated from the frequency ratio of two isotopic species. The arguments above are valid specifically for isolated molecules, and refer to the fundamental transition of the molecules.

An ideal experiment for obtaining information concerning the Group II MX_2 molecules would require gas-phase conditions (to deal with isolated molecules) and low temperatures (in order to observe the fundamental transition, and not transitions to or from excited states, the so-called "hot bands"). As is well known, all the species dealt with here are solid at ambient temperatures. For gas-phase experimentation, the molecules are heated to high (sometimes very high) temperatures. This leads to a serious problem, since at high temperatures it is not possible to observe only the absorption due to the fundamental transitions. For this reason the technique of investigating these molecules in solid inert gas matrices at very low temperatures is important.

The purpose of the present discussion is to review the experimental work which has been carried out and to examine critically the results and their reliability. For related reviews see refs. 1a, 1b. The experimental frequencies reported in the literature for both the gas phase and matrices are summarized in Table 1.

B. COMPARISON OF GAS-PHASE AND MATRIX MEASUREMENTS

Most of the measurements of vibrational frequencies in the gas phase have been performed by Klemperer and co-workers [2–5] and Baikov [6,7]. However, there is not even one molecule for which all three frequencies are reported. The absorption bands given in the literature are very wide, and the absorption maxima are not definitive. Therefore, the frequencies of absorption quoted have a large error. This is true even for species with high vapour pressure at moderate temperatures, such as the mercury halides [2]. Also, the rotational structures are not resolved in the experimental spectrum. These facts tend to indicate that is is not feasible as yet to decide the exact frequency values of the fundamental transitions. This argument is reinforced by examining cases where similar absorptions are quoted in different investigations. For $CdCl_2$ the frequency ν_3 in the gas phase is assigned [3] as 427 cm^{-1} and in another work [5] as 409 cm^{-1}. Similarly for $MgCl_2$ we find 597 cm^{-1} (ref. 4) and 588 cm^{-1} (ref. 8). The values of the bending frequencies ν_2 of some fluorides [6] appear at very low energies, but the results quoted are estimates only, with appreciable uncertainty owing to the low sensitivity of the detecting devices in this region.

In inert gas matrix experiments (see discussion in ref. 1b) the absorption bands are narrow and sharp. Detailed measurements were performed by Mann and co-workers[9, 10], Loewenschuss et al.[11, 12], Hastie et al.[13–15] and Snelson[16]. Owing to the low temperatures used in this technique, the vibrational absorption frequency corresponds to the fundamental transition. No rotational structure is observed, since the molecule, embedded in the matrix, cannot rotate. The disadvantage of this technique is that absorption frequencies are shifted, usually towards lower energies. This emerges from examination of the absorption bands measured in several matrices. In all measurements[11, 13, 14, 16], absorption is shifted to lower frequencies when going from neon to argon to krypton (see Table 1). Snelson[16] and Baikov[6, 7] concluded from this that the gas-phase frequency has a higher value than the frequency observed in a neon matrix. This is a useful empirical observation. However, from the experimental frequencies it can be seen that the gas-phase absorption, though not accurate, is in some cases lower than the matrix value[6, 7, 16]. Thus, in the MgF spectrum[9], the fundamental transition frequency (710 cm^{-1}) is lower than the krypton matrix frequency value (740 cm^{-1}). From comparison of gas-phase and matrix measurements it seems that the gas-phase frequencies cannot always be determined by reference to matrix measured frequencies. It is seen from Table 1 that there are marked differences be-

