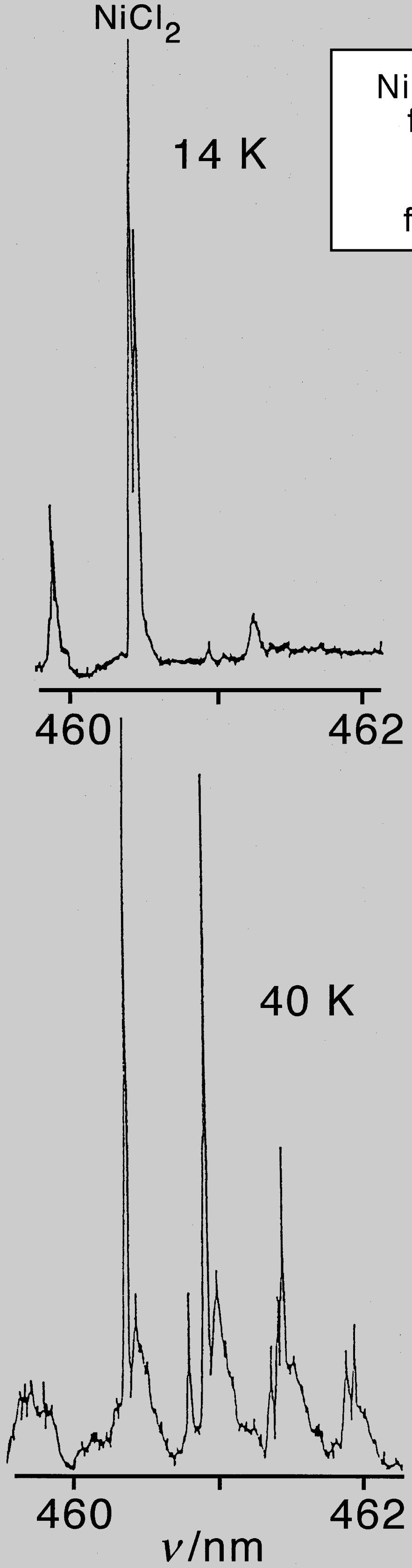
Structure and Spectra

of s-, d-, and f-block halides, oxides, and hydrides.
Presented here are data for two dichlorides.

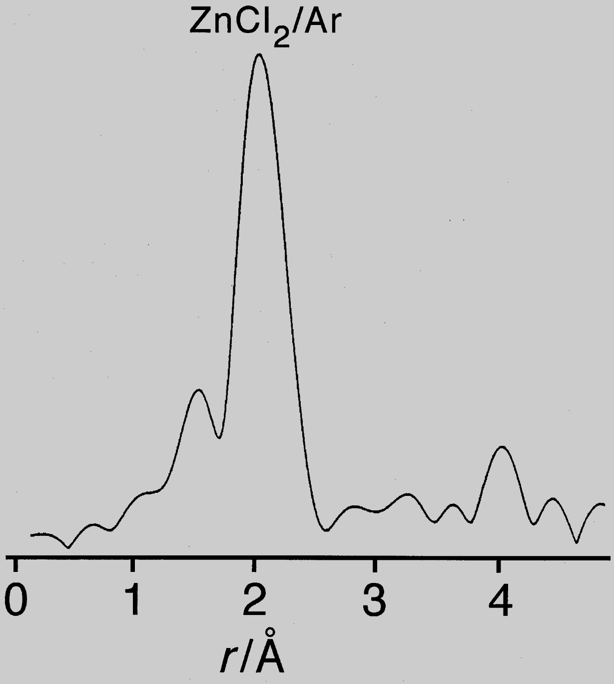
cold molecular beam
laser-induced fluorescence



Ni-Cl = 2.05607(13) Å
for the ground state

= 2.0958(15) Å
for the excited state

matrix
EXAFS Fourier transform



r = interatomic distance

Zn-Cl = 2.053(2) Å in Ar
= 2.081(2) Å in N_2

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A Critical Appraisal of the Experimental Data on the Molecular Structure and Spectra of Halides, Oxides, and Hydrides of the s-, d-, and f-Block Elements

Ian R. Beattie*

An understanding of the electronic structure of small molecules is of importance in many areas of chemistry. It enables theoreticians to improve methods and databases, and experimentalists to interpret more complex systems. Many simple compounds of the s-, d- and f-block elements are rather involatile solids or unstable under normal conditions. Hence, gas-phase data are difficult to obtain. Electron diffraction at high temperatures has been used extensively on the more stable compounds, notably the halides. However, for reasons outlined below this technique is sometimes open to criticism. High-resolution spectroscopy can be applied at temperatures up to about 700 °C for molecules with larger rotational constants. Alternatively, electronic spectra can be recorded at very high resolution by using "cold" molecular beams, but interpretation of the data is by no means simple. Microwave spectroscopy requires the presence of a permanent electric dipole, and many of the molecules of interest are not thought to be polar. For these reasons, many studies use matrix-isolation techniques. Of these, matrix-isolation IR spectroscopy with partial isotopic substitution has been the most widely used (and is perhaps the easiest from an experimental point of view). However, energy levels are affected by the surrounding matrix, and even the noble gases can cause changes in molecular geometry. This review attempts to put conflicting strands of evidence in context and suggests new experiments for determining the electronic structure and detailed molecular geometry of key molecules.

Keywords: electronic structure · gas-phase chemistry · laser spectroscopy · matrix isolation · structure elucidation

1. Introduction

A knowledge of the geometry and electronic spectra of small molecules of the s-, d-, and f-block elements is an essential prerequisite to understanding their chemistry. There are many experimental and theoretical papers on this topic. This review attempts to select experimental studies that enable clear-cut conclusions to be drawn. It is biased towards compounds that are not easily studied in the gas phase and those whose structures can be regarded as anomalous (that is, other than linear, trigonal-planar, or tetrahedral for MX_2, MX_3, and MX_4, respectively).

