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BOND DISTANCES AND ESTIMATED BENDING FREQUENCIES OF SOME FIRST ROW TRANSITION METAL DIHALIDDES: ELECTRON DIFFRACTION STUDIES

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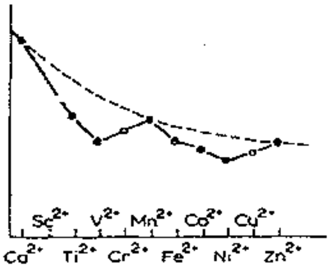
CONTENTS

A. INTRODUCTION

The physico-chemical behaviour of transition metal dihalides has been well studied [1] and their properties are understood by established theories of electronic structure and bonding [2]. The present review mainly deals with electron diffraction studies of some first row transition metal dihalides aimed primarily at establishing the geometry of these molecules. From these studies information on the electronic structure can only be gained indirectly, but there is some correlation which can be demonstrated by the following example. Consider the variation of ionic radii with atomic number in a series of ions of the same charge as shown by Fig. 1 [2]. The points for Ca, Mn and Zn are connected, i.e. atoms with a spherically symmetrical distribution of *d* electrons; the ionic radii of the other atoms are smaller than interpolation would yield from the Ca—Mn—Zn line. As is well known, the non-uniform distribution of *d* electrons around the nuclei is the reason for this phenomenon. As the shielding of one *d* electron by another from the nuclear charge is imperfect, there is a contraction in the ionic radii.

The question then arises whether this is followed by variations in the respective geometrical parameters which can be directly determined. The dichloride molecules are suitable for such a comparison and the data available so far on their bond lengths in the vapour phase seem to be consistent with the trend described above as seen in Fig. 2.



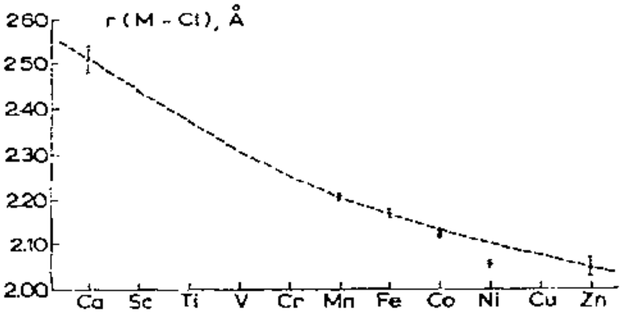


Fig. 1. Relative ionic radii (in octahedral environment) in the first series of transition metals after Cotton and Wilkinson [2].

Fig. 2. The average bond lengths determined for some transition metal dihalides by electron diffraction; the length of the vertical bar indicates the experimental uncertainty; the dashed line connects the data points for $CaCl_2$, $MnCl_2$ and $ZnCl_2$.

There are, however, very few transition metal dihalides whose molecular geometries have been determined in contrast with the relatively larger number of studies on the more complicated organic transition metal complexes (see e.g. Ref. 3). It is to be stressed that we are concerned with vapour phase data since the vapour phase is the only phase where the intramolecular forces are solely responsible for the structural choice. Considering the experimental difficulties encountered in studying transition metal dihalide structures in the vapour phase, it is not so surprising that the data are scarce.

B. THE MOLECULAR CONFIGURATION

Structural information concerning molecular shape and symmetry and obtained by other techniques will be summarized before discussing the electron diffraction studies in more detail. This is necessary since the electron diffraction data cannot be interpreted without additional information or assumptions.

The main question is, of course, whether the transition metal dihalide molecules are linear or bent.

Klemperer and coworkers [4—6] developed a unique technique to determine the electric polarity of molecules in high temperature vapours by electric deflection of molecular beams with mass spectrometric detection. Information concerning the molecular configuration is obtained since only polar molecules are deflected by an inhomogeneous electric field.

The molecular beam deflection experiments [4] on the fluorides of manganese, cobalt and nickel indicated that these molecules have no permanent electric dipole moment, and, accordingly, their equilibrium configuration can be assumed to be linear. The same observation was made for manganese chloride.

The structural properties of transition metal dihalides are often compared with those of alkaline earth metal dihalides. According to molecular beam deflection studies by Wharton et al. [4] the combination of large alkaline earth metal atoms and small halogen atoms favours a bent configuration. The difluorides of barium, strontium and calcium are all polar (bent configuration), while $BaCl_2$ and $SrCl_2$ are polar and $CaCl_2$ is non-polar (linear configuration). The molecular configurations of alkaline earth metal dihalides determined from the molecular beam deflection studies are compiled in Table 1.

