PROGRESS IN
STEREOCHEMISTRY

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PREFACE

INTEREST in stereochemical problems has been growing during the last few years. This interest was strikingly demonstrated by the attendance at the Symposium on Dynamic Stereochemistry held in Manchester in March 1954. No major work on stereochemistry has appeared since Freudenberg's great textbook of 1933. To write a complete textbook today would be almost an impossibility, even with a large team of contributors. We have therefore tried in this volume to discuss a few of the recent advances in the field. These are chiefly stereochemical problems or concepts which were unknown at the time of Freudenberg's book, or which have developed very largely since 1933.

In an endeavour to correlate the different chapters of the book, which cover widely scattered fields in physical, inorganic, organic and biological chemistry, a draft of each chapter was circulated to all the other contributors, and much valuable criticism resulted. We hope that by this means we have linked the chapters together, where possible, and avoided serious overlaps. The literature has been covered up to late 1953, and in some cases to early 1954. A few important additional references which have appeared while the book has been passing through the press are listed on pages 366-9.

We should like to thank the many colleagues—including our fellow-authors—who have read typescripts and proofs of the various chapters, or who have supplied unpublished information; we are grateful also to the authors and publishers of diagrams which have been reproduced from other books and journals. (A list of these is given overleaf.)

The editor is particularly indebted to Professor D. H. R. Barton, F.R.S., for many helpful discussions during the preparation of this book, to Dr P. B. D. de la Mare and Mr A. A. Wright for their kind help in reading the proofs, to Miss June Felton for much secretarial work and for assistance with the Index, and to the staff of Messrs Butterworths the publishers for their constant and willing help at all stages of the production.

<div align="right">W. KLYNE</div>

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THE SHAPES OF SIMPLE MOLECULES

A. D. Walsh

In this chapter it is proposed to deal with the shapes of the simplest polyatomic molecules. The stress will be primarily upon the experimental results that are now available, upon the empirical generalizations that can be made from these results, and upon what can be said from a theoretical point of view to explain those generalizations. It is desirable, however, to begin with a brief indication of the main methods that have been used to determine molecular shapes.

MAIN METHODS OF DETERMINING THE STRUCTURES OF MOLECULES

These methods are three in number: (*a*) the diffraction of x-rays, (*b*) the diffraction of electrons, (*c*) spectroscopic methods.

X-Ray Diffraction

This method is usually only of practical importance when the substance to be examined can be obtained as a crystal at temperatures fairly close to room temperature (perhaps down to $-15°C$), though a few studies have been made at lower temperatures. For this reason it has been applied more to fairly large molecules than to the simplest polyatomic molecules. Since, however, many simple ions exist in crystals at room temperature, x-ray diffraction has often been the main source of information about the shapes of these (*e.g.*, the nitrite, nitrate and carbonate ions). The method does not usually fix the relative positions of hydrogen atoms; but, particularly in fixing the positions of heavier atoms, it is capable of high accuracy. Usually, the bond length values obtained have been considered reliable to about $0·02$ Å but only the more recent analyses have been carried out with sufficient precision to justify this figure. During recent years, realization of errors introduced by the techniques used to interpret the diffraction photographs and careful estimation of those errors have improved the reliability of results and the precision with which they can be stated (see Jeffrey and Cruickshank, 1953). It should be emphasized, however, that the structure of a substance in the solid form is not necessarily the same as that of gaseous molecules of the substance. For example, nitrogen pentoxide in the solid state is an

assembly of equal numbers of NO_2^+ and NO_3^- ions (Grison, Eriks and de Vries, 1950); but in the gas phase consists of covalently bound molecules of probable structure

$$O_2N-O-NO_2$$
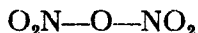
(Maxwell, Mosley and Deming, 1934). Further, the bond lengths of a molecule may not be exactly the same in a crystal as in the gas phase; though unless the crystal forces are strong (*i.e.* the crystal has a high melting point), the difference is not expected to be considerable. Iodine is one of the few substances which has been studied both in the solid state by x-ray methods and in the gas phase by spectroscopic methods. From the x-ray studies the bond length is reported as 2·70 Å, but from analysis of the electronic spectrum as 2·666(6) Å. The discrepancy is probably partly real because it appears that in the solid something approaching chemical bonds exists between one molecule and another (Townes and Dailey, 1952).

For details of the x-ray diffraction method, the reader should consult *e.g.* Bunn (1945) or Lonsdale (1948), and, for results, the successive volumes of *Structure Reports*, issued by the International Union of Crystallography.