1.1. Matrix Isolation

The isolation of reactive molecules in an inert matrix at cryogenic temperatures allows their study by a variety of physical techniques. The resulting spectra are greatly simplified compared with gas-phase data because all the molecules are in their ground vibrational and electronic states and rotational motion is effectively quenched. An important source of reference for such experiments up to 1985 is a bibliography by Ball et al.,[1] which is currently being updated. Almond and Downs[2] give a detailed tabulation covering mainly 1977–1986 and include a survey of the techniques that can be applied to species isolated in cryogenic matrices. Similar information is given in a review by Perutz,[3] who commented that "one of the key deficiencies…is the lack of bond length information". Since then (1985) it has been shown that for the dichlorides of Cr, Fe, Ni, and Zn, extended X-ray absorption fine structure (EXAFS) analysis can determine bond lengths in dilute matrices to an accuracy of about one-tenth that obtained in routine single-crystal X-ray studies.[4]

Infrared spectra of matrix-isolated molecules enable the identification of individual isotopomers, and this leads to information on bond angles and molecular symmetry. Optical spectroscopy has been less extensively used. A study[5] on $CuCl_2$ isolated in neon elegantly demonstrates the presence of three distinct matrix sites and illustrates the strengths and weaknesses of this approach. The ESR spectra of matrix-

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[*] Prof. I. R. Beattie
The Physical and Theoretical Chemistry Laboratory
South Parks Road
Oxford OX1 3QZ (UK)
Fax: (+44) 1865-275410
E-mail: beattie@physchem.ox.ac.uk

isolated species might be expected to reveal the ground-state electronic configuration of molecules with one or more unpaired electrons, provided the transitions occur within the range of the spectrometer. However, for linear molecules only Σ states are observed in matrices; Weltner and co-workers. have summarized much of the available data.[6]

1.2. Matrix Effects

In matrix-isolation spectroscopy the effects of the medium can be appreciable, and electronic states are usually affected more than vibrational states. Jacox[7] has tabulated the ground-state vibrational fundamentals of many diatomic molecules in the gas phase and in solid matrices. As examples, the alkali metal halides in argon matrices show red shifts of 6.3–11.2% relative to their gas-phase values. In a nitrogen matrix the shift for LiBr is 24.5%, which in many systems would be taken as evidence of complex formation.

In 1985 Perutz[3] pointed out that there was only one claim[8] for a violation of the principle that molecular symmetry should not be altered by changing the matrix: “$CsUF_6$ which appears to have Cs^+ bound to one face of the UF_6^- octahedron in argon, but to an edge in nitrogen matrices”. This work was extended[9] to $CsNbF_6$, whereby the strength of the matrix interaction was “calibrated” by observing the splitting of the antisymmetric stretching band of ClO_4^- in molecular $KClO_4$ isolated in each of the matrix gases under study. It was proposed for $CsNbF_6$ that edge binding occurs in nitrogen and carbon monoxide, but facial binding in neon, argon, and oxygen (Figures 1 and 2). Both forms occur in xenon. As the molecules concerned are fluoro derivatives of heavy elements, no data on isotopomers are available. There are many other papers in which site effects, molecular orientation, and dependence of shape on the matrix gas are discussed. Examples include LaF_3,[10] WO_2,[11] ScF_2,[12] $BaCl_2$,[13] NbX_5 and TaX_5 (X = Cl, Br),[14a] $NiCl_2$,[15] and $NiBr_2$.[16] In 1984 Arthers and Beattie[17] showed that the IR spectrum of thorium tetrachloride in a neon matrix could be interpreted on the basis of the expected T_d molecular symmetry, while the spectrum in krypton indicated a substantial distortion.

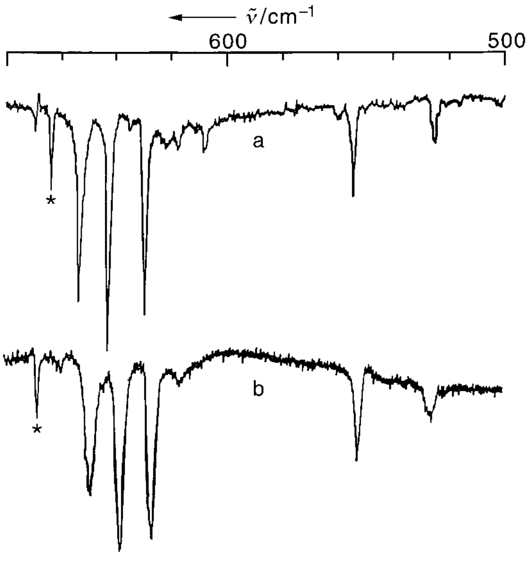


Figure 1. The IR spectrum ($500-680\,cm^{-1}$) of $CsNbF_6$ isolated in nitrogen a) and carbon monoxide b).[9] * = matrix isolated CO_2. Reproduced with the permission of The Royal Society of Chemistry.

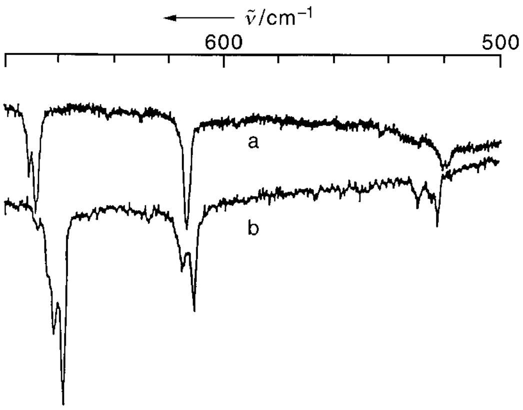
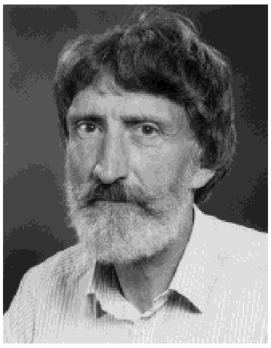


Figure 2. The IR spectrum ($500-680\,cm^{-1}$) of $CsNbF_6$ isolated in neon a) and argon b).[9] The apparent splitting of the highest frequency band in (a) arises from an inverse CO_2 band. Reproduced with the permission of The Royal Society of Chemistry.

1.3. Gas-Phase Studies

Electron diffraction can give A–B interatomic distances for AB_n species, but at higher temperatures the B–B



Until recently Ian Beattie was a Professor at Southampton University. Prior to this he was at the Inorganic Chemistry Laboratory and Oriel College in Oxford. He has now returned to Oxford, but this time to the Physical and Theoretical Chemistry Laboratory. His research has mainly been concerned with molecular species derived from compounds that are solids or are polymeric under ambient conditions (examples include $CsClO_3$, $NiCl_2$, WOF_4). This has necessitated the use of many spectroscopic techniques together with the development of a vibrational analysis programme (SOTONVIB) applicable to crystals and molecules. There was still time to look for interesting species such as XeI^+ (in 1957) and most recently mercury in an oxidation state higher than +2—both unsuccessful! Currently he is working with Professor J. M. Brown on high-resolution spectroscopy of small inorganic molecules in molecular beams.

distances are less reliable as the raw data is averaged over all thermal vibrations. Essentially, angles are more easily deformed than chemical bonds. A review by Hargittai[18] on the molecular geometry of gas-phase metal halides covers electron diffraction up to 1988 and includes spectroscopic data in the gas phase and in matrices.

Similarly, absorption or emission spectra of the vapors above heated solids are complicated by the occupation of many rotational, vibrational, and even electronic energy levels, and the bands tend to be broad complexes made up of a forest of individual lines. Problems occur for isothermal cells with containment, window materials, and gaskets. In the case of Raman spectroscopy, which can be carried out routinely in fused silica ampoules up to about 1000 °C, the strong Q branches can lead to narrower bands than those in the corresponding IR spectra.[19] However silica (like many materials) is relatively reactive at high temperatures,[20] and species such as $ThCl_4$ can lead to the generation of $SiCl_4$ as a substantial impurity.

