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The Concept of Vibronic Interactions in Present-day Chemistry

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The present review deals with the chemical aspects of a new concept in the structure and properties of molecules and crystals, namely the concept of vibronic interactions, where the movements of the electrons and the nuclei are not described separately, and account is taken of the mixing of electronic states by the displacements of the nuclei. The applications of this concept to the description of vibronic structure by means of orbital vibronic constants, vibronic reactivity, and chemical activation on coordination, and to electron-conformational interactions, have been examined. The concept of vibronic interactions provides a basis for a deeper understanding of the origins of the structure and transformations of molecular systems.
The bibliography contains 48 references.

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I. INTRODUCTION

The structure and properties of a molecular system are determined by the motion of its electrons and nuclei, and the interaction between them. The principal laws governing this motion were established in the thirties, immediately after the discovery of quantum mechanics. Because of the mathematical difficulties, restricting but physically justified approximations are introduced in the quantum-mechanical description of the properties of molecules. The most general of these is the Born–Oppenheimer adiabatic approximation (see, for example, Refs.1 and 2), according to which, in view of the very large difference between the masses of the electrons and the nuclei, and hence the appreciable difference in their rates of movement, it is possible to establish the steady motion of the electrons for each instantaneous position of the nuclei. In other words, the electrons follow the motion of the nuclei in inertialess fashion (adiabatically), and the nuclei move in the averaged field created by the electrons.

Thus in this approximation the electrons are assigned only the general ("classical") role of the sources of the average electrostatic field, and the details of the electronic structure do not appear in the description of the motion of the nuclei.

Also in the thirties, some of the most obvious departures from the adiabatic approximation were understood. In 1934, Landau, in a conversation with Teller, first put forward the idea that when there is electronic degeneracy (two or more electronic states with the same energy), the nuclear configuration may be unstable, and undergo spontaneous deformation. This idea, subsequently verified by Jahn and Teller for all types of (non-linear) molecules, formed the basis of the Jahn–Teller theorem, whose consequences are now widely used to analyse the structure and properties of polyatomic systems.[1–5] When the so-called Jahn–Teller effect operates, the electrons do not follow the nuclei adiabatically, and the state of the latter is determined not by the average field of the electrons but by its details, which depend, in particular, on the nature of the degeneracy. The consequent complex relationship between the electronic and nuclear movements is the first and an extremely significant departure from the adiabatic approximation. Cases of degeneracy in the ground state of a molecule are themselves fairly frequent, and their number increases greatly when account is taken of excited states (without which a sufficiently complete study of the structure and properties of molecules is impossible).

In 1957, Opik and Pryce[6] were the first to point out that phenomena analogous to the Jahn–Teller effect may be encountered when there is quasi-degeneracy (pseudo-degeneracy), when for some nuclear configuration of the core of the electronic energy levels are fairly close, but do not coincide as in the case of degeneracy (Jahn–Teller pseudo-effect). The criterion for this pseudo-degeneracy contains the relationship between three parameters of the system, so that the concept of similarity in electron energies becomes relative (see below for more details). Thus the Jahn–Teller pseudo-effect in principle covers all molecular systems, without exception, and the only problem is that in some systems the effect is small and can be neglected.

The theory of the Jahn–Teller effect and pseudo-effect and its applications began to be developed intensively in the early sixties, and has grown into a new field in the physics and chemistry of molecules and crystals, encountered fairly frequently in the literature under the general name of the Jahn–Teller effect (although the term "vibronic effects" is more appropriate). The fields of application of these effects cover the whole of spectroscopy, from Mössbauer via the ultraviolet, visible, and infrared ranges to the entire range of radiofrequency spectroscopy (EPR, NMR, NQR), polarisability and magnetic susceptibility, crystal chemistry, and crystal physics, including such important branches as the nature of the formation of crystal structures, structural phase transformations in ferroelectricity, and reactivity (orbital symmetry rules).

In recent years a new field has begun to develop, in which vibronic interactions are taken into account to explain the origin of the effects of the mutual influence of molecular groups in their chemical binding (coordination), both in the case of chemical reactions and more particularly in the case of the influence of a catalyst.[3,7–10] This trend introduces fundamentally new elements into the allowance for the effects of vibronic interaction, extending them to the case of molecular transformations. With the inclusion of this trend, the approach overall becomes a concept which from a definite viewpoint analyses all the properties of molecules, including their transformations. The mathematical basis of this concept involves abandoning the adiabatic approximation, or taking systematic account of vibronic interactions (see below). To obtain a deeper general understanding of the phenomens, the new concept takes a more systematic account of the role of the electrons and the details of the electronic structure, in the production of the nuclear configuration and its dynamics, and the influence of the latter on the spectral and stereochemical properties and reactivity of molecules.

In a vertain sense, the systematic "introduction" of this concept into chemistry develops a new and more fruitful way of thinking for research workers. In fact, all courses on the structure of molecules present the adiabatic approximation, according to which the electrons follow the nuclei adiabatically, and the nuclei move in the average field of the electrons, and with very few exceptions it is not pointed out that in most cases this picture is incorrect. This creates in research workers a restricting stereotype, according to which the electrons, as already noted, are assigned the classical role of the sources of the electrostatic field, and the extremely important details of the electronic structure of the valence shell related to quantum effects are ignored completely. In the process, the understanding of how changes in the structure of the valence shell of a molecule lead to a change in the nuclear configuration, and a correct understanding of the nature of chemical transformations, are lost. The new concept based on the non-adiabaticity of the interactions of electrons and nuclei (taken into account by the vibronic mixing of different electronic states) directs the thinking of research workers to a more adequate reflection of the structure and properties of polyatomic systems and their chemical transformations.

The present review characterises briefly the essential features of the concept of vibronic interactions and various aspects of its applications in present-day chemistry. The analysis of the latter, for lack of space, has been restricted to examples from chemical reactivity and activation in catalysis, and electron-conformational effects. The review does not deal with the many applications of this concept in spectroscopy, which have developed particularly extensively in the form of new branches of electronic spectroscopy and EPR, or with problems of crystal chemistry, structural Jahn–Teller phase transformations, and ferroelectricity (cooperative effects). These and other interesting aspects of this topic can be found in the literature (see Refs.1–4 and the detailed bibliography in Ref.5).