TABLE 1

Experimental frequencies of Group II MX_2 molecules

Molecule	Gas			Neon			Argon			Krypton			Assigned to other species
	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3	
BeF_2		$825^{a}, 345^{c}$	1520^{a}		333^{b}	1545^{b}		317^{b}	1528^{b}		311^{b}	1524^{b}	$290^{b}, 830^{b}, 1250^{b}$
$BeCl_2$		482^{a}	1113^{a}		238^{b}	1123^{b}			1109^{b}			1100^{b}	$640^{b}, 870^{b}$
$BeBr_2$					207^{b}	993^{b}			985^{b}				
BeI_2						872^{b}			877^{b}				
$^{24}MgF_2$		160^{c}	825^{d},		254^{b}	865^{b}		243^{b}	$840^{b}, 842^{c}$	478^{e}	$238^{b}, 242^{c}$	$836^{b}, 837^{e}$	$740^{b,e}, 490^{b,e}, 450^{e}$
$MgCl_2$		295^{a}	$597^{a}, 588^{f}$								109^{h}		
$MgBr_2$			490^{f}										
$^{40}CaF_2$		115^{c}	575^{d}	504^{b}		581^{b}	489^{b}		561^{b}	$487^{b}, 485^{g}$	163^{g}	$555^{b}, 554^{g}$	$370^{b,g}, 530^{b,g}$
$CaCl_2$			395^{d}			414^{i}			394^{i}		90^{h}		
$CaBr_2$			330^{d}										
CaI_2			290^{d}										
$^{88}SrF_2$		100^{c}	455^{d}	469^{b}		471^{b}	447^{b}		450^{b}	$439^{b}, 441^{g}$	82^{g}	$443^{b}, 442^{g}$	$305^{b}, 360^{b}$
$SrCl_2$			300^{d}				275^{j}		308^{j}		60^{h}		
BaF_2		95^{c}	415^{d}	437^{b}		413^{b}	421^{b}		398^{b}	$416^{b}, 413^{g}$		$392^{b}, 390^{g}$	320^{b}
$BaCl_2$			265^{d}	262^{j}	62^{j}	268^{j}	226^{j}	61^{j}	$234^{j}, 247^{j}$				
$^{64}ZnF_2$						772^{k}			763^{k}		151^{l}	758^{l}	$710^{k}, 680^{k}, 430^{l}, 660^{l}$
$ZnCl_2$	361^{m}	295^{n}	516^{o}					105^{l}	512^{l}		102^{l}	505^{l}	$150^{l}, 270^{l}, 425^{l}, 120^{l}$
$ZnBr_2$	230^{m}	225^{n}	$400^{n}, 413^{o}$								73^{l}	404^{l}	$326^{l}, 227^{l}, 146^{l}$
ZnI_2	168^{m}		340^{o}								62^{l}	346^{l}	$193^{l}, 272^{l}$
CdF_2											123^{p}	662^{p}	$384^{p}, 475^{p}$
$CdCl_2$			$409^{n}, 427^{o}$								89^{p}	419^{p}	371^{p}
$CdBr_2$			315^{o}								62^{p}	319^{p}	$163^{p}, 190^{p}, 270^{p}$
CdI_2			265^{o}									270^{p}	$153^{p}, 222^{p}$
HgF_2											172^{p}	642^{p}	$384^{p}, 586^{p}, 660^{p}$
$HgCl_2$	355^{q}		413^{r}								107^{p}	411^{p}	
$HgBr_2$	220^{q}		293^{r}					73^{p}	297^{p}		73^{p}	294^{p}	$286^{p}, 261^{p}$
HgI_2	155^{q}		237^{o}								63^{p}	238^{p}	223^{p}

(1) In the case of matrix splitting, only one component is cited. (2) The frequencies are rounded off to three significant figures. (3) Frequencies are tabulated as assigned in the original reference. (4) Frequency units in cm^{-1}.

[a] Ref. 4; [b] Ref. 16; [c] Ref. 6; [d] Ref. 7; [e] Ref. 9; [f] Ref. 8; [g] Ref. 10; [h] D. White, private communication; [i] Ref. 15; [j] Ref. 14; [k] Ref. 13; [l] Ref. 11; [m] Ref. 21; [n] Ref. 5; [o] Ref. 3; [p] Ref. 12; [q] Ref. 20; [r] Ref. 2.

tween gas-phase and matrix absorptions assigned to ν_2 for $CaCl_2$, MgF_2 and SrF_2, and similar arguments hold for the assigned ν_3 frequencies of MgF_2 and BaF_2. In the Group IIB metal halides the differences between gas-phase and matrix values are smaller. This seems to be coincidental when the great uncertainty in assigning absorption frequencies from gas-phase measurements is considered.