It should be noted here that the alkaline earth metal dihalide molecules were all considered to be linear in early electron diffraction studies [7]. As Wharton et al. [4] have already pointed out, however, the uncertainty of the bond angle determination was especially large for molecules with small halogen atoms (small atomic number — small electron scattering ability); later investigations established a bent configuration. There is no real contradiction between the experimental data if the large error limits assigned to the electron diffraction results are considered [7]. The molecular structures of alkaline earth metal dihalides will have to be reinvestigated by means of the up-to-date technique of electron diffraction.

Since none of the transition metal difluorides studied by Büchler et al. [5] were found to be polar, it was assumed on the basis of analogy with the alkaline earth metal dihalides that all the other dihalides are also of linear configuration. *

Vibrational spectroscopy is the other experimental technique invoked to establish the shape (and symmetry) of transition metal dihalide molecules. Only the antisymmetric stretching frequency, ν_3, could be determined for the monomeric species from the infrared spectra of the gaseous samples [8—10].

Matrix isolation infrared spectroscopic experiments were later performed by Thompson and Carlson [11] to augment the above mentioned data ex-

TABLE 1

The molecular configurations of alkaline earth metal dihalides as determined from the molecular beam deflection experiments [4]

	F	Cl	Br	I
Mg	linear	linear	linear	
Sr	bent	linear	linear	linear
Ca	bent	bent	linear	linear
Ba	bent	bent	bent	bent

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* Note however that not all transition metal dihalides are linear. In general both bent and linear geometries occur, see e.g. the established bent structures of TiF_2 (F—Ti—F, 130°) [48] and ZrF_2 (F—Zr—F, 120° ± 4°) [49].

TABLE 2

Infrared frequencies of some transition metal dihalides determined for gaseous or matrix isolated species

	ν_2 (cm^{-1})		ν_3 (cm^{-1})		
	Neon matrix	Argon matrix	Gas	Neon matrix	Argon matrix
MnF_2	132 [a]	125 [a]		722 [a]	700 [a]
FeF_2	148 [a]	141 [a]		758 [a]	731 [a]
CoF_2	158 [a]	151 [b]		746 [b]	723 [b]
NiF_2	143 [a]	140 [a]		801 [b]	780 [b,g]
$MnCl_2$		83 [c]	467 [d]	484 [f]	467 [c,h]
$FeCl_2$		88 [c]	492 [d]		494 [c], 493 [h]
$CoCl_2$		94.5 [c]	493 [d]		492 [c], 493 [h]
$NiCl_2$		85 [c]	505 [e], 516 [d]		521 [c,f,g,h]
$NiBr_2$		69 [c]			414 [c]

[a] Ref. 44. [b] Ref. 45. [c] Ref. 11. [d] Ref. 9. [e] Ref. 8. [f] Ref. 46. [g] Ref. 10. [h] Ref. 47.

tending the spectroscopic measurements to regions lower than the 200 cm^{-1} limit of the earlier investigations. These experiments provided more precise values for the ν_3 frequency and, for the first time, values for the bending frequency ν_2 of the monomers. The frequencies determined from the infrared spectra of gaseous and matrix-isolated species are collected in Table 2.

The most important spectroscopic argument in favour of the linear structure is the absence of a symmetric stretching frequency in the infrared spectra. From the simple valence field equations Thompson and Carlson [11] estimated these frequencies of the dichloride molecules studied to be in the region of 316 to 350 cm^{-1} or higher depending on their departure from linearity. Since no positive evidence for the existence of this band could be found in this region, it was concluded that they are either too weak for detection or infrared inactive because of a strictly linear geometry. These measurements were thus entirely consistent with the spectra expected for linear or nearly linear dihalide configurations. Additional evidence for linear geometry is provided from isotopic shifts in vibrational spectra [11,46].

C. THE ELECTRON DIFFRACTION EXPERIMENTS *

So far five transition metal dihalides have been investigated by electron diffraction. The results of these studies will be summarized below but the discussion obviously bears some relation to the Budapest results.