II. VIBRONIC INTERACTIONS

The examination of some general equations will help to introduce the terminology and notation. The stationary Schrodinger equation for a molecular system $H\Psi = E\Psi$ can be considered, and the Hamiltonian H represented as the sum of three terms:

$$H = H_Q + H_r + V(r, Q) \qquad (1)$$

where H_r is the part of the Hamiltonian that depends only on the coordinates of the electrons, H_Q the operator of the kinetic energy of the nuclei, and $V(r,Q)$ the operator of the electron–nucleus and nucleus–nucleus interactions (r and Q denote the sets of coordinates of the electrons and nuclei respectively).

It is assumed that a solution of the Schrodinger equation has been found for fixed positions of the nuclei ($H_Q = 0$):

$$[H_r + V(r, Q)]\varphi_k(r, Q) = \varepsilon_k(Q)\varphi_k(r, Q)\,. \qquad (2)$$

In this case the energy levels $\varepsilon_k(Q)$ and wavefunctions $\phi_k(r,Q)$ depend on the coordinates of the nuclei as parameters. The complex wavefunction $\Psi(r,Q)$ can be sought as the expansion with respect to the series of functions $\phi_k(r,Q)$:

$$\Psi(r, Q) = \sum_k \chi_k(Q)\cdot\varphi_k(r, Q) \qquad (3)$$

Substituting $\Psi(r,Q)$ in the equation $H\Psi = E\Psi$ and taking account of Eqn.(2) gives an infinite system of equations for

the functions $\chi(Q)$:

$$[H_Q + \varepsilon_m(Q) - E]\chi_m(Q) - \sum_k A_{mk}\chi_k(Q) = 0$$
$$m = 1, 2, \ldots \quad (4)$$

Here, A_{mk} are the matrix elements of the so-called non-adiabaticity operator. These quantities depend on the derivatives of the functions $\phi_j(r,Q)$ with respect to the coordinates of the nuclei Q.[2] This is an effect of non-adiabaticity with the mixing of different electronic states.

If the electronic functions depend little on the coordinates of the nuclei Q, the terms A_{mk} in Eqn.(4) are small and can be neglected. The system of equations (4) then takes the form

$$[H_Q + \varepsilon_m(Q) - E]\chi_m(Q) = 0, \; m = 1, 2, \ldots \quad (5)$$

For each electronic wavefunction it is possible to construct $\Psi_m(r,Q)$ as the product

$$\Psi_m(r, Q) = \varphi_m(r, Q)\chi_m(Q).$$

The function $\chi_m(Q)$ has the significance of the wavefunction describing the motion of the nuclei. This is the adiabatic approximation.

The nature of the adiabatic approximation can be discussed from another viewpoint. The operator $V(r,Q)$ can be expanded in a series with respect to small displacements Q in the region of the point $Q = 0$:

$$V(r, Q) = V(r, 0) + \sum_\alpha \left(\frac{\partial V}{\partial Q_\alpha}\right)_0 Q_\alpha + \frac{1}{2}\sum_{\alpha,\beta}\left(\frac{\partial^2 V}{\partial Q_\alpha \partial Q_\beta}\right)_0 Q_\alpha Z_\beta + \ldots \quad (6)$$

The non-zero terms in this equation (linear, quadratic, etc.) are called the operators of the electronic–vibrational or vibronic interaction. The solution of the electronic Schrodinger equation taking account of only the zeroth term of the expansion (6), $V(r,0)$, gives wavefunctions $\phi(r,0)$ and energy levels $\varepsilon(0)$ which are independent of Q (simple adiabatic approximation). For small displacements of the nuclei Q, the dependence of the electronic wavefunction on Q is determined according to perturbation theory by the matrix elements of the linear terms of the vibronic interaction

$$F_\alpha^{(ij)} = \left\langle \varphi_i(r, 0) \left| \left(\frac{\partial V}{\partial Q_\alpha}\right)_0 \right| \varphi_j(r, 0) \right\rangle \quad (7)$$

which are called the linear vibronic constants. Thus the simple adiabatic approximation is equivalent to neglecting the vibronic interaction. On the other hand, systematic allowance for vibronic interaction automatically takes account of non-adiabaticity. It can be shown[2] that the physical significance of this conclusion is preserved in the complete adiabatic approximation.

Thus in the general case, when account is taken of vibronic interaction, the complete wavefunction is represented in the form of Eqn.(3), including excited states. In other words, vibronic interactions "mix" the ground and excited electronic states of the molecule, obtained in the simple adiabatic approximation for fixed positions of the nuclei.

A criterion of the applicability of the adiabatic approximation is provided by the strong inequality

$$\varepsilon_2 - \varepsilon_1 \gg \hbar\omega \quad (8)$$

where $\hbar\omega$ is the quantum of the vibrations in the ground electronic state, and $\varepsilon_2 - \varepsilon_1$ the lowest energy of electronic excitation.

If criterion (8) is fulfilled, then allowance for the vibronic terms in the expansion (6) leads only to small corrections to the quantities found in the adiabatic approximation. If however this criterion is not fulfilled, then allowance for vibronic interactions leads to qualitatively new effects. To classify and analyse these effects it is convenient to use the adiabatic potential surface (or curves), that is the energies of the electronic terms as functions of the nuclear displacements. Fig.1 gives three types of adiabatic potential in the range of the intersection or approach of two electronic terms (for convenience, the one-dimensional case is considered). The greatest breakdown of the adiabaticity criterion takes place when $\varepsilon_2 = \varepsilon_1$ (the case of degeneracy of the electronic state), when the inequality (8) is not fulfilled for any values of $\hbar\omega$. For this case, Jahn and Teller, on the basis of Landau's idea, proved that (in present-day terms) at the point of electronic degeneracy (that is in a nuclear configuration for which the energies of two or several electronic states coincide), the adiabatic potentials do not have a minimum (Fig.1*a*), so that the nuclear configuration is unstable.