Allavena et al.[17] calculated the apex angle and force constants of SO_2 from matrix frequencies, and found that these values were close to gas-phase values. It was concluded that for the Group IIA fluorides a similar calculation will also give apex angles and force constants of the gas-phase or isolated molecules. In Table 2 we compare apex angles calculated from the isotope effect[10, 17] and those calculated from the three vibrational frequencies (ref. 1a, eqn. II (192)) of SO_2 and the fluorides. Table 2 demonstrates the fact that while for SO_2 there is agreement between angles calculated from the isotope effect and those calculated from the frequencies, and also fair agreement between gas-phase and matrix calculations, for the fluorides the angles calculated from matrix frequencies do not agree with those calculated from the isotope effect. We shall show in the next section that apex angles calculated from the isotope effect are reasonable. It seems that apex angles (as well as force constants) calculated from the three matrix frequencies are doubtful. Thus it does not seem advisable to make analogies between SO_2 and the fluorides nor between gas-phase and matrix frequency values, since for at least some triatomic molecules this analogy does not hold (Table 2).

From the above argument it is evident that, with the experimental techniques commonly used at present for infrared measurements, it is not possible to determine accurately the fundamental transition frequency of isolated MX_2 molecules. Matrix IR measurements are more informative than the gas-phase measurements. We shall refer next to the matrix technique[1b] and try to examine its advantages and shortcomings.

C. THE ISOTOPE EFFECT

This is a valuable tool for determining force constants and apex angles of molecules. If it is assumed that these constants do not change on isotopic substitution, then all the force constants and the apex angle of a molecule can be obtained from measurements on the various isotopes. Since the molecules dealt with here are relatively heavy, their isotope effect is small, and an instrument with high resolving power is needed. It is not possible to

TABLE 2

Apex angle calculations

	From isotope effect	From three frequencies
(Gas) SO_2	121° 09′	122° 16′
(Krypton matrix) SO_2	120° 06′	120° 56′
(Krypton matrix) MgF_2	158°	Imaginary
(Krypton matrix) CaF_2	140°	115°
(Krypton matrix) SrF_2	108°	91°

observe any isotope effect in these molecules in the gas phase, owing to the wide absorption bands observed in the spectrum, and hence this effect has only been observed in inert gas matrix measurements. Its major application has been in determining the molecular constants of the fluorides by using different isotopes of the metal atom[9, 10, 16]. For the fluorides the method is relatively simple, since the fluorine atom has only one isotope. For chlorides the method is somewhat more complicated since the chlorine atom has two abundant isotopes (see, for example[15], $CaCl_2$).

There exists the problem of assignment of bands in the isotopic measurements. A commonly used criterion is to assign closely spaced bands according to their intensities. The greater the relative abundance of an isotopic species, the greater its absorption intensity. It is of course possible to measure isotopic species separately by carefully establishing identical conditions for the various measurements, as is reported[11] for $ZnCl_2$.

According to the Teller–Redlich product rule, the determination of apex angles in these molecules depends only on the antisymmetric vibration frequency ν_3. It is possible to calculate the apex angle if it is assumed that the ratio of frequencies ν_3 measured in matrices is equal, as a good approximation, to the same ratio of the fundamental transition frequencies. It is possible to check this assumption by looking at the isotope effect for the symmetric frequencies ν_1 (stretching) and ν_2 (bending). The ratio between these frequencies in different isotopes of the same atom depends only on the atomic masses in the molecules (see Herzberg[1a], eqn. II (306)). In Table 3 a comparison is made between the ratio of experimental frequencies and the ratio calculated from atomic masses. The calculations were carried out for only two molecules, because only for these molecules were sufficient data available.

Agreement between the calculated and experimental isotope effects is fairly good. The difference can partly be attributed to anharmonicity, which was not taken into consideration in the frequency values (see, for comparison, Table 52 in ref. 1a). There is no apparent reason to assume a different isotope effect for different frequencies of the same molecule. We then conclude that the isotope effect may be used for the antisymmetric ν_3 frequency ratio and may be applied to the determination of the apex angle in matrix measurements. Some support for this argument can be obtained from the ν_3 isotope effect of the linear $ZnCl_2$ molecule[11]. In this case agreement is found between the calculated and experimental isotope effects.