The main distinguishing feature of the electron diffraction experiments on transition metal dihalides is that relatively high temperature (~700—800°C) conditions are needed to produce sufficient vapour pressures for the desired

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* For an up-to-date review of the electron diffraction technique see Ref. 12.

electron scattering intensities. The single most important difficulty to overcome in these experiments is connected with creating the high temperature conditions without producing an electromagnetic field that would appreciably disturb the electron beam. In this review we are not concerned with the details of the electron diffraction experiments, and indicate only the type of nozzle systems employed in the individual studies with the necessary references for detailed description of the technique used.

Compound	Nozzle system	Laboratory	Ref.
$MnCl_2$	"radiation"	Budapest	13, 4, 20
$FeCl_2$	"electron bombardment"	Moscow	15
$CoCl_2$	"radiation"	Budapest	13
$NiCl_2$	"resistance"	Corvallis	16
$NiBr_2$	"radiation"	Budapest	13, 4, 20

Typical molecular intensity and radial distributions are shown in Figs. 3 and 4, respectively.

Before discussing the results of the electron diffraction analyses we note that the vapour composition of the compounds in question has been examined by mass spectrometry [17] at temperatures not much lower than those of the electron diffraction experiments. The vast majority of the vapour phase species were found to be monomeric. Dimeric species could not be detected at all for nickel chloride and bromide, while a small quantity of dimers has been shown to be present for the other compounds. The partial pressures of the monomers and dimers are compiled for some compounds in Table 3. According to the mass spectrometric studies of iron(II) chloride

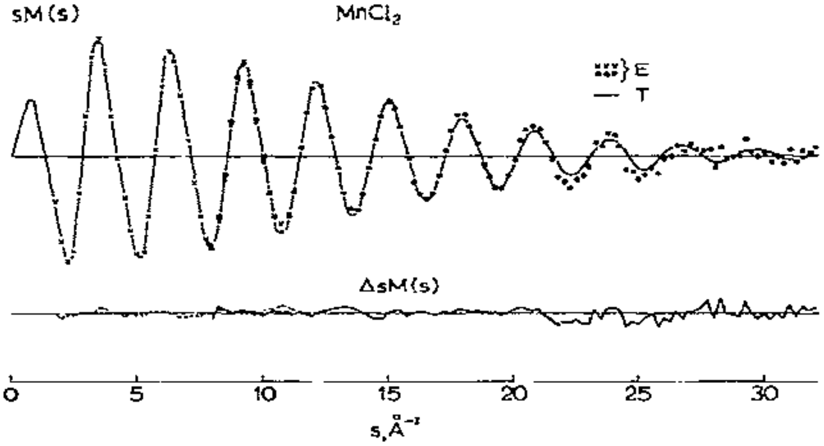

Fig. 3. Experimental (E) and theoretical (T) molecular intensities for manganese(II) chloride. The theoretical curve was computed from parameters given in Tables 4 and 5.

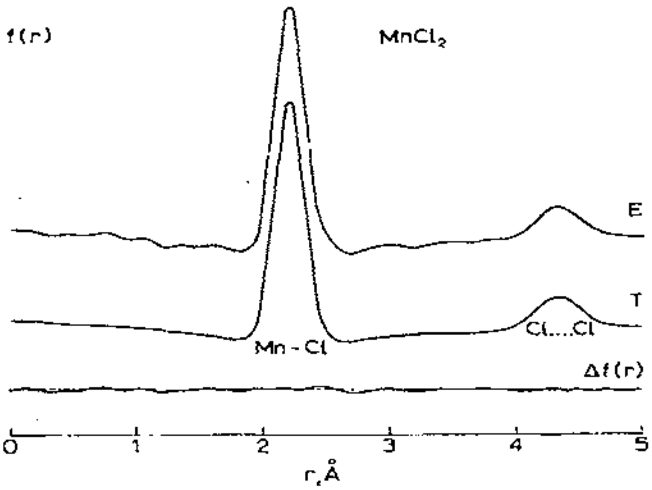

Fig. 4. Experimental (E) and theoretical (T) radial distributions for manganese(II) chloride obtained by Fourier-transforming the molecular intensities shown in Fig. 3.

[18] and bromide [19], their vapours predominantly contain monomers and dimeric species are only present in very small concentrations.

Assuming that the vapour composition is the same under the conditions of the electron diffraction experiments as in the mass spectrometric studies, it can be concluded that the electron scattering originated exclusively from monomers in the case of nickel(II) bromide; but even for manganese(II) and cobalt(II) chlorides the dimer content remains below 1.5%. Thus the contribution of the dimeric species to the electron scattering can be ignored, and is assumed not to cause appreciable error compared with other experimental uncertainties.

