Russian Chemical Reviews **62** (6) 527–538 (1993)
©1993 Russian Academy of Sciences and Turpion Ltd

UDC 539.19 + 547.117

The molecular spectra and structure of the oxides of boron and aluminium

A V Nemukhin, L V Serebrennikov

Contents

I. Introduction	527
II. General characteristics	527
III. Methods of study	528
IV. The structure and spectra of X_mO_n molecules	529
V. Summary	537

Abstract. The results of theoretical and experimental studies of the molecular structure of the oxides of boron and aluminium X_2O_3, X_2O_2, X_2O, and XO_2 (X = B, Al), carried out mainly by spectroscopic methods using matrix-isolation techniques, and also by quantum-mechanical calculations, have been reviewed. The bibliography contains 70 references.

I. Introduction

The present review gives the results of experimental and theoretical studies of the molecular structure of the oxides of boron and aluminium X_mO_n (X = B or Al, $m + n < 6$). The compounds X_mO_n are of both fundamental and applied interest. Thus in the published[1] 'league table' of the chemical elements (involving a comprehensive survey of the importance of the chemical elements in nature, industry, and chemical science), the elements O, B, and Al occupy leading positions.

The literature on the molecular structure of the oxides of boron and aluminium is fairly extensive, and covers a period of more than thirty years. Although it is too early to say that all problems have been resolved, our ideas about the structure of the molecules X_mO_n are fairly well developed. They are based primarily on the results of experimental spectroscopic studies and quantum-chemical calculations. One of the aims of the present review is to show the extent to which it is possible to accept the conclusions of both the experimental and the theoretical studies, which agree with one another in many respects, but not all.

The analysis of the structure of these chemical compounds must involve the question of the similarity and differences in the structure of the oxides of boron and aluminium, and possible explanations. We understand that any 'explanation of the regularities of chemical structure' is provisional, and depends primarily on the level of theory regarded as basic: whether it is sufficient to carry out the analysis using, say, the differences in the electronegativities, dimensions, and polarisabilities of the atoms, or some other parameters, or whether it is necessary to take account of completely different characteristics of the systems.

A V Nemukhin, L V Serebrennikov Chemistry Department, Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow.
Fax (7-095) 939 01 26

Received 17th February 1973
Uspekhi Khimii **62** (6) 566–578; translated by D A Paterson

The theoretical analysis of this present review is based mainly on the molecular orbital model of the theory of electronic structure, with particular attention to the interpretation of the localised molecular orbitals and to such characteristics as the effective charges on the atoms. Analysis of the influence of effects of electron correlation on molecular structure will be regarded as especially important.

II. General characteristics

According to the canonical rules of chemistry, the principal oxide of an element X of group III is X_2O_3. The first studies of the composition of the vapour over solid B_2O_3 and Al_2O_3 showed, however, that oxide molecules with other stoichiometries exist: XO, X_2O, XO_2, and X_2O_2.[2] Later quantum-chemical calculations established that all these systems correspond to stable minima on the potential energy surfaces. Moreover, many of them have several equilibrium configurations of the nuclei. Correspondingly, the experimental spectra relate to different isomers of the molecules. The existence of the higher oxides B_3O_3, Al_3O_3, and Al_2O_4,[3,4] and even exotic species such as Al_3O and Al_4O,[5] has been predicted theoretically. The wide variety of compositions is one of the characteristics of the molecules X_mO_n.

Fig.1 compares the geometric configurations of the most stable isomers of the molecules X_2O, XO_2, X_2O_2, and X_2O_3. The characteristics of the geometric structure of each of the molecules will be discussed in detail later. Here we would only point out that the molecules X_mO_n show not only a variety of compositions but also a variety of geometric forms. It is not always easy to reach a definite conclusion about the geometry of a molecule; this is illustrated by the lively debate about the shape of B_2O_3.[6–9] It is still not completely clear which isomer of AlO_2, linear or cyclic, corresponds to the most stable configuration.[10] The compounds of this class provide a good illustration of one of the traditional problems of the structural chemistry of molecules with 3–5 atoms, namely the question of whether the linear or angular (or cyclic) configuration is preferred. In general, for the oxides X_mO_n we can expect a combination of ionic and covalent bonding, with ionic bonding predominating for the aluminium oxides. Thus linear structures, giving the minimum $O^- - O^-$ and $X^+ - X^+$ repulsion, are generally not unexpected. Angular configurations may be favoured, however, by the effects of sp^2 hybridisation of the boron and oxygen atoms.

Quantum-chemical calculations show that the difficulty of distinguishing between the linear and angular configurations of X_mO_n molecules is related to the flatness of the potential energy surfaces along the deformation coordinates.

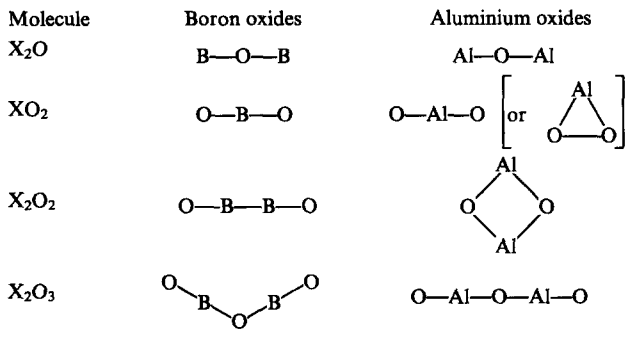


Figure 1. Geometric configurations of the ground-state isomers of the polyatomic molecules X_mO_n.

The structural formulae given in Fig. 1 indicate that the vibrational spectra of the molecules should contain characteristic bands which can be assigned to the groups X—O (in different positions), X—O—X, and O—X—O. The regularities observed in the vibrational spectra, particularly in the high-wavenumber stretching region, represent another characteristic of the molecules of this class.

III. Methods of study

As noted in the Introduction, the present review is based on the results of experimental spectroscopic studies and quantum-chemical calculations. In the present section we shall discuss briefly the possibilities provided by these approaches, mainly to understand how reliable they are for predicting the structure of the molecules B_mO_n and Al_mO_n.

1. Experimental methods

The difficulties in the study of the polyatomic oxides of boron and aluminium are related to the fact that in the equilibrium vapour above the corresponding condensed phases, only the molecules B_2O_3, B_2O_2, and Al_2O are present in quantities sufficient for study by non-resonance spectroscopic methods. Moreover, although resonance methods, for example laser-induced fluorescence (LIF), can be used to study products at low concentrations, with rare exceptions they do not give sufficient information for reaching reliable conclusions about the geometry and vibrational constants of poly-atomic molecules. Thus the data required for the interpretation of the spectra and structure of these materials have been obtained mainly using the methods of the spectroscopy of thermodynamically non-equilibrium systems — inert matrices in which chemical reactions are taking place, and beams obtained by the non-equilibrium (most frequently laser-pulse) volatilisation of appropriate targets. Here we shall discuss mainly data obtained by matrix studies, since almost all the fundamental experimental results on the oxides of boron and aluminium have been obtained from these studies.

The following experimental scheme is now generally accepted.

1. A non-equilibrium situation is created in a system containing boron (or aluminium) and oxygen. This may be a matrix of an inert gas or nitrogen, into which are introduced metal atoms and clusters, volatilised from a Knudsen cell or from the surface of a solid target by a laser, and molecules of an oxidant (oxygen, nitrous oxide, hydrogen peroxide, ozone, etc.). In another version, the products of the non-equilibrium volatilisation of an oxide target are deposited in the matrix.

2. The infrared or Raman spectra of the specimen obtained are recorded by the methods of low-temperature vibrational spectroscopy.

3. The matrix is subjected to external treatment — photolysis, controlled heating ('annealing'), or simple storage for a long time at a constant temperature — after which the changes in the spectra are recorded.

4. When the elements being studied have stable isotopes, the entire cycle of studies is repeated with isotope-enriched specimens.

5. Attempts are then made to obtain an internally consistent assignment of all the bands, or the strongest bands, in all the spectra, relating them to molecules with definite composition.

6. For those molecules whose existence has been established in the previous stage, the experimental wavenumbers and the measured isotope shifts are used to solve the vibrational problem in the harmonic approximation, to determine the symmetry of the equilibrium configuration and to estimate the missing vibrational wavenumbers.

Thus the reliability of the results of the experimental studies depends mainly on the quality of the interpretation of the observed spectra. The complexity of this problem is due to two factors. Firstly, the composition of the products of matrix chemical reactions depends significantly on temperature, the matrix material, and the concentration of the starting materials, and this leads to poor reproducibility of the results. Frequently, papers by different authors give quite different spectra for the same systems. Secondly, the optical properties of the matrices, particularly those containing metals, are very far from ideal, and this leads to various distortions of the spectra, such as displacement and splitting of the bands, and, which is most important, to a significantly non-linear dependence of the intensity of the bands on the concentration of the corresponding products.

We shall not discuss these problems (details can be found elsewhere[11]), and here we merely formulate the general position which we shall subsequently maintain: an individual specific result of an experimental study may prove to be incorrect when a more extensive study or a technically improved study is carried out, but for a sufficiently large number of molecules consisting of the same atoms, the general picture obtained in a systematic study with wide variation of the conditions and methods can apparently be taken as reliable. Thus in the examination of specific molecules we shall try to pick out not the differences between different authors, which naturally represent the principal topic for discussion in experimental and theoretical studies, but the results which can now be regarded as established.

2. Quantum-chemical calculations

According to the present-day ideas, structural data for molecules made up of a small number of atoms from the start of the periodic table should be obtained by non-empirical approaches with allowance for the effects of electron correlation. Calculations of this kind have been carried out for practically all the systems examined in the present review.[3,4,10] It is of course appropriate to discuss the results obtained by other approaches.

When carrying out quantum-chemical calculations, it is necessary to choose correctly the basis set of atomic orbitals (AO) and the method for taking account of electron correlation. It is then necessary, for the given version of the calculation to find the geometric configurations corresponding to stable minima on the potential energy surface (PES) of the molecule, to estimate the differences between the energies of the different minima (if several are found), and to calculate the wavenumbers and intensities for the normal vibrations, for example in the harmonic approximation. This calculation scheme can be simplified, by neglecting correlation effects, that is restricting the treatment to the self-consistent field (SCF) approximation, by introducing pseudo-potentials and excluding explicit consideration of the core electrons, and by using semi-empirical schemes.

