Translated from *Uspekhi Khimii*, 47, 101-126 (1978)

U.D.C. 539.27

Electron Diffraction Studies on Stereochemically Non-rigid Molecules

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Electron diffraction data for the structures and potential energy functions of molecules with a certain type of intramolecular motion—high-amplitude motion—are analysed in detail and the fundamental characteristics of such motion and the conditions for its experimental observation are formulated. Important structural-chemical consequences of high-amplitude motion and the urgent need for a comprehensive investigation of stereochemically non-rigid molecules are demonstrated.
The bibliography includes 201 references.

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I. INTRODUCTION

Owing to the comparative simplicity of the experimental technique and methods and the possibility of investigating complex molecules (including non-polar molecules), modern gas-phase electron diffraction is of primary importance for the analysis of molecular structures. The main information which can be derived by electron diffraction concerns the geometrical parameters characterising the steric structure as well as the mean square amplitudes of the vibrations of pairs of nuclei. The application of this method in the study of organic and inorganic molecules led to the accumulation of extensive experimental data on molecular structures in the gas phase (see, for example, the compilation in Ref. 1 as well as the relevant reviews[2-10]).

A special type of intramolecular motion of nuclei—the so called high-amplitude motion—has been detected by electron diffraction only in a comparatively small number of molecules; however, it is difficult to overestimate the importance of detailed investigation of this phenomenon for many branches of modern chemistry.

The high-amplitude motion of nuclei is characterised by low frequencies (usually below 100 cm^{-1}) and is reflected specifically in the structure, dipole moments, and other molecular properties. This is manifested in the study of spectra, thermodynamic properties, the behaviour of molecules in electric fields, and other experimental research. Investigations in recent years have provided many examples of the manifestation of complex intramolecular motions of nuclei in compounds of different classes. In this connection, the problem has been assuming increasing current chemical importance in the interpretation of data derived by a wide variety of experimental methods, in the theoretical study of the geometrical and electronic structures of polyatomic molecules, in the calculations of thermodynamic functions of substances, etc.

This review deals with a limited topic—the electron diffraction study of molecules with a complex motion of nuclei (high-amplitude vibrations)†; studies of internal rotation have been excluded, to some extent arbitrarily, because there already exists an independent and exhaustive literature on this problem (see, for example, the review of Bastiansen et al.[15] and the monograph of Orville-Thomas[16]).

II. THE GENERAL CHARACTERISTICS OF THE HIGH-AMPLITUDE MOTION AND THE CONDITIONS FOR ITS EXPERIMENTAL OBSERVATION

It is difficult to define rigorously the concept of "high-amplitude motion" because the nuclear shifts in molecules do not vary continuously. The convention has been adopted that one speaks of the high-amplitude motion of nuclei in those cases where the nuclear shifts are much larger than in the usual motion in "quasi-rigid" molecules, where the nuclei execute small oscillations about the corresponding equilibrium positions[17-19]. Large nuclear shifts arise when periodic internal rearrangements of individual atoms or whole molecular fragments take place in the molecule. The transition of the system of nuclei from one steric configuration to another—the so called hindered motion—constitutes in fact high-amplitude

† Among the experimental methods for the investigation of processes involving intramolecular motion, NMR also plays an important role. In particular, extensive information has been obtained by this method about the high-amplitude motion of nuclei in the condensed phase (see the relevant reviews[11-14]).

motion and the molecules where such transitions occur are referred to as stereochemically non-rigid‡.

In principle any molecules with identical nuclei can have several steric configurations differing from one another as a result of nuclear transpositions, provided that these transpositions are not equivalent to the rotation of the molecules as a whole. In addition, each non-planar molecules can have left- and right-hand configurations whose interconversion requires inversion. Thus the motion of nuclei in the majority of molecules is generally speaking characterised by potential functions (in the general case potential surfaces) with two (or more) minima corresponding to different steric configurations of the nuclei and separated by potential barriers.

We shall now consider the conditions under which high-amplitude motion is possible in principle and can be observed experimentally.

(a) If the potential function minima are fairly deep (i.e. the barriers between the minima are high), one may assume that a definite steric configuration of the nuclei corresponds to each potential energy minimum.

A quantitative criterion of the fundamental distinguishability of a particular configuration of the nuclear system is (Bersuker [30], p.192):

$$\tau \geqslant T\,, \tag{1}$$

$$\Delta E \geqslant 2\hbar\omega, \tag{1a}$$

where τ is the "lifetime" of the configuration corresponding to the potential minimum, T the period of the vibrations at the minimum, ΔE the depth of the minimum, and ω the vibration frequency at the minimum. When condition (1) or (1a) is fulfilled, the configuration of the nuclei corresponding to the given minimum is fairly long-lived, quasi-stationary, and in principle can be distinguished experimentally. For an approximate description of the nuclei in the configuration corresponding to the potential energy minimum, the thoroughly developed model of quasi-rigid molecules is applicable [17-19].

In the case under consideration the equilibrium configuration corresponding to the potential minimum is a characteristic of the steric arrangement of the nuclei. The transitions of the system fron one minimum to another can occur as a result of tunnelling through the potential barrier, but such transitions are not always observed experimentally.

If the thermal energy of the molecules kT is greater than the height of the potential barrier, there is an appreciable increase of the population of the upper (above the barrier) vibrational levels. In order to characterise the geometrical configuration of the molecule in these states, it is necessary to know values averaged with respect to the vibrations, which differ appreciably from the equilibrium values corresponding to the potential minima. A typical example of such a case is provided by the ammonia molecule for which there exists two equilibrium nuclear configurations arising when the nitrogen atom is reflected in the plane containing the hydrogen atoms. The vibrational and rotational spectra of the molecules as well as electron diffraction data can be interpreted satisfactorily on the hypothesis of a quasi-rigid pyramidal molecular model, while tunnelling is revealed by the inversion-induced splitting of the vibrational levels in the spectra.

If all the potential barriers separating energetically equivalent configurations are very high (virtually impossible to overcome), one can ignore the existence of all the potential minima except one. The molecular state at this minimum will be stationary and the transitions of systems from one minimum to another will hardly occur.

(b) If the minima in the potential function are shallow (the barriers between the minima are low), i.e. Eqn.(1a) does not hold, then the nuclear system does not possess a definite symmetry and is not characterised by a stable stationary configuration corresponding to the potential minimum. The equilibrium configuration loses the significance of a characteristic of the steric arrangement of the nuclei. In this case individual configurations corresponding to various minima of this type are in principle indistinguishable and the system merely executes periodic virtually unhindered transitions from one configuration to another (or others), i.e. high-amplitude motion arises. As an illustration, one may quote the cyclopentane molecule. In this molecule the motion of the ring nuclei during vibrations can be described as continuous transitions between ten configurations with C_2 symmetry and ten configurations with C_S symmetry ("pseudorotation" of the ring; see Section V below), none of which is a stable equilibrium configuration of the ring.

It is seen from the above examples that in reality one encounters most frequently cases where the total potential energy function possesses at the same time very high barriers, separating the minima from one another, the transitions between which cannot be neglected, and one (or a few) relatively low barriers. For this reason, as a rule only part of the molecule is stereochemically non-rigid in the above sense and the nuclear system executes high-amplitude motion only along one or several but not all vibrational coordinates. Thorson and Nakagawa [31] introduced the concept of quasi-symmetry for molecules with high-amplitude nuclear motion. For example, molecules characterised by a continuous reversible transition from a bent to a linear configuration and conversely are regarded as quasi-linear (quasi-linearity relative to the deformation angle; the molecule is quasi-rigid relative to the other vibrational coordinates).

We shall analyse in greater detail the conditions under which high-amplitude motion may be observed experimentally. Evidently the characteristic time of the experimental method employed should play an important role in this. Indeed, individual nuclear configurations, corresponding to the potential minimum, will be experimentally indistinguishable when the characteristic time τ' of the given experimental method (the time of the effective interaction between the molecular system investigated and the external perturbation) is greater than the lifetime τ of the individual configurations (see Bersuker [30], p.190), i.e.

$$\tau' > \tau, \tag{2}$$

In this case there is sufficient time during the measurement for the system to undergo repeated transitions from one set of configurations to another, and an average pattern is recorded experimentally. It is easily seen that the fulfilment of condition (2) is facilitated by low values of τ, i.e. low energy barriers between individual configurations.