Nevertheless, rotationally resolved spectra can be obtained from hot gases. Limiting features include background luminescence, the rotational constant of the molecule under study, and Doppler and pressure broadening. In 1991 Frum et al.[21] reported "...the first complete rotational analysis of a dihalide molecule" by the use of IR emission spectroscopy. The molecule was BeF_2 and the temperature about 700 °C. Under asssumption of a linear molecule, the Be–F bond length (r_e) was 1.37297(9) Å. Only one rotational constant is available as both Be and F are monoisotopic.

Electronic absorption spectra can usually be obtained at appreciably lower pressures than those needed to obtain IR spectra. However, by far the most sensitive technique at these shorter wavelengths is fluorescence spectroscopy, which is dependent on the quantum yield and the fourth power of the wavelength. By using tunable narrow-linewidth laser excitation and high-resolution spectrometers to disperse the resultant fluorescence it is possible to obtain rotationally resolved spectra from species such as $CuCl_2$ even at temperatures as high as 750 °C.[22] In essence, one rovibronic transition is excited in these experiments.

Microwave spectroscopy has not been extensively used owing to the need for a permanent molecular electric dipole. However, there is some elegant work by Törring et al. on the molecules KCN (T-shaped)[23] and $LiNaF_2$ (cyclic)[24] at high temperature. These techniques give at most three rotational constants. Any further information on geometry can only be obtained by isotopic substitution of an effective atom in the molecule.

An elegant way of examining high-temperature molecules at cryogenic temperatures in the gas phase is to make use of "cold" molecular beams.[25] In our experiments a pressure of about 2 atm of an inert gas (normally argon) is maintained in contact with the sample in an alumina tube. The argon, seeded with the molecule under examination, is allowed to expand through an orifice (ca. 250 μm in diameter) into a rapidly pumped chamber at a residual pressure of about 0.2 Torr.[26] In this way rotational temperatures on the order of 10 K can be obtained for molecules vaporized at about 1000 °C. After leaving the nozzle, the molecules rapidly enter a collision-free zone, so that their trajectories are essentially linear, with velocities in the region of 500 $m\,s^{-1}$, and are translationally cooled to about 1 K. This can lead to the virtual elimination of Doppler broadening. Since vibrations are more difficult to freeze the vibrational temperatures are usually on the order of 100–200 K. Fluorescence is usually the chosen technique for detection because of the low number density in the beam. By crossing the molecular beam with a tunable narrow-band laser and monitoring the total fluorescence as a function of excitation frequency it is possible to obtain rotationally resolved laser-induced fluorescence (LIF) or excitation spectra (similar to absorption spectra). The main disadvantage of the technique, when only the total fluorescence is measured, is that it gives information on the excited state rather than the ground state. If the fluorescence is dispersed, again at rotational resolution, ground-state data can be obtained. However, the fluorescence is frequently weak, and the signal to noise ratio may not be high enough to give the required resolution.

$FeCl_2$,[27] $CoCl_2$,[27] $NiCl_2$,[26, 28] and $CuCl_2$[29] were studied in molecular beams by LIF. Figure 3 shows the R branches and part of the P branches of $^{58}NiCl_2$ and $^{60}NiCl_2$ in the LIF spectrum of natural-abundance $NiCl_2$. This is thought to be a $^3\Sigma$–$^3\Sigma$ transition of the linear molecule involving one quantum of the symmetric stretch and three quanta of the bend. There is no Q branch because there is no change in angular momentum. Earlier information obtained from matrix isolation[30] or gas-phase[31] electronic (including fluorescence) spectra can be of value in interpreting high-resolution electronic spectra and in selecting appropriate molecules for study.

Cavity ringdown spectroscopy[32] allows absorption experiments to be performed on molecular beams and enables the study of energy levels that are not observed by fluorescence

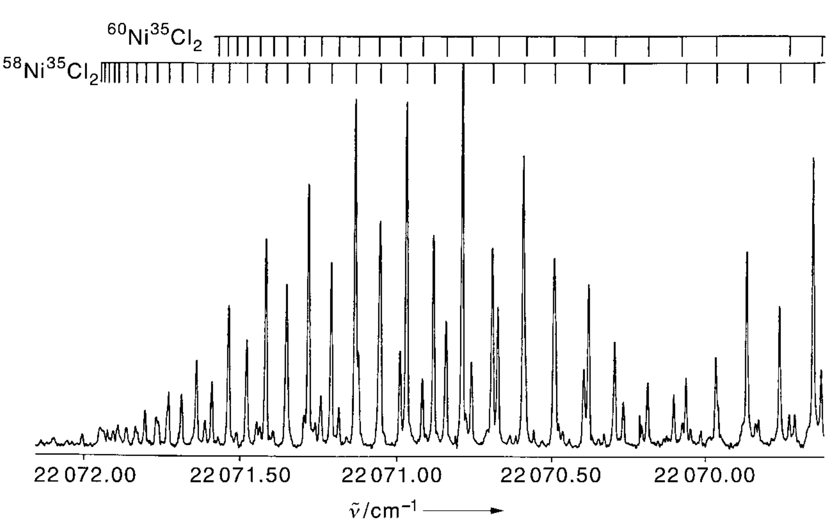


Figure 3. Part of the electronic (LIF) spectrum of jet-cooled $NiCl_2$ at rotational resolution.[28b]

spectroscopy. In principle, it yields ground-state constants directly. A recent paper[33] reports the use of this technique in the infrared at a number density of only about 10^{12} cm^{-3}. Finally, the development of very sensitive electron diffraction techniques may allow the molecules of interest here to be studied in cold molecular beams.[34]

2. Halides

Halides occupy a major portion of this review because in many cases their vaporization occurs at a relatively low temperature to give mainly monomers. In the first-row transition series pressures of about 1 Torr can be obtained for $CrCl_2$ at around 850 °C and as low as 700 °C for $NiCl_2$. With Ti and V disproportionation is a serious problem, and $CuCl_2$ readily loses chlorine.

2.1. Dihalides

2.1.1. Determination of Bond Angles

Since ^{19}F and ^{127}I are the only naturally occurring isotopes of fluorine and iodine and the shift from ^{79}Br to ^{81}Br is only two mass units in eighty this discussion concentrates on the chlorides. Note that ^{45}Sc, ^{55}Mn, and ^{59}Co are monoisotopic, while ^{51}V is 99.75 % abundant. For a matrix-isolation experiment the presence of ^{35}Cl and ^{37}Cl enables the number of chlorine ligands to be established; a characteristic 9:6:1 triplet demonstrates the presence of two equivalent chlorine atoms if natural-abundance chlorine is present.