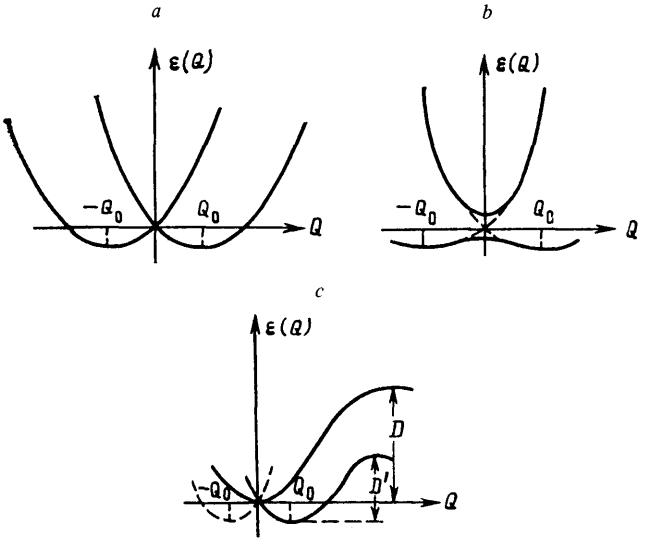


Figure 1. Schematic representation of the three principal cases of vibronic effects: *a*) case of degeneracy (Jahn–Teller effect), *b*) case of pseudo-degeneracy (Jahn–Teller pseudo-effect), *c*) case of electronic rearrangement or vibronic effects at large distances.

Fig.1 also shows that the minima of the adiabatic potential correspond to distorted configurations. This does not mean, however, that it is possible to detect a distorted configuration of the nuclei instead of a highly symmetrical configuration by direct measurements. In fact, there are always two or more of these minima (sometimes an infinite number—a continuum of minima), with equivalent energies, which complement one another in such a way that overall, the original symmetry is preserved. Thus the so-called Jahn–Teller effect reduces not simply to distortion of the geometry of the molecule but to extremely complex nuclear core dynamics which give rise to a whole range of new effects and regularities.[1-5] Because this feature was neglected, until about 1960 all attempts to detect directly the distortions of a system related to the Jahn–Teller effect, generally speaking, were unsuccessful. At about this time, the present author[1-3] observed one of the clearest manifestations of the complex dynamics of molecular systems with allowance

for vibronic effects—the existence of pulsating motions in which molecules spontaneously (and at a definite frequency) change between configurations corresponding to different equivalent minima of the adiabatic potential (similar to those given in Fig. 1*a*). This new phenomenon, together with the observed effects and regularities (and applications) based on it, was registered (in 1978) in the USSR as scientific discovery No. 202.[11]

A situation similar to that arising when $\varepsilon_1 = \varepsilon_2$ is found at a point of the nuclear configuration where the energy levels ε_1 and ε_2 are fairly close to one another (Jahn–Teller pseudo-effect, Fig. 1*b*). Here, together with effects which are consequences of the Jahn–Teller theorem, various new regularities appear.[1-5]

The similarity in energy observed for nuclear displacements in a certain direction Q is fairly characteristic. It was recently shown[12-14] that mixing of the electronic states is the only source of dynamic instability in molecular systems (and that it may be considerable even for large differences $\varepsilon_2 - \varepsilon_1 \cong 10$ eV). This result is important for interpreting the stereochemical properties of molecular systems[3,15] and transition states in chemical reactions,[3,12] and for explaining the nature of structural (including ferroelectric) phase transformations in crystals,[16,17] the "plasticity" of the coordination sphere of certain transition metals, and distortion isomers.[18,19]

Finally, in the last case, illustrated in Fig. 1*c*, there may be effects which appear at large distances from the point of degeneracy (or pseudo-degeneracy). Different situations relating to this case are discussed in more detail below.

III. DESCRIPTION OF MOLECULAR STRUCTURE BY MEANS OF ORBITAL VIBRONIC CONSTANTS

From the above discussion, it follows that the effects of the vibronic mixing of different electronic states are determined by the vibronic constants (7). These can be written in a more convenient form by making use of the symmetry properties of the molecules. If the coordinates of the displacements of the nuclei used in the expansion (6) are the generalised symmetry coordinates (or normal coordinates) $Q_{\Gamma\gamma}$, which transform as the row γ of the irreducible representation Γ of the symmetry point group of the molecule, then the linear vibronic constant can be written as

$$F_{\tilde{\Gamma}\tilde{\gamma}}^{(\Gamma\gamma,\Gamma'\gamma')} = \left\langle \Gamma\gamma \left| \left(\frac{\partial V}{\partial Q_{\tilde{\Gamma}\tilde{\gamma}}} \right)_0 \right| \Gamma'\gamma' \right\rangle \qquad (9)$$

where $|\Gamma\gamma\rangle$ and $|\Gamma'\gamma'\rangle$ denote the electronic wavefunctions for fixed positions of the nuclei, transforming as the corresponding rows of the irreducible representation. If the mixed states are not degenerate, then the representations Γ and Γ' each contain only one row γ and γ'. In this case $\tilde{\Gamma}$ is also non-degenerate, and the symbols for the row γ are omitted in $F_{\tilde{\Gamma}}^{(\Gamma,\Gamma')}$. If however one or both of these states is degenerate, then there exist several vibronic constants, corresponding to the number of possible combinations of the rows of the representations. These constants, however, differ from one another only in a numerical factor (the Clebsch–Gordan coefficients), obtainable from Tables.[2,3] Thus the vibronic mixing of two (any) states is described essentially by one vibronic constant.

Some of the vibronic constants have a clear physical significance. In particular, the diagonal linear vibronic constant $F_{\tilde{\Gamma}}^{(\Gamma\Gamma)} \equiv F_{\tilde{\Gamma}}^{\Gamma}$ is equal to the force with which the electronic cloud in the state Γ deforms the core in the direction of the symmetrised (normal) displacement $\tilde{\Gamma}$. The molecule is obviously in an equilibrium (but not necessarily stable) state when $F_{\tilde{\Gamma}}^{\Gamma} = 0$ for all $\tilde{\Gamma}$.