On the other hand, when

$$\tau' < \tau, \tag{3}$$

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‡ The term "stereochemically non-rigid molecules" was introduced by Muetterties [20-27]. In the NMR system other terms are also widely used in the description of the high-amplitude intramolecular motion, for example, "fluctuating molecules" [11], "degenerate intramolecular rearrangement" [13,28], "autoisomerisation" [29], etc.

then a separate configuration is manifested in the measurement with a lifetime τ (provided that it is distinguishable in principle; see above). The times τ' are different for different experimental methods (see Table) and the results of the measurements therefore depend primarily on the method employed [the rule governing the relation with the means of observation (see Bersuker [30], p. 191)].

The characteristic times τ' of certain physicochemical methods [20]*.

Method	τ', s
Electron diffraction	10^{-18}
Neutron diffraction	10^{-18}
X-Ray diffraction	10^{-18}
Ultraviolet spectroscopy	10^{-15}
Visible spectroscopy	10^{-14}
Infrared and Raman spectroscopy	10^{-13}
ESR	10^{-4} - 10^{-8}
NMR	10^{-1} - 10^{-9}
NQR	10^{-1} - 10^{-8}
Mössbauer spectroscopy	10^{-7}
Deflection of molecular beams in electric field	10^{-6}

*The characteristic time of the electron diffraction experiment quoted was obtained by the authors of the review and differs from the value (10^{-20} s) in the literature [13,20].

On the other hand, since the lifetime depends on the vibrational state v at the minimum potential ($\tau = \tau_v$), the fulfilment of conditions (2) and (3) is also determined by the conditions of the measurements, for example, temperature [the rule governing the relation with the conditions of measurement; (see Bersuker [30], p. 190]. Thus the values of τ_v are high at low temperatures and condition (3) may hold for the given τ', i.e. a separate configuration with a lifetime τ_v is observed experimentally. At higher temperatures, higher vibrational levels begin to be populated and τ_v diminishes, which promotes the transition to condition (2) and an average pattern reflecting the high-amplitude motion is manifested experimentally.

The knowledge of the potential function describing the motion of the nuclei in the molecule can yield the complete characteristics of the behaviour of the nuclei, including their high-amplitude motion. However, a rigorous quantum-mechanical solution of the problem of the derivation of such a potential function in the general case is impossible because of the difficulties in the solution of the Schrödinger equation for the electronic states of complex molecules, which cannot as yet be overcome. Additional difficulties in the solution of this problem can be due to the possible deviations from the adiabatic approximation, since there is reason to believe that the vibronic interaction, which has a particularly marked effect when the electronic states are degenerate (the Renner and Jahn–Teller effects) or pseudodegenerate (the Jahn–Teller pseudoeffect), plays a major role in complex intramolecular motion of nuclei. These problems have been examined in detail by Renner [32], Jahn and Teller [33], van Vleck [34], Öpik and Pryce [35], Liehr [36], Longuet-Higgins [37,38], Bersuker [30,39–43], and many other workers (for further details, see the relevant monographs [30,44,45] and reviews [38, 43]). Despite these difficulties, useful information about the potential energy functions may be obtained by LCAO-MO calculations [30,46].

The most promising approach to a quantitative description of the motion of nuclei in the case under consideration consists at present in separating the high-amplitude motion from other types of nuclear motion, specifying a definite type of potential function, and solving the corresponding Schrödinger equation for the vibrational and rotational states of the molecule. However, even this more specific problem is complicated, since the thoroughly developed procedure for calculations in terms of normal coordinates and the standard expansion of the potential energy function in terms of these coordinates is of only limited applicability in this instance. A promising approach involves the use of more general curvilinear coordinates with a corresponding increase in the complexity of the expression for the kinetic energy operator and generalisation of the concept of reduced mass. However, these methods have so far been used only in the study of three-, four-, and five-atomic molecules and molecules with pseudorotation in the rings (see, for example, Refs. 47–53). Still more complicated cases, where it is impossible to separate high-amplitude motion from other types of nuclear motion, have not so far been considered.

The application of electron diffraction to the study of stereochemically non-rigid molecules yielded in all cases a qualitative pattern of nuclear motion and sometimes also complete quantitative information about the parameters of the potential functions of such motion. Quantitative data have in fact been obtained only in relatively simple cases where the potential function depends on only one vibrational coordinate (the one-dimensional vibrational problem). In this case there is a complete analogy with internal rotation. This made it possible to employ in the structural analysis of stereochemically non-rigid molecules the classical form of the probability density function, proposed previously [54,55] in relation to internal rotation. The parameters of the potential energy function are determined in most cases by the method of least squares. Either calculated and experimental scattering intensities (radial distribution functions) [56–58], or calculated and experimental vibration amplitudes, or the internuclear distance contraction effects [59] were then compared.

Since the contribution to the intensity of the scattering of electrons by pairs of nuclei executing high-amplitude motion decays rapidly with increase in the scattering angle, it is sometimes useful and effective to analyse low-angle scattering [60–62].

III. QUASI-LINEAR MOLECULES

The motion of nuclei in quasi-linear molecules is one of the simplest cases of high-amplitude motion, because the only vibrational coordinate describing this motion is the change in the deformation angle α. The dependence of potential energy of the quasi-linear molecule on α is illustrated in Fig. 1. One must note that α varies in the region of positive values ($0 < \alpha < \pi/2$), because the configurations corresponding to the potential minima illustrated in Fig. 1 can be derived from one another by the appropriate rotation of the molecule as a whole. The vibrational potential therefore has actually only one minimum, two minima arising on the curve in Fig. 1 when one considers the section of the potential surface taking into account both the deformation vibration and the rotation of

the molecule as a whole. This type of situation holds for any planar molecules (see Herzberg[17], pp. 39, 239).

The carbon suboxide molecule C_3O_2 [O(1) = C(2) = C(3) = C(4) = O(5)] is the most thoroughly investigated of the quasi-linear molecules. In the first modern electron diffraction study on the C_3O_2 molecule § [63] unusually high values of the so called "contraction effect" (see Cyvin[64], Chapter XIV) and the vibration amplitudes of pairs of nuclei, the distances between which vary during the deformation vibration, were already observed. The measured quantities did not agree with the theoretical calculations in terms of the approximation of low-amplitude harmonic vibrations[65]. In their experiments at different temperatures (237, 290, and 508 K) the authors[63] attempted to determine the temperatures of the C_3O_2 vapour flowing from the nozzle on the basis of the measured vibration amplitudes and contraction effects. Despite the failure of this attempt, the conclusion that the ν_7 deformation vibration of the C=C=C fragment is not described by a harmonic function must be regarded as an important result of this study[63]. The equation proposed[63] for the potential is (Fig. 1)

$$V(q) = Aq^4 + Bq^2, \qquad (4)$$

where A and B are constants and q represents half the deviation of the C=C=C angle for the linear value:

$$q = \frac{180^\circ - \angle(C{=}C{=}C)}{2}.$$

According to the authors' estimate, the barrier for the linear configuration is in the range 40–255 cm^{-1}.

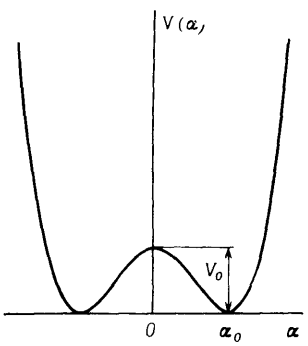


Figure 1. The potential function for the deformation vibration of quasi-linear molecules.

The C_3O_2 molecule was thoroughly reinvestigated by electron diffraction in another study[59], attention being concentrated on the potential function of the deformation vibration of the C=C=C fragment. Using this function, as defined by Eqn. (4), Tanimoto et al.[59] obtained the following expression by analysing the experimental data

$$V(Q_7) = (24 \pm 5) Q_7^4 - (100 \pm 31) Q_7^2, \qquad (5)$$

where $Q_7 = (\sin\alpha)/0.145$ is the vibrational coordinate of the deformation of the C=C=C fragment (α has the same significance as q in the previous notation). The positions of the potential minima correspond to $\alpha_0 = \pm 12^\circ$ and the height of the potential barrier at $\alpha = 0$ is 100 ± 47 cm^{-1}, the electron diffraction data proving virtually insensitive to the presence or absence of this barrier.