The bond angle 2θ in XY_2 can be calculated from Equation (1)[35]

$$\left(\frac{\tilde{\nu}_3}{\tilde{\nu}_{3i}}\right)^2 = \left(\frac{1}{M_y}+\frac{2}{M_x}\sin^2\theta\right)\Big/\left(\frac{1}{M_{yi}}+\frac{2}{M_{xi}}\sin^2\theta\right) \qquad (1)$$

where i refers to an isotopomer and $\tilde{\nu}_3$ is the antisymmetric stretching frequency. Using the observed frequencies rather than the harmonic frequencies of the isotopomers inevitably leads to errors, but by making reasonable assumptions[36] it can be shown that substitution at X in XY_2 leads to a lower limit for the bond angle, while substitution at Y leads to an upper limit. The effects of anharmonicity can be appreciable, as is demonstrated for the diatomic molecule NiO isolated in argon matrices.[37] Four isotopomers were examined, and the following differences between calculated (without corrections for anharmonicity) and observed isotope shifts determined (the second figure in each case is the total shift): 0.12, 2.86 ($^{58/60}$Ni^{16}O); 0.06, 3.06 ($^{58/60}$Ni^{18}O); 0.45, 36.32 (^{58}Ni$^{16/18}$O); 0.40, 36.52 cm^{-1} (^{60}Ni$^{16/18}$O). For a polyatomic molecule such differences could lead to large errors in the bond angle calculated with Equation (1).

For an XY_2 molecule, the $\sin\theta$ function becomes less sensitive to changes in θ as the bond angle nears 180°, and this makes the assignment of linearity or nonlinearity increasingly difficult. This is illustrated in Figure 4 on the basis of calculations with Equation (1). The effect of increasing the mass of the central atom X is also clear. With bands of the order of 1 cm^{-1} full width at half-height, which frequently may not be fully resolved, attainment of the required accuracy is by no means easy.

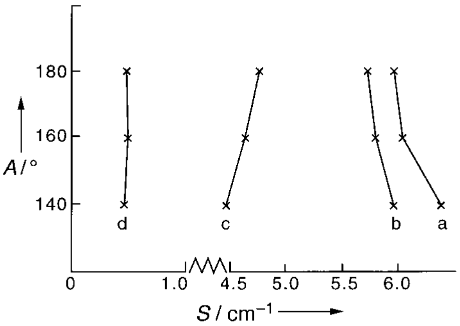


Figure 4. Calculated shifts S of ν_3 for an XY_2 molecule with an isotopic mass change of two units as a function of bond angle A. a) ^{56}Fe$^{35/37}$Cl$_2$; b) Yb$^{35/37}$Cl$_2$; c) $^{56/58}$Fe^{35}Cl$_2$; d) $^{172/174}$Yb^{35}Cl$_2$. (ν_3 for ^{56}Fe^{35}Cl$_2$ taken[40] as 493 cm^{-1}; ν_3 for Yb^{35}Cl$_2$ taken[39] as 296 cm^{-1}; arbitrary mass change for Yb from 172 to 174).

If the symmetry of MCl_2 in the all-^{35}Cl or all-^{37}Cl form is $D_{\infty h}$ or C_{2v}, ν_3 and ν_1 (the symmetric stretch) have different symmetries and do not interact. However, for the ^{35}Cl^{37}Cl isotopomer the symmetry is lowered to $C_{\infty v}$ or C_s. This means that the ν_3 and ν_1 modes of M^{35}Cl^{37}Cl can interact. As the mass of the central atom increases, the difference between ν_3 and ν_1 becomes smaller, and the vibrational coupling becomes stronger. As $\tilde{\nu}_3$ is generally higher than $\tilde{\nu}_1$, the central component (M^{35}Cl^{37}Cl) of the ν_3 triplet is shifted to a higher frequency, while the central component of the ν_1 triplet is shifted to lower frequency. This behavior can be used to determine whether the observation of two stretching frequencies is due to two matrix sites or the presence of bands for both ν_1 and ν_3 in the IR spectrum. If ν_1 and ν_3 can both be unambiguously identified, the relative intensities of their bands can also be used to obtain information on bond angles[38] [Eq. (2)], provided no interaction occurs with the bending mode and the change in dipole moment is along the bond axis.

$$\frac{I_{\nu_3}}{I_{\nu_1}} = \tan^2\theta(M_X+2M_Y\sin^2\theta)/(M_X+2M_Y\cos^2\theta) \qquad (2)$$

A combination of isotope shifts and the ratio of the intensities of the ν_1 and ν_3 bands was used to show that $YbCl_2$ is nonlinear,[39] with an estimated bond angle of 126 ± 5°. The authors commented (1983) that "…as far as we are aware this is the first unambiguous result showing nonlinearity for a transition element dichloride molecule". We might add "in an argon matrix".

On the subject of linearity of dichlorides the behavior of $NiCl_2$, which is almost certainly linear in the gas phase, will be considered. In very careful experiments in argon matrices, Green et al.[40] determined a bond angle of 161°, although the observed shifts in $\tilde{\nu}_3$ for isotopic substitution of chlorine, which give an upper limit for the angle, were only 0.04 (^{58}Ni$^{35/37}$Cl$_2$) and 0.03 cm^{-1} (^{60}Ni$^{35/37}$Cl$_2$) relative to those calculated for a linear molecule. A later paper[15] reported similar results in argon, but in nitrogen a major shift of over 90 cm^{-1} occurred in the position of ν_3, and a bond angle of

130° was reported. In this work separate samples of $Ni^{35}Cl_2$ and $Ni^{37}Cl_2$ were simultaneously vaporized to obtain the frequencies of these components without the added complication of an intense $Ni^{35}Cl^{37}Cl$ peak. Similar results were obtained for $NiBr_2$ in nitrogen by Young,[16] who used both EXAFS (145°) and isotope shift (125°) to obtain the bond angle. Again the difference between $\tilde{\nu}_3$ in argon and $\tilde{\nu}_3$ in nitrogen was large.

2.1.2. The Elements Calcium to Zinc

In 1979 Drake and Rosenblatt[41] wrote a comprehensive review entitled "Trends in Structures and Vibrational Frequencies of MX_2 and MX_3 High Temperature Halide Vapors". At that time TiF_2 was a key molecule as it was thought to be strongly nonlinear,[42] with a bond angle of about 120°. However, as deduced by Beattie et al.,[43] the bands in the IR spectrum of TiF_4 were incorrectly[42] attributed to TiF_3, and bands due to TiF_3 were assigned to TiF_2. Thus the derived bond angle of about 120° referred to TiF_3, not TiF_2. The error resulted from the ready disproportionation of TiF_3, which leads to the quite volatile TiF_4 and an involatile solid, together with the lack of data for fluorine isotopes, which meant that the number of ligands could not be determined from isotopomer distribution patterns. The remaining evidence for nonlinearity in TiF_2 arises from the ESR spectrum in a matrix, which shows that the molecule is not rigorously cylindrical.[44] It appears that a similar error arose in the VF_3/VF_2 system, for which data on isotopes are unavailable for both metal and ligand.[45]

These results emphasize the care that is necessary in interpreting data on fluorides when more than one oxidation state of the metal may be involved. Even when relevant mass spectrometric data are available, the differences between the pressures used in mass spectrometers ($<10^{-7}$ Torr), matrix-isolation IR spectroscopy (ca. 10^{-3} Torr), and conventional electron diffraction (ca. 1 Torr) make comparisons difficult. Changes in vaporization conditions can lead to alterations in the composition of the gas phase, as can expansion through an orifice from a higher pressure to a lower pressure. An additional problem, notably with fluorides, is the frequent loss of one (or more) ligands during ionization, so that the parent ion may not be observed in the mass spectrum.