Diffraction of Electrons

This method has the great advantage that it can be applied to determine the structures of simple substances that are gaseous at room temperature. It has been so applied to a very large number of substances [see the extensive tables compiled by Allen and Sutton (1950) for results obtained up to that date]. On the other hand, the accuracy obtainable is often much less than in methods (*a*) and (*c*). Like the x-ray method, method (*b*) does not locate hydrogen atoms accurately in the presence of much heavier atoms. Furthermore, once the experimental work is completed, a model has to be set up which, calculation shows, would lead to the same scattering pattern as observed. By trial and error, the model is adjusted until agreement of calculated and observed patterns is obtained. It is then not always certain that the *only* model which would yield good agreement with the observed pattern has been obtained. Partly because of this and partly because of over-optimistic guesses at probable errors, many of the earlier results obtained by electron diffraction have had to be revised. To take but one example out of the many possible, the ClF_3 molecule was reported as a regular pyramid (see Allen and Sutton, 1950), but is now found by x-ray diffraction and microwave methods to be planar and of a slightly distorted T-shape. Values obtained for interbond angles are usually subject to greater uncertainty than values for bond lengths. For example, in the SO_2 or ClO_2 molecules the S or Cl

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atom has a much greater scattering power than the O atoms. As a result, the two S—O or Cl—O terms in the scattering equation have much more effect on the diffraction pattern than has the single O—O term. Hence, any alteration in the bond angle assumed makes little difference to the theoretical intensity curve; and the S—O or Cl—O distances can be obtained much more accurately than the OSO or OClO angles. It is therefore not particularly surprising that the OClO angle in chlorine dioxide was first reported as 137° (Pauling and Brockway, 1935), but has later (Dunitz and Hedberg, 1950) been revised to $116 \cdot 5 \pm 2 \cdot 5°$. Even in ozone, where the atoms do not differ in weight, the apex angle has been reported (Shand and Spurr, 1943) as $127 \pm 3°$, but has since been determined by more accurate, microwave, methods as 117°.

In recent years, considerable improvement in experimental techniques [especially the introduction of the so-called sector method (Finbak, 1941; Finbak and Hassel, 1941; and Debye, 1939), used particularly by the Norwegian School (Viervoll and Hassel, 1947)], in methods of interpreting the experimental data (*e.g.* Viervoll, 1947; and Karle and Karle, 1949), and attention to freeing the results of systematic errors and estimating the random errors (Cruickshank and Viervoll, 1949), have led to great advances in the reliability of results. In a particularly favourable case (the C—Br length in CBr_4) studied by the sector method the standard deviation has been estimated as only $\pm 0 \cdot 004$ Å (Cruickshank and Viervoll, 1949); but in general the bond length values obtained are not to be trusted to more than about $0 \cdot 02$ Å, and are usually reliable only if determined in the last few years. At best the accuracy of the bond angle values reported is only plus or minus a few degrees. The uncertainty attaching to all the earlier results should be borne in mind when considering data from electron diffraction studies presented later in this chapter.

For details of the electron diffraction method, the reader should consult the above references and also Pirenne (1946) and Beach (1950).

Spectroscopic Methods

These methods fall into three main divisions: (*i*) the study of rotation spectra, (*ii*) the study of vibration-rotation spectra, and (*iii*) the study of electronic spectra.

Rotation Spectra

The rotation spectra of molecules lie in the so-called microwave region *i.e.* at wavelengths from about 5 to 0·5 cm. The elaboration of radar . during the war led to a rapid development of this field in the post-1945

period. For a general account of the methods used, the reader should consult Gordy, Smith and Trambarulo (1953). The method yields the moments of inertia of molecules. These in general are not sufficient to determine all the bond lengths and angles in a molecule; but since the lengths and angles are expected to be the same for isotopic molecules, combination of the moments of inertia determined for isotopic molecules may lead to a complete structure determination. The moments of inertia are yielded with very high accuracy because the resolving power in the microwave region is very great. Spectral lines as close as 4×10^{-6} cm^{-1} can be separated. In other words, micro-wave frequencies can be measured to an accuracy of about 1 in 10^{6}.