Using Eqn. (5) for the potential of the deformation vibration of the C=C=C fragment and the harmonic approximation for other types of vibration, the authors[59] obtained a satisfactory agreement between the calculated and experimental mean square vibration amplitudes and contraction effects. The vibrational-rotational ν_7 band was also calculated by Eqn. (5) and its maximum proved to be at 70 cm^{-1}, which differs slightly from the experimental value 63 ± 2 cm^{-1}.[66,67]

The deformation vibration of the C=C=C fragment has been examined theoretically[68] on the basis of spectroscopic and electron diffraction data. Using the method of Thorson and Nakagawa[31], Clark and Seip[68] established by solving the Schrödinger equation for the vibrational and rotational states of the molecule that a potential function of the type

$$V(r) = 2400r^2 + \frac{14000}{2.2 + r^2}, \qquad (6)$$

where $r = \alpha r$[C(3)=O(5)] with minima at $\alpha_0 = \pm 10.8^\circ$ and a barrier 50.6 cm^{-1} high at $\alpha = 0$, describes satisfactorily both spectroscopic and electron diffraction data. Calculation of the position of the absorption band maximum corresponding to the ν_7 vibration by Eqn. (6) yields a value in the range 65–69 cm^{-1}, in good agreement with the experimental value $\nu_7 = 63 \pm 2$ cm^{-1}.[66,67] The parameters of the calculated peak of the radial distribution curve, corresponding to the distance between the oxygen atoms, agree just as well with the results of the electron diffraction experiment at 237 and 508 K.

It has also been concluded[68] that electron diffraction data are not unduly sensitive to the detailed form of the potential describing the ν_7 vibration. The potential function (6) and equations of the type

$$V(r) = \text{const}, \text{ when } |\alpha| < 10.8^\circ \text{ and}$$
$$V(r) = 2400r^2 + \frac{14000}{2.2 + r^2}, \text{ when } |\alpha| \geqslant 10.8^\circ \qquad (7)$$

describe with almost equal accuracy the experimental peak of the radial distribution curve corresponding to the distance between the oxygen atoms.

Another important result obtained in the above investigation[68] was that the use of the classical probability density function

$$P(\alpha) = N e^{-\frac{V(\alpha)}{kT}}$$

leads to virtually the same parameters of the peak on the radial distribution curve corresponding to the distance between oxygen atoms as the quantum-mechanical expression based on the use of 93 vibrational-rotational wave functions in combination with the Boltzmann distribution.

Numerous spectroscopic studies on the carbon suboxide molecule[66,67,69–74] demonstrated a complex structure of the absorption spectra. The absorption bands were assigned and the fine structure and the complex shape of the bands as well as the presence of numerous "hot" bands were explained by experimenters on the basis of potentials of types (4)–(6) for the ν_7 vibration. The problem of the C_3O_2 molecular structure therefore appeared to be solved in broad outline.

§ We shall not consider the earlier electron diffraction studies (see, for example, the compilation in Ref. 1).

However, a high-resolution infrared spectrum (0.3 cm^{-1}) was obtained in 1973 in the range 20–80 cm^{-1} as well as the Raman spectra of the C_3O_2 molecule in the vapour phase and in the crystalline state [75]. Analysis of the set of experimental data obtained enabled the authors [75] to suggest that the absorption frequency observed in the region of 61 cm^{-1} may be assigned to the 0,0 → 2,2 vibrational-rotational transition. The frequency ν_7 was found to be 22 cm^{-1} in contrast to the results of all previous studies. The new value of ν_7, obtained in the most accurate of the known investigations [75], throws doubt on the validity of the interpretation of the previous spectroscopic and electron diffraction data. It may be that one must resort to the concept of a strong vibronic interaction in the C_3O_2 molecule (the Jahn–Teller pseudoeffect) in order to eliminate the discrepancy observed between electron diffraction and spectroscopic data. At any rate, it appears desirable to repeat the electron diffraction and spectroscopic studies of the carbon suboxide molecule, the correct interpretation of which may serve as a key to the interpretation of the experimental data for many other molecules of different classes.

Among the electron diffraction studies where the experimental data were also interpreted from the standpoint of the quasi-linear model, mention should be made of the investigation of silyl isocyanate ($H_3Si-N=C=O$) and silyl thioisocyanate ($H_3Si-N=C=S$) molecules [76] as well as indium subselenide and subtelluride [77,78]. The usual harmonic approximation for the potential function of the deformation vibration of the silyl thioisocyanate skeleton agrees with experimental data, while for the silyl isocyanate molecule agreement with experiment is achieved using a potential of the type

$$V(\alpha) = -300\alpha^2 + 1090\alpha^4 \qquad (8)$$

with minima at $\alpha_0 = \pm 28°$ and a barrier 20 cm^{-1} high at $\alpha = 0$.

An electron diffraction study of the high-temperature indium subselenide and subtelluride vapours [77,78] established that the deformation vibrations are described by the potential functions

$$V(\alpha) = 12816\alpha^4 - 3280\alpha^2 \ (In_2Se), \qquad (9)$$

$$V(\alpha) = 18080\alpha^4 - 3376\alpha^2 \ (In_2Te). \qquad (10)$$

The first function has minima at $\alpha_0 = \pm 21°$ and a barrier 210 cm^{-1} high at $\alpha = 0$. Analogous data were obtained also for the second function: $\alpha_0 = \pm 18°$ and a barrier 157 cm^{-1} high.

IV. BICYCLIC MOLECULES

Electron diffraction studies on bicyclo[2,2,2]octane [57] and triethylenediamine [79] showed that these molecules have a "quasi-D_{3h}" symmetry, i.e. there is a possibility of high-amplitude torsional vibrations about the C_3 axis (see Fig. 2). These vibrations are described satisfactorily by a potential function of the type

$$V(\Phi) = k_2\Phi^2 + k_4\Phi^4, \qquad (11)$$

where Φ for the bicyclo[2,2,2]octane molecule is the dihedral angle between the C(1)C(2)C(3) and C(2)C(3)C(4) planes—the so called torsional angle. The potential for the triethylenediamine molecule has a similar form. The energy barriers in the torsional vibrations were found to be 35 cm^{-1} [57] and 30 cm^{-1} [79] for bicyclo[2,2,2]octane and triethylenediamine respectively, and the mean square values of the angle Φ are 12.8° and 11.0° respectively.

The electron diffraction data agree well with the results of X-ray diffraction studies on the same molecules [80,81]. The substitution of one hydrogen atom in bicyclo[2,2,2]-octane and triethylenediamine by a chlorine atom increases the barriers to 46.8 and 66.8 cm^{-1}, while the equilibrium angles Φ_e are respectively 16.2 and 16.4° according to the results of microwave studies on the above molecules [82,83].

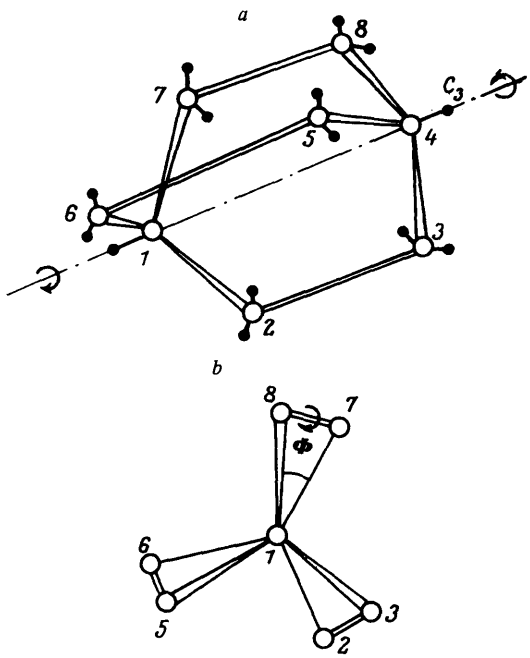


Figure 2. Torsional vibrations in the bicyclo[2,2,2]-octane molecule: *a*) configuration with D_3 ["quasi"–D_{3h}) symmetry; *b*) view along the C_3 axis.