In the discussion of theoretical results and their comparison with experimental data, it is not always easy to estimate the consequences of a given simplification. For example, in calculations of vibrational wavenumbers by the SCF method with scaling, that is in fact with semi-empirical corrections, in a number of cases it is possible to obtain better agreement with the line positions in the experimental spectrum than when various correlation approaches are used.

The structural characteristics of Al_mO_n and B_mO_n molecules have been calculated[3,4] using 6-31GF* basis sets (that is valence-split sets with the addition of polarisation AO) by SCF methods and second-order Moeller–Plesset perturbation theory (MP2). This procedure (MP2/6-31GF*) is now generally accepted, and should give an uncertainty of not more than 2% for the equilibrium geometric parameters and 5% for the vibrational frequencies. For the relative energies of the isomers and all other calculated energy differences, the situation is generally not so favourable, and the upper limit of the uncertainties in the worst cases may be appreciably higher.

The interpretation of the results of calculations of molecular properties in the MO LCAO approximation is facilitated considerably by analysing the electronic structure in terms of the so-called natural bond orbitals.[12] This involves the use of the methods of quantum chemistry to model familiar Lewis structures reflecting the structure of molecules by means of bonds and lone pairs. We shall make extensive use of this representation in the discussion of the properties of the molecules of the oxides of boron and aluminium.

IV. The structure and spectra of X_mO_n molecules

Specific molecular systems X_mO_n will be discussed in the following order. We shall examine first the geometric configuration of the ground-state isomer and its vibrational spectrum, and then other possible geometric configurations (for the boron and aluminium compounds separately). In each concluding section we shall formulate the common and distinguishing details of the structure of the oxides B_mO_n and Al_mO_n mainly on the basis of an analysis of the electronic structure.

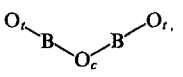
1. X_2O_3 molecules

We begin with the principal oxide of group III elements—X_2O_3. Fig. 1 shows that the ground-state isomers of the B_2O_3 and Al_2O_3 molecules have different geometric configurations—angular for B_2O_3 and linear for Al_2O_3. The simple explanation of this result is the more ionic character of the aluminium compounds, leading to the formation of linear structures. The path to this conclusion has been fairly complex, and other configurations, primarily trigonal bipyramidal, have been examined, but the accumulated experimental and theoretical data correspond to the structures given in Fig. 1.

The first studies of the infrared spectra of B_2O_3 vapour were published in the mid nineteen-fifties, when there was interest in the combustion products of boron compounds. Most progress in the study of the structure of the B_2O_3 molecule was made, however, using spectroscopic matrix and electron diffraction methods.[8,9,13–16] The first studies were carried out in the early nineteen-sixties,[13–15] and quantum-chemical calculations to establish the structure of B_2O_3 were carried out at the same time.[6,7,17–19] This was possibly one of the first examples of this complex approach to the solution of problems of molecular structure.

Boric oxide is a fairly convenient material for study by matrix-isolation infrared spectroscopy. The only problem in the assignment of the bands in the spectrum of this molecule was due to the presence of boric acids in the vapour above B_2O_3. This difficulty was overcome by systematic fractional volatilisation.[8] The complete infrared spectrum of natural boric oxide and all isotopic forms of the molecule with ^{10}B and ^{18}O have now been obtained.[8,13] For the molecules obtained by matrix reactions, the degree of reliability which has been achieved in the assignment of the frequencies in the infrared spectrum has not been obtained. Thus the B_2O_3 molecule provides an ideal 'calibration' system for determining the extent of the agreement that can now be obtained between the results of quantum-chemical calculations and the data obtained by infrared spectroscopy and electron diffraction.

The first quantum-chemical calculations for the B_2O_3 molecule by the non-empirical SCF method with a small basis set of AO[17] and by the semi-empirical INDO method[18] gave geometric configurations with C_{2v} symmetry. The results of several independent non-empirical calculations[6,7,19] in the SCF approximation with different AO basis sets, showing fairly good agreement with one another, were published in 1980 and 1981. The latest non-empirical studies of the B_2O_3 molecule were apparently carried out in 1992 (using the SCF method and MP2 perturbation theory with 6-31GF* basis sets),[4] and they did not lead to new qualitative changes in the earlier conclusions about the equilibrium geometry of the molecule



although the quantitative changes in the parameters were appreciable.

Table 1 compares the results of calculations of the equilibrium geometric parameters of the molecule with the C_{2v} configuration with data obtained by electron diffraction.[9] Comparison of the last two rows of Table 1 shows the very good quantitative agreement between the experimental and theoretical approaches. For this example we can estimate the uncertainties in the non-empirical calculations of the equilibrium internuclear distances in the MP2/6-31GF* approximation for the molecules being considered as 0.01 Å (that is about 1%).

It should nevertheless be remembered that the path to these consistent results was complex, and considerable work was required. Thus the electron diffraction data have been repeatedly refined as new measurements were made.[9,15,20,21] Difficulties were also encountered in the calculations; in particular, it has been emphasised that to to obtain a non-linear equilibrium structure it is necessary to include polarisation AO in the basis set.[7]

The vibrational wavenumbers of the B_2O_3 molecule for the principal isotopic form ($^{11}B_2{}^{16}O_3$) are given in Table 2, which compares the values calculated in the harmonic approximation (SCF or MP2 with different basis sets), the results of spectral studies in low-temperature matrices,[8,16] and the results of a combined treatment of data obtained by gas-phase electron diffraction and molecular spectroscopy by an original method which gives an estimate of the frequencies.[19]

The calculated intensities of the infrared bands and a qualitative description of the modes of the B_2O_3 molecule are given in Table 3. The position of the strongest ν_2 band in the infrared spectrum is known from spectroscopic studies of B_2O_3 in inert matrices [2061 cm^{-1} (Ref. 8) or 2062.3 cm^{-1} (Ref. 16)]. Isotope replacement $^{11}B \rightarrow {}^{10}B$ leads to a displacement [2061→2128 or 2062.3→ 2130.5 cm^{-1} with $R(10/11) = 1.033$], but the absence from the spectrum of the band corresponding to the mixed composition $^{10}B^{11}BO_3$ remains somewhat puzzling.

Table 1. Calculated and experimental (from gas-phase electron diffraction data) equilibrium geometric parameters of the B_2O_3 molecule (distances R in Å, angles Φ in °).

Method	R_{O_c-B}	R_{B-O_t}	$\Phi(B-O_c-B)$	$\Phi(O_t-B-O_c)$	Ref.
SCF/OST-3GF	1.363	1.237	137.5	176	6
SCF/4-21GF*	1.324	1.188	136.0	178.3	7
SCF/[4*s*2*p*1*d*]	1.330	1.191	137.1	178.8	7
SCF/6-31GF*	1.313	1.189	145.5	180	4
MP2/6-31GF*	1.334	1.221	136.1	177.6	4
Gas-phase electron diffraction	1.323	1.219	137.5	173.4	9

Note. The experimental uncertainties are: $\Delta R_{O_c-B} = \pm 0.008$, $\Delta R_{B-O_t} = \pm 0.007$ Å, $\Delta\Phi(B-O_c-B) = \pm 6.3°$, $\Delta\Phi(O_t-B-O_c) = \pm 4.4°$.

Table 2. Theoretical and experimental vibrational wavenumbers of the B_2O_3 molecule (cm^{-1}).

Vibration	Symmetry	Calculated data					Experiment	
		OST-3GF[6]	4-21GF*[4]	6-31GF*			Spectroscopy[8]	Electron diffraction[9]
				SCF	SCF(0.9)[a]	MP2		
ν_1	A_1	2201	2314	2272	2045	2100		2057
ν_2	B_1	2164	2293	2283	2055	2125	2061	2060
ν_3	B_1	1258	1308	1356	1220	1227		1099
ν_4	A_1	713	817	779	701	756		1050
ν_5	A_1	462	597	583	525	529	518	566
ν_6	A_2	429	462	508	457	466		288
ν_7	B_2	415	518	552	497	488	489	273
ν_8	B_1	378	491	501	451	456	462	512
ν_9	A_1	99	108	79	71	87	73	102

[a] Here and subsequently the column 'SGF(0.9)' gives wavenumbers obtained by the SCF/6-31GF* method by scaling with a factor 0.9.

From MP2/6-31GF* calculations,[4] the isotope shift $^{11}B_2O_3 \rightarrow {}^{10}B_2O_3$ [2125 $cm^{-1} \rightarrow$ 2197 cm^{-1}, $R(10/11) = 1.034$] shows good agreement with the experimental data. Estimates of the intensities with the calculated[4] force-constant matrix show that the band due to the mixed isotopic form $^{10}B^{11}BO_3$ should be fairly close to the $^{10}B_2O_3$ band, and this may make its identification difficult. However, this does not explain the absence of the band due to the mixed isotopic form from the spectrum despite the high intensity expected from the theoretical calculations. Oxygen isotope replacement $B_2^{16}O_3 \rightarrow B_2^{18}O_3$ for the ν_2 band gives a consistent picture for experiment [2062.3 $cm^{-1} \rightarrow$ 2024.1 cm^{-1}, $R(16/18) = 1.019$] and theory [MP2/6-31GF*, 2125 cm^{-1}, 2089 cm^{-1}, $R(16/18) = 1.017$].

For the ν_7 band, the measured[8] isotope shift $^{10}B_2O_3 \rightarrow {}^{11}B_2O_3$ is 489 $cm^{-1} \rightarrow$ 505 cm^{-1}, $R(10/11) = 1.033$; the theoretical (MP2/6-31GF*) shift is 488 $cm^{-1} \rightarrow$ 504 cm^{-1}, $R(10/11) = 1.033$. The experimental shift for oxygen $B_2{}^{16}O_3 \rightarrow B_2{}^{18}O_3$ [489 $cm^{-1} \rightarrow$ 480 cm^{-1}, $R(16/18) = 1.019$] also coincides with the calculated shift [488 $cm^{-1} \rightarrow$ 479 cm^{-1}, $R(16/18) = 1.019$].