The accuracy with which moments of inertia can be deduced from these frequencies is limited by uncertainty in the value of Planck's constant, the latter only being known to about 1 part in 10^{4}. The accuracy with which bond lengths can be deduced from the moments of inertia may be further limited when, as is usually the case, data for isotopic molecules have to be combined. Strictly, the moments of inertia referring to the equilibrium point of a potential curve or surface should be used, for the equilibrium internuclear distances (r_e) depend only on the force field which is justifiably assumed to be unchanged by isotopic substitution. The moments of inertia referring to the lowest vibrational level are less appropriate because the mean internuclear distances (r_o) change with zero-point amplitude and so with isotopic substitution. r_o differs from r_e because the vibrations are not harmonic, so that a potential curve is not symmetrical about r_e.

In addition, one has to remember that, even though for a simple harmonic vibration the mean internuclear distances are not altered by the zero-point motion, the mean of the squares of the distances from the centre of gravity is altered; and it is on this latter quantity that the moment of inertia depends. The r_o values obtained from spectra are thus effective values of a special kind and not simply average values of r in the lowest vibrational level. It is the moments of inertia referring to the lowest vibrational level that are obtained directly from micro-wave spectra and are commonly used, reducing the accuracy of the derived bond length values. The correction may be important, since the computed bond lengths are very sensitive to any change of inter-nuclear distance on isotopic substitution. It is true that even for r_o the equality of bond lengths for isotopic molecules holds to within 0·002 Å; but a change of mean internuclear distance of 0·001 Å on substitution of mass 33 for mass 32 may lead to an error of 0·03 Å in the value of the derived bond length (Whiffen, 1950). Errors of 0·005 Å may also be introduced by uncertainty of the exact isotopic masses.

Unless allowance has been made for the zero-point effects, bond lengths derived from isotopic moments of inertia should not be trusted to better than 0·01 Å.

In order to correct the mean moments of the lowest vibrational level to the equilibrium moments, it is necessary to know the moments in the higher vibrational levels and to extrapolate to zero vibrational energy. This is not generally possible in the microwave region. However, where bond lengths and angles have been determined by microwave studies, they are usually more accurate and reliable than data from other sources except those obtained from the study of vibration-rotation spectra (see below). Further advantages are that the method can be used to obtain other important data such as the magnitudes of dipole moments (by use of the Stark effect) and nuclear spins. On the other hand, except in special cases (*e.g.* O_2), the method can only be applied to molecules with a permanent dipole moment. However, this in itself may provide a way of deducing molecular shape. Thus, since the H_2O molecule has a pure rotation spectrum, it must have a dipole and cannot therefore be linear.

Vibration-rotation spectra are not restricted to polyatomic molecules with a permanent dipole moment. Vibration spectra are studied, under low resolution, by the use of either Raman or infra-red techniques. The selection rules that determine the number of 'lines' obtained in the Raman and infra-red spectra depend very much upon symmetry. Thus a linear triatomic molecule BAB has two strong lines in its infra-red spectrum and only one strong line (of a different frequency) in its Raman spectrum. The two spectra are complementary. It is in fact always true that if a molecule has a centre of symmetry then a strong line obtained in the Raman spectrum will not be obtained in the infra-red spectrum and vice versa; though of course care has to be taken not to be misled by chance coincidences. This mutual exclusion rule affords a simple method of determining whether a molecule has a centre of symmetry. Furthermore, the polarization of the scattered light in the Raman effect also depends upon the molecular symmetry. By studying the number and polarization of strong lines in the Raman and infra-red spectra it is thus often possible to say at once whether a given molecule is linear or non-linear. As an example, sulphur dioxide has three strong infra-red absorption frequencies; and these frequencies also occur in the Raman spectrum (though two happen here to be rather weak). It is concluded therefore that the SO_2 molecule is not linear. (It is always desirable that such deductions be checked by alternative arguments, for sometimes absorption frequencies may not be observed in the infra-red or Raman spectra simply because they are not strong enough and not because they are forbidden on account of a symmetry property of the molecule.)