V. ORGANIC MOLECULES WITH FIVE-MEMBERED RINGS AND INORGANIC HALIDES

1. Pseudorotation in Five-membered Rings of Organic Molecules

The concept of "pseudorotation" was introduced for the first time by Pitzer and coworkers [84–86] in order to account for the high entropy of gaseous cyclopentane. According to this concept, there is a continuous migration ("rotation") of the maximum deformation of the plane of the ring along the latter in the cyclopentane molecule and not simply out-of-plane vibrations. These vibrations represent the motion of the atomic nuclei without a significant contribution to the rotational moment of the molecule. The pseudorotation of five-membered rings is a more complex intramolecular motion than the deformation of linear molecules or torsional vibrations in bicyclic systems described above. This motion can be described by two

vibrational coordinates, the phase Φ and the amplitude q of the pseudorotation linked by the expression

$$Z_j = \sqrt{\frac{2}{5}} q \cdot \cos\left[2\left(\frac{\pi}{5} j + \Phi\right)\right], \qquad (12)$$

where q is the deviation of the nucleus of the carbon atom from the plane (two-dimensional vibrational problem).

If it is assumed that the change in the coordinate q is described by the harmonic potential function

$$V(q) = \frac{k}{2}(q - q_0)^2 \qquad (13)$$

and that pseudorotation takes place virtually freely, it is possible to separate the motions along the two coordinates. Pitzer and coworkers [85] established on the basis of this approximation that $q_0 = 0.472$ Å for this molecule.

Further thermodynamic studies on cyclopentane [87-89] as well as semiempirical quantum-mechanical calculations of the energy of this compound [90-92] confirmed Pitzer's dynamic model. However, direct experimental confirmation of pseudorotation in cyclopentane was obtained for the first time in a study of the infrared spectrum of this compound [93]. The same workers [93] determined $q_0 = 0.479$ Å, which agrees well with the thermodynamic value found previously by Pitzer and coworkers [84-86].

According to modern ideas about the structure of five-membered rings, pseudorotation may be regarded as the superposition of two types of motion: the out-of-plane ring vibrations where one of the atoms is displaced from the plane (the "envelope" conformation with C_S symmetry) and torsional ring vibrations where two atoms are displaced simultaneously from the plane (the "half-chair" conformation with C_2 symmetry) [47,94] (Fig. 3). Pseudorotation can therefore be described as continuous transitions between configurations with C_2 and C_S symmetries (in all, ten configurations for each type of symmetry in a single pseudorotation cycle).

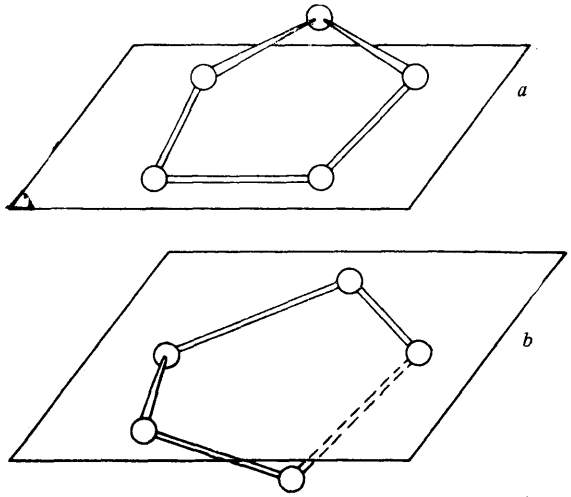


Figure 3. Conformations of five-membered cyclic molecules: *a*) "envelope" type (C_S symmetry); *b*) "half-chair" type (C_2 symmetry).

An electron diffraction study on cyclopentane [95] agreed fully with thermodynamic [84-86] and spectroscopic [93] studies and confirmed Pitzer's ideas concerning the complex motion of the nuclei in the molecule. However, the authors of the electron diffraction study [95] used a somewhat different dynamic model, where a vector S_j (j = 1, 2, ..., 5), defining the instantaneous position of a ring carbon atom, was introduced. During pseudorotation, each carbon atom moves in the vertical plane, passing through the given atom and the centre of the ring, the distance between the carbon atom and the centre of the ring being constant. Pseudorotation is also described by the two vibrational coordinates q and Φ, but in the given model the marked dependence of the C–C bond lengths on the displacement Z_j is eliminated. It was found that $q_g = 0.427$ for the effective displacement of the carbon atom from the plane (the subscript g denotes a value averaged with respect to temperature under the conditions of the electron diffraction experiment), which is somewhat less than the value obtained previously by Pitzer and coworkers [84-86] and in a spectroscopic study [93]. The equilibrium value $q_e = 0.438$ Å was also calculated [95] for the adopted anharmonicity constant of the out-of-plane vibrations $a = 2.0$ Å^{-1}. The difference between the values of q obtained in the electron diffraction [95] and spectroscopic [93] studies can be explained by the fact that the molecular parameters determined spectroscopically and by electron diffraction have a different physical significance (see, for example, Kuchitsu and Cyvin [6]).

Ab initio quantum-mechanical calculations on the cyclopentane molecule [96] confirmed the conclusion that the motion which depends on the angle Φ is virtually free and that $q_e = 0.43$ and 0.48 Å agrees well with the value determined by the electron diffraction method [95]. According to the authors' estimate [96], the height of the barrier separating the two configurations is in the range 4–8 kcal mole^{-1}.

Molecules containing a double bond [sic! a heteroatom?] in the five-membered ring have also been studied by electron diffraction: tetrahydrofuran [97-99], and 3-bromotetrahydrofuran [100]. In the first study [97], devoted to tetrahydrofuran and carried out at an earlier stage of the development of the electron diffraction method, only the planar model of the molecule was considered. A later investigation [98] established that the molecule has a non-planar structure. However, a satisfactory agreement between the theoretical and experimental intensity curves was not obtained for the individual models with C_S and C_2 symmetry (Fig. 3). Best agreement was achieved when the "envelope" and "half-chair" conformations were superimposed: $\alpha_1 C_S + \alpha_2 C_2$ (here α_1 and α_2 are the percentage contents of the forms with C_S and C_2 symmetry respectively) with $\alpha_1 \simeq \alpha_2$. This finding was interpreted [98] as evidence for the virtually free pseudorotation, the difference between the energies of the two conformers (C_S and C_2) being small and amounting to 0–3 kcal mole^{-1}.

A model of the pseudorotation of the five-membered ring, analogous to that used [95] for cyclopentane, was resorted to in an electron diffraction study [99] undertaken to interpret the experimental data for the tetrahydrofuran molecule. In this case too the model eliminates a marked dependence of the C–C and C–O bond lengths on the vibrational coordinates q and Φ. The average value of q_g was found to be 0.38 ± 0.02 Å, which is somewhat less than the spectroscopic value $q_0 = 0.470 \pm 0.025$ Å.[101]

Nevertheless one should note that the results of electron diffraction studies do not permit the conclusion whether or not the molecule is statically distorted or whether pseudorotation takes place in it. However, it has been established spectroscopically [48] that the C_2 form is energetically more favourable, while the C_S form has an energy higher by 1277 cm^{-1}.

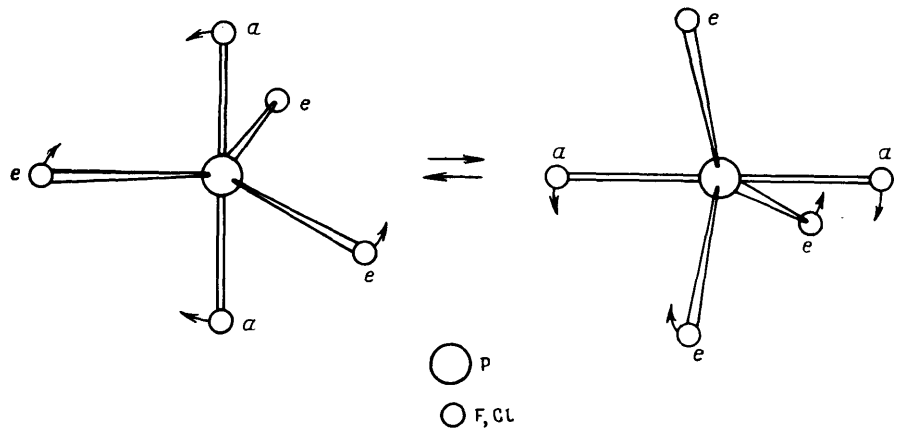


Figure 4. Schematic representation of the pseudorotation in the molecules of the phosphorus pentahalides PF_5 and PCl_5.