TABLE 3

Isotope effect

Molecule	$\dfrac{\nu_1^{(i)}\ \nu_2^{(i)}}{\nu_1\ \ \nu_2}$	$\dfrac{\omega_1^{(i)}\ \omega_2^{(i)}}{\omega_1\ \ \omega_2}$
MgF_2	0.981	0.976
CaF_2	0.982	0.978

ν – experimental frequencies

ω – harmonic frequencies of fundamental transitions

It should not be deduced from the above arguments that an accurate value of the apex angle can be derived. Rather, a range is obtained, which is sometimes quite large[9, 10], owing to the fact that the frequency shift of an isotopic species is not a sufficiently sensitive function of the apex angle. Hastie et al.[13] calculated an apex angle for ZnF_2 lower than 180°, while Loewenschuss et al.[11] predict a linear molecule from the isotope effect (both measurements were of course carried out in matrices). Snelson[16] found the isotope effect of MgF_2 to indicate linearity. Mann et al.[9] obtained for the same molecule an apex angle of about 160°. It is clear then that the determination of apex angle values from the isotope effect requires very careful and precise work. Snelson's measurements[16] are accurate to within $\pm 1\ cm^{-1}$, and consequently his apex angle value is accurate within ± 30°. In the case of Mann et al.[9] the frequency values are much more accurate ($\pm 0.05\ cm^{-1}$) and thus the apex angle is given with an error of ± 5°. Only with such very accurate measurements is it possible to distinguish between a linear and a bent configuration for MgF_2.

It therefore seems advisable to be cautious about conclusions from isotope-effect measurements. When a bent configuration of a molecule is well established (e.g. CaF_2, SrF_2, $SrCl_2$), the apex angle value is still subject to a sizeable error, due primarily to anharmonicity[15].

D. OTHER METHODS OF GEOMETRY DETERMINATION

Apart from spectroscopic measurements, the molecular geometries have been studied by electron diffraction[18], and by the deflection of a molecular beam in an inhomogeneous electric field[19]. A detailed discussion will not be given here since these methods for determining geometries have been discussed in the literature. From electron diffraction measurements it was concluded that all the molecules in question are linear[17]. However, it is by now widely accepted that since the error in determining apex angles by this method is large (up to 40° in some measurements) it is scarcely possible to decide from it whether a molecule is linear or bent.

A more sensitive technique is due to Klemperer and co-workers[19]. However, this method does not give apex angles, and the effect observed is qualitative. This work indicates the fluorides of calcium and strontium, strontium chloride, and all the barium halides to be bent, which does not contradict the spectroscopic measurements. In addition, in almost all molecules where no indication of bending is observed, spectroscopic measurements indicate linearity (e.g. the Group IIB halides). The deflection method is reliable when definite indications of bent molecules are obtained, since this is based on an observable effect. Conclusions on linearity by this technique are less reliable since they are based on lack of an observable effect. Thus, in the case of MgF_2, Klemperer and co-workers[19] concluded the molecule is linear. Mann et al.[9] deduced from the vibrational spectrum of the molecule in inert gas matrices that it is bent. In the next section we shall try to explain this apparent contradiction.

Some brief remarks on geometries from theoretical approaches seem appropriate. An examination of the experimental geometries of all Group II dihalides[19] leads to the conclusion that a trend towards bending is observed for heavier metal atoms and lighter halogen atoms. The method developed by Walsh[22] for MX_2 molecules predicts a linear configuration for all the molecules. Orbitals of type *s* and *p* only of the central metal atom are considered. Refinement of Walsh's method by including *d* orbitals[23, 24] of the metal atom leads to a possibility of bending in the heavier metal halides, namely the halides of Ca, Sr and Ba. This improves the agreement with experimental results. The trend of geometry on halide substitution can be qualitatively explained by the electronegativity of the halides[23]. This seems to be a rather intuitive approach, and further theoretical work seems called for.