Two other cases of apparent nonlinearity arose from electron diffraction studies[46] on VCl_2 and $CrCl_2$, which gave bond angles in the region of 110°. However, the results are in doubt because of the possibility of disproportionation and/or oligomers in the gas phase, as shown by subsequent matrix-isolation experiments.[47, 48] From a review on the molecular geometry of gas-phase metal halides[18] it appears that renewed analysis of the electron diffraction data does not give clear evidence for the nonlinearity of these two dichlorides.

Inspection of Figure 4 shows that the bond angles of 161°, 157°, and 161° reported[40] for $FeCl_2$, $CoCl_2$, and $NiCl_2$, respectively, cannot be reliably differentiated from linearity. We are then left with very little evidence of nonlinearity in the first-row transition element dihalides. The bond angle of 152° found for NiF_2[49] in an argon matrix represents a lower limit. In 1988 Bukhmarina et al.[50] assigned this molecule a linear $D_{\infty h}$ geometry on the basis of a combination of IR and Raman spectroscopy in neon and argon matrices. This leaves a) the ESR spectrum of TiF_2 in neon, which shows that the molecule does not have cylindrical symmetry[44] and b) a suggestion, based on the third law entropy, that $CrCl_2$ is nonlinear.[51] However this is at best an indirect method,[52, 53] and the linearity found in matrix studies appears to be more reliable.[48]

Even with gas-phase rotational data the proof of exact linearity for an XY_2 molecule is by no means easy, as may be seen from a recent paper on $CuCl_2$,[29] in which the bond angle determined from extensive experiments is 173°. Under the assumption of linearity, the bond length (r_e) in the $^2\pi_{g(3/2)}$ ground state was 2.0353 Å, and values of 371.693(2) and 525.897(4) cm^{-1} were obtained for ω_1 and ω_3 of the $^{63}Cu^{35}Cl_2$ isotopomer.

With regard to the calcium halides, there seems to be no doubt that CaF_2 is nonlinear in a neon matrix[54] (and several other matrices), although the angle of 140° represents a lower limit as the isotopic substitution was at calcium. At the other end of the transition series, there is little evidence for nonlinearity of the zinc dihalides.[55] Finally, anyone who wishes to appreciate the problems of matrix-isolation vibrational spectroscopy on compounds of this type is referred to an excellent paper by Lesiecki and Nibler on MgF_2.[56]

2.1.3. Heavier Elements

SrF_2, like CaF_2, was reported to be strongly bent, with a bond angle of 108° in krypton,[57] although the isotope data were taken from two different spectra because of band overlap. In the case of $SrCl_2$ the bond angle is slightly greater (120°), again in a krypton matrix.[58] A report[59] on the surprising stability of YF_2 showed that earlier matrix studies incorrectly identified this molecule as YF_3, which was reduced by the tantalum cell.

There is much less work on the second- and third-row transition series, mainly because of the lack of simple dihalides. The lanthanides Sm, Eu, and Yb form rather stable species in the +2 oxidation state, and there is evidence that the dichlorides are strongly bent.[13, 39, 60] However in only one case[39] was the identification of ν_1 confirmed by isotopic shift data for both ν_1 and ν_3, while for Sm[60] and Eu[13] isotope data could only be obtained in nitrogen, which is known to cause bending in $NiCl_2$[15] and $NiBr_2$[16].

2.2. Trihalides

For the trihalides of the lighter transition elements there is little evidence of structures other than D_{3h}, except for one very recent paper[61] entitled "The Structure of the Free MnF_3 Molecule—A Beautiful Example of the Jahn–Teller Effect", in which a C_{2v} structure was proposed on the basis of the electron diffraction data of the gas. Although this work and the related[62] matrix-isolation IR and Raman studies appear to have been carried out with great care, many of the problems discussed above also apply to these experiments.

In the case of the lanthanide trihalides, the situation is extremely confusing, as is shown by a collection of literature data by Molnár and Hargettai.[63] In particular, work by Hastie, Hauge, and Margrave[10, 64] appears in a number of instances to be in direct conflict with that by De Kock et al.[65, 66] An added complication in these studies is the orientation of the molecule in the matrix.[10, 67]

2.3. Tetrahalides

The tetrahalides are a particularly interesting group as any distortion from T_d symmetry results in at least a partial lifting of the triple degeneracy of ν_3 and ν_4, the antisymmetric stretching and bending vibrations, respectively. As the bands in matrix spectra are usually quite narrow, this is a sensitive way of studying distortions. A detailed study of thorium tetrachloride with a variety of $^{35}Cl/^{37}Cl$ isotopomer distributions demonstrated that even the inert gas krypton could have major effects on the vibrational spectrum.[17, 68] In krypton matrices excellent agreement between calculated and observed spectra was found for a C_{2v} model with bond angles of 110° and 160° (Figure 5). However, in a neon matrix the data could be interpreted in terms of the expected T_d model, with ν_1 and ν_3 effectively coincident, and partial occupation of a second type of site. There is thus unambiguous evidence for a change of symmetry between two noble gas matrices.

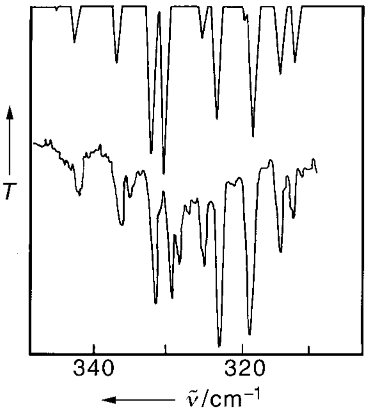


Figure 5. Calculated (upper trace) and observed (lower trace) IR spectra of $ThCl_4$ (^{35}Cl:^{37}Cl ratio 1:2) in a krypton matrix.[68] T = transmission.