Apart from the electron diffraction determination of the molecular structure of 3-bromotetrahydrofuran, Smith et al.[100] also calculated the energies of its conformations by the Westheimer–Hendrickson method. They showed that the best agreement between the theoretical and experimental intensities is achieved on the hypothesis of almost free pseudorotation of the ring. The small energy differences between different conformations (of the order of 0.5 kcal $mole^{-1}$), found by conformational analysis, confirmed the results obtained by electron diffraction.

The electron diffraction data for other molecules with five-membered rings showed that the replacement of the oxygen atom by S, SiH_2, Se, CO, and GeH_2 leads to a greater stability of the C_2 form, the heteroatom or atomic group being displaced from the plane of the ring by approximately 20° during the vibrations[102]. The energy difference between the C_2 and C_S forms increases in the above sequence according to spectroscopic data[103-105].

2. Pseudorotation in Inorganic Halides

Pseudorotation in inorganic halides is a three-dimensional analogue of the high-amplitude intramolecular motion in five-membered cyclic organic molecules. Using these molecules as an example, it is possible to demonstrate that the characteristic duration of the experiment, which is different for different physicochemical methods used to study this problem (see Table), is significant for the observation of high-amplitude intramolecular motion.

An electron diffraction study of the PF_5 [106,107] and PCl_5 [107] molecules established that halogen atoms occupy two different positions—axial (*a*) and equatorial (*e*). The molecular model is described by the D_{3h} symmetry point group and the bond lengths P–X(a) > P–X(e) (X = F or Cl). However, the NMR spectrum of PF_5 [108] indicates the complete equivalence of the fluorine atoms in the (*a*) and (*e*) positions, which served as the basis for the hypothesis of intramolecular exchange of fluorine atoms[14,109,110]. Analogous results have been obtained for the PCl_5 molecule[111-113]. The discrepancy between the electron diffraction and NMR measurements can be accounted for by the fact that the characteristic time of the NMR experiment (see Table) is apparently significantly longer than the time required for the exchange of fluorine atoms. Only the average picture of the intramolecular motion is therefore observed in this instance. On the other hand, it may be that the characteristic time of the electron diffraction experiment (see Table) is shorter than the exchange time of the halogen atoms. Because of this, at each instant the electron diffraction method records only the "instantaneous" picture of the scattering process in which halogen atoms occupy only the two most probable positions relative to the phosphorus atom, i.e. (*a*) and (*e*). For the same reason, the electron diffraction method cannot distinguish the possibilities involving the intramolecular motion in PF_5 and PCl_5 molecules as a result of which halogen atoms change places, on the one hand, or the static non-equivalence of the positions of these atoms, on the other.

Berry[109] and other workers[21-23,25,114-116] put forward the hypothesis that the exchange of axial and equatorial halogen atoms in phosphorus halides is a three-dimensional analogue of the pseudorotation in the five-membered rings of organic molecules (Fig. 4). Analysis of the Raman spectra of the PF_5 molecule in the gas phase made it possible to determine the pseudorotation barrier as 5.7 kcal $mole^{-1}$.[117]

As in phosphorus pentahalides, pseudorotation is observed in the heptafluorides of rhenium (ReF_7) and iodine (IF_7). The first electron diffraction study of the IF_7 molecule, carried out[118] using a visual method for estimating the electron scattering intensities, established that the nuclear configuration in this molecule is close to that of a pentagonal bipyramid (D_{5h} symmetry) in which five fluorine atoms are located in the equatorial plane, two fluorine atoms are on the axis, and the iodine atom is in the centre. According to LaVilla and Bauer[118], the fluorine atoms in the equatorial plane, which form a five-membered ring, are involved in a pseudorotatory motion, analogous to that described above for atoms in the rings of organic molecules.

The electron diffraction study of the IF_7 [119,120] and ReF_7 [119,121] molecules was repeated by Bartell and coworkers. Analysis of the results made it possible to establish reliably that the geometry of these molecules corresponds to the D_{5h} symmetry only approximately. Comparison of the theoretical intensity curve corresponding to the proposed model having D_{5h} symmetry with the experimental curve showed that the mean square vibration amplitudes for the non-bonded fluorine atoms

[$l_g(Fe...Fe)$ = 0.254 Å and $l_g(Fa...Fe)$ = 0.236 Å were obtained for ReF_7] are unduly high compared with the usually observed amplitudes for non-bonded pairs of atoms [cf. ReF_6 molecule [122]: $l_g(Fe...Fe) \simeq l_g(Fa...Fe)$ = 0.091 Å].

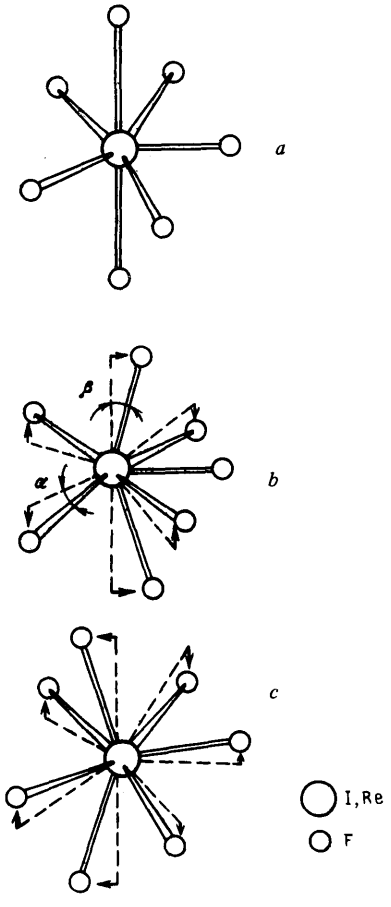


Figure 5. Models of the IF_7 and ReF_7 molecules with different symmetries: *a*) D_{5h}; *b*) C_2; *c*) C_S. The arrows in parts *b* and *c* indicate the directions of the deviations from the configuration with D_{5h} symmetry.

Bartell and coworkers [120,121] considered the following two alternative types of models of the IF_7 and ReF_7 molecules. In the first type static deformation is postulated—the displacement of fluorine atoms from the plane of the five-membered ring—described by the relation

$$\alpha_j = \alpha^0 \cos\left[2\left(\frac{2}{5}\pi j + \Phi_e\right)\right], \quad (14)$$
$$j = 1, 2, \ldots, 5,$$

where α^0 is the maximum angular deviation of fluorine atoms from the equatorial plane and Φ_e is the phase of the displacement of the same atoms. For $j = n\pi/10$ (n is an integer), we obtain a molecular model with C_S symmetry, while $j = (2n + 1)\pi/10$ yields a model with C_2 symmetry.

The angular displacement of the axial fluorine atoms is described by an analogous relation:

$$\beta_i = \beta^0 \cos\left[2\left(\frac{2}{5}\pi i + \Phi_a\right)\right], \quad (15)$$

where β^0 is the maximum angular displacement of fluorine atoms from the C_5 axis, and Φ_a the phase of the displacement of the same atoms. From symmetry considerations, we have $\Phi_a = 4\Phi_e$. It was found that $\alpha^0 = 7.51$ and $\beta^0 = 4.55°$ for IF_7 and $\alpha^0 = 8.78$ and $\beta^0 = 7.65°$ for ReF_7. The molecular models are illustrated in Fig. 5. It is noteworthy that, both for models with C_S and C_2 symmetries and for their superposition $\alpha_1 C_S + \alpha_2 C_2$ with different statistical weighting factors α_1 and α_2, the factors governing the discrepancies between theoretical and experimental intensity curves proved to be fairly close, so that it was impossible to select any one of these models or their superposition.