E. MATRIX EFFECTS

In extreme cases the possibility should be borne in mind that the effect of matrix environment may perhaps result in bending a molecule which is linear in the gas phase. The spectrum[9] of MgF_2 in argon and krypton matrices indicates a bent structure, while gas-phase geometry measurements[19] indicate linearity. Similar arguments apply to ZnF_2, for which matrix measurements[13] indicate a bent structure (but the anharmonic factor may not be negligible in this case[13, 15]), while the measurements of Klemperer and co-workers[19] indicate a linear molecule. Whether these differences are really due to matrix effects or to the low sensitivity of the geometry determination techniques is hard to decide at present.

The assignment of bands in the infrared spectrum is also made complicated by so-called matrix splitting. The difficulty arises from the fact that there is no quantitative explanation for this effect. A typical example of such splitting is encountered in the matrix spectrum[9] of MgF_2. In the krypton matrix spectrum a triplet is observed in the absorption band, attributed to the antisymmetric stretching vibration ν_3. A similar multiplet, but consisting of four branches, is observed in the same band measured in an argon matrix. This splitting covers a wide range, extending 5.5 cm^{-1} in the ν_3 absorption band of $^{24}MgF_2$ in the argon matrix. The apex angle determination of the molecule is not affected, because each component of the multiplet exhibits the same isotope effect[9]. However, the multiplet makes it impossible to assign an accurate value to the vibration frequency. Another complication arises from the fact that the matrix splitting appears only in certain absorption bands and in certain matrices. In BeF_2 the ν_2 and ν_3 bands are clearly split in all matrices[16]. In other molecules splitting is observed only in the ν_3 band, while for the ν_1 and ν_2 bands no such effect is observed. This is encountered especially in the fluorides[9, 10, 16]. The spectrum of SrF_2 clearly demonstrates the difficulty of assignment of absorption bands due to matrix splitting. In the ν_3 absorption frequency region[10] of SrF_2, splitting attributed to the matrix effect appears. With an instrument of high resolving power, the ν_1 symmetric frequency could be observed in this region (the difference between ν_1 and ν_3 for SrF_2 is about 1 cm^{-1}) by the use of different isotopes of Sr separately. The matrix splitting of ν_3 overlaps the ν_1 band, and thus complicates the assignment of this latter band (see Fig. 5, ref. 10). Again, some uncertainty is involved in the assignment[14] of ν_1 in $BaCl_2$, partly due to the matrix effect on ν_3.

In the spectrum of ZnF_2 a matrix splitting of ν_3 is observed in neon[13], but not in argon[13] or krypton[11]. It does not seem possible to assign this split to a ν_1 absorption as this would require both a very bent geometry and an unusually large k_{12} interaction. In TiF_2 splitting of ν_3 and detection of ν_1 have been reported[25].

To conclude, it is worthwhile mentioning a case in which the matrix absorption band depends on the experimental conditions, namely the temperature of the vapour. Hastie et al.[14] report a shift of 13 cm^{-1} in the frequency band of superheated $BaCl_2$ trapped in an argon matrix. If this phenomenon is common to other related molecules, it leads to a serious difficulty in the determination of the exact value of a given vibrational frequency.

F. THE SYMMETRIC STRETCH FREQUENCY

According to the selection rules of triatomic symmetric molecules in the infrared, the frequency absorption ν_1 appears only in the spectrum of bent molecules. The experimental data existing in this respect should be handled carefully. In gas-phase measurements Baikov[6, 7] did not observe a ν_1 frequency for some fluorides known to be bent[19]. Although observed in the Raman measurements[20, 21] there is not even one experimental absorption assigned[2–7] to ν_1 in infrared measurements, whether the molecule is linear or bent. It is concluded that available spectroscopic gas-phase data cannot provide a criterion for the geometry of the triatomic molecules. While a ν_1 absorption was not detected in bent molecules[6, 7], there exist spectra of apparently linear molecules that show absorptions which can be assigned to ν_1. In the gas-phase spectrum[4] of $MgCl_2$ an absorption band was found at about 295 cm^{-1} (it was originally assigned to the bending frequency ν_2, but this should appear at a much lower frequency). This band may be assigned to ν_1, thus indicating a bent configuration. Geometry determinations indicate[19] a linear structure for $MgCl_2$, but owing to the limited sensitivity of the experimental techniques a bent structure cannot be ruled out. Similar arguments[4] could be applied to BeF_2 and $BeCl_2$. However, since dimers of $MgCl_2$, BeF_2 and $BeCl_2$ are known to be present in the gas phase from mass spectrometric measurements, the above bands can also be attributed to these species.