Finally, for the ν_5 band the experimental shifts are:[8] for $^{11}B_2O_3 \rightarrow {}^{10}B_2O_3$, 518 $cm^{-1} \rightarrow$ 538 cm^{-1}, $R(10/11) = 1.039$; for $B_2{}^{16}O_3 \rightarrow B_2{}^{18}O_3$, 518 $cm^{-1} \rightarrow$ 510 cm^{-1}, $R(16/18) = 1.016$. The corresponding theoretical estimates are:[4] for $^{11}B_2O_3 \rightarrow {}^{10}B_2O_3$, 529 $cm^{-1} \rightarrow$ 548 cm^{-1}, $R(10/11) = 1.036$, and for $B_2{}^{18}O_3$, 529 $cm^{-1} \rightarrow$ 521 cm^{-1}, $R(16/18) = 1.015$.

The isotope shifts have not been obtained for the remaining two measured frequencies (ν_8 and ν_9).

Since the assignment of the known bands is fairly reliable, it is possible to discuss the accuracy of the theoretical calculations of the wavenumbers of the B_2O_3 molecule. It is appropriate to compare the values calculated by the 4-21GF* and 6-31GF* methods with the experimental spectroscopic data (Table 2). The calculations using the OST-3GF basis set are of considerable historical interest, but the frequencies estimated from experimental electron diffraction data are not all sufficiently reasonable, apparently because of the incorrect choice of reference spectral data.

Table 3. Intensities (km mol^{-1}) of the bands in the infrared spectra and the assignment of the vibrations of the B_2O_3 molecule (the symbols for the modes correspond to those in Table 2).

Mode	Intensities		Assignment
	SCF/4-21GF*	MP2/6-31GF*	
ν_1	68.5	38.0	B–O_t (symmetric stretch)
ν_2	1263.6	963.7	B–O_t (antisymmetric stretch)
ν_3	102.5	108.8	B–O_c (antisymmetric stretch)
ν_4	24.0	13.8	B–O_c (symmetric stretch)
ν_5	131.6	75.1	mixed deformation
ν_6	0	0	anti-phase out of plane
ν_7	16.7	100.6	in-phase out-of-plane
ν_8	21.2	11.6	O_c–B–O_t (deformation)
ν_9	14.0	8.5	B–O_c–B (deformation)

In the SCF approximation, the basis-set effects (the change from 4-21GF* to 6-31GF*) are fairly tyical—the frequencies differ by 10%. The change to the MP2 correlation method lowers the frequencies, and comparison of the data obtained by MP2 and SCF (0.9) methods shows that the use of the popular scaling factor 0.9 for the frequencies calculated in the SCF approximation, covering both correlation and anharmonic corrections,[22,23] in this case leads to values very close to those obtained by the MP2 method (see Table 2). At the very least, the SCF approximation with scaling shows no unique advantages over MP2 in this case, although the frequencies calculated in the SCF approximation with scaling are slightly closer to the experimental data for ν_2, ν_5, and ν_9.

Direct comparison of the calculated and measured wavenumbers is naturally made difficult by the fact that the theoretical values are obtained using the harmonic model and relate to the free molecule, while the experimental data correspond to the real vibrations of the molecule in a matrix environment. It is usually assumed that both the anharmonic and the matrix effects are small, so that the comparison of the frequencies obtained using the MP2 approximation with the experimental spectroscopic data (Table 2) is fully justified. The positions of the strong ν_2, ν_7, and ν_5 bands are effectively reproduced in the MP2/6-31GF* calculation; the differences between the results and the experimental wavenumbers do not exceed 3% (the published[6,9] assignment of the experimental[8] wavenumbers 518 cm^{-1} to B_1 and 462 cm^{-1} to A_1 is incorrect). The values of the ν_8 wavenumbers differ by the same amount. For the B–O_c–B deformation ν_9 with the lowest frequency, slightly greater differences between the experimental and theoretical results are observed, as expected.

The flatness of the PES along the given deformation coordinate (which gives grounds for regarding this molecule as quasi-linear) is responsible for the previously noted difficulties encountered in the quantum-chemical calculations[4,6,7] and for the difficulty in the interpretation of the electron diffraction data.[9,15,20,21] According to published calculations,[6,7] the barrier to inversion, that is the difference between the linear and equilibrium (C_{2v}) configuration, does not exceed 2.5 kcal mol^{-1}. Under these conditions it is fairly difficult to determine the equilibrium valence angle and the frequency of the deformation. Appreciable anharmonicity corrections can also be expected for the ν_9 vibration.

Even by increasing considerably the possible range of uncertainties for the wavenumbers calculated in the MP2/6-31GF* approximation, for example to 10%, it is not

possible to obtain from the calculated data a band in the Raman spectrum in the region of 1062 cm^{-1}, assigned[8] to the B_2O_3 molecule. The absence from the experimental infrared spectrum of the ν_3 band (theoretical wavenumber 1227 cm^{-1}), which should be fairly strong, and the strong ν_2 band due to the mixed isotopic form $^{10}B^{11}BO_3$ also remains unexplained.

An intensive search has been made[4] for other stationary points on the PES of the ground state of B_2O_3, but no structures other than the configuration with C_{2v} symmetry were found.

According to SCF and SCF-X_α SW calculations,[6] the excited states of B_2O_3 are fairly high; the estimated vertical excitation energies are 6–7 eV.

Thus calculation and experiment on the whole give similar pictures of the structure and infrared spectrum of the B_2O_3 molecule. Quantitative agreement is even obtained for the positions and intensities of a number of the spectroscopic bands. The differences noted above are also observed, however.

In contrast to B_2O_3, there are very few experimental data for the Al_2O_3 molecule. The vapour above solid aluminium oxide apparently does not contain free Al_2O_3 molecules.[2] A large number of products are formed in the reaction of atomic aluminium with oxygen in argon and nitrogen matrices.[24–30] Attempts have been made to assign various bands in the infrared and Raman spectra of these products to Al_2O_3. Characteristic features of the infrared spectra of the Al + O_2 system in published studies[26,27] are the 1101, 1095 cm^{-1} doublet in dilute nitrogen matrices, and the 1101, 1095, 1092 cm^{-1} triplet in concentrated matrices. The less intense 502 , 492 cm^{-1} doublet is recorded under the same conditions. These two bands have been provisionally assigned to the vibrations of a linear Al_2O_3 molecule with $D_{\infty h}$ symmetry. The doublet band at 1031, 1024 cm^{-1} in the Raman spectrum has been assigned to the same linear molecule.

The band at 1211.2 cm^{-1} in the infrared spectrum of the products of the reaction of aluminium volatilised by a laser from solid Al_2O_3 with oxygen in an argon matrix was recently assigned[30] to the O–Al–O–Al–O molecule. The band at 1101 cm^{-1} was assigned to a molecule with the composition AlO_3 in which two oxygen atoms are joined to one another and the third is a terminal atom. The author cited previously assigned this band to an unsymmetrical aluminium dioxide molecule.

From semi-empirical MNDO quantum-chemical calculations, it was suggested[26] that there exist a number of molecular isomers with the composition Al_2O_3, and the band at 964 cm^{-1} in the infrared spectrum was assigned to one of these which was completely unsymmetrical.

According to non-empirical calculations,[3,31] the ground-state minimum on the PES of Al_2O_3 corresponds to the linear symmetrical $D_{\infty h}$ structure

$$O_t-Al-O_c-Al-O_t\,.$$

Table 4 gives the results of quantum-chemical calculations of the equilibrium internuclear Al–O distances by SCF and MP2 methods. From calculations for the B_2O_3 molecule and other similar molecular systems, the uncertainties in the calculated equilibrium distances in the MP2/6-31GF* approximation should be about 0.01 Å.

Table 4. Equilibrium internuclear distances (Å) in the linear molecule $O_t-Al-O_c-Al-O_t$.

Method of calculation	R_{O_c-Al}	R_{Al-O_t}	Ref.
SCF/(10*s*6*p*1*d*,7*s*3*p*)/[6*s*4*p*1*d*,4*s*2*p*]	1.641	1.561	31
SCF/(12*s*8*p*1*d*,9*s*5*p*1*d*)/[6*s*4*p*1*d*,4*s*2*p*1*d*]	1.657	1.565	31
SCF/6-31GF*	1.666	1.571	3
MP2/6-31GF*	1.691	1.626	3

The wavenumbers and intensities of the vibrations of the linear Al_2O_3 molecule are given in Table 5. The results of two independent calculations by the SCF method with basis sets of comparable quality[3,31] practically coincide. As with B_2O_3, scaling the wavenumbers gives values close to the results obtained in the MP2 approximation with the same basis set. The correlation of the calculated wavenumbers with the experimental spectra in this case, however, is not so successful as in the case of B_2O_3.

Table 6 gives the wavenumbers and the corresponding isotope ratios $R(16/18)$ of the isotopic forms of the Al_2O_3 molecule for those bands in the spectra to which the experimental data are assigned. The band recorded[30] at 1211.2 cm^{-1} apparently in fact corresponds to the $\nu_1(\Sigma_u)$ vibration of O–Al–O–Al–O. The agreement between the isotope ratios is almost quantitative, and the experimentally determined ν_1 wavenumber coincides with that calculated by the SCF method with scaling, and with the wavenumber obtained by the MP2/6-31GF* method to within 3%. The bands observed[26,27] at 1101, 502 (infrared), and 1031 cm^{-1} (Raman) possibly correspond to other compounds or to a molecule with a different structure.

The assignment of the bands is fairly obvious: the pairs ν_1, ν_2 and ν_3, ν_4 correspond to the vibrations of terminal $Al-O_t$ and central $Al-O_c$ groups respectively. All the deformations have fairly low wavenumbers, particularly the ν_7 vibration (40–50 cm^{-1}) describing the deformation about the central oxygen atom. The section of the PES along this coordinate is even flatter than that for B_2O_3.