In addition to linear vibronic constants, it is possible to introduce quadratic, cubic, etc. vibronic constants. It is possible, for example, to define the quadratic vibronic constants. The general expression for a matrix element of the coefficient of the quadratic terms in the expansion (6) can be written as:

$$K_{0\tilde{\Gamma}\tilde{\gamma}}^{(\Gamma\Gamma')}(\Gamma_1 \times \Gamma_2) = \frac{1}{2} \left\langle \Gamma \left| \left\{ \left(\frac{\partial^2 V}{\partial Q_{\Gamma_1} \partial Q_{\Gamma_2}} \right)_0 \right\}_{\tilde{\Gamma}\tilde{\gamma}} \right| \Gamma' \right\rangle . \qquad (10)$$

Here, the shaped brackets denote tensor convolution, that is a combination of the second derivatives with respect to the coordinates $Q_{\Gamma_1\gamma_1}$ and $Q_{\Gamma_2\gamma_2}$, which transforms as the row $\tilde{\gamma}$ of the representation $\tilde{\Gamma}$ contained in the product of the representations $\Gamma_1 \times \Gamma_2$. The totally symmetric part of the diagonal element (10) denoted $K_{0\tilde{\Gamma}}^{\Gamma}$) has a completely clear physical significance; it defines the curvature of the adiabatic potential (force constant) of the system $K_{\tilde{\Gamma}}^{\Gamma}$, corresponding to the coordinates $Q_{\tilde{\Gamma}}$:[2,3]

$$K_{\tilde{\Gamma}}^{\Gamma} = K_{0\tilde{\Gamma}}^{\Gamma} - 2 \sum_{\Gamma'}{}' |F_{\tilde{\Gamma}}^{(\Gamma\Gamma')}|^2 / \Delta_{\Gamma'\Gamma} \qquad (11)$$

where $\Delta_{\Gamma'\Gamma}$ is equal to half the difference between the energies of the states Γ and Γ'; $\Delta_{\Gamma'\Gamma} = (1/2)(\varepsilon_{\Gamma'} - \varepsilon_{\Gamma})$. Thus keeping for $K_{0\tilde{\Gamma}}^{\Gamma}$ the earlier description as the curvature of the surface or the force constant (the curvature of the surface at the equilibrium point, where $F_{\tilde{\Gamma}}^{\Gamma} = 0$, coincides with the force constant), all the remaining matrix elements (10) (namely the non-totally-symmetric parts $\tilde{\Gamma} \neq A_1$ of the diagonal elements $\Gamma = \Gamma'$ and all the off-diagonal elements) can be called quadratic vibronic constants and denoted $G_{\tilde{\Gamma}}^{(\Gamma\Gamma')}$. $(\Gamma_1 \times \Gamma_2)$.

Similarly, it is possible to derive cubic vibronic constants, some of which (or their combinations) make a direct contribution to the anharmonicity of the system.

An important step towards chemical applications of the theory of vibronic interactions can be taken by introducing orbital vibronic constants. In the molecular orbital (MO) method it is possible to introduce linear, quadratic, etc. vibronic constants for each orbital state. For this purpose the MO energy levels and MO wavefunctions can be denoted ε_i and $\psi_i(\mathbf{r})$ respectively, and use can be made of the additive operator of the electron–nucleus interaction (N is the number of nuclei):

$$V = \sum_i V_i(\mathbf{r}_i);\ V_i(\mathbf{r}_i) = -\sum_\alpha \frac{e^2 Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \frac{1}{N} \sum_{\alpha,\beta} \frac{e^2 Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} . \qquad (12)$$

By analogy with the integral constant (8), the linear orbital vibronic constant (OVC) is then determined from the equation:

$$f_{\tilde{\Gamma}}^{(ij)} = \left\langle \psi_i(\mathbf{r}_i) \left| \left(\frac{\partial V_i}{\partial Q_{\tilde{\Gamma}}} \right)_0 \right| \psi_j(\mathbf{r}_i) \right\rangle . \qquad (13)$$

In exactly the same way, by analogy with Eqn. (9), the orbital matrix elements of the quadratic terms of the vibronic interaction are written as:

$$k_{0\tilde{\Gamma}\tilde{\gamma}}^{(ij)}(\Gamma_1 \times \Gamma_2) = \frac{1}{2} \left\langle \psi_i(\mathbf{r}_i) \left| \left\{ \left(\frac{\partial^2 V_i}{\partial Q_{\Gamma_1} \partial Q_{\Gamma_2}} \right)_0 \right\}_{\tilde{\Gamma}\tilde{\gamma}} \right| \psi_j(\mathbf{r}_i) \right\rangle . \qquad (14)$$

Here also, the totally symmetric part of the diagonal element $i = j$ with $\tilde{\Gamma} = A_1$ and $\Gamma_1 = \Gamma_2 = \tilde{\Gamma}$, $k_{0\tilde{\Gamma}}^{(ii)} \equiv k_{0\tilde{\Gamma}}^{i}$ makes a direct contribution to the orbital force constant, and the

non-totally symmetric (for degenerate MO) and off-diagonal elements are the orbital quadratic vibronic constants $g_{\bar{\Gamma}}^{(ij)}(\Gamma_1 \times \Gamma_2)$.

The physical significance of the orbital constants can be considered. First of all it can be seen that the diagonal linear OVC $f_{\bar{\Gamma}}^{(ii)} \equiv f_{\bar{\Gamma}}^{i}$ has the significance of the force with which an electron situated in the ith MO deforms the original nuclear configuration in the direction of the symmetrised coordinate $Q_{\bar{\Gamma}}$ (or $Q_{\bar{\Gamma}\bar{\gamma}}$ for degenerate coordinates) minus the corresponding part of the repulsion in this direction (see Eqn.(12)). It is difficult to determine the orbital components directly from experimental data. It is therefore of interest to find the relationship between these orbital contributions and the corresponding integral quantities for the molecule as a whole. This can be done using the combination theorem,[7,9] according to which

$$F_{\bar{\Gamma}\bar{\gamma}}^{\Gamma} = \sum_i q_i^{\Gamma} f_{\bar{\Gamma}\bar{\gamma}}^{i} \qquad (15)$$

where q_i^{Γ} represents the occupation numbers of the MO (0, 1, or 2) in the state Γ of the molecule. In other words, the total force with which the electron cloud acts on the nuclear core (in a certain direction $Q_{\bar{\Gamma}\bar{\gamma}}$) is equal to the sum of the contributions from each MO. An analogous relationship applies for the diagonal quadratic OVC.