The authors [120,121] put forward a dynamic pseudorotation model as the second possible interpretation of the experimental data for the ReF_7 and IF_7 molecules. It can be described as a continuous transition from the configuration with C_2 symmetry to one with C_S symmetry (Fig. 5). The motion of fluorine atoms in the equatorial plane is analogous to that on pseudorotation in the cyclopentane molecule. As a consequence of the strong interaction of vibrations of the e_2'' and e_1' type, the motion of the fluorine atoms in the equatorial plane is correlated with the motion of the axial atoms. Such interaction can be represented as the maximum "avoidance" of the fluorine atoms in the equatorial position involved in free pseudorotation by the axial fluorine atoms in the coordination sphere of the central atom.

Thus the electron diffraction method made it possible to establish unambiguously in this case also whether or not the observed distortion of the ReF_7 and IF_7 molecules is static, or whether a dynamic pseudorotation model is valid. However, the use of other experimental methods supports the dynamic model.

The effective dipole moment of the ReF_7 molecule, which increases as the temperature is reduced, has been observed by the method involving the deflection of the molecular beam in a homogeneous electric field [123]. A similar but less pronounced effect was found in the same study [123] also for the IF_7 molecule. These data, which disprove the quasi-rigid structure and demonstrate the temperature dependence of the results of the dipole moment measurements, support the dynamic stereochemically non-rigid molecular model. Furthermore, NMR studies of $Re^{19}F_7$ and $I^{19}F_7$ melts [124] indicate the complete equivalence to fluorine atoms in these compounds. Apart from the pseudorotation of the five-membered ring in these molecules, one may therefore also expect the occurrence of an intramolecular rearrangement leading to the exchange of the equatorial and axial fluorine atoms.

The study of the infrared and Raman spectra of IF_7 [125,126] and ReF_7 [125,127] supported a molecular model with D_{5h} symmetry. However, this does not conflict with the dynamic molecular model under consideration because an average pseudorotation pattern was apparently manifested in the spectroscopic experiment owing to the fact that its characteristic time (see Table) exceeds the time required for the intramolecular exchange.

Pseudorotation of a still more complex type may be postulated in the xenon hexafluoride molecule. The problem of the structure of this molecule has been discussed in a number of studies [128-131]. However, on the

basis of theoretical analysis alone it was impossible to reach a conclusion about the molecular structure of XeF_6. X-Ray diffraction study did not permit the solution of the problem, because the compound does not form single crystals[132]. Spectroscopic investigations[133,134] likewise did not allow definite structural conclusions. The XeF_6 molecule was studied by electron diffraction several times[135-139]. A particularly detailed and thorough investigation was carried out by Bartell and Gavin[138,139] and their results are therefore described below.

The main conclusion which they reached[138,139] is that the molecular structure of XeF_6 in the gas phase cannot be described from the standpoint of a quasi-rigid model with O_h symmetry. Analysis of a wide variety of molecular models (O_h, C_{2v}, C_{3v}, D_{3d}, and C_s) and their linear combinations enabled them to establish that two alternative models may be reconciled with experimental data: (1) a static distortion model (with C_{2v}, C_{3v}, and C_s symmetry); (2) a dynamic model. According to the latter, the deformation vibrations with t_{1u} and t_{2g} symmetry in the XeF_6 molecule interact which leads to the correlation of the motions of the axial and equatorial fluorine atoms and to a distortion of the octahedron to give configurations with C_{2v}, C_{3v}, or C_{4v} symmetry. According to the authors[138,139], motion of this type can explain the virtual absence of an electrical dipole moment of the molecule[140,141] (the dipole moment measurements were performed by the method involving the deflection of a molecular beam by an inhomogeneous electric field), the unusual shapes, and anomalous half-widths of infrared absorption bands[130], as well as entropy data[142].

The nature of the dynamic distortions in the XeF_6 molecule can be clearly described by assuming that it resembles in some way three-dimensional pseudorotation in which fluorine atoms deviate from the octahedral positions by 5–10° as if striving to avoid certain regions in the coordination sphere of the Xe atom. In conformity with the Gillespie–Nyholm theory[143,144] (the theory of the repulsion of the electron pairs in the valence shell), the authors[138,139] identified these regions with the position of the lone electron pair of the Xe central atom, which migrates continuously in its coordination sphere from the position on the diagonal of the square formed by the equatorial fluorine atoms to the centres of the faces of the octahedra formed by one axial and two equatorial fluorine atoms (Fig. 6).

It is noteworthy that, although the idea of a stereochemically active lone electron pair does in general explain correctly the type of distortions in the molecule, nevertheless the theory of the repulsion of the electron pairs in the valence shell predicts much more pronounced distortions of the octahedron than are observed experimentally.

Claassen et al.[145] investigated the infrared, ultraviolet, and Raman spectra of XeF_6 in a matrix and in the gas phase, the Raman spectra and the spectra in the visible and ultraviolet regions being studied as a function of temperature. The authors suggest that, under the experimental conditions, the XeF_6 molecules exist in three electronic states ("electronic isomers"[148]): $^3A_{2u}$ (D_{3h} symmetry), ^3A_u or ^3B_u (C_{2v} symmetry), and A_{1g} (O_h symmetry). They showed[145] that all the spectra which they observed may be interpreted on the hypothesis of three "electronic isomers" of the XeF_6 molecule between which thermodynamic equilibrium is established in the course of approximately 10 min at 100°C. Evidently a reinterpretation of the electron diffraction data from the standpoint of the existence of the XeF_6 molecule in different electronic states is of undoubted interest. The interpretation of the molecular structure of XeF_6 in such a case requires in essence that one resorts to the Jahn–Teller pseudoeffect, since conditions under which the pseudoeffect is manifested may exist in the molecule[146-149].

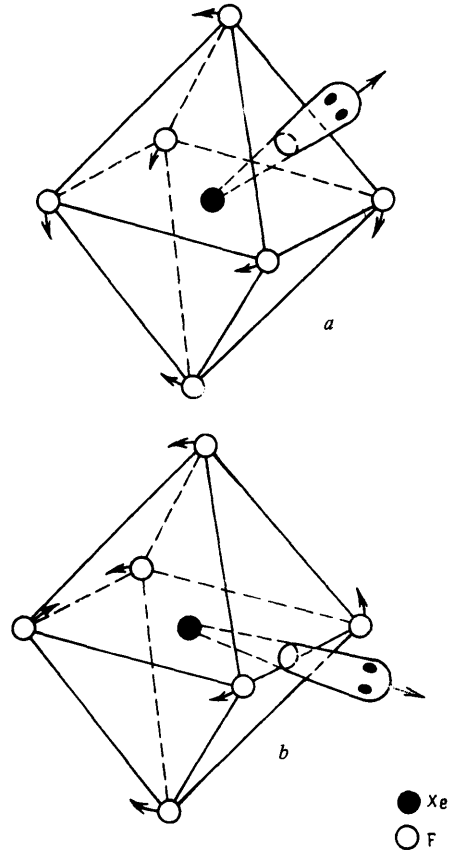


Figure 6. A model of the XeF_6 molecule. The possible positions of the lone electron pair on a face (*a*) and edge (*b*) of the octahedron and the directions of the distortions of the latter caused by the electron pair are shown.

The dynamic pseudorotation in the ReF_7, IF_7, and XeF_6 molecules described above should presumably be characterised by low frequencies. The following frequencies in the above molecules may be estimated from the electron diffraction data: 4.4 cm^{-1} (ReF_7); 5 cm^{-1} (IF_7); 10 cm^{-1} (XeF_6). Consequently the contribution of the pseudorotation to the thermodynamic functions of the given substances should be very considerable.