The presence of more than one type of site is a major problem in matrix-isolation spectroscopy, notably when a decision on stereochemistry relies on the observation of a totally symmetric mode in the IR spectrum. Although the tetrahalides often give IR bands that apparently show at least partial resolution of a degeneracy,[69] there do not appear to be any cases where this cannot be explained by "matrix effects". A possible exception is UF_4, which has been carefully examined[70] in terms of a Jahn–Teller distortion. The situation is again somewhat complicated by the orientation of the molecule within the matrix.[71]

2.4. Pentahalides

The greater volatility of the pentahalides means that conventional gas-phase techniques can be applied to many of these molecules, and they are therefore of less interest in this review. However, for the pentafluorides very strong association can occur through fluorine bridges to give oligomers which are not easily broken down to the monomers even in the gas phase.[72] Recently it was shown that $NbCl_5$, $NbBr_5$, $TaCl_5$, and $TaBr_5$ adopt a square-pyramidal geometry in nitrogen matrices, while a variety of conformers are found in argon matrices.[14a] Species such as UF_5 and MoF_5 apparently adopt a square-pyramidal geometry in these matrices.[73, 74]

3. Oxides

Vaporization of metal oxides frequently requires high temperatures and in many cases results in the loss of oxygen and the formation of metal atoms and/or diatomic MO as the gaseous species. The precise behavior is critically dependent on the oxygen partial pressure. In certain cases the desired gaseous oxide may be obtained by passing oxygen over the metal or a lower oxide. Examples include Ag_2O[75], PtO_2,[76] CrO_3,[77] and OsO_3.[78] Easily vaporized oxides often give polymeric vapors, and examples that demonstrate the tendency towards tetrahedral coordination include V_4O_{10}[79] and $(MO_3)_n$ (M = Cr,[77] Mo, W).[80] Although matrix-isolation IR spectroscopy is particularly attractive for oxides because of the large relative mass change from ^{16}O to ^{18}O and the high frequency of most metal oxygen vibrations, generating gaseous oxides in a systematic fashion analogous to the work on the halides is difficult. Also, there are fewer ligands in oxides than in halides for a given formal charge of the metal atom, so that matrix interactions may be more important.

The rate of reaction of gaseous metal atoms of the first-row transition series with (di)oxygen has been studied[81] and correlated with the presence of a d^ns^1 configuration. For Sc, Ti, and V, transfer of oxygen atoms occurs, while for Cr (d^5s^1) the reaction shown in Equation (3) is observed.

$$Cr + O_2 + Ar \longrightarrow Cr(O_2) + Ar \qquad (3)$$

It is not clear whether OCrO is formed, and no LIF data could be obtained. Cobalt, which has a low-lying s^1 ($3d^84s$, ^4F) state, reacts slowly, while Ni has some 22 % population of an s^1 ($3d^94s$, ^3D) state at room temperature. An alternative approach to obtain information on the energy levels of the neutral molecule[82, 83] is to use negative ion photoelectron spectroscopy (NIPES). The resolution is not high, so no information on bond angles is available (for example, for CrO_2 $\tilde{\nu}_1 = 895 \pm 20$, $\tilde{\nu}_2 = 220 \pm 20$ cm^{-1}). There are few papers dealing with electronic spectra of oxides in matrices, and even less information is available for the gas phase.[84]

3.1. Dioxides

Recent work, notably by Andrews et al., has dramatically altered our knowledge of dioxides. For example, reliable high-quality IR spectroscopic data are now available for all the dioxides from calcium through to zinc. The results were obtained by reaction of laser-ablated metal atoms with oxygen followed by cocondensation with argon to give a matrix that could be studied by spectroscopy. The resulting bond angles (given here without error ranges) show an interesting dependence on the central element: Ca[85] 140°, Sc[86] 128°, Ti[87] 113°, V[88] 118°, Cr[89] 128°, Mn[90] 135°, Fe[91] 158°, the rest (Co[92], Ni,[93] Cu,[94] Zn[95]) linear. There is, not unexpectedly, a dramatic change in the simple valence force field (SVFF) stretching force constant derived from $\tilde{\nu}_3$ for CaO_2 through ScO_2 to TiO_2 (1.4 to 3.1 to 5.4 in units of $10^2\,\mathrm{N\,m^{-1}}$). Overall, the value of this force constant for Ti through to Ni is around 5.6. It starts to fall at CuO_2 (4.2) and is 3.5 for ZnO_2, which resembles CaO_2 in having a maximum likely metal oxidation state of +2. The decrease in the metal–oxygen distance from calcium to zinc presumably leads to the higher force constant.

For a nonlinear molecule XY_2[35] [Eq. (4)]

$$4\pi^2\nu_3^2 = \left(\frac{1}{M_Y} + \frac{2}{M_X}\sin^2\theta\right)k \qquad (4)$$

where k is the SVFF stretching force constant, and 2θ the bond angle. For ν_1, neglecting interaction with the deformation ν_2, a similar expression holds in which $\sin^2\theta$ is replaced by $\cos^2\theta$. For a bond angle of 90°, the ν_1 and ν_3 bands [according to Eqs. (2) and (4)] will have the same intensity and frequency since $\sin^2\theta = \cos^2\theta$. Figure 6 shows the dramatic change in the difference between $\tilde{\nu}_3$ and $\tilde{\nu}_1$ from CrO_2 to MnO_2, which is associated with a decrease in the difference between the observed position of the $M^{16}O^{18}O$ component and that calculated from the mean of the $M^{16}O_2$ and $M^{18}O_2$ positions. Both of these effects are brought about principally by changes in bond angle.

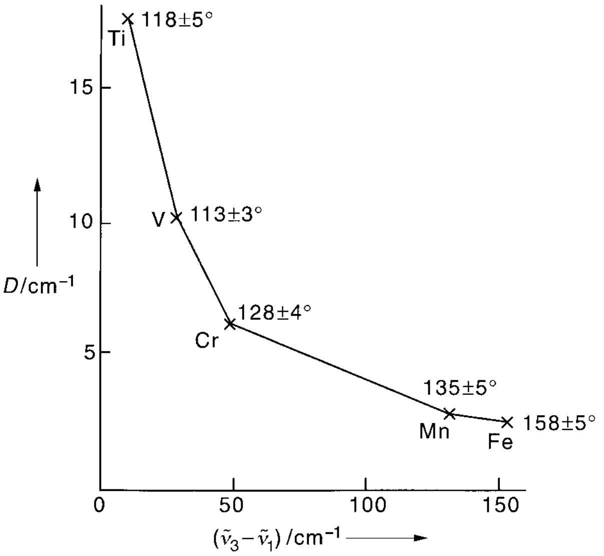


Figure 6. The effect of the O-M-O bond angle on the stretching frequency of metal dioxide molecules (D = difference between the frequency of the $M^{16}O^{18}O$ component of ν_3 and that calculated from the mean of the $M^{16}O_2$ and $M^{18}O_2$ frequencies).