The derivation of the analogous relationships for the off-diagonal OVC is more complicated, since the latter depend on the excited states. In the approximation of "frozen orbitals" (in this approximation, in an excitation $\Gamma \to \Gamma'$ associated with a change in the state of one electron $i \to j$, the states of the other electrons do not change), it has been shown[3] that

$$F_{\bar{\Gamma}\bar{\gamma}}^{(\Gamma\Gamma')} = f_{\bar{\Gamma}\bar{\gamma}}^{(ij)}, \qquad (16)$$

$$K_{\bar{\Gamma}}^{\Gamma} = \sum_i q_i^{\Gamma} k_{\bar{\Gamma}}^{i}, \qquad (17)$$

$$k_{\bar{\Gamma}}^{i} = k_{0\bar{\Gamma}}^{i} - 2\sum_j{}' |f_{\bar{\Gamma}}^{(ij)}|^2/\Delta_{ji} \qquad (18)$$

where $\Delta_{ji} = (1/2)(\varepsilon_j - \varepsilon_i)$.

It can be seen that in the approximation of frozen orbitals, the off-diagonal OVC coincide with the total vibronic constants, and the force constants of the molecule can also be represented additively in terms of the orbital contributions, although the latter also involve other orbitals. Analogous equations can be derived for the cubic and other contributions of higher orders.

The orbital vibronic constants supplement the data on the electronic structure of molecules in the one-electron MO approximation (the set of one-electron energy levels and wavefunctions is a stationary or static picture) with important information on the action of the electrons on the nuclear core (the dynamic picture). The description of the electronic structure of molecules in MO terms is at present the most adequate and the most easily applied in practice. It can be used to analyse chemical processes in convenient and clear terms, facilitating a deeper understanding of their nature. In this approximation, however, no account is taken of the influence of the electron cloud on the positions of the nuclei, so that it is not clear whether the configuration of the nuclei will be the equilibrium configuration for the given electron distribution. Moreover, this static picture does not indicate how the configuration of the nuclei changes with change in the electronic structure.

Allowance for the vibronic constants makes it possible to eliminate most of this unsatisfactory feature of the description of the electronic structure: the integral vibronic constants characterise the deforming forces and force constants corresponding to the given electronic structure. The orbital vibronic and force constants characterising the contributions of the individual MO to these dynamic characteristics are particularly useful. Knowing the orbital vibronic and force constants, it is possible to predict the behaviour of the nuclear core with change in the electronic structure: the change in its equilibrium configuration, force constants, anharmonicity constants, etc. These data can be used to predict the nature of the change in reactivity. Thus the orbital and vibronic and force constants supplement considerably the static description of the electronic structure in the MO approximation.

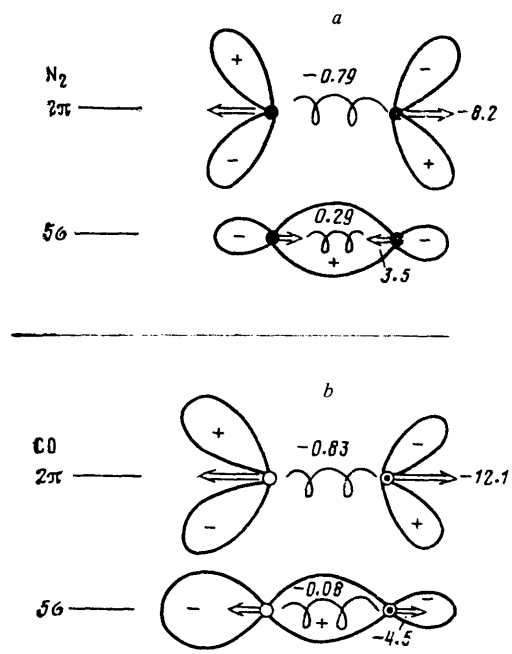


Figure 2. Illustration of the vibronic structure of molecules: *a*) 5σ HOMO (bonding) and 2π LUMO (antibonding) of the N_2 molecule; *b*) HOMO and LUMO of the CO molecule; HOMO—weakly antibonding, LUMO—strongly antibonding. The contribution of the orbital electrons to the deforming force is shown by arrows, figures in 10^{-4} dyn; the contribution to the force constant is shown by the spring, figures in 10^6 dyn cm^{-1}.

In Fig.2, the concept of the structure of polyatomic systems described above is illustrated for the highest occupied MO (HOMO) 5σ and the lowest unoccupied MO (LUMO) 2π of the simplest diatomic molecules N_2 and CO (the numerical characteristics of these MO are discussed in section IV). Fig.2 shows that in the N_2 molecule, the electron in the 5σ MO "attracts" the nuclei with a force $f_R^{5\sigma}(N_2) = 3.51 \times 10^{-4}$ dyn

(R is the distance between the nuclei), whereas in the CO molecule the electron in the analogous orbital "repels" the nuclei with a force $f_R^{5\sigma}(CO) = -4.5 \times 10^{-4}$ dyn. The electrons in the 2π orbitals "repel" the nuclei with a force $f_R^{2\pi}(N_2) = -8.18 \times 10^{-4}$ dyn and $f_R^{2\pi}(CO) = -12.1 \times 10^{-4}$ dyn.

The contributions to the force constant (shown as springs in Fig.2) have the following values (dyn cm^{-1}):

	5σ	2π
N_2	$0.23 \cdot 10^{-6}$	$-0.73 \cdot 10^{-6}$
CO	$0.08 \cdot 10^{-6}$	$-0.83 \cdot 10^{-6}$

These data show first of all that the 5σ orbital in the N_2 molecule is bonding, and that in CO is antibonding, whereas the 2π MO are antibonding in both molecules. Moreover, the above data contain quantitative information on the degree of bonding or antibonding character of each MO and its contribution to the deforming force and the force constant of the bond. As already noted, this information is particularly valuable in the analysis of the influence of the rearrangement of the electron cloud on the behaviour of the nuclear core (see section IV).

In the case of polyatomic molecules, the orbital and force vibronic constants carry much richer information than the simple representation of the bonding or antibonding character of the MO. Thus in accordance with the rules of group theory, the orbital linear vibronic constant $f_{\bar{\Gamma}}^{(ij)} = \langle i | (\partial V / \partial Q_{\bar{\Gamma}})_0 | j \rangle$ is non-zero if the product of the representations Γ_i and Γ_j according to which the ith and jth MO transform, contains the representation $\bar{\Gamma}$ corresponding to the symmetrised direction $Q_{\bar{\Gamma}}$. For different Γ_i and Γ_j, the representation Γ can be any one. For $i = j$ the representation Γ is contained in the symmetrised square $[\Gamma_i \times \Gamma_i]$, so that if the ith MO is non-degenerate, the representation $\bar{\Gamma}$ is totally symmetric. In other words, the electrons in the non-degenerate MO deform the molecule without changing its symmetry. The MO are also bonding or antibonding, depending on the sign of $f_{\bar{\Gamma}}^{ii}$. For degenerate MO the product $\Gamma_i \times \Gamma_j$ contains not only the totally symmetric but also non-totally symmetric representations, so that the electrons in the degenerate MO can deform the molecule with a change in its symmetry (in complete correspondence with the Jahn–Teller theorem[2]). Moreover, in accordance with Eqn.(18), which contains $f_{\bar{\Gamma}}^{(ij)}$, the "softening" of the molecule brought about by the orbital electron can take place in any direction (depending on the mixed states i and j with small Δ_{ji}).