TABLE 3

The monomeric and dimeric vapour pressures of some transition metal dihalides; the mass spectrometric data of Schoonmaker et al. [17]

	T (K)	P_{MX_2} (atm)	$P_{M_2X_4}$ (atm)
$CrCl_2$	985	2.73×10^{-5}	0.308×10^{-5}
$CrBr_2$	931	1.79×10^{-5}	0.378×10^{-5}
$MnCl_2$	888	6.15×10^{-5}	0.074×10^{-5}
$MnBr_2$	848	9.09×10^{-5}	0.135×10^{-5}
FeI_2	714	0.62×10^{-5}	0.121×10^{-5}
$CoCl_2$	817	1.61×10^{-5}	0.024×10^{-5}
$CoBr_2$	771	0.74×10^{-5}	0.034×10^{-5}

TABLE 4

Average values of internuclear distances (r_g, Å) and the shrinkage (δ_g, Å) determined for transition metal dihalides by electron diffraction. The temperature of the experiment is also indicated. For the meaning of uncertainties consult the cited references.

	r_g (M—X) (Å)	r_g (X· · ·X) (Å)	δ_g (Å)	T (°C)
$MnCl_2$ [a]	2.205 ± 0.005	4.324 ± 0.015	0.085	800
$FeCl_2$ [b]	2.17 ± 0.01			
$CoCl_2$ [c]	2.120 ± 0.005	4.125 ± 0.021	0.115	750
$NiCl_2$ [d]	2.056 ± 0.004	4.018 ± 0.076	0.094	800
$NiBr_2$ [e]	2.212 ± 0.005	4.326 ± 0.013	0.098	670

[a] Ref. 20. [b] Ref. 21. [c] Ref. 22. [d] Ref. 16. [e] Ref. 23.

D. THE ELECTRON DIFFRACTION RESULTS AND THEIR INTERPRETATION

The internuclear distances and mean amplitudes of vibration determined so far for transition metal dihalides by electron diffraction are collected in Tables 4 and 5, respectively. In order to discuss the molecular geometries in more detail, the physical meaning of the internuclear distance parameters has to be examined *. The r_g parameters given in Table 4 are average values of the internuclear distances and are closely related to the distance parameters r_a that are directly determined from the least-squares analysis based on the electron diffraction molecular intensities. To a good approximation [26]

$$r_g \approx r_a + l^2/r_a$$

where l^2 (or $\langle \Delta z^2 \rangle$) is the mean square amplitude of vibration. The r_g distance corresponds to the centre of gravity of the probability distribution

TABLE 5

Mean amplitudes of vibration (l (Å)) determined for transition metal dihalides by electron diffraction. For the meaning of uncertainties consult the cited references.

	l (M—X) (Å)	l (X· · ·X) (Å)
$MnCl_2$ [a]	0.082 ± 0.005	0.152 ± 0.012
$CoCl_2$ [b]	0.082 ± 0.005	0.158 ± 0.010
$NiCl_2$ [c]	0.079 ± 0.006	0.203 ± 0.047
$NiBr_2$ [d]	0.084 ± 0.005	0.164 ± 0.011

[a] Ref. 20. [b] Ref. 22. [c] Ref. 16. [d] Ref. 23.

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* For details and further references see e.g. the review by Kuchitsu and Cyvin [25].

function $P(r)$, where $P_{ij}(r)\mathrm{d}r$ is the probability that the r_{ij} distance is found between r and $r + \mathrm{d}r$.

The relationship between the average internuclear distance (r_g) and the equilibrium internuclear distance (r_e) can be expressed in the following way

$$r_g = r_e + \delta r + \langle \Delta z \rangle + \frac{\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle}{2\, r_e} + \cdots$$

The equilibrium distance (r_e) corresponds to the position of the minimum of the potential energy function of the hypothetically motionless molecule. The above relationship refers to a Cartesian coordinate system whose z-axis coincides with the equilibrium internuclear axis and whose origin is the equilibrium position of one of the two nuclei involved. The term δr represents the centrifugal distortion due to the rotation of the molecule. The term $\langle \Delta z \rangle$ expresses the deviation of the distance between the average positions of the nuclei due to anharmonicity. The quantities $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ are the mean square perpendicular amplitudes and they are finite even if only harmonic vibrations are performed.