In matrix measurements there is at least one example in which a ν_1 frequency may be assigned to an absorption band, namely[12] HgF_2. In the spectrum of this molecule the unclassified absorption at 660.5 cm^{-1} may be assigned to ν_1 (similar assignment is possible for the absorption at 586 cm^{-1}, see ref. 11b). Such an assignment is reasonable, since there is no other explanation for this absorption (HgF or dimers perhaps?). The existence of the ν_1 frequency indicates a bent structure, and this contradicts the assumption that all mercury halides are linear. The spectrum referred to above was taken in a krypton matrix, another example of the possibility of a "matrix effect" that bends the molecule. The above arguments about HgF_2 well illustrate the uncertainty involved in the interpretation of spectroscopic measurements.

Another example is ZnF_2. Hastie et al.[14] calculated from the isotope effect an apex angle smaller than 180° (but see Sect. E), though they (as well as Loewenschuss et al.[11]) did not find any absorption that could be attributed to ν_1. It seems that no decision can be made at this stage as to whether this fact is due to the insensitivity of the isotope effect or to the inability to observe ν_1 (because of a "matrix effect", or an overlap with other absorptions – see next section). It is claimed[14] that at apex angles close to 180° absorption assignable to ν_1 is not easily detected. This is not always so since in the case of MgF_2, with an apex angle[9] of 160° or more, the ν_1 absorption is readily observed when using a proper technique.

An examination of the ν_1 frequencies measured in krypton matrices (Table 1) shows that the ν_1 frequency of MgF_2 is lower than that of CaF_2, while from the ν_1 frequencies of the other fluorides (Sr, Ba) an inverse order is expected. This illustrates the uncertainty involved in the assignment of ν_1 frequencies. In the mercury halides (except for the fluoride) agreement exists between the ν_1 frequency calculated from matrix spectra[12] and the experimental Raman frequency[20], confirming the suggested linearity of the molecules. Similar agreement, though not as good, is encountered in the zinc halides[11, 21]. The relatively small differences in ν_1 may be attributed partly to the frequency shift caused by the matrix.

G. DIMER AND POLYMER SPECIES

With present experimental inert gas matrix techniques, the appearance of species other than monomer MX_2 molecules is difficult to avoid. In most matrix investigations the existence of dimer and polymer species is reported. Absorptions due to these species complicate the assignment of bands of the monomer molecules. The problem is most pronounced in cases of overlap of absorptions of the monomer and other species. A remarkable example is found in the spectrum of MgF_2. Snelson[16] overlooked the ν_1 absorption frequency of the monomer molecule around 480 cm^{-1}. Only with better resolution[9] could this absorption band be detected. This suggests some uncertainty in assigning bands observed in the spectrum of BeF_2. In the gas-phase measurements, an absorption around 825 cm^{-1} was detected[4], which may be assigned to ν_1. Snelson[16] attributed a similar band observed in a matrix spectrum to a polymer species. Nevertheless, such an absorption due to ν_1 may exist, though the overlapping polymer band makes its observation difficult. (In MgF_2 the ν_1 was also masked by a polymer band, see above.) A similar problem is encountered in the zinc halides. The bands of $ZnCl_2$ and $ZnBr_2$, observed in the gas phase[5] at 295 cm^{-1} and 225 cm^{-1} respectively, could be assigned to the symmetric ν_1 frequency, although assignment of these bands to the dimers is also possible. Thus the failure to observe these absorptions in the matrix spectra[11] may be attributed to the overlap of dimer or polymer species, which absorb in the same region. The assignment of these bands to ν_2 by Klemperer and co-workers[5] is believed to be incorrect, since the ν_2 vibration appears[11] at a much lower frequency. In the previous section a linear structure was proposed for $ZnCl_2$ and $ZnBr_2$, while here the possibility of bending arises. It is not intended to solve the problem here, but rather to point out the complicated nature of assigning absorption bands and geometries for some of the molecules under discussion.