VI. JAHN–TELLER MOLECULES¶

Vanadium tetrachloride. The electron diffraction study of the VCl_4 molecule[150,151] was undertaken in order to determine its possible Jahn–Teller distortions, predicted on the basis of studies of the spectra of this compound[152–155] as well as theoretical calculations[45,156–160]. It was impossible to observe significant deviations of the VCl_4 structure from a regular tetrahedron[150,151], although, according to Morino and Uehara[150], the tetrahedron may deviate by 0.05 Å in the direction of the ν_2 stretching vibration. However, the greater amplitude of the vibrations of the Cl...Cl pair of nuclei in the VCl_4 molecule compared with $TiCl_4$ as well as certain other features of the structure and the vibrational spectrum of VCl_4 support, according to the authors[150], the operation of this effect. It appears that the Jahn–Teller distortions of the VCl_4 geometry are small and their measurement corresponds to the limit of the power of the modern electron diffraction method.

Vanadium hexacarbonyl. The molecules of vanadium and chromium hexacarbonyls have been investigated by electron diffraction[161]. Analysis of the experimental data established that the mean square vibration amplitudes of the vanadium atom in the $V(CO)_6$ molecule relative to the environment consisting of carbonyl groups are much higher than the corresponding values for the $Cr(CO)_6$ molecule. This was explained by the Jahn–Teller effect in the $V(CO)_6$ molecule. Schmidling[161] tested two types of models corresponding to the Jahn–Teller distortions of the nuclear configuration—of the Eg type (D_{4h} symmetry) and the T_{2g} type (D_{3d} symmetry). Best agreement was achieved for the model with D_{3d} symmetry and the deviation of the CO group in the direction towards the threefold axis was found to be 5.3°.

Rhenium hexafluoride. An electron diffraction study of the ReF_6 molecule established[122] that its geometrical configuration is described by the symmetry point group O_h. However, a spectroscopic study by Brand et al.[162] indicated the possibility of a Jahn–Teller distortion of this molecule, the displacement of the fluorine atom leading to trigonal (t_{2g} symmetry) distortions of the octahedron to the extent of 0.046 Å. The energy of the Jahn–Teller distortions was found to be 74 cm^{-1}. It is at present apparently difficult to explain the cause of the difference between the conclusions reached in the spectroscopic[162] and electron diffraction[122] studies. Nevertheless one may point out that Jacob and Bartell[122] observed a discrepancy between the theoretical and experimental intensities, which they were able to account for satisfactorily by the effects due to three-atom intramolecular scattering.

¶ The classification of different types of high-amplitude motion employed in the present review is to a large extent arbitrary and is a result of the author's endeavour to reflect the main ideas, terminology, and explanations of the observed effects in the literature quoted. However, as already mentioned to some extent, the results of many of the studies of stereochemically non-rigid molecules discussed in Sections II–V may be accounted for on the hypothesis of a Jahn–Teller pseudoeffect in the molecules and the latter may be regarded as being of the Jahn–Teller type. This also applies to the exposition below.

VII. BIS(CYCLOPENTADIENYL)BERYLLIUM

According to electron diffraction studies[163,164], the two cyclopentadiene rings in the $(C_5H_5)_2Be$ molecule are parallel to one another and mutually staggered, the distance between them being 3.375 ± 0.010 Å. The Be atom is located on a fivefold symmetry axis, which is the same as the two cyclopentadienyl groups, and can occupy two alternative positions at a distance $h_1 = 1.472 \pm 0.06$ Å from one ring and $h_2 = 1.903 \pm 0.008$ Å from the other.

It may be that the structural characteristics of this compound, observed in the electron diffraction experiment, are due to the manifestation of the Jahn–Teller pseudoeffect and that the beryllium atom oscillates between the cyclopentadiene rings along the fivefold symmetry axis. The potential curve describing such motion has two minima corresponding to different distances of the beryllium atom from the planes of the cyclopentadiene rings. This interpretation of the electron diffraction data[163,164] makes it possible to determine the "lifetime" of each configuration, which is 10^{-12}–10^{-13} s according to Ionov and Ionova[165], and the most probable barrier to the transition between the two configurations is in the range 1.4–2.9 kcal $mole^{-1}$.

VIII. MOLECULES OF OXYACID SALTS AND CERTAIN COMPLEX HALIDES

Electron diffraction studies on a number of alkali metal and thallium(I) metaborates[166–168], sulphates[169–171], chromates[169], perrhenates[172,173], molybdates[171,174], and nitrates[175–178] as well as complex compounds of the type $M^IM^{II}Hal_4$[179–181] and $M^I\ {}^{II}Hal_3$[182] (Hal = halogen and M^I, M^{II}, and M^{III} are Group I–III metals) yielded experimental data which have many characteristic features in common. In particular, it was observed that the electron diffraction patterns of these compounds contain only a limited amount of information about the position of the metal atom relative to the acid residue in molecules of the oxyacid salts and relative to the $M^{III}Hal_4$ (or $M^{II}Hal_3$) fragment in the complex compounds, revealed mainly in the region of low scattering angles. This situation is observed for both light and heavy atoms and cannot be explained simply by their low scattering capacity. A similar phenomenon has been called the "elution" effect[183]. It appears that it can be explained in many instances by an increase of the mean square vibration amplitudes of certain pairs of nuclei as a consequence of the increase in the populations of the excited vibrational levels of the molecule[183]. This appears to be a quite natural consequence of the influence of the high experimental temperature, particularly when the molecule executes low-frequency vibrations.

However, the above explanation, which is valid within the framework of the quasi-rigid molecular model, is inadequate for the salts of oxyacids and the complex compounds, because it is difficult to account for the above features of the experimental data simply by an increase in the populations of the excited vibrational levels. It appears much more natural to postulate a continuous change in molecular configuration as a result of the displacement of the metal atom relative to the quasi-rigid fragment (the acid residue, $M^{III}Hal_4$, or $M^{II}Hal_3$). Such a dynamic stereochemically non-rigid molecular model is apparently a general characteristic feature of the structures of many oxyacid salts and complex halides and

possibly also other classes of compounds. We shall now consider the results of the electron diffraction studies in greater detail.

The electron diffraction patterns of alkali metal metaborates [166-168] in general correspond to the symmetrical linear BO_2 fragment and the low contribution to the overall scattering by the metal atom hinders the determination of its position. In electron diffraction studies on caesium [169,171], potassium [169], and thallium(I) [170,171] sulphates, potassium chromate [169], and thallium(I) nitrate [177,178], agreement between the experimental and theoretical density curves within the framework of a single quasi-rigid model can be achieved only for anomalously high vibration amplitudes of the metal atom relative to the oxygen atoms of the acid residue (l_g = 0.15–0.25 Å). The fragment of the acid residue then has a structure close to that of a regular tetrahedron for salts of the type M_2EO_4 (E = S or Cr; M = K, Cs, or Tl) or of an equilateral triangle in the case of thallium(I) nitrate (the non-equivalence of the angles at the central atom has been estimated [166-177] as ±5°, while the possible non-equivalence of the bond lengths does not exceed 0.1 Å). An electron diffraction study of the $TlNO_3$ molecule established [177] that best agreement between the theoretical and the experimental intensity curves is attained for a superposition of models of this molecule having different symmetries ($\alpha_1 C_S$ + $\alpha_2 C_{2V}$ + $\alpha_3 C_{3V}$) with the greatest contribution by the model with C_{2V} symmetry (α_2 = 71%).

Thus, in conformity with electron diffraction data, in the oxyacid salts quoted above there is a high symmetry of the acid residue in combination with a high mobility of the metal atom. This picture of the structures of many oxyacid salts has been confirmed by spectroscopic data. Thus studies of the infrared spectra of the vapours of the metaborates of certain elements [184-186] failed to detect the vibration frequency of the metal atom relative to the BO_2 fragment and the observed frequencies in the range 600 to 1940 cm^{-1} are due to the vibrations of the BO_2 group and were found to be almost independent of the metal atom to which the group is attached. Similar results, indicating a weak dependence of the NO_3 and SO_4 vibrations on the nature of the metal atom, were obtained also in studies of the infrared spectra of univalent metal nitrates in a matrix [187] and in the gas phase [188] and of univalent metal sulphates [189].