The question of the isomers of the Al_2O_3 molecule has been examined.[3,26,31] According to quantum-chemical calculations, the at first sight attractive trigonal bipyramidal model must be rejected, since the energy of this configuration is too high compared with the linear form (more than 200 kcal mol^{-1} in the MP2/6-31GF* method); moreover, the D_{3h} structure does not correspond to a minimum on the PES. The configurations found by the semi-empirical MNDO method[26] were not confirmed by subsequent non-empirical calculations.[3]

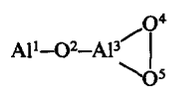
Of considerable interest is one of the equilibrium configurations of Al_2O_3 found by the SCF/6-31GF* and MP2/6-31GF* methods,[3] namely the planar structure with C_{2v} symmetry

Table 5. Calculated wavenumbers (cm^{-1}) and infrared intensities (in curly brackets, km mol^{-1}) of the vibrations of the linear molecule O–Al–O–Al–O.

Vibration	Symmetry	SCF [31]	SCF/6-31GF* [3]	SCF (0.9)	MP2/6-31GF* [3]
ν_1	Σ_u		1345	1211	1242 {387}
ν_2	Σ_g	1269	1263	1137	1130
ν_3	Σ_u		1016	914	924 {105}
ν_4	Σ_g	461	459	413	428
ν_5	Π_u	326	324	292	250 {116}
ν_6	Π_g	197	209	188	175
ν_7	Π_u	72	55	50	36 {20}

Table 6. Theoretical and experimental wavenumbers of the isotopic forms of the linear Al_2O_3 molecule and the corresponding isotope ratios $R(16/18)$ (given in brackets).

Positions of the bands and isotope ratios $R(16/18)$						Assignment	Ref.
$^{16}O_2$		$^{16}O_2+{}^{18}O_2$		$^{18}O_2$			
1211.2	1206.1	1200.0	1187.4	1183.1	1172.9	$\nu_1(\Sigma_u)$ (expt)	30
(1.000)	(1.004)	(1.009)	(1.020)	(1.025)	(1.033)		
1242		1230	1217		1202	$\nu_1(\Sigma_u)$ (theor)	3
(1.000)		(1.009)	(1.020)		(1.033)		
1101					1068	$\nu_1(\Sigma_u)$ (expt)	26
(1.000)					(1.031)		

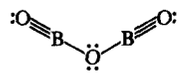


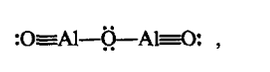
whose energy is higher than that of the linear form by only 11 kcal mol^{-1} in the SCF method, or 32 kcal mol^{-1} in the MP2 method. Experience suggests that the MP2 approximation should give a value for the energy difference which is too large, so that the C_{2v} structure being considered should correspond to an energy of $\sim$20 kcal mol^{-1}, which does not exclude its presence in Al + O_2 matrix reactions. The presence of a similar structure was suggested in the interpretation of electron diffraction data for B_2O_3, but was rejected.[9] According to MP2/6-31GF* data, the equilibrium geometric parameters of the C_{2v} Al_2O_3 molecule are: $R_{Al^1-O^2}$ 1.745, $R_{O^2-Al^3}$ 1.683, $R_{Al^3-O^4}$ and $R_{Al^3-O^5}$ 1.723 Å, $\Phi(O^4-Al^3-O^5)$ 59°.

One of the vibrations of the C_{2v} isomer, 1146 cm^{-1} (MP2/6-31GF*) or 1109 cm^{-1} (SCF/6-31GF* with a scaling of 0.9), should be extremely intense in the infrared spectrum.[3] The corresponding wavenumber might be observed in the experimental spectra.[26,27,30] The electronic structure of this compound is effectively described by the formula $Al^+(AlO_3)^-$.

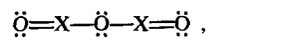
Thus with reference to the structure of the Al_2O_3 molecule there remain a fairly large number of unanswered questions, particularly regarding the experimental data.

Formally, the Lewis structures of the B_2O_3 and Al_2O_3 molecules coincide:[3,4]

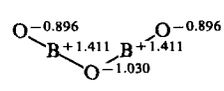


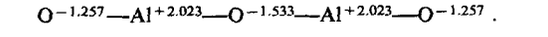


(it is of course possible to use the alternative description



since the boundary between the orbital of the lone pair of the terminal oxygen atom and one of the π-orbitals of the $X-O_t$ bond is somewhat provisional). The pictures of the effective charges on the atoms, obtained by analysis of the populations of the natural orbitals,[3,4] however, differ significantly:





The Mulliken populations[7,31] for systems of this kind give effective charges which are much too low.[12] As expected, the contribution of ionic components to the interaction is greater for aluminium oxide. This also explains the differences in the equilibrium geometric configurations and the lower frequency of the deformation involving the central oxygen atom for Al_2O_3.

The greater contributions of the covalent components to the characteristics of the B–O bonds in B_2O_3 are reflected in the higher values of the force constants (MP2/6-31GF*):

f_{B-O_t} = 13.7 mdyn Å^{-1} $\quad f_{Al-O_t}$ = 6.68 mdyn Å^{-1}

f_{B-O_c} = 7.94 mdyn Å^{-1} $\quad f_{Al-O_c}$ = 4.95 mdyn Å^{-1}

In both molecules, B_2O_3 and Al_2O_3, the dominant correlation effects should be associated with excitations of the type $\pi(X-O_t)\rightarrow\pi^*(X-O_t)$,[3,4,32] leading finally to an increase in the equilibrium internuclear $X-O_t$ distances obtained in the correlation approaches, compared with the results obtained by the SCF method (see Tables 1 and 4). This effect is greater for Al_2O_3 [$\Delta R_{corr}(Al-O_t)$ = 0.06 Å, $\Delta R_{corr}(B-O_t)$ = 0.03 Å]; this can be related to the smaller difference between the energies of the orbitals $\pi(X-O_t)$ and $\pi^*(X-O_t)$ for the $Al-O_t$ bonds, compared with $B-O_t$.

2. X_2O_2 molecules

Fig. 1 shows that the configurations of the ground-state isomers with the composition X_2O_2 for boron and aluminium are fundamentally different: a linear structure with a B–B bond for B_2O_2 and a cyclic structure for Al_2O_2. Both theoretical and experimental data indicate the existence of other X_2O_2 isomers with low energies. Future more accurate studies will possibly alter present conclusions about the configurations of the ground-state isomers. Nevertheless, it is clear that for oxides with this stoichiometry the differences between the structures of the molecules containing boron and aluminium are considerable.

The B_2O_2 molecule has been studied in parallel with B_2O_3, since mass-spectrometric studies[33] show that when elemental boron is added to solid boric oxide B_2O_3, B_2O_2 molecules predominate in the vapour above the mixture. Until recently, only one isomer had been characterised experimentally. For this isomer, two vibrational wavenumbers were obtained (1898 cm^{-1} and 213 cm^{-1}), and all possible isotope shifts measured. It was concluded that this isomer has a symmetrical linear structure, the force field was calculated, and the frequencies of forbidden transitions in the absorption spectrum were estimated.[34,35] These data were subsequently confirmed[36] in a study of the photoelectron spectra of B_2O_2 vapour. The two bands (at 2048 cm^{-1} and 1408 cm^{-1}) found in recent studies[16,37] of the reactions of atoms in boron clusters with oxygen and water in inert matrices were assigned to the unsymmetrical linear isomer B–O–B–O. In a study of the mass spectra[38] of the vapour above B_2O_3 it was concluded that the compound B_2O_2 corresponds to the unsymmetrical isomer B–O–B–O.

Semi-empirical and non-empirical SCF calculations with the minimum basis set OST-3GF predicted[39,40] that the ground-state

Table 7. Geometric parameters (Å) and relative energies ΔE/kcal mol^{-1} of the linear molecules O–B–B–O and B–O–B–O.

Method of calculation	O–B–B–O		$B^1–O^2–B^3–O^4$			ΔE	Ref.
	R_{B-O}	R_{B-B}	$R_{B^1-O^2}$	$R_{O^2-B^3}$	$R_{B^3-O^4}$		
SCF/4-31GF	1.196	1.631	1.337	1.314	1.202	16.8	36
SCF/6-31GF*	1.182	1.667	1.306	1.311	1.190	19.9	4, 36
MP3/6-31GF*	1.201	1.647	–	–	–	29.5	36
MP2/6-31GF*	1.218	1.636	1.317	1.332	1.220	40.0	4

Semi-empirical and non-empirical SCF calculations with the minimum basis set OST-3GF predicted[39,40] that the ground-state isomer should have the linear symmetrical structure O–B–B–O.

The parameters of the equilibrium configurations of the linear systems O–B–B–O and B–O–B–O, calculated in a fairly good approximation (SCF and MP with generally accepted basis sets),[4,36] are given in Table 7. As with B_2O_3, we expect that the MP2/6-31GF* method makes it possible to predict internuclear distances with an uncertainty of about 0.01 Å. Comparison with the data in Table 1 shows that for all the molecules (B_2O_3, O–B–B–O, and B–O–B–O) the distances from boron to the terminal oxygen agree within this uncertainty and are equal to 1.22 Å.

The vibrational frequencies and infrared intensities for the two isomers are compared in Table 8. As in the previous examples, noteworthy features are the similarity in the frequencies calculated by the SCF(0.9) and MP2 methods, and the fact that the calculated harmonic frequencies of the MP2/6-31GF* approximation coincide with the measured values in the infrared spectrum (ν_2 and ν_5) for the ground-state isomer O–B–B–O. The published[16,34,35,37] $^{16}O \rightarrow {}^{18}O$ and $^{11}B \rightarrow {}^{10}B$ isotope shifts in different combinations for the ν_2 band are reproduced almost quantitatively by the calculations. The large differences for the ν_3 and ν_4 bands can be explained, since the wavenumbers forbidden in the infrared spectrum were predicted[35] with molecular force constants estimated from known bands. Comparison of the results of different calculations[4,36] shows the very large difference between the ν_1 and ν_2 vibrational wavenumbers obtained by the MP2 and MP3 methods with the same basis set 6-31GF* (in the SCF method, the corresponding values are identical).