Passing now to the second- and third-row transition elements, the earlier members are, like those of the first row, strongly nonlinear: Zr and Hf (113°);[87] Nb (108°), Ta (106°);[96] Mo (122°), and W (124°).[97] It is noteworthy that in the case of molybdenum, with seven isotopes of natural abundance greater than 9%, it was possible to use 16 (symmetrical) $^{16}O_2$ or $^{18}O_2$ species to calculate an upper limit to the angle (125°), and more than 40 isotopomers to calculate a lower limit (119°). RuO_2 was reported[98] to have a bond angle of 149°, and if RhO_2 and IrO_2 are linear, as indicated by ESR measurements,[99] then the general pattern for the second- and third-row transition element dioxides appears to be similar to that established for the first row.

Several lanthanide oxides can be vaporized at very high temperatures to give gas-phase MO_2, and this behavior appears to correlate with the value of the fourth ionization potential of the metal. Both CeO_2 and TbO_2 (d^0f^0 and d^0f^7) have spherically symmetrical inner shells and are nonlinear (146 ± 2° and 121 ± 2°).[100] Although the angle for CeO_2 (isoelectronic with BaF_2) is large and the assignments of two IR bands reverse those in an earlier paper,[101] the authors present a consistent argument for nonlinearity. Praseodymium dioxide, which has a central atom with a partially filled f shell, is a linear molecule.[100]

In the case of the actinides ThO_2 (d^0f^0) is nonlinear (122.5 ± 2°),[100] while UO_2[102] and PuO_2[103] both have partially filled shells and are linear. This work on the lanthanides and actinides is mainly from the group at Argonne National Laboratory, and the IR spectra are of high quality. There are laser ablation experiments by Wilson and Andrews, analogous to those on the first row transition element dioxides, which confirm the earlier work on CeO_2 and indicate that PrO_2, NdO_2 (similar to UO_2), and SmO_2 (similar to PuO_2) are linear. However, EuO_2 and GdO_2 were found to be nonlinear surprisingly, with acute angles of approximately 90° and 97°, respectively.[104]

3.2. Trioxides

Of the trioxides, MoO_3 was reported[105] to be pyramidal (C_{3v}). However the $^{16}O_2$ to $^{18}O_2$ frequency shift of the assumed ν_3 band in this difficult experiment was only shifted 0.2 cm^{-1} from that calculated for a planar molecule (neglecting interaction with the E′ bend). Further, the assignment of ν_1 has been questioned.[97] If MoO_3 were planar this would agree with data on WO_3[11] and RuO_3,[98] both reported as D_{3h}. UO_3 is exceptional in that it is apparently T-shaped in argon matrices and, as a result, has been extensively studied.[102]

4. Hydrides

The situation with regard to hydrides is perhaps the least satisfactory, although as a group they are the most tractable from the point of view of theoretical calculations and spectroscopic rotational analysis. The terms $\left(\frac{2}{M_X}\sin^2\theta\right)$ and $\left(\frac{2}{M_X}\cos^2\theta\right)$ for ν_3 and ν_1 in Equation (4) are small compared with $1/M_Y = 1$ or 0.5. Essentially the ν_1 and ν_3 bands of MH_2 and the ν_{M-H} band of HMD will all lie within a narrow frequency range, well separated (by a factor of about $\sqrt{2}$) from the corresponding bands of MD_2 and HMD. Hence, isotopic shift data are usually not useful in determining bond angles. For the dihydrides the determination of bond angle therefore relies on the relative intensities of the ν_1 and ν_3 bands [ca. $\tan^2\theta$ according to Eq. (2)]. The occupation of two different matrix sites by a linear MH_2 molecule also leads to two bands in the stretching region. However, the difficulty is resolved because in this case each MHD molecule gives rise to two stretching vibrations, so that a total of four bands is observed for the mixed isotopomer, rather than the two expected for a nonlinear molecule in a single matrix site.

This approach gave a tentative value of 168° for CaH_2;[106] however, the spectroscopic data are very complex. In the case of TiH_2 Chertihin and Andrews[107] report a value for $\tilde{\nu}_3$ but note that a band previously assigned[108] to ν_1 was of variable intensity in their spectra. It is thus possible that TiH_2 is linear. There is disagreement about VH_2. Van Zee, Li, and Weltner[109] find "no indications of VH_2 being nonlinear" by ESR spectroscopy, although a previous paper[108] reported a strongly bent molecule ($127 \pm 5°$). The situation with CrH_2 is equally confused as the HD species were observed as doublets in the latest paper,[110] while MnH_2 is probably linear.[111, 112] Fortunately, at this point some definitive experiments were performed. In 1996 groups in Bonn and Oxford announced the identification of FeH_2 in the gas phase by IR spectroscopy.[113] FeH_2 was produced in a dc electric discharge through helium doped with hydrogen and iron pentacarbonyl. The discharge was probed with a CO laser by Zeeman modulation of the energy levels of FeH_2. This laser magnetic resonance experiment characterized the molecule as linear in its ground electronic state ($^5\Delta$) with a ν_3 fundamental frequency of 1674.7196(4) cm^{-1} and an Fe–H distance of 1.665 Å. The bending vibration of FeD_2 occurred at 229 cm^{-1}.[114] The latest matrix IR results[115] also indicate a linear molecule in argon, in contrast to earlier work in xenon,[116] which gave a bond angle of "around 117°". In the cases of CoH_2[117] and ZnH_2,[106, 118] IR data show them to be close to linear or linear in a matrix, although for CoH_2 the ESR spectrum was interpreted[119] in terms of a strongly bent molecule. However, there is one very interesting result. From IR studies in argon matrices doped with hydrogen, it has been reported[120] that nickel atoms insert directly into H_2 to give NiH_2, with a bond angle close to 90°. For most other metals only excited atoms react with H_2, again the preferred mechanism being insertion. The bending frequency of NiH_2 is high (771 cm^{-1}), comparable to that of linear ZnH_2 (631 cm^{-1}) but more than twice those of FeH_2 and CoH_2 (335 and 380 cm^{-1}) all in argon matrices. The anomalous behavior of this molecule is further emphasized in Figure 7, which plots the SVFF force constants of MH_2 [from ν_3 in Eq. (4)] for the elements Ca to Zn (except Sc and Cu). By contrast, photodetachment spectroscopy on MnH_2^-, FeH_2^-, CoH_2^-, and NiH_2^- led to the suggestion that all the neutral dihydrides are linear.[121]

A number of higher and heavier hydrides has been reported.[122] However, in view of the difficulties outlined above and the lack of systematic studies, it is not possible to make any useful comments other than to note that several of the heavier ones appear to be nonlinear (MH_2) or pyramidal (MH_3).