The average internuclear distance (r_g) is not the same as the distance between the average positions of the atomic nuclei, that is

$$r_\alpha = r_e + \langle \Delta z \rangle$$

differing from the equilibrium distance because of anharmonicity. The parameter r_α refers to the thermal equilibrium corresponding to a given temperature. Thus for the ground state

$$r_\alpha^0 = r_e + \langle \Delta z \rangle_0$$

The average distance parameter, r_g, is the most convenient way to characterize the average length of a chemical bond [27]. It has no such descriptive geometrical meaning, however, for distances between non-bonded atoms because of the effects of perpendicular vibrations. For instance, for a strictly linear triatomic molecule MX_2, the X · · · X distance will be shorter than twice the M—X bond length in terms of the r_g parameters. This effect was first observed experimentally by Bastiansen and coworkers for several linear molecules [28—30], and an important theoretical contribution concerning this effect was made by Morino [31]. The effect is called shrinkage or very often the Bastiansen—Morino shrinkage effect [32].

On the other hand, for the distances between non-bonded atoms (as well as for bond angles), the best representation is in terms of the parameters that correspond to the distances between the average positions of the nuclei since they are free of the effects of the perpendicular vibrations.

As is demonstrated by the radial distribution of manganese(II) chloride in Fig. 4 and seen in more detail in Table 4, the value of r_g (X · · · X) is smaller than twice the value of r_g (M—X). Since the equilibrium configuration of $MnCl_2$ can be assumed to be linear on the basis of evidence from other physical techniques (see above), this is a consequence of the shrinkage effect due

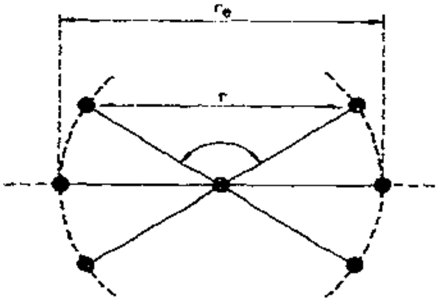

Fig. 5. Perpendicular vibrations and the origin of the shrinkage effect in MX_2 molecules; r_e = equilibrium distance, r = instantaneous distance during vibration. Because of the bending vibrations, the average internuclear distance, $r_g = \int r(\gamma)P(\gamma)d\gamma$ is less than the equilibrium distance; here $P(\gamma)d\gamma$ expresses the probability that the angle X—M—X lies between γ and $\gamma + d\gamma$.

to the perpendicular vibrations. Figure 5 is provided for illustration.

In order to calculate the value of the bond angle X—M—X from the distances, the simple expression

$$\angle \text{X—M—X} = \arcsin \left[\frac{r(\text{X}\cdots\text{X})}{2\,r(\text{M—X})}\right]$$

is used. However, only a so-called effective bond angle, $\angle_G$, can be obtained by simply applying the average values of internuclear distances

$$\angle_G\ \text{X—M—X} = \arcsin \left[\frac{r_g(\text{X}\cdots\text{X})}{2\,r_g(\text{M—X})}\right]$$

and not the average value of the bond angle, $\angle_g$, that would refer to the thermal equilibrium corresponding to a given temperature, as was shown by Kuchitsu [33]. The value of $\angle_G$ has no well-defined physical meaning. On the other hand, the average value of the bond angle can be expressed in the following way *

$$\angle_g\ \text{X—M—X} = \langle \arcsin r(\text{X}\cdots\text{X})/2\,r(\text{M—X})\rangle_T$$

where T indicates that averaging for a given temperature is to be taken according to the Boltzmann distribution considering all the vibrational levels.

Unfortunately, we cannot calculate the values of $\angle_g$ X—M—X, or their deviation from those of $\angle_G$ X—M—X. The large differences between the values of $\angle_G$ X—M—X and 180°, viz.

	$180° - \angle_G$ X—M—X
$MnCl_2$	23°
$CoCl_2$	27°
$NiCl_2$	25°
$NiBr_2$	24°

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* The corresponding analytical expressions are discussed by Kuchitsu [33].

clearly indicate the importance of the perpendicular vibrations. The values of the shrinkage

$$\delta_g = 2\, r_g(\mathrm{M{-}X}) - r_g(\mathrm{X\cdots X})$$

are also given in Table 4.