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Vibration-rotation Spectra

These are studied by the use of high resolution infra-red techniques. Until the recent development of photoconductive infra-red detectors (lead sulphide, selenide and telluride), much higher resolution was obtainable if the spectrum was detected by photographic means than by *e.g.* thermocouples. For the study of the rotational fine structure of a vibration band it has therefore been desirable to use bands in the so-called photographic region of the infra-red. The difficulty was that the strong infra-red bands usually occur at longer wavelengths than those of the photographic region, the bands occurring in the latter region being the comparatively weak higher overtone and combination bands. During recent years Herzberg and his co-workers, and others, have overcome this difficulty by the use of very long absorbing paths obtained by repeated reflections of the light. The rotational fine structure of a vibration band depends upon the symmetry of the molecule and upon the particular vibration change responsible for the band. Particular vibration changes, for a linear molecule for example, are labelled $\Sigma-\Sigma$, $\Pi-\Sigma$, $\Pi-\Pi$, *etc.* $\Sigma-\Sigma$ bands have simple P and R branches [corresponding to changes of the rotational quantum number (J) by -1 and $+1$] with one rotation line missing between the two, while $\Pi-\Sigma$ and $\Pi-\Pi$ bands have in addition a Q branch (corresponding to $\Delta J = 0$). For molecules with a centre of symmetry, alternate rotation levels are symmetric and anti-symmetric with respect to an exchange of the identical nuclei. In consequence there is an alternation in the intensities of successive rotation lines (or alternate lines are missing if the nuclear spins are zero). Conversely, when a simple band with P and R branches only is observed, one knows at once that the molecule is linear; and when an intensity alternation (or alternate missing lines as with CO_2) is observed with that molecule, one knows that the molecule has a centre of symmetry. These conclusions can be drawn immediately from the appearance of the bands under high resolution without detailed measurements. From the observation of $\Sigma-\Sigma$ bands in this way it has been shown, for example, that the electronic ground states of N_2O, CO_2, C_2H_2 and diacetylene are all linear, and that the last three have a centre of symmetry. The absence of an intensity alternation shows that N_2O has the configuration NNO and not NON.

Detailed measurement yields the moments of inertia of the molecules. For CO_2, the moment of inertia yields directly the C=O bond length. For other molecules, the bond lengths and angles can be obtained by using also the moments of inertia of isotopic molecules. For example, two isotopic species are obviously required for the C_2H_2 molecule; two for the C_2H_4 molecule; and three for the diacetylene molecule. As regards C_2H_2, both C_2HD and C_2D_2 have been studied, thus over-determining the structure. For diacetylene, however,

no isotopic molecules have yet been studied and so, although the moment of inertia is known accurately, it is not yet possible to deduce from it the bond lengths except on the basis of such assumptions as that the C—H and C≡C lengths are identical in diacetylene and acetylene. The remarks made above about the importance of distinguishing between r_0 and r_e values apply just as much to bond lengths derived from vibration-rotation spectra as to those derived from microwave spectra. However, the study of vibration-rotation spectra has the advantage of allowing one to investigate the effect of vibration on the rotational constants and so to eliminate the influence of zero-point vibration*. The r_e values may then be accurate to about 0·001 Å. CO_2, C_2H_2, C_2H_4, CH_4 and C_2H_6 form examples of molecules wherein very accurate values of bond lengths have been determined from vibration-rotation spectra; see TABLES 1–4 (pp. 10–23). These molecules are all ones where the microwave method could not be applied because of the absence of a permanent dipole moment. It is most satisfactory that where a molecule with a permanent dipole has been studied—e.g. HCN and HCNO—the very accurate moments of inertia obtained from the vibration-rotation bands agree excellently with the also very accurate values from microwave spectra. For details of the infra-red work, the reader should consult Herzberg (1945).

Electronic Spectra

The study of electronic spectra is not confined to any particular class of molecule, except that it is usually only with gases that a structure determination can be made. It has the advantage that it is capable of yielding not only the shape of the ground state but also that of the upper electronic state. Our knowledge of the shapes and sizes of molecules has usually been confined to the ground electronic states. Knowledge of the shapes and sizes of excited states has only recently begun to accumulate and is still in its infancy. Yet from the point of view of a theoretical understanding of the factors that influence molecular shape and size it is most desirable that more knowledge of excited states should be obtained. The possible electronic-vibration bands that may appear are governed by selection rules that depend upon the symmetries of the equilibrium forms of both lower and upper states. It is often possible therefore to say something about the symmetries of the lower and upper states from a vibrational analysis of an electronic band system. For example, vibrational analysis of the 2600 Å system of benzene indicates that the molecule has a symmetry at least close to that of a regular hexagon in both combining states.

*For the ground state of the H_2 molecule r_0 is about 2 per cent greater than r_e. Rather similar differences apply to the r_0 and r_e values in the ground states of the CO_2 and C_2H_2 molecules.