Virtually analogous results were obtained in electron diffraction studies on the $NaAlF_4$, [179] $KAlCl_4$, [180] $KYCl_4$, and $TlInCl_4$ [181] molecules. It was established that the $MHal_4$ fragments in these compounds have a configuration close to that of a regular tetrahedron [within the limits of the errors in the measurements of the angles, which have been estimated [179-181] as ±5°, and the possible non-equivalence of the M^{III}–Hal bond lengths (<0.1 Å)]. The univalent metal atoms are located on a line perpendicular to one of the edges of the tetrahedron. An electron diffraction study of M^IBeF_3 molecules (M^I = Na or K) [182] showed that the BeF_3 fragment has a configuration close to that of an equilaterial triangle and that the metal atom is located within the plane of the triangle on a line perpendicular to one of its sides. A characteristic feature of the studies on complex salts of both types is anomalously high vibration amplitudes of the metal atom relative to the quasi-rigid $M^{III}Hal_4$ or $M^{II}Hal_3$ fragment (for example, 0.19 Å in $TlInCl_4$ [181]). This makes it possible to treat the observed configurations as the most probable and the molecular structures of these compounds should be described with the aid of a dynamic stereochemically non-rigid molecular model, fully analogous to the model discussed above in relation to oxyacid salts.

The results of *ab initio* quantum-chemical calculations on the LiNC molecule by Clementi and coworkers [190,191], *ab initio* calculations on the $LiBO_2$ molecule [102], calculations by the LCAO-MO semiempirical method on the $LiNO_3$ and $TlNO_3$ molecules [193], as well as calculations on the dependence of the electrostatic energy of the interaction between the cation and anion on the spatial position of the metal ion for $CsNO_3$ and $TlReO_4$ molecules, carried out [194] using an ionic model (Fig. 7), are of undoubted interest in connection with the problem under consideration.

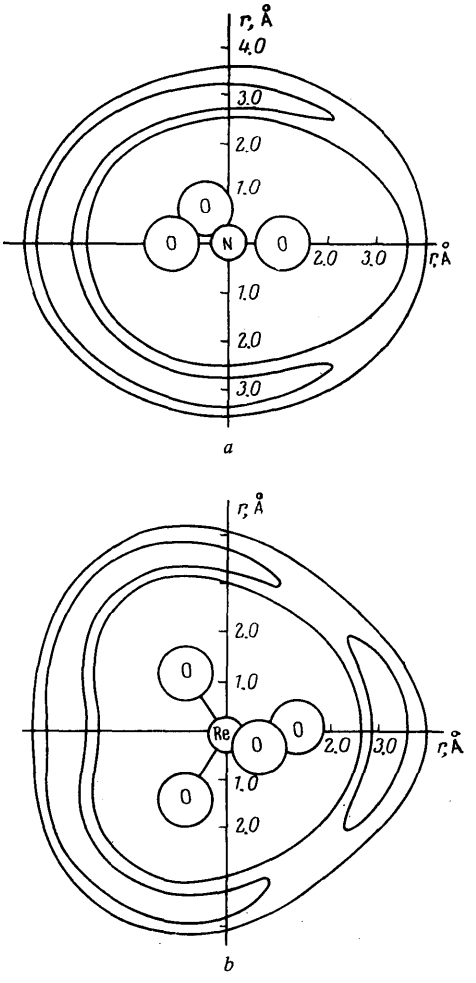


Figure 7. A map of the potential energy surface for the motion of the metal atom relative to the acid residue: *a*) $CsNO_3$; *b*) $TlReO_4$.

The electronic structure of the LiNC molecule has been calculated [191] for different positions of the metal atom relative to the NC fragment. The calculated maps of the energy surfaces for the motion of the Li atom showed that there is virtually no energy barrier between the Li–C≡N

and Li–N≡C configurations. On thermal excitation (energy about 0.3 eV), the Li atom rotates freely about the NC group.

Virtually analogous results were obtained also in quantum-chemical calculations on $LiBO_2$ [192] and $TlNO_3$ [193] molecules.

Thus the results of quantum-chemical calculations have fully confirmed the conclusions reached in electron diffraction studies concerning the stereochemical non-rigidity of the molecules of many oxyacid salts.

This exhausts, for the present, the list of electron diffraction studies in which experimental data were clearly interpreted from the standpoint of the stereochemically non-rigid molecular model. However, one cannot rule out the possibility that experimental studies on many organic and inorganic compounds, in the explanation of the results of which a quasi-rigid molecular model has been used, can also be interpreted from the standpoint of the stereochemically non-rigid molecular model.

IX. CONCLUSION

The extensive experimental electron diffraction data available at the present time have shown, in agreement with the results derived by other physicochemical methods, that complex nuclear motions are executed in molecules of different classes, namely high-amplitude motions. They lead to important chemical consequences.

In the first place this concerns the classical ideas about the geometrical configurations of molecules and their symmetry. The classical structural theory is based in essence on the coordinates of the minima in a multidimensional potential energy surface, whose set forms a fixed geometrical configuration with a definite point symmetry, and not on physically determined spatial positions of the nuclei in the molecule. Therefore, if a nucleus in the molecule executes a high-amplitude motion, then under certain conditions (see Section II) the positions of the potential energy minima lose the significance of the spatial characteristics of the nuclear system and the molecular structure cannot be described, in principle, by a time-invariant geometrical configuration with fixed positions of the nuclei (and its point symmetry). In this case only the solution of the corresponding wave equation for the motion of the nuclei (if necessary, taking into account non-adiabatic corrections) and the determination of the probability density function for the distribution of the nuclei yields an adequate (although not unduly clear) picture of the structure. With the aid of this function, it is possible, in principle, to calculate the probability of any location of the nuclei. In this connection one must mention Liehr's study [36], where the quasi-rigid molecular model was subjected to a serious criticism and an attempt was made to develop a more general approach to the description of nuclear subsystems, including the construction of the complete potential energy surface.

The next problem which must be considered concerns the nature of the chemical bond in stereochemically non-rigid molecules. We shall examine it in relation to salts of oxyacids and complexes. It was shown above that in molecules of these compounds there is virtually free rotation of the metal atom about the acid residue or the $M^{III}Hal_4$ and $M^{II}Hal_3$ fragments. This shows that the theory of the chemical bond, in particular the theory of directional valence, is unsuitable for the description of the electronic structures of these molecules.

A specific feature of the chemical bond involving the metal atom in the compounds under consideration is its delocalisation in the molecule—its dynamic, distributed nature. This is not a bond between any pair of atoms, but a bond formed by the metal atom with the acid residue (or the $M^{III}Hal_4$ and $M^{II}Hal_3$ fragments) as a whole. In order to stress this feature of the bond, Clementi [191] suggested that it be called a polytopic bond and that the molecules containing such bonds should also be referred to as "polytopic" molecules. The nature of the polytopic bond is apparently close to that of the bond in ionic crystals, where there is also no appreciable bond directionality.

Another characteristic feature of the chemical bond under consideration consists in the relatively weak distorting influence of the metal atom on the acid residue (or $M^{III}Hal_4$ and $M^{II}Hal_3$ fragments), which is a consequence of the migration of the metal atom. However, according to thermodynamic studies (see, for example, Cubicciotti [195]), there are no grounds for the assumption that this bond is energetically weak and that the corresponding molecule is thermally unstable.

We may note that the experimental and theoretical studies which have been carried out have in essence merely posed the problem of polytopic bonds and that the multiplicity of questions which have arisen still require an answer. For example, the elucidation of the role of vibronic interactions in high-amplitude motions may be regarded as a problem of this kind. If the vibronic interaction is intense, the electronic spectra of molecules cannot be treated separately from nuclear motion, which leads to the necessity for a radical revision of the ideas about the nature of the chemical bond.

The accumulation of experimental data on stereochemically non-rigid molecules is important also for many other chemical problems. Thus tunnelling effects play an appreciable role in the kinetics of chemical reactions, particularly at low temperatures. The problem was formulated for the first time by Bourgin in 1929 [196] and was analysed in detail theoretically in a number of other studies [197–200]. Pearson [201] attempted to regard the activation energies of uni- and bi-molecular reactions on the basis of the analysis of the orbital symmetries of the electronic states of the molecules involved in the reaction and the influence of close excited electronic states. This approach is extremely important for the understanding of the mechanisms of intramolecular rearrangements.

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