The observation[16,37,38] of the unsymmetrical isomer B–O–B–O is also confirmed by non-empirical calculations. From the isotope shifts, the experimental[37] bands at 2048 cm^{-1} and 1408 cm^{-1} agree with the calculated values 2123 cm^{-1} and 1488 cm^{-1} for ν_1 and ν_2 respectively:

ν_1, $R(16/18) = 1.016$ and $R(10/11) = 1.034$ from experiment, and $R(16/18) = 1.017$ and $R(10/11) = 1.035$ from calculation; ν_2, $R(16/18) = 1.034$ and $R(10/11) = 1.019$ from experiment, and $R(16/18) = 1.035$ and $R(10/11) = 1.019$ from calculation (MP2/6-31GF*).

The differences between the theoretical and experimental wavenumbers are 4% for ν_1 and 6% for ν_2, which are slightly greater than those observed in the previous examples. The question of the magnitude of the energy of the isomer B–O–B–O relative to that of O–B–B–O remains unresolved, that it is not clear whether it is sufficiently low for it to be possible to obtain the isomer B–O–B–O experimentally.

As has been suggested,[40] the cyclic isomers of B_2O_2 also correspond to stationary points on the PES of the ground state,[4,36] but their energies differ from that of the ground-state configuration O–B–B–O by more than 60 kcal mol^{-1}.

The presence of the compound Al_2O_2 in the vapour above solid aluminium oxide has been confirmed by mass spectrometry.[2] The interpretations of the infrared spectra of the products of matrix reactions of aluminium with oxygen, assigned to Al_2O_2, are contradictory. For a long time, the band at 496 cm^{-1} (or 498 cm^{-1}) was assigned to an Al_2O_2 molecule with a rhomb-shaped configuration.[41,42] According to Serebrennikov and coworkers,[24,25] this band belongs to a cyclic isomer of Al_2O_2, and this was confirmed in recent experiments.[30] An infrared band at 691 cm^{-1} and (provisionally) a Raman band at 713/721 cm^{-1} have been assigned[26,28] to a vibration of the square isomer of Al_2O_2; the infrared bands at 640 cm^{-1} and 545 cm^{-1} and the Raman band at 563 cm^{-1} were assigned to the rhomb-shaped isomer. In the work cited,[30] the bands in the infrared spectrum were assigned only for the linear isomer Al–O–Al–O: 1176/1169/1167, 945/943/940 cm^{-1}. The band at about 943 cm^{-1} has been assigned[26] to this isomer.

A number of quantum-chemical calculations have been carried out for Al_2O_2.[3,43–45] SCF calculations using pseudopotentials[43] for the molecule gave three stationary points on the PES: the ground-state isomer corresponds to an almost square configuration with D_{2h} symmetry, the isomer with the rhomb-shaped configuration has an energy 37 kcal mol^{-1} higher, and the third isomer is the linear molecule Al–O–Al–O. From the calculated vibrational wavenumbers it was concluded that the experimental band at 496 cm^{-1} can be assigned to the ground-state square isomer of Al_2O_2. Calculations have been carried out[44] by non-empirical SCF (with different basis sets) and MP2/6-31GF* methods. It was confirmed that the ground-state equilibrium configuration is square, and that the linear Al–O–Al–O (10.2 kcal mol^{-1} higher) and rhomb-shaped (71.5 kcal mol^{-1}) configurations have higher energies. As before, one of the vibrational wavenumbers of the ground-state isomer, found only in the SCF approximation (476 cm^{-1} without scaling), was compared with the experimental data. Attention was drawn[45] to the fact that in the square configuration the energy of the triplet state is fairly close to that of the singlet state.

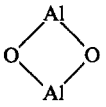
The equilibrium geometric parameters and the wavenumbers and intensities of the vibrations have been calculated[3] in the SCF and MP2 approximations with the basis set 6-31GF*. For the geometries and wavenumbers in the SCF approximation

Table 8. Wavenumbers (cm^{-1}) and intensities (in curly brackets, km mol^{-1}) of the vibrations of the molecules O–B–B–O and B–O–B–O

Method	O–B–B–O					B–O–B–O					Ref.
	$\nu_1(\Sigma_g)$	$\nu_2(\Sigma_u)$	$\nu_3(\Sigma_g)$	$\nu_4(\Pi_g)$	$\nu_5(\Pi_u)$	$\nu_1(\Sigma)$	$\nu_2(\Sigma)$	$\nu_3(\Sigma)$	$\nu_4(\Pi)$	$\nu_5(\Pi)$	
SCF/4-31GF	2253	2031	639	547	236	2206	1458	843	553	176	36
MP3/6-31GF*	2222	2052	628	432	216						36
SCF/6-31GF*	2314	2131	631	538	235						4
SCF(0.9)	2083	1918	568	484	212						4
MP2/6-31GF*	2073	1898 {40}	625	501	215 {41}	2123 {597}	1488 {516}	828	478 {53}	50	4
Experiment	2060[a]	1898	585[a]	410[a]	213						35
		1899				2048	1408				16, 37

[a] Estimated from the force field.

Table 9. Equilibrium geometric parameters of the lower isomers of Al_2O_2

Molecule	Method of calculation	Parameter			Ref.
		R_{Al-O}/Å	Φ(Al−O−Al)/°	Φ(O−Al−O)/°	
 singlet	SCF	1.764	90.6	89.4	43
	SCF/6-31GF*	1.741	87.9	92.1	3,44
	MP2/6-31GF*	1.780	86.3	93.7	3,44
triplet	SCF2/6-31GF*	1.737	88.3	91.7	3
D_{2h}	MP2/6-31GF*	1.776	86.3	93.7	3
$Al_t-O_c-Al_c-O_t$	SCF	1.743 (Al_t-O_c); 1.670 (O_c-Al_c); 1.591 (Al_c-O_t)	–	–	43
$C_{\infty v}$	SCF/6-31GF*	1.718 (Al_t-O_c); 1.658 (O_c-Al_c); 1.574 (Al_c-O_t)	–	–	3,44
	MP2/6-31GF*	1.735 (Al_t-O_c); 1.692 (O_c-Al_c); 1.628 (Al_c-O_t)	–	–	3,44

and the geometries in the MP2 approximation, the values obtained for the two lower isomers agreed completely with published data.[44] The characteristics of the vibrations calculated in the MP2/6-31GF* approximation, however, make necessary a radical re-examination of the previous interpretation.

The geometric parameters of the Al_2O_2 isomers of lowest energy are given in Table 9. Table 9 does not give results for the second rhomb-shaped configuration, although it is of considerable interest from the viewpoint of structural theory, or results for the other linear isomers obtained, O−Al−Al−O, Al−O−O−Al, and Al−Al−O−O,[3] since the energies of all these configurations are too high compared with the energy of the ground-state isomer (more than 70 kcal mol^{-1}) for them to be observed experimentally.

For the cyclic (almost square) isomer, noteworthy features are, firstly, the small deviations of the valence angles from 90° at the aluminium and oxygen atoms, and, secondly, the similarity in the equilibrium configurations of the molecule in the singlet and triplet states. Comparison of the internuclear distances for the linear isomer $Al_t-O_c-Al_c-O_t$ with the distances in the linear molecule $O_t-Al_c-O_c-Al_c-O_t$ (see Table 4) shows (like the comparison of the data for O−B−B−O and B_2O_3) that the Al_c-O_t distances coincide to within 0.01 Å (1.63 Å, MP2/6-31GF*); the Al_c-O_c distances also coincide (1.69 Å). The Al_t-O_c distance in $Al_t-O_c-Al_c-O_t$ (1.74 Å) is greater than the distance within the fragment O−Al−O. The Al−O bond length in the ring is even longer (1.78 Å).

The relative energies of the lower isomers of Al_2O_2 calculated[3] by the SCF and MP2 methods with the 6-31GF* basis set are shown in Fig. 2. These results show the importance of allowing for the effects of electron correlation in the Al_2O_2 system; on going beyond the one-electron model, the qualitative conclusions about the structure of the molecule change. It is known that the MP2 approximation does not always give energy differences sufficiently accurately, and calculations at a higher level (for example by the MP4 method or the method of bound clusters) may in principle change the relative energies of the linear and cyclic structures. The results obtained, however, provide sufficient grounds for assigning the experimental data to both structures.

Table 10 gives the experimental vibrational wavenumbers for the cyclic Al_2O_2 molecule; the calculated wavenumbers, infrared intensities, and isotope ratios for the singlet and triplet states of the almost square isomer are indicated. As in other examples, the wavenumbers calculated in the SCF/6-31GF* approximation are systematically greater than the corresponding values calculated in the MP2/6-31GF* approximation with a factor close to 0.9. For the ν_3 vibration of the singlet isomer, however, an extremely unusual situation is observed; there is a dramatic change in both the wavenumber (476 →690 cm^{-1}) and intensity of the vibration when corrections for correlation effects are introduced. It is for this reason that earlier attempts to correlate the theoretical wavenumbers calculated in the SCF approximation[43,44] with the experimental data led to an erroneous assignment of the observed band at 496 cm^{-1} to the Al_2O_2 molecule. We shall return to the discussion of the role of correlation effects in the cyclic Al_2O_2 molecule. Meanwhile, we are justified in assigning to the almost square molecule the intense band in the infrared spectrum at 691 cm^{-1}, as previously proposed.[28] The situation is more complex for the other suggestions made in the work cited.[28] The most active vibration in the Raman spectrum is the ν_5 vibration with a wavenumber of about 516 cm^{-1} and an isotope ratio R(16/18) = 1.020. The possibility of assigning the experimental band at 563 cm^{-1} to this vibration[28] cannot be excluded. For the other bands in the infrared and Raman spectra,[28] appropriate assignments were not made.

Table 11 gives the vibrations of the linear Al−O−Al−O molecule. Comparison with experimental data[30] shows that there is practically no doubt about the assignment of the bands at 1176.3 cm^{-1} and 945.5 cm^{-1} (or the bands close to them for

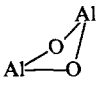
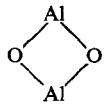
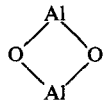
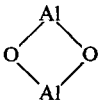
Molecule	Energy/cal mol^{-1}	Molecule	Energy/cal mol^{-1}
O—Al—Al—O	104		72
		O—Al—Al—O	70
 singlet	37.7		
Al—O—Al—O	21.4	Al—O—Al—O	10.4
 triplet	0.0	 triplet singlet	8.2 0.0

Figure 2. Relative energies of the lower isomers of Al_2O_2, calculated in the SCF/6-31GF* (on the left) and MP2/6-31GF* (on the right) approximations.