Application of the Franck-Condon principle and observation of the intensities observed in vibrational progressions may also lead to conclusions about the shape and size of the excited state relative to the ground state. For example, in the 2600 Å absorption of benzene the intensities observed in vibrational progressions involving the breathing frequency of the carbon hexagon have led to the conclusion (Craig, 1950) that in the equilibrium form of the upper state each side of the hexagon has expanded by 0·037 Å. If an electronic transition covers an extensive range of the spectrum one may deduce that the size, and perhaps the shape, of the excited state differ markedly from the ground state. In the near ultra-violet absorption of carbon disulphide long progressions in what is probably the bending frequency of the upper state have been observed; strongly suggesting that the initially linear molecule has become bent in the equilibrium form of the upper state (Mulliken, 1935). A vibrational analysis of an electronic band system may lead to the determination of force constants controlling the vibrations in the upper state; and so, by empirical relations between force constants and bond lengths, to dimensions of the upper state. This method has been applied by Garforth, Ingold and Poole (1948) to the 2600 Å system of benzene, yielding upper state C—C lengths in good agreement with the work of Craig quoted above.

It is always desirable that a vibrational analysis should be supplemented if possible by rotational fine structure analysis of the various bands; partly because the 'origins', and so the accurate vibrational frequency separations, can be fixed only by rotational analysis, and partly because the fine structure analysis yields the polarization of the bands and so checks the vibrational analysis. Further, if the rotational fine structure can be resolved, it may lead to a determination of the moments of inertia of both the upper and lower states; in principle, therefore, especially if isotopic molecules are also studied, it can lead to a determination of the bond lengths and angles in both combining states. Such a fine structure analysis for an electronic-vibration band has, for example, been carried out for certain bands in the near ultra-violet absorption spectrum of formaldehyde (Dieke and Kistiakowsky, 1934); and partially for the 2491·Å band of nitrogen dioxide (Harris and King, 1940). Nitrogen dioxide is a sufficiently simple molecule for the moments of inertia to yield the bond lengths and angles without study of isotopic molecules. Even without detailed measurement of the fine-structure lines or even if the fine structure is not completely resolved, it is often possible to deduce something about the change of equilibrium dimensions in the upper state relative to the lower. Thus from the observed degradation of the so-called J and K fine structure of the 3900–3400 Å absorption bands of sulphur dioxide, one can conclude (Metropolis, 1941) that the upper state has a

slightly increased apex angle and S—O length. Similarly, one can conclude from certain emission bands of CF_2 (Venkateswarlu, 1950) that the molecule is not linear in either electronic state and has a larger apex angle in the upper than in the lower (ground) state.

It is important to bear in mind that polyatomic molecules differ from diatomic molecules in that, on electronic excitation, the shape in the equilibrium position may change. There are as yet few cases where the shape of a molecule in an electronically excited state is definitely known. However, in addition to the example of the carbon disulphide 3980–2767 Å absorption mentioned above, the following may be mentioned. The upper electronic state of the 2400–2100 Å acetylene absorption bands, unlike the ground state of acetylene, is non-linear; it has a planar, centrosymmetric, zigzag, form (King and Ingold, 1953). The first excited state, unlike the ground state, of the HCN molecule is probably bent; while the first excited state, unlike the ground state, of the HCO radical is probably linear (Ramsay, 1953). An emission band system believed to be due to carbon dioxide molecules (which are linear in their ground state), and occurring in flames of carbon monoxide, almost certainly involves molecules with a bent configuration (see Mulliken, 1942a; Walsh, 1953b). The upper state of the formaldehyde fluorescence bands, unlike the ground state, is probably slightly non-planar (Walsh, 1953f). The lowest-energy absorption transition of ethylene probably leads to a shape of the C_2H_4 molecule wherein the arrangement of bonds around each carbon atom is slightly non-planar and one CH_2 group has been twisted through $90°$ relative to the other (Mulliken, 1942b; Walsh, 1953i).

There is unfortunately no good modern book which deals with the electronic spectra of polyatomic molecules; the reader who desires more information on the theoretical side should consult Sponer and Teller (1941).

The above methods of determining the shapes of molecules do not exhaust the ways of obtaining information. Other methods, notably the study of dipole moments also have their importance. For a recent tabulation of the dipole moments of molecules, see Wesson (1948). The list should especially be supplemented by values obtained from microwave spectra and listed in the references given in the dis-cussion above of these spectra. The above methods, however, represent the main sources of our knowledge.

RESULTS FOR THE GROUND STATES OF MOLECULES

Where limits of error are quoted in TABLES 1–4, they are as given by the original authors and do not necessarily imply that the present author believes them to be justified.