The relatively large values of the mean amplitudes of vibration (Table 5) are not surprising in the light of the high temperature experimental conditions. The consequence of the large vibrational amplitudes appears as a relatively strong damping of the electron diffraction molecular intensities as seen in Fig. 3.

E. ESTIMATION OF THE BENDING FREQUENCIES

Assuming a strictly linear equilibrium configuration, it is possible to estimate the bending vibrational frequency, ν_2, from the shrinkage effect for the MX_2 molecule. Mean amplitudes of vibration determined by electron diffrac-

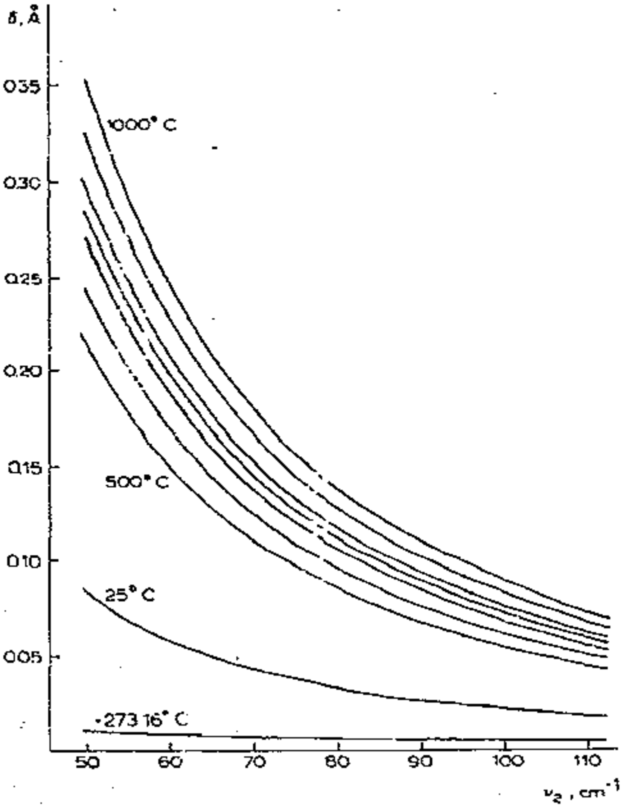

Fig. 6. Shrinkage (δ) vs. bending frequency (ν_2) curves calculated for a series of temperatures.

tion have been utilized before in spectroscopic analyses as additional data along with observed frequencies. A similar approach is possible with the shrinkage effect. The accuracy requirements for the experimental data, however, are usually too high to make these data really useful [34]. The situation becomes more favourable as the temperature of the experiment increases and also when low frequencies are involved. This is illustrated by Fig. 6 after Cyvin [35].

For simple molecules it may be possible to determine some of the vibrational frequencies from the electron diffraction data. In particular, all frequencies may be obtained in principle for linear MX_2 molecules [32].

Well before the matrix isolation infrared spectroscopic studies [11] on the transition metal dihalides, Brewer et al. [36] estimated the bending vibrational frequencies ν_2 for many MX_2 molecules as part of their thermodynamic investigations. These values, around 50 cm^{-1}, have been used by Nagarajan [37] and also by Cyvin and Vizi [38,39] to calculate the shrinkage values at different temperatures. These calculations yielded extremely large values (around 0.3 Å for 1000 K).