Table 10. Wavenumbers (cm^{-1}) and infrared intensities (in curly brackets, km mol^{-1}) of the cyclic isomer of Al_2O_2 [the isotope ratios $R(16/18)$ for complete replacement $^{16}O \rightarrow {}^{18}O$ are given in round brackets].

Vibration	Al_2O_2 (singlet)			Al_2O_2 (triplet)	
	SCF/6-31GF* [3,44]	MP2/6-31GF* [3]	experiment[28]	SCF/6-31GF* [3]	MP2/6-31GF* [3]
$\nu_1(A_g)$	861	782 (1.041)		868	784
$\nu_2(B_{2u})$	819 {198}	772 {110} (1.036)		827	759 {104}
$\nu_3(B_{1u})$	476 {828}	690 {193} (1.036)	691 (1.028)	811	738 {349}
$\nu_4(B_{3g})$	664	622 (1.035)		680	624
$\nu_5(A_g)$	553	516 (1.020)		565	524
$\nu_6(B_{3u})$	327 {45}	308 {51} (1.037)		322	276

(MP2/6-31GF*) frequencies differ by not more than 3%, although the difference between the intensities is much greater.

In contrast to the X_2O_3 systems, the structures of the B_2O_2 and Al_2O_2 molecules differ considerably. The two lowest isomers of B_2O_2 are the Lewis structures of the linear configuration:[4]

$$:O{\equiv}B-B{\equiv}O: \quad \text{and} \quad :B-\ddot{O}-B{\equiv}O: .$$

The contributions of ionic interactions are not so large, as follows, for example, from the effective natural charges of the ground-state isomer

$$O^{-0.824}-B^{+0.824}-B^{+0.824}-O^{-0.824} .$$

For Al_2O_2 the situation is more interesting. The Lewis structures of the linear isomer Al–O–Al–O obtained with Hartree–Fock and correlation (MP2) electron densities can be represented as follows:

$$:Al:\ddot{O}-Al{\equiv}O: \text{ (SCF)} \qquad :Al{\equiv}O-Al{\equiv}O: \text{ (MP2)},$$

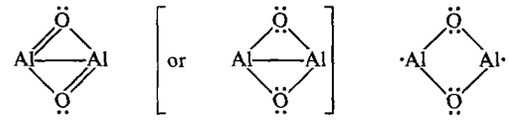
reflecting the general trend in the change in the electronic structure of aluminium oxides — correlation effects lead to an increase in the covalent character of the bond.[3]

Naturally, because of the appreciably higher effective natural charges

$$Al^{+0.867}-O^{-1.595}-Al^{+2.007}-O^{-1.278},$$

the structures with X–X contacts are less favourable for aluminium than for boron (the ground-state linear isomer is O–B–B–O for B_2O_2, and Al–O–Al–O for Al_2O_2). Allowance for correlation effects leads to a lowering of the energy of O–X–X–O relative to X–O–X–O (Table 7 and Fig. 2), but in the case of Al_2O_2 this lowering is insufficient for the O–Al–Al–O isomer to be regarded as sufficiently low-lying. In the limit of a completely ionic description, the linear molecule Al–O–Al–O can be represented as $Al^+[O-Al-O]^-$. The fragment $[O-Al-O]^-$ is identified in the Al_2O_2 and Al_2O_3 molecules both from the geometric parameters and from the vibrational frequencies.

The Lewis structures for the cyclic isomer of Al_2O_2 in the singlet and triplet states can be represented as follows:[3]



singlet triplet

In this picture, the highest occupied and lowest unoccupied MO for the singlet state are the orbitals $\sigma(Al-Al)$ and $\sigma^*(Al-Al)$ with an extremely small energy gap between them (0.1 a.u.). This leads to the marked changes in the energies and in the vibrational wavenumbers of the molecule observed on going beyond the SCF approximation.[3,32] The triplet state corresponds to a biradical structure with unpaired electrons on Al. The rigid framework of Al–O σ-bonds is responsible for the similarity in the geometries and vibrational frequencies of the cyclic Al_2O_2 molecule in the two spin states.

3. X_2O molecules

Of all the polyatomic oxides X_mO_n, the compounds with the composition X_2O are apparently the least puzzling. There is almost no doubt that the ground-state isomers correspond to the linear symmetrical configurations X–O–X. For quantum-chemical calculations, these triatomic systems are not very complex, and sufficiently reliable theoretical results can be expected. From the experimental viewpoint also, there is no doubt about the correctness of the understanding of the structure of the B_2O and Al_2O molecules.

There is only one published experimental study in which, in an investigation of the reaction of atomic boron with water, the bands in the infrared spectrum were assigned to the matrix-isolated B_2O molecule.[37] From the behaviour of the band at about 1420.5 cm^{-1} on isotope replacement it was concluded that the molecule in the matrix has a linear or almost linear symmetrical configuration.

Table 11. Wavenumbers (cm^{-1}) and infrared intensities (in curly brackets, km mol^{-1}) for the linear isomer of Al_2O_2 [the isotope ratios $R(16/18)$ for the replacement $^{16}O \rightarrow {}^{18}O$ are given in round brackets].

Vibration	SCF/6-31GF* [3,44]	MP2/6-31GF* [3]	Experiment [30,26]
$\nu_1(\Sigma)$	1301	1183 {276} (1.014; 1.015; 1.030)	1176.3 (1.013; 1.030)
$\nu_2(\Sigma)$	1020	946 {233} (1.018; 1.034; 1.051)	945.5; 943 (1.019; 1.034; 1.051)
$\nu_3(\Sigma)$	497	468	
$\nu_4(\Pi)$	281	225 {56}	
$\nu_5(\Pi)$	72	49	

Table 12. Vibrational wavenumbers (cm^{-1}) of the B–O–B molecule and the isotope ratios for the replacements $^{10}B \rightarrow {}^{11}B$ [$R(10/11)$] and $^{16}O \rightarrow {}^{18}O$ [$R(16/18)$] for the strong ν_1 band.

Method	Wavenumber/cm^{-1}			$R(10/11)$	$R(16/18)$	Ref.
	$\nu_1(\Sigma_u)$	$\nu_2(\Sigma_g)$	$\nu_3(\Pi_u)$			
SCF/6-31GF*	1585	1126	120			4
SCF(0.9)	1426.5	1013	108			4
MP2/6-31GF*	1496	1052	111	1.021	1.034	4
MP2/6-311GF**	1456	1043	24			4
Experiment	1420	–	–	1.020	1.033	37

In a study of the gas-phase oxidation of atomic boron by NO_2 and N_2O molecules, the authors[46] tried to assign the chemiluminescence spectrum to the B_2O molecule, supposedly in the form of the unsymmetrical isomer B–B–O (if the vibration with wavenumber 582 cm^{-1} can be associated with this molecule), although the assignment of the experimental spectrum to B_2O_2 is not excluded.

Quantum-mechanical calculations by the SCF method[39,47] predict a linear symmetrical equilibrium configuration, while the energy of the other linear isomer B–B–O should be appreciably higher. According to recent calculations for B_2O, carried out by SCF and MP2 methods,[4] the equilibrium internuclear distance in the linear symmetrical molecule B–O–B is 1.313 (SCF/6-31GF*), 1.333 (MP2/6-31GF*), or 1.329 Å (MP2/6-311GF**), demonstrating again that for these compounds the MP2/6-31GF* method predicts the bond lengths with an uncertainty of not more than 0.01 Å.

The vibrational wavenumbers of the B_2O molecule are compared in Table 12. The experimentally determined wavenumber of the ν_1 vibration is close to that calculated by the MP2/6-31GF* method (error ~5%). Comparison of the wavenumbers calculated by the MP2/6-31GF* and MP2/6-311GF** methods shows that they are fairly sensitive to the basis set, particularly for the ν_3 deformation. The low wavenumber of the deformation indicates a very flat section for the PES along this coordinate, confirming the arguments[37] about the possible quasi-linearity of B–O–B in the matrix. However, the proposed[37] assignment of the emission spectrum[46] to B–O–B is of course excluded. There is more justification for assigning the observed chemiluminescence[46] to the O–B–B–O molecule.

The strong band of the matrix-isolated Al_2O molecule at 992 cm^{-1} (992.8 cm^{-1} according to recent measurements[30] in an argon matrix) with an isotope ratio $R(16/18) = 1.045$, assigned to the antisymmetric stretch, is well known and reliably established.[25,29,30] The electronic spectrum of the gas phase has also been used to estimate the wavenumber of the symmetric stretch (471 cm^{-1}).[48] The bands at 472 cm^{-1} and 475 cm^{-1} in the Raman spectra of the argon and nitrogen matrices were assigned to this vibration.[27,49] In the earliest studies[49] it was pointed out that the wavenumber of the Al–O–Al deformation should be low (below 190 cm^{-1}).

Many non-empirical calculations have been carried out for the Al_2O molecule.[3,5,43,44,50–52] All the data agree in predicting a linear symmetrical equilibrium configuration Al–O–Al. Some of the calculation results are given in Table 13. The positions of the strong ν_1 band in the infrared spectrum and the corresponding isotope ratios $R(16/18)$ obtained by calculation (MP2/6-31GF* or the scaled SCF/6-31GF* wavenumber) and by experiment show very good agreement. The agreement between the calculated ν_2 frequency and that estimated from the electronic spectra is also satisfactory.

Electron diffraction studies of the Al_2O molecule in the gas-phase electron diffraction laboratory of the Chemistry Department of Moscow State University led to the conclusion that the molecule has an angular configuration with an Al–O–Al angle of about 140°. This conclusion is evidently a consequence of the extremely low deformation frequency of the molecule.

Table 13. Equilibrium distance R_{Al-O} (in Å) and vibrational wavenumbers of the Al–O–Al molecule.