TABLE 1. TRIATOMIC MOLECULES

No. of valency electrons	Molecule	Shape	Inter-bond angle	Bond lengths Å	Method	Ref.
			(A) AH_2 molecules			
8	H_2O	Isosceles triangle	θ_e, 104°27′ θ_o, 105°3′	r_e, 0·958 r_o, 0·957	Vibration-rotation spectra	1
	H_2S		θ_o, 92°16′	r_o, 1·334		2*
	H_2Se		~90°	1·49	Vibration-rotation spectra +Badger's Rule	98
	H_2Te		~90°	1·69		
			(B) HAB molecules			
10	HCN	Linear		r_o(CH),1·059, r_o(CN),1·157	Vibration-rotation spectra	3
				r (CH),1·061, r (CN), 1·157	Microwave spectra	22
14	HOBr HOCl	Expected to be triangular				
			(C) BAB and BAC, non-hydride, molecules			
15	CO_2^+			r_o, 1·177	Electronic emission spectrum	5
16	CO_2			r_e, 1·159	Vibration-rotation spectra	1
	CS_2			r_o, 1·554	Electronic spectra	4
	OCS			(CO), 1·164 (CS), 1·559		27, 29
	OCSe			(CO), 1·159 (CSe), 1·709		28
	TeCS			(TeC), 1·904 (CS), 1·557		112
	ClCN	Linear		(ClC), 1·629 (CN), 1·163	Microwave spectra	26, 25
	BrCN			(BrC), 1·790 (CN), 1·158		25
	ICN			(IC), 1·995 (CN), (1·158)		25
	N_2O			(NN), 1·126 (NO), 1·191		90
	NCS^-			(NC), 1·25 (CS), 1·59	x-Ray diffraction	71
	NCO^-				Vibration spectra	1
	BO_2^-					1
	N_3^-					1
	NO_2^+				General expectations and vibration spectra	6
	$ZnCl_2$, $ZnBr_2$				Vibration spectra	1
	ZnI_2			2·42±0·02	Electron diffraction	104
	$CdCl_2$			2·23±0·03		105
	$CdBr_2$			2·39±0·03		105

* Only one band so far analysed; hence θ_e and r_e cannot be given.

TABLE 1. TRIATOMIC MOLECULES (continued)

No. of valency electrons	Mole-cule	Shape	Inter-bond angle	Bond lengths Å	Method	Ref.
16	CdI_2	Linear		2.60 ± 0.02		104
				2.56 ± 0.03		105
	$HgCl_2$			2.34 ± 0.01	Electron	106
				2.27 ± 0.03	diffraction	107
	$HgBr_2$			2.44 ± 0.01		106
	HgI_2			2.61 ± 0.01		106
	$ClHgBr$, $ClHgI$, $BrHgI$				Vibration spectra	1
	$AgCl_2^-$, $AuCl_2^-$				x-Ray diffraction	113
	UO_2^{2+}				x-Ray diffraction + vibration spectra	7a 7b
17	NO_2		$154\pm4°$	1.28	Electronic spectrum	8
			$132\pm3°*$	1.20 ± 0.02	Electron diffraction	9
18	SO_2	Isosceles triangle	$119° 2.1'$	1.432	Microwave spectra	10
			$119° 53'$	1.432		80
	O_3		$117°$	1.277		11
			$116° 49'\pm30'$	1.278 ± 0.003		103
	NO_2^-	Triangular	$114\pm4°$	1.25 ± 0.04	x-Ray diffraction	12
			$115°$	1.23 ± 0.02		13
	FNO		$110°$	(NF), 1.52 (NO), 1.13	Microwave spectra	114
	$ClNO$		$116\pm2°$	(NO), 1.14 ± 0.02 (NCl), 1.95 ± 0.01		19
	$BrNO$		$117\pm3°$	(NO), 1.15 ± 0.04 (NBr), 2.14 ± 0.02	Electron diffraction	19
	$SnCl_2$, $SnBr_2$, SnI_2; $PbCl_2$, $PbBr_2$, PbI_2					105
19	ClO_2	Isosceles triangle	$116° 30'$	1.49	Electron diffraction	14
20	F_2O		$101° 30'\pm90'$	1.38 ± 0.03	Vibration-rotation spectra + electron diffraction	95, 96
	Cl_2O		$110° 48'$	1.70		14
	Cl_2S		$101\pm4°$	1.99 ± 0.03	Electron diffraction	16
			$103\pm3°$	2.00 ± 0.02		17
	Br_2Te		$98\pm3°$	2.51 ± 0.02		18
	$(BrF_2)^+$ $(ICl_2)^+$	Expected isosceles triangle				

* R. A. Spurr, using the electron diffraction data of (44) found θ, 141°; r, 1.21Å [quoted by (99)].