IV. VIBRONIC REACTIVITY AND CHEMICAL ACTIVATION ON COORDINATION IN CATALYSIS

Vibronic effects may have a significant influence on the reactivity of a molecular system. Thus as can be seen, for example, from Eqn.(11), as a result of vibronic mixing the curvature of the adiabatic potential of the ground state decreases by an amount F^2/Δ. This decrease in the curvature of the adiabatic potential surface evidently leads to a decrease in stability (in the limit ($F^2/\Delta > K_0$) the system becomes unstable) and to an increase in reactivity.

This last statement requires explanation. First of all it is necessary to give a quantitative definition of the reactivity of molecules, and even this is an extremely difficult task. Reactivity should obviously characterise the rate of the elementary act of a chemical reaction, so that it is natural to try to relate it to the activation energy of the reaction. The latter, however, may depend not only on the given molecule but also on the molecule with which it reacts.

In the study of the change in the reactivity of a given molecule under the influence of vibronic effects or a change in its electronic structure, a measure of its reactivity in a given chemical reaction is provided by the quantity D, the activation energy of the given reaction, associated with the activation of the molecule being considered (see the discussion in Refs.3 and 10). To determine D it is necessary to know the ascending section of the potential energy curve along the reaction coordinate from its minimum to the maximum of the barrier. Comparison of these sections, constructed with and without allowance for vibronic effects, other conditions being equal, shows that the vibronic effects decrease considerably the activation energy of the reaction taking place along the coordinate Q active in the Jahn–Teller effect or pseudo-effect, that is along the displacements of the nuclei for which the vibronic mixing of the electronic states is a maximum.

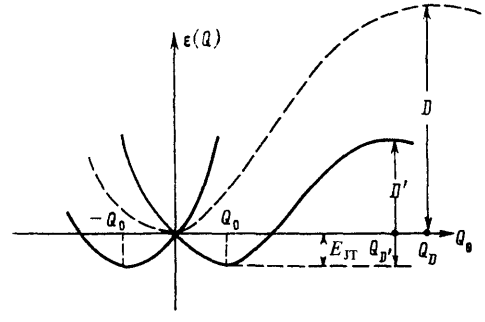


Figure 3. Adiabatic potential in the direction of the coordinate Q_θ active in the Jahn–Teller effect, at large distances, illustrating the lowering of the activation energy $\Delta D = D' - D$ for the reaction taking place in this direction, compared with the same reaction in the absence of the Jahn–Teller effect (broken curve).

This conclusion is illustrated in Fig.3 for the case where there is a Jahn–Teller effect in the original highly symmetrical nuclear configuration $Q = 0$, and the system at this point does not have an energy minimum with respect to the nuclear displacements described by the generalised coordinate Q; the displacements at the point $Q = \pm Q_0$ at which the initial nuclear configuration is distorted have minimum values. It can readily be seen that the change in the activation energy in this case may be considerable, since the points Q_0 and Q_D are not very far from one another (the distortions due to the Jahn–Teller effect are of the order of tenths of an Ångstrom unit, and the distances to the activation barrier are usually greater, but not by much; in any case, they are quantities of the same order of magnitude).

An example is provided by substitution or unimolecular decomposition in an octahedral complex of a transition metal having a doubly degenerate E term, for example for copper(II), for which a strong Jahn–Teller effect is observed. As a result of the Jahn–Teller effect, the adiabatic potential of the system has three minima,[1-4] at which the octahedron is elongated along a tetragonal axis so that the two ligands on the four-fold axis are at a greater distance than the other four. In the tetragonal coordinates Q_θ and Q_ε,[1,2]

the distortion (elongation of the octahedron) takes place along the coordinate Q_θ, which is thus the coordinate along which the activation energy of the reaction decreases (relative to the other directions, other conditions being equal).

Thus these reactions should take place in the direction of the displacements Q_θ for which the two axial ligands move apart (and the four equatorial ligands approach one another). For a unimolecular reaction, this means the dissociation of two ligands in the *trans*-position, and for substitution it means the replacement of these two ligands, giving *trans*-substituted complexes. In other words, when elongated octahedra are formed (during the pulsations), the two ligands in the *trans*-position are less strongly held and are more susceptible to attack by substituting reagents.[20]

This result agrees completely with available experimental data obtained in the study of the behaviour of octahedral complexes of copper(II) in solution or in the gas phase. Thus these complexes first lose two ligands in the *trans*-position to give a square-planar structure, and substitution reactions give only *trans*-substituted complexes (an exception is provided by bidentate ligands, which can only form bonds in two *cis*-positions). On the other hand, it can readily be seen that in this system, if other conditions are equal the Jahn–Teller effect is suppressed, the rate of replacement is lowered considerably; this has also been confirmed experimentally.[21] According to the theory, similar effects should be expected for octahedral complexes of Cr^{II}, Mn^{II}, Ag^{II}, and other systems with an E term.

Other terms (or other nuclear configurations with an E term) will correspond to other mechanisms of this reaction. They can be examined qualitatively from the distortions expected as a result of the Jahn–Teller effect and pseudo-effect. In particular, for a tetrahedral system with a T term (of the type CH_4^+), which as a result of the Jahn–Teller effect should be expected to give four minima of the adiabatic potential with one elongated bond and three shortened bonds, dissociation and replacement with a lowered activation energy can be expected at this elongated bond.