Method	R_{A-O}	Wavenumber/cm^{-1}			$R(16/18)$	Ref.
		$\nu_1(\Sigma_u)$	$\nu_2(\Sigma_g)$	$\nu_3(\Pi_u)$		
SCF	1.691	1076	553	126	–	51
SCF	1.723	1012	531	129	–	43
SCF/6-31GF*	1.703	1043	549	112	–	3, 5, 44
GF2/6-31GF*	1.733	988	513	90	1.045	3, 5
Experiment	–	992.8	471; 472; 475	–	1.045	30, 47, 27, 69

The other possible isomer of the molecule, namely Al–Al–O, has a fairly high energy (more than 80 kcal mol^{-1}) relative to Al–O–Al.[3,5]

Comparison of the details of the electronic structures of the B–O–B and Al–O–Al molecules does not lead to any unexpected features.

The more ionic character of the bonding for Al, which can be seen by comparing the natural charges on the atoms,[3,4]

$$B^{+0.645}-O^{-1.290}-B^{+0.645} \qquad Al^{+0.830}-O^{-1.660}-Al^{+0.830},$$

is responsible for certain differences in the descriptions of the systems. The Lewis structures of aluminium oxide, obtained with the Hartree–Fock (SCF) and correlation (MP2) densities,[3] indicate an increase in the covalent contributions when allowance is made for electron correlation

$$:Al:\ddot{O}:\ Al: \text{ (SCF)} \qquad :Al-\ddot{O}-Al: \text{ (MP2)}.$$

For the boron oxide, the description at the level of the Lewis structures is fairly obvious:

$$B\equiv O-B: \quad \leftrightarrow \quad :B-O\equiv B: .$$

In both molecules, correlation effects are responsible for an increase in the equilibrium internuclear distance X–O (0.02 Å for X = B, 0.03 Å for X = Al), which is slightly smaller than for the other oxides.

4. XO_2 molecules

Species with the composition XO_2 are formed and play an extremely important role in the oxidation of boron and aluminium. A fairly large amount of experimental information on XO_2 molecules has been obtained, including spectral data for the matrix-isolated molecules. From the theoretical viewpoint, the analysis of the XO_2 systems is much more complex than that for the molecules of the other oxides examined above. This is due chiefly to the fact that these molecules have open electron levels; moreover, methods of calculation based on the single-configuration representation of electronic wave-functions are generally speaking inadequate in the present application.

The results of experimental and theoretical studies indicate that the equilibrium configuration of the BO_2 molecule is the linear symmetrical configuration.

The vibrational wavenumbers of the BO_2 molecule, obtained by different methods, are given in Table 14. In this case it is possible to compare the experimental results for the gas phase[53–57] and the matrix-isolated molecules.[14,16,58] Most information has been obtained for the ν_1 antisymmetric stretch. The vibration frequencies of the molecule in the gas phase has been measured extremely accurately, and the shifts observed in matrix-isolation experiments are estimated relative to this quantity. According to the latest measurements,[16] the shifts differ considerably, depending on the material of the matrix and (presumably) on the type of capture position. The maximum deviation from the gas-phase value for ν_1 is ~20 cm^{-1} (not more than 2%).

Thus the characteristic uncertainties in the vibrational wavenumbers calculated by present-day methods of quantum chemistry (MP2/6-31GF*) (about 3%) are close to the relative shifts in the wavenumbers as a result of the matrix environment. For the ν_3 deformation, the matrix shifts have even higher values. Since modelling the matrix shifts is extremely difficult,[60,61] the agreement between the experimental molecular spectra, obtained for these compounds primarily under matrix-isolation conditions, and the theoretically calculated spectra cannot have a higher accuracy than that already noted (3–5%).

There have been few non-empirical calculations of the properties of the BO_2 molecule. For the ground electronic state $X^2\pi_g$, Lomp and coworkers[59] calculated the equilibrium internuclear distance B–O in the linear molecule—1.34 Å (SCF/OST-3GF) and 1.26 Å {SCF/[9*s*5*p*]/(4*s*2*p*)} (experimental value 1.265 Å [53])—and also the harmonic frequencies of the ν_2

Table 14. Vibrational wavenumbers (cm^{-1}) for the BO_2 molecule (the oblique lines separate wavenumbers associated with different positions of capture of the molecule by the matrix).

Method	Wavenumber/cm^{-1}			Ref.
	ν_1 (Σ_u)	ν_2 (Σ_g)	ν_3 (Π_u)	
Experiment (gas phase)	1278.3	1070	464	53–57
Experiment (matrix isolation)	1276	–	–	14
	1299.3/1282.8/1274.6 (Ar)	–	398.2/446.6 (Ar)	16
	1285.5/1300.7 (Kr)	–	394.6 (Kr)	16
	1292.2 (Xe)	–	–	16
Calculation SCF/OST-3GF	–	1079	464	59

and ν_3 vibrations (Table 14). In the calculations, considerable difficulty was encountered in obtaining symmetrically stable solutions of the electronic equation.

The AlO_2 molecule has been detected among the products of the reaction of aluminium with oxygen in an argon matrix. For this molecule, a cyclic structure with an O–Al–O angle of 30–50° was proposed, as for all the dioxides of the group III elements.[24] Evidence in support of this interpretation is provided by the presence in the infrared spectrum of a band at 1096 cm^{-1}, close to the wavenumber of the O_2^- vibrations (1089 cm^{-1}). It has been suggested[24] that the molecule has an ionic structure $Al^+O_2^-$. The band at 496 cm^{-1} was assigned to this structure. The remaining wavenumber was estimated at 550 cm^{-1}. Subsequent studies[25,26] showed that in the matrix reactions of aluminium with oxygen, another isomer of the molecule is formed, namely the linear O–Al–O. The wavenumber of the antisymmetric stretch in the infrared spectrum (918 cm^{-1}) was assigned to this isomer, and the laser fluorescence spectra gave the wavenumbers of the symmetric stretch (635 cm^{-1}) and the deformation (70 cm^{-1}).[70]

In other studies of the matrix reactions of aluminium with oxygen,[29] the formation of an unsymmetrical isomer of AlO_2 with a C_s structure was assumed; later,[30] the wavenumber 496.3 cm^{-1} in the infrared spectrum was assigned to a cyclic configuration, and the wavenumber 1129.5 cm^{-1} to the linear O–Al–O isomer.

Nonempirical quantum-mechanical calculations for the AlO_2 molecule are difficult, due to the symmetry instability of the Hartree–Fock equations.[10,62,63] To construct the potential surfaces of this system it is necessary to use many-configuration approximations, and in the last case also considerable difficulties are encountered, particularly in the estimation of the vibrational frequencies. The many-configuration SCF method (MC SCF) combined with the pseudo-potential approximation has been used[62] to model the field of the core electrons. It was established that of the two molecular configurations examined—the cyclic configuration and the linear unsymmetrical Al–O–O—the cyclic form corresponds to the energy minimum. Its equilibrium geometric parameters and the wavenumbers of the harmonic vibrations were estimated (Tables 15 and 16). The methods of configuration interaction (CI) and many-particle perturbation theory (PT) with basis sets of restricted dimensions have been used[63] to examine both the cyclic and the linear symmetric isomers of the AlO_2 molecule. These calculations indicate only that these isomers have similar energies.

Table 15. Geometric parameters of the AlO_2 molecule (distances in Å, angles in °) and difference between the energies (kcal mol^{-1}) of the linear and cyclic isomers.

Method of calculation	Linear isomer R_{Al-O}	Cyclic isomer R_{Al-O}	Φ(O–Al–O)	Energy difference	Ref.
MC SCF	–	1.97	38	–	62
CI, PT	1.72	1.88	41	1.2	63
MC SCF	1.67	1.93	42	6.0	10

Table 16. Experimental and calculated vibrational wavenumbers of the AlO_2 molecule (cm^{-1}).

Molecule		Wavenumber/cm^{-1}			Ref.
		ν_1	ν_2	ν_3	
	calculation	1081	591	277	10
		1394	528	242	62
	experiment	1096	496	–	24
		–	496.2	–	30
O–Al–O	calculation	932	582	75	10
		978	659	92	63
	experiment	918	635	70	24

The MC SCF method (the version of the complete configurational space of the active orbitals) was also used by Nemukhin and Almlof,[10] but with allowance for all the electrons, in contrast to the work of Rubio and coworkers.[62] The orbitals were represented using basis sets specially designed for calculations with allowance for correlation effects, the so-called atomic natural orbitals of the type (20*s*13*p*5*d*)/[6*s*5*p*2*d*] for Al and (13*s*8*p*5*d*)/[5*s*4*p*1*d*] for O. It was concluded that on the potential surface of the ground state of the molecule ($^2A_2$) there are two minimum points separated by a high barrier (~60 kcal mol^{-1}), and that the energy of the linear symmetrical form is 6 kcal mol^{-1} lower than that of the cyclic configuration. More accurate estimates of the ratio of the energies of the linear and cyclic forms apparently require additional calculations with a more detailed allowance for correlation effects, but it can be taken as established that both isomers may be formed in matrix reactions of aluminium with oxygen. The linear and cyclic isomers of AlO_2 are described by appreciably different electron configurations, and are characterised by different distributions of the effective charges.[10]

The experimental and theoretical vibrational wavenumbers for the two isomers are compared in Table 16. Unfortunately, the non-empirical calculations for this system were carried out using a scheme different from that used for the other oxides examined (here, generally speaking, the single-configuration SCF and MP2 approximations are inapplicable), so that we cannot use the regularities noted above. Overall, the theoretical and experimental wavenumbers show agreement but the agreement is not yet quantitative.

In the comparison of the properties of BO_2 and AlO_2 in the linear configurations, the significant difference in the wavenumbers of the deformation is noteworthy: 464 cm^{-1} for O–B–O and 70 cm^{-1} for O–Al–O.

5. XO molecules

Information on the diatomic oxides BO and AlO at the level mainly developed in the present review (geometry, vibrational wavenumbers) is already given in reference works,[64] and therefore is not discussed here. In connection with the questions dealt with above, we would merely refer to new spectral studies of matrix-isolated BO and AlO molecules.[16,30,65] From these data it follows

that the experimental matrix shifts for BO and AlO have different signs. For example, in argon matrices the shift of the principal vibrational wavenumber of BO is -7 cm^{-1} (1854.7 cm^{-1} relative to the gas-phase value of 1862.1 cm^{-1}),[16] while that for AlO is 10 cm^{-1} (975 cm^{-1} compared with 965 cm^{-1} for the gas phase).[30,65]

One may also mention fairly detailed studies of the potential energy curves of diatomic oxides by non-empirical methods of quantum chemistry,[66–68] which show significant changes in the electronic structure with change in the internuclear distance.