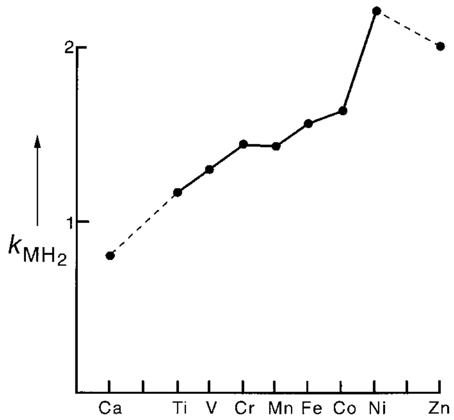


Figure 7. Plot of the stretching force constant k for the dihydrides of elements Ca to Zn (without Sc and Cu). Values refer to argon matrices, except for CaH_2, which was studied in krypton.

5. Summary and Outlook

In 1989[43] we wrote a paper entitled "Do Any AB_n Molecules Have Anomalous Shapes?" The title was intended to be provocative and to emphasize the potential importance of host–guest interactions in matrices. In 1988[68] we wrote: "Guests likely to be strongly affected by the host matrix would be those where the central atom is co-ordinatively unsaturated and where bonding forces are not highly directional in character."

Table 1 summarizes the bond angles found for metal dioxides (OMO) isolated in argon matrices for which well-resolved IR spectra were obtained for the $^{16}O/^{18}O$ molecules. In their experiments on the dioxides of the metals from Ca to Zn,[85–95] Andrews et al. found a gradual change from CaO_2 at about 140° (similar to CaF_2 in argon) through ScO_2 at 128° to TiO_2 at 113°. This decreasing angle is reflected in the increase in formal charge from +2 to +4 and possibly represents

Table 1. Bond angles [°] of MO_2 species in argon matrices determined by means of $O^{16}/^{18}O$ substitution[a]

Sc	Ti	V	Cr	Mn	Fe	Co to Zn		
128	113	118	128	135	158	180		
Y	Zr	Nb	Mo	Tc	Ru			
	113	108	122		149			
La	Hf	Ta	W	Re	Os			
	113	106	124					
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb
	146	180	180		180	ca. 90	ca. 97	121
Ac	Th	Pa	U	Np	Pu			
	122		180		180			

[a] Of the dihalides, $^{40/44}CaF_2$* (Ne, Ar, Kr, 143–139°), $^{86/88}SrF_2$* (Kr, 108°), $^{86/88}Sr^{35/37}Cl_2$ (Kr, 120°), and $Yb^{35/37}Cl_2$ (Ar, 126°) are nonlinear; of the dihydrides, NiH_2 is nonlinear (Ar, ca. 90°; an asterisk denotes the lower limit of an angle).

increasing interaction with the matrix. As the electronegativity difference between the metal and oxygen decreases, the bond angle widens up to CoO_2, and all subsequent dioxides up to and including ZnO_2 are linear. Again, one of many possible explanations is that the bending is induced by the matrix, although it could equally well be argued that these strongly bound molecules are unlikely to be appreciably affected by their surroundings. A comment by Lessen and Brucat[123] is apposite: "the potential well depth of VAr^+ is sufficently strong as to be similar to the more chemically relevant solvent water". As expected the binding energy of such species increases with the polarizability of the inert gas.[124] It is also interesting that in the sequence $FeCl_2$, $CoCl_2$, $NiCl_2$ in nitrogen matrices[125] there appears to be a gradual decrease in bond angle from 150° in $FeCl_2$ to 130° in $NiCl_2$. As these molecules are all thought to be linear in argon, this again suggests a gradual change in matrix interactions. Against this view, calculations by Andrews and co-workers frequently show excellent agreement between theory and experiment for the first-row transition element dioxides.

This leaves the question of which experiments are most likely to resolve these controversies. For the first-row transition metal dihalides, the only molecule that shows evidence of a nonlinear structure is TiF_2.[44] A laser ablation experiment on titanium, seeded in an argon stream doped with fluorine, followed by cocondensation and IR spectroscopy could settle this point. The spectra of TiF (gas), TiF_3, and TiF_4 (in matrices) are all known, and titanium has several naturally occurring isotopes. For the halides of Ca, Sr, and Ba, a high-temperature gas-phase microwave spectrum of SrClF could establish whether it is worth pursuing the pure dihalides. This technique could also be used for the lanthanide dihalides, notably YbClF.

In the case of oxides the difficulty of obtaining species in the gas phase means that, unless an alternative approach is found, it may be necessary to work at the very high temperatures required to generate vapors of, for example, CeO_2 or UO_3, with all the attendant problems that this entails.

Of the dihydrides, NiH_2 is the most interesting in that it shows both high force constants and a strongly nonlinear molecule. A reaction analogous to that used to generate gaseous FeH_2, but with $[Ni(CO)_4]$ instead of $[Fe(CO)_5]$, is being actively pursued.

Most of this review has been concerned with ground-state molecules. Matrix-isolation techniques allow the synthesis of many interesting species, and their IR spectra frequently give information on molecular geometry. Gas-phase studies are much more difficult both in the formation of the required molecule and in the recording and analysis of the spectra. However, it is only by obtaining detailed information on molecular energy levels and geometry that comparison with increasingly reliable[126] theoretical calculations will be possible. In particular density functional theory (which is nearly as old as quantum mechanics) is establishing a reputation for speed and reliability for compounds of the transition elements.[127] It is also salutory to recall that although the ground and several excited electronic states of CaOH are linear,[128] "the F state is bent, the first bent and strongly covalent state of CaOH to be observed".

Perhaps as a finale to this review a quote by Friedman-Hill and Field[129] is relevant: "Truly heroic analyses of the spectra of these molecules have still left many questions unanswered…" and they were referring to diatomic gases.

Addendum

Several relevant papers have been published since submitting this Review. One of these represents a major advance: the recording of the microwave spectrum of ZrO_2 giving a bond length of 1.7710 ± 0.0007 Å and a bond angle of $108.11 \pm 0.08°$ for the ground-state molecule in the gas phase.[130] As the corresponding matrix-isolation experiment[87] gave an upper limit of $113 \pm 5°$ for the bond angle while that calculated was 112°, the value of 108° gives confidence in both the matrix data and the calculations on similar strongly bonded dioxides.

The value of 128° used in Table 1 of this Review for ScO_2 is now thought[131] to be due to ScO_2^- (isoelectronic with CaF_2). IrO_2[132], RhO_2,[133] and PtO_2[134] are all reported as linear, while the more weakly bound YO_2 and LaO_2 are nonlinear[135] with ν_1 showing an anomalously high intensity and frequency relative to ν_3. There are now data on all the lanthanide dioxides apart from Pm, Er, and Lu.[136] This work (which agrees with earlier data on Ce, Pr, and Tm) gives Nd, Sm, Dy, and Yb as linear while Eu, Gd, Ho, and Tm are strongly bent (from isotopic data or intensity measurements on ν_1 and ν_3). Finally the low-lying electronic states of WO_2 have been probed using NIPES,[137] while the vibrational and electronic energy levels of many oxides and hydrides have been tabulated by Jacox.[138]

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