In some cases it is possible to obtain quantitative estimates of the change in the reactivity of molecules (the decrease in the activation energy of the chemical reaction) as a result of vibronic interactions.[7–10] The above example of an octahedral system with an E term can be considered. To analyse the ascending part of the adiabatic potential along the reaction coordinate, it can be approximated by a polynomial of the third degree:[3,7–10]

$$\varepsilon(Q) = aQ + bQ^2 + cQ^3 \ . \qquad (19)$$

Without allowance for vibronic effects, the curve has a minimum at the origin of coordinates, and $\varepsilon(Q)$ is described by the expression

$$\varepsilon(Q) = \frac{1}{2}KQ^2 - \gamma Q^3 \qquad (20)$$

where K is the force constant, and γ takes account of the deviations from harmonicity. With allowance for vibronic effects, the curve has the form

$$\varepsilon'(Q) = FQ + \frac{1}{2}K'Q^2 - \gamma' Q^3 \qquad (21)$$

where F is the linear vibronic constant corresponding to the Jahn–Teller effect, which for the case of an E term is related to the stabilisation energy E_{JT} (Fig. 3) by the relationship: $E_{JT} = F^2/2K$.

In the case being considered, the greatest contribution to the change in the form of the adiabatic potential along the coordinate Q_θ is made by the linear terms of the vibronic interaction.[2] To estimate the effect, therefore, the changes in the force constant and the anharmonicity constant in this direction are neglected. In this case $K' = K$ and $\gamma' = \gamma$, and the change in the activation energy $\Delta D = D' - D$ is given by the following expression (more detailed calculations are given below):

$$\frac{\Delta D}{D} = -3p\left(1 - p + \frac{p^2}{3}\right) \qquad (22)$$

where $p = (4E_{JT}/3D)^{1/2}$.

It can be seen that the change in the activation energy as a result of the Jahn–Teller effect is considerable. For example, for $E_{JT}/D = 0.1$, $(\Delta D/D) \cong 0.7$, that is the activation energy is lowered by 70%. It should be emphasised that this decrease in the activation energy takes place only in a definite direction, namely in the direction of the coordinates active in the Jahn–Teller effect or pseudo-effect (in the case being considered in the direction of the coordinate Q_θ for which two ligands in the *trans*-position are moved apart). Thus when there are strong vibronic effects in one or both reacting systems, the reaction mechanism is dictated by these effects.

The following general question arises from the vibronic reactivity examined above. If it is known how the vibronic effects, by decreasing the stability, increase the reactivity, that is lower the activation energy of chemical reactions in definite directions, is it not possible to change the reactivity of a molecule in a required direction by external influences (perturbations)? In other words, knowing the vibronic structure, it might be possible, using the concept of vibronic interactions, to develop methods for the vibronic activation of molecular systems. It is possible to given an affirmative answer to this question, and one method of studying the chemical activation of molecules, based on vibronic theory, is examined below.

The orbital vibronic constants introduced in section III, and the picture of the vibronic structure of molecules developed from it, provide a good base for a new approach to the problem of chemical transformations, and in particular to a deeper understanding of the nature and to a semi-quantitative description of the action of one molecular system on the reactivity of another during the reaction between them.[7–10,22–24] This last feature is particularly important in catalysis, where the coordination of a reagent molecule to the active centre of a catalyst (homogeneous or heterogeneous) leads to a marked change in its activity (reactivity) with respect to the chemical reaction with another atom or molecule (or unimolecular decomposition). In view of the importance of this catalytic aspect of the problem and to introduce a more specific content, the discussion here will deal chiefly with the problem of the activation of molecular systems in their reaction with a catalyst, although, as shown below, the proposed approach can also be applied to other aspects of the problem of molecular transformations.

As noted above, the diagonal linear orbital vibronic constant $f^i_{\bar{\Gamma}\bar{\gamma}}$ characterises the force with which an electron in the ith MO deforms the core in the direction of the symmetrised displacements $Q_{\bar{\Gamma}\bar{\gamma}}$, minus the fraction of the nuclear repulsion force in this direction corresponding to one electron. The total force deforming the molecule in this direction (the integral diagonal vibronic constant $F^\Gamma_{\bar{\Gamma}\bar{\gamma}}$) in the state Γ is determined by the combination rule (15), from which it can be seen that if the system in the given configuration of the nuclei in the direction of the symmetrised coordinate $Q_{\bar{\Gamma}\bar{\gamma}}$ is stable, the following equality applies

$$F^\Gamma_{\bar{\Gamma}\bar{\gamma}} = \sum_i q^\Gamma_i f^i_{\bar{\Gamma}\bar{\gamma}} = 0 \qquad (23)$$

that is the generalised forces produced as a result of the action of the electrons on the nuclear configuration in the direction $\bar{\Gamma}\bar{\gamma}$ are compensated at the equilibrium point, although for each MO this force, generally speaking, is non-zero, and the forces f^i are different for different orbitals (the force of nuclear repulsion in a given direction for a given nuclear configuration is constant, and is independent of the orbital, whereas the electron distribution changes significantly from one orbital to another).

It can be seen from Eqns.(17) and (18) that formally, there is also a combination rule for the orbital force constants: the curvature of the adiabatic potential surface in a given direction $K_{\bar{\Gamma}}^{\Gamma}$ is equal to the sum of the orbital contributions $k_{\bar{\Gamma}}^{i}$. Unlike the linear vibronic constants, however, the force constant $k_{\bar{\Gamma}}^{i}$ is determined not only by the given orbital but also by the contributions of vibronic mixing with other orbitals. Of the latter, it is necessary to take into account only the unoccupied or partly occupied orbitals, since the contributions of the vibronic mixing of completely filled orbitals appear twice with opposite signs in the expression for $K_{\bar{\Gamma}}^{\Gamma}$, and compensate one another.

Any effect of a given molecular system on another (van der Waals interaction, hydrogen bonding, static polarisation, chemical bonding with sharing of electrons, oxidation, reduction, excitation, ionisation, coordination) begins with a change in the less inert (more mobile) electron distribution in it, which then leads to changes in the more inert nuclear configuration. If the change in the electronic structure is sufficiently small, it can be described in a first approximation by the change in the electron populations of the MO, Δq_i. So long as the values of Δq_i are not too large (of the order of one electron), it is possible, in Koopmans' approximation (the approximation of frozen orbitals), to use this description (in fact, as a result of the change in the interelectronic repulsion, change in q_i also leads to a change in the wavefunctions of the MO, but this effect is of second order with respect to Δq_i; it can be included at the cost of a marked increase in the complexity of the equations).