V. Summary

One of the principal conclusions from the comparison of the results of studies of the oxides X_mO_n (X = B, Al) is that these compounds show a great variety of compositions and molecular geometries. For practically all the systems X_2O_3, X_2O_2, X_2O, and XO_2 we can now formulate definite conclusions about the structure, based on the experimental spectra of the molecules and the results of quantum-chemical calculations. For these compounds it may be concluded that the accuracies of the determination of the equilibrium geometric parameters and the vibrational frequencies from experiment and from calculation are comparable.

Most of the differences in the structures of the oxides of boron and aluminium can be attributed to the more ionic character of the Al–O bond in the compounds Al_mO_n; the balance of the ionic and covalent contributions depends considerably on allowance for correlation effects, which increase the covalent components. Aluminium oxides, to a greater extent than boron oxides, are characterised by the existence of low-lying isomers with the same stoichiometry.

Most of the unresolved theoretical questions remaining relate to the BO_2 and AlO_2 molecules. From the experimental viewpoint, the situation for the Al_2O_3 and Al_2O_2 molecules is least satisfactory.

For a more complete understanding of the processes accompanying the reactions of atoms and clusters of boron and aluminium with oxygen or other oxidants in the gas phase and under matrix-isolation conditions it is extremely important to study systems of the type $(XO)_n$ and $(XO_2)_n$ with $n > 2$.

References

1. P G Nelson *J. Chem. Educ.* **68** 732 (1991)
2. R D Srivastava, M Farber *Chem. Rev.* **78** 627 (1978)
3. A V Nemukhin, F Weinhold *J. Chem. Phys.* **97** 3420 (1992)
4. A V Nemukhin, F Weinhold *J. Chem. Phys.* **98** 1329 (1993)
5. A I Boldyrev, P v R Schleyer *J. Am. Chem. Soc.* **113**, 9045 (1991)
6. N G Rambidi, N F Stepanov, Yu G Abashkin, A I Berezin, A I Dement'ev, B I Zhilinskii, V K Mikhalko, V I Pupyshev, V Ya Simkin, I A Topol' *Zh. Strukt. Khim.* **22**, 29 (1981)
7. H Sellers, J Boggs, A V Nemukhin, J Almlof *J. Mol. Struct. (THEOCHEM)* **85** 195 (1981)
8. L V Serebrennikov, Yu N Sekachev, A A Maltsev *High Temp. Sci.* **16** 23 (1983)
9. V P Spiridonov, A G Gershikov, E Z Zasorin, A A Ivanov *High Temp. Sci.* **16** 325 (1983)
10. A V Nemukhin, J Almlof *J. Mol. Struct. (THEOCHEM)* **253** 101 (1992)
11. G V Chertikhin, I L Rozhanskii, L V Serebrennikov *Vestn. Mosk. Univ., Ser. 2: Khim.* **29**, 27 (1988)
12. A E Reed, R B Weinstock, F Weinhold *J. Chem. Phys.* **83** 735 (1985)
13. W Weltner, J R W Warn. *J. Chem. Phys.* **37** 292 (1962)
14. A Sommer, D White, M J Linevsky, D E Mann. *J. Chem. Phys.* **38** 87 (1963)
15. P A Akishin, V P Spiridonov *Dokl. Akad. Nauk SSSR* **131**, 557 (1960)
16. T R Burkholder, L Andrews *J. Chem. Phys.* **95** 8697 (1991)
17. J F Chiang, D R Witman *Theor. Chim. Acta* **17**, 155 (1970)
18. M A Ali, A J Shaikh *J. Mol. Struct.* **13** 179 (1972)
19. A I Dementjev, N G Rambidi, V Ya Simkin, I.A.Topol *J. Mol. Struct.* **68** 199 (1980)
20. Yu S Ezhov, S M Tolmachev, V P Spiridonov, N G Rambidi *Teplofiz. Vys. Temp.* **6** 68 (1968)
21. Yu S Ezhov, S M Tolmachev, V P Spiridonov, N G Rambidi *Zh. Strukt. Khim.* **11** 527 (1970)
22. G Fogarasi, P Pulay *Ann. Rev. Phys. Chem.* **35** 191 (1984)
23. B A Hess, L J Schaad, P Carsky, R Zahradnik *Chem. Rev.* **86** 709 (1986)
24. L V Serebrennikov, S B Osin, A A Maltsev *J. Mol. Struct.* **81** 25 (1982)
25. L V Serebrennikov, A A Mal'tsev *Vestn. Mosk. Univ., Ser. 2: Khim.* **26** 137 (1985)
26. I L Rozhanskii, G V Chertikhin, L V Serebrennikov, V F Shevel'kov *Zh. Fiz. Khim.* **62**, 2351 (1988)
27. I L Rozhanskii, L V Serebrennikov, V F Shevel'kov *Zh. Fiz. Khim.* **64** 521 (1990)
28. G V Chertikhin, L V Serebrennikov, V F Shevel'kov *Zh. Fiz. Khim.* **65** 1078 (1991)
29. S M Sonchik, L Andrews, K D Carlson *J. Phys. Chem.* **89** 2009 (1983)
30. L Andrews *J. Phys. Chem.* **96** 10182 (1992)
31. V G Solomonik, V V Sliznev *Zh. Neorg. Khim.* **32** 1301 (1987)
32. A V Nemukhin, F Weinhold *J. Chem. Phys.* **97** 1095 (1992)
33. M G Inghram, R F Porter, W A Chupka *J. Chem. Phys.* **25** 498 (1956)
34. Yu N Sekachev, L V Serebrennikov, V S Nikitin, A A Mal'tsev *Vestn. Mosk. Univ., Ser. 2: Khim.* **20** 589 (1979)
35. L V Serebrennikov *Vestn. Mosk. Univ., Ser. 2: Khim.* **22** 606 (1981)
36. B M Ruscic, L A Curtiss, J Berkovitz *J. Chem. Phys.* **80** 3962 (1984)
37. L Andrews, T R Burkholder *J. Phys. Chem.* **95** 8554 (1991)
38. R J Doyle *J. Am. Chem. Soc.* **110** 4120 (1988)
39. R L DeKock, M R Barbachyn *Inorg. Nucl. Chem.* **43**, 2645 (1981)
40. A I Dement'ev, S S Kramarenko, N F Stepanov *Zh. Strukt. Khim.* **24** 99 (1983)
41. P A Finn, D M Gruen, D L Page *Adv. Chem. Ser.* **158** 30 (1976)
42. M A Douglas, R H Hauge, J L Margrave *High Temp. Sci.* **16** 35 (1983)
43. J Masip, A Clotet, J M Ricart, F Illas, J Rubio *Chem. Phys. Lett.* **144** 373 (1988)
44. L Bencivenni, M Pelino, M Ramondo *J. Mol. Struct. (THEOCHEM)* **253** 109 (1992)
45. A V Zaitsevskii, G V Chertikhin, L V Serebrennikov, N F Stepanov *J. Mol. Struct. (THEOCHEM)* in press
46. T C Devore, J R Woodward, J L Gole *J. Phys. Chem.* **92** 6919 (1998)
47. T S Zyubina, O P Charkin, A S Zyubin, V G Zakchevskii *Zh. Neorg. Khim.* **27** 558 (1982)
48. M A Douglas, R H Hauge, J L Margrave *High Temp. Sci.* **16** 35 (1983)
49. A Snelson *J. Chem. Phys.* **74** 2574 (1970)
50. E L Wagner *Theor. Chim. Acta*, **32** 295 (1974)
51. V G Solomonik, I G Sazonova *Zh. Neorg. Khim.* **30** 1939 (1985)
52. A M Mebel', T S Zyubina *Zh. Neorg. Khim.* **32** 1285 (1987)
53. J W C Johns *Can. J. Phys.* **39** 1738 (1961)
54. D K Russell, M Kroll, D A Dows, R A Beaudet *Chem. Phys. Lett.* **20** 153 (1973)
55. D K Russell, M Kroll, R A Beaudet *J. Chem. Phys.* **66** 1999 (1977)
56. K Kawaguchi, E Hirota, C Yamada *Mol. Phys.* **44** 509 (1981)
57. A Maki, J B Burkholder, A Sirha, C J Howard *J. Mol. Struct.* **130** 238 (1988)
58. L V Serebrennikov *Vestn. Mosk. Univ., Ser. 2: Khim.* **16** 363 (1975)
59. P E Lomp, V Ya Simkin, N F Stepanov *Izv. Akad. Nauk Est. SSR* **32** 286 (1983)
60. A I Krylova, A V Nemukhin, N F Stepanov *J. Mol. Struct. (THEOCHEM)* **262** 55 (1992)
61. L V Serebrennikov *Vestn. Mosk. Univ., Ser. 2: Khim.* (in the press)
62. J Rubio, J M Ricart, F Illas *J. Comput. Chem.* **9** 836 (1988)
63. A V Zaitsevskii, S A Bogdanova, A I Dement'ev, V Ya Simkin *Vestn. Mosk. Univ., Ser. 2: Khim.* **31** 604 (1990)
64. K P Huber, G Herzberg *Molecular Spectra and Molecular Structure* Vol. 4 *Constants of Diatomic Molecules* (Translated into Russian) (Moscow: Mir, 1984)
65. S J Bares, M Haak, J W Nibler *J. Chem. Phys.* **82** 670 (1985)
66. A V Nemukhin, J Almlof, A Heiberg *Chem. Phys.* **57** 197 (1981)
67. J Almlof, A V Nemukhin, A Heiberg *Int. J. Quantum Chem.* **20** 655 (1981)
68. B H Lengsfield, B Liu *J. Chem. Phys.* **77** 6083 (1982)
69. I V Ovchinnikov, L V Serebrennikov, A A Mal'tsev *Zh. Fiz. Khim.* **59** 1558 (1985)
70. I L Rozhanskii, L V Serebrennikov, V F Shevel'kov *Vestn. Mosk. Univ., Ser. 2: Khim.* **29** 560 (1988)