From the experimental work performed thus far, it cannot generally be concluded with certainty whether a molecule is linear or slightly bent. This continuing uncertainty undoubtedly requires improvement of the techniques for determining molecular geometries. It would seem that high resolving power is one of the important requirements (at least in isotopic measurements) for properly solving the spectra of the Group II metal dihalide molecules. However, it should be stressed that at present the anharmonicity uncertainty is greater than limitations of resolution.

ACKNOWLEDGEMENT

The authors would like to thank Dr. J.W. Hastie for his many useful remarks and comments.

APPENDIX

It is useful for comparison purposes to add a few remarks concerning the first-row transition metal dihalides. Since the method for determining frequencies is the same as in the Group II dihalides (and is subject to the same criticism) we shall confine ourselves to remarks concerning geometries as deduced from spectroscopic data. The frequencies obtained for transition metal and some other fluorides and chlorides in the gas phase and in neon and argon matrices are summarized in Table 4.

TABLE 4*

Experimental frequencies of transition metal and other selected MX_2 molecules**

	Gas		Neon			Argon		
Molecule	ν_1	ν_3	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3
ScF_2					700^a			685^a
TiF_2				176^b	751^b	643^b	171^b	741^b
VF_2					743^a			733^a
CrF_2				151^a	680^a		155^a	654^a
MnF_2				132^a	722^a		125^a	700^a
FeF_2				148^a	758^a		141^a	731^a
CoF_2				158^a	746^c		151^a	723^c
NiF_2				143^a	801^c		140^a	$780^{c,d}$
CuF_2				188^a	766^c, 769^e		183^a	744^c
GeF_2	692^f	663^f	685^f		655^f	676^f	262^a	648^f
$ScCl_2$								466^g
$TiCl_2$					486^g		122^g	458^g
VCl_2					491^g			481^g
$CrCl_2$					493^g		110^g	458^g, 493^h
$MnCl_2$		467^j			484^g		83^i	$467^{h,i}$
$FeCl_2$		492^j					88^i	$494^{g,i}$, 493^h
$CoCl_2$		493^j					94^i	492^i, 493^h
$NiCl_2$		505^k, 515^j			530^g		85^i	$521^{d,g,h,i}$
$CuCl_2$		496^j						
SiF_2	855^l	872^l	851^m		865^m	843^m		853^m
$SiCl_2$						513^n		502^n
$PbCl_2$			326^o	81^o	304^o	321^o		299^o
EuF_2			474^o	113^o	452^o	458^o		435^o
$EuCl_2$			276^o		287^o	270^o		282^o

* The remarks at the foot of Table 1 also apply here.

** Only the frequencies of the most abundant isotope are considered.

[a] Ref. 26; [b] Ref. 25; [c] Ref. 13; [d] Ref. 29; [e] Ref. 30; [f] Ref. 33; [g] Ref. 15; [h] Ref. 32; [i] Ref. 28; [j] Ref. 31; [k] Ref. 8; [l] Ref. 34; [m] Ref. 36; [n] Ref. 35 (the assignments are somewhat uncertain); [o] Ref. 14.

The tendency towards linearity when going from a lighter to a heavier halide is encountered, as in the Group II dihalides. Thus, all the transition metal dichlorides are quoted as linear (see, for example, ref. 15). Among the difluorides of these metals, it is evident that TiF_2, at least, is bent[25], the evidence consisting both of the isotope effect and an observable ν_1. Some other difluorides are also considered to have a bent structure[26], but these are estimates only. This trend seems to be a rather general rule, since it applies to the heavier lanthanide dihalides as well (EuF_2 and $EuCl_2$ in ref. 14).

No distinctive trend can be found for the metals[26]. While for the Group II dihalides, the heavier the metal the more bent the molecule, no such behaviour is encountered in the transition metals. In fact, by examining the table in ref. 26, the configuration of the difluorides as a function of the atomic weight is quite random. It should be noted here that the geometries quoted were (when not estimated) determined from the isotope effect in inert gas matrices, and the limitations inherent in this method should be borne in mind.

No attempt will be made to explain theoretically the configurations of the various molecules. However, attention is drawn to the fact that Hayes' reasoning[23] (s–p and s–d separations) does not apply here (see discussion[27] and comparison between CaF_2 and MnF_2).

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