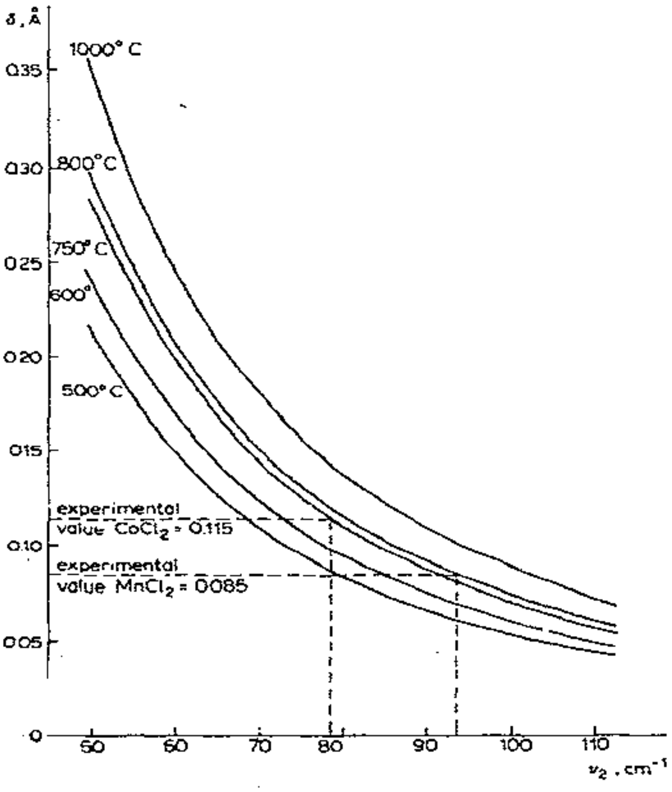

Fig. 7. Shrinkage (δ) vs. bending frequency (ν_2) curves for $CoCl_2$ and $MnCl_2$ and the experimental values.

TABLE 6

Measured and estimated bending frequencies (ν_2 (cm^{-1}))

	From the shrinkage effect, electron diffraction	Matrix isolation infrared spectroscopy, Thompson and Carlson [11]	Estimation by Brewer et al. [36]
$MnCl_2$	93	83	47
$FeCl_2$		83	49
$CoCl_2$	78	94.5	49
$NiCl_2$		85	51
$NiBr_2$	69	69	40

The values of the shrinkage observed in the electron diffraction studies suggested appreciably higher bending frequencies. Accordingly, the shrinkages were calculated by Cyvin's procedure. As is illustrated by Fig. 7, the crossing point of the line corresponding to the experimentally determined shrinkage and the shrinkage vs. ν_2 curve corresponding to the temperature of the experiment readily yields the bending frequency consistent with the electron diffraction data. The results given in Table 6 thus demonstrate a useful method of estimating low frequencies by means of the electron diffraction technique.

It seems to us important to discuss some uncertainties in connection with estimating the ν_2 values from electron diffraction data. The shrinkage vs. bending frequency calculations are based on the assumption that these molecules have a strictly linear equilibrium configuration. This assumption, in turn, originates from the results of the molecular beam deflection studies according to which these molecules are non-polar. However, as pointed out recently by Eliezer and Reger [40], this method does not give bond angles and the observed effect is qualitative. On the other hand, in almost all cases where the molecular beam deflection experiments show the molecules to be non-polar, the vibrational spectroscopic evidence confirms linearity *. Unfortunately, however, the limit of deviation from linearity which would be undetected by the molecular beam deflection technique is not known.

Comparison of the ν_2 values estimated from the electron diffraction results is further complicated by the uncertainties of the spectroscopic data obtained by means of the matrix isolation technique. The frequency shifts due to matrix effects may be of the magnitude of the differences between the electron diffraction and spectroscopic ν_2 values.

It is also important to note that the shrinkage vs. bending vibration frequency calculations are based on the assumption of small harmonic vibra-

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* The well-known exception is MgF_2 for which a linear structure was suggested from molecular beam deflection experiments [5], while an appreciably bent structure was suggested on the basis of infrared spectra produced by the matrix isolation technique [41]. Recent ab initio calculations [42] favour a linear configuration.

tions. The molecules discussed in this review perform large amplitude vibrations and it does not seem probable that anharmonicity can be ignored. Unfortunately the effect on the results of using such crude approximations is not known.

It is also difficult to estimate the accuracy of the shrinkage obtained from the electron diffraction data. The total errors of the internuclear distances, however, seem to be too large to use for the shrinkage since, for the latter, important systematic errors cancel.

An important unknown in the electron diffraction experiment is the vibrational temperature of the vapour. The temperature of the nozzle is measured. It has been shown (see e.g. Ref. 43), however, that the vibrational temperature of the vapour can be considered to be the same as the nozzle temperature for a great variety of nozzle geometries that certainly include those applied in the experiments for the transition metal dihalides. On the other hand, the ranges of temperatures used in these studies are much higher than those for which this problem was thoroughly studied [43]. At the same time it can be stated that there is no systematic trend in the differences between the spectroscopic and electron diffraction ν_2 values which would indicate a systematic error in judging the experimental temperature. Conversely, knowing the value of ν_2 from spectroscopic measurements for a strictly linear molecule, the vibrational temperature of the vapour in the electron diffraction experiment could be determined on the basis of the shrinkage vs. bending frequency plots.

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