The new values of the orbital populations $q_i^{\Gamma} + \Delta q_i$ naturally lead to a change in the electron distribution and to decompensation of the orbital deforming forces and force constants. Thus if initially the system was in equilibrium with $F_{\bar{\Gamma}} = 0$ and $K_{\bar{\Gamma}} > 0$ (here and subsequently, for convenience, the index of the state Γ is omitted), then replacing q_i by $q_i + \Delta q_i$ in Eqns.(15) and (17) gives (here and subsequently, q is in units of e)

$$F_{\bar{\Gamma}} = \sum_i \Delta q_i f_{\bar{\Gamma}}^{i} , \qquad (24)$$

$$\Delta K_{\bar{\Gamma}} = K'_{\bar{\Gamma}} - K_{\bar{\Gamma}} = \sum_i \Delta q_i k_{\bar{\Gamma}}^{i} + \sum_{i,j}{}' q_i \Delta q_j |f_{\bar{\Gamma}}^{(ij)}|^2/\Delta_{ji} . \qquad (25)$$

Thus a rearrangement of the electron cloud in which there is a change in the populations of some orbitals produces a non-zero deforming force $F_{\bar{\Gamma}}$ in the symmetrised direction $Q_{\bar{\Gamma}}$; in this direction the corresponding $f_{\bar{\Gamma}}^{i}$ (for which $\Delta q_i \neq 0$) are non-zero (deforming effect), and the force constant changes by $\Delta K_{\bar{\Gamma}}$ (softening effect). It can immediately be stated how the direction of the deforming force depends on the symmetry of the i^{th} orbital, which transforms according to the representation Γ_i: as already noted $f_{\bar{\Gamma}}^{i}$ is non-zero if $[\Gamma_i \times \Gamma_i]$ contains $\bar{\Gamma}$. If Γ_i is not degenerate, then $\bar{\Gamma}$ can only be totally symmetric, that is non-degenerate MOs deform the molecule only along the totally symmetric displacements, without changing their symmetry. For non-degenerate Γ_i the representation $\bar{\Gamma}$ may also be non-totally-symmetric, but only in the same way as in the Jahn–Teller effect.[2] $\bar{\Gamma}$ for $\Delta K_{\bar{\Gamma}}$ may be either, particularly as a result of the second term of the sum (25), in which $f_{\bar{\Gamma}}^{(ij)}$ is non-zero if $\bar{\Gamma} \quad \Gamma_i \times \Gamma_j$. Analogous equations can be written for the change produced by electron rearrangement in the anharmonicity constants, etc.

The deforming forces and the changes in the force constants and anharmonicity constants produced under the influence of electron rearrangement explain naturally the change in the reactivity of the molecule and its activation, and, when the changes are sufficiently large, its chemical transformation. It will be shown below how it is possible to determine approximately the quantitative dependence of these changes on the degree of electron rearrangement. However, from Eqns.(20) and (21), it is already possible to reach various general conclusions about the conditions corresponding to the greatest influence of electron rearrangement in coordination. Thus it follows from these equations that the deforming and softening effect of the coordination centre on a given molecule is linearly dependent on the orbital charge transfer Δq_i. The total transfer $\Delta q = \sum_i \Delta q_i$ cannot be large, from thermodynamic considerations. Thus the values of Δq_i can in principle be large if bond formation between the coordination centre and the given molecule involves more than one orbital and if Δq_i have different signs for different orbitals.

In the case, frequently encountered, where the orbitals most active in chemical bond formation are two in number, namely the bonding HOMO (for which $f^{(1)} > 0$) and the antibonding LUMO ($f^{(2)} < 0$), the orbital charge transfers have different signs: $\Delta q_1 < 0$ and $\Delta q_2 > 0$. Overall, for example, the deforming force from Eqn.(24) is equal to:

$$F = \Delta q_1 f^{(1)} + \Delta q_2 f^{(2)} = -(|\Delta q_1 \| f^{(1)}| + |\Delta q_2 \| f^{(2)}|) , \qquad (26)$$

In other words, in this case the sum of the absolute magnitudes of the contributions of the two orbitals is taken (the situation for the contributions to the change in the force constant ΔK is analogous). Thus the greater the absolute magnitude of the orbital charge transfers of different sign, the greater the effect of one molecule on the other in the case being considered. When more than two orbitals are active in bond formation, the number of favourable combinations increases with increase in the vibronic influence, but the total transfer Δq remains small. This leads to a conclusion about the role of many-orbital bonds in the vibronic effect of one system on another (in particular in catalysis). From this viewpoint, the unique role of transition metals (and lanthanides) in catalysis is attributed to the possible formation of many-orbital bonds by these elements and their compounds with other molecular formations.

If the resulting deforming force F and the change in the force constant $\Delta K = K' - K$ and the anharmonicity constant $\gamma' - \gamma$ are known, Eqns.(20) and (21) can be used to obtain the following relationships (Q_0 is the displacement of the minimum of the potential energy curve as a result of the action of the deforming force F, and Q_D and Q_D, the positions of

the maxima of the barrier before and after coordination; see Fig. 3): [7-10]

$$D = K^3/54\gamma^2;\ Q_D = K/3\gamma = (6D/K)^{1/2};\ Q_{D'} = K'/3\gamma' - Q_0 \qquad (27)$$
$$Q_0 = (K'/6\gamma')\{1 - [1 + (12\gamma' F/(K')^2]^{1/2}\},$$

$$D' = (K' - 6\gamma' Q_0)^3/54(\gamma')^2 = (K')^3/54(\gamma')^2 - K'Q_0/3\gamma' + 2K'Q_0^2 - 4\gamma' Q_0^3$$
$$\Delta D = D' - D = -D[1 - (K'/K)^3(\gamma/\gamma')^2] - (K')^2 Q_0/3\gamma' + 2K'Q_0^2 - 4\gamma' Q_0^3. \qquad (28)$$

The last equation can be simplified. The coefficients of the cubic terms γ can be expressed in terms of the spectroscopic corrections for anharmonicity ωx, [25] which in many cases are known from experimental data. Thus $\gamma/\gamma' = \beta^{1/2}(K/K')^{3/2}(\hbar\omega'/\hbar\omega) = \beta^{1/2}(K/K')$, where $\beta = \omega x/\omega' x'$ (when the electron rearrangements are not too great, β is close to 1). Finally:

$$\Delta D = -D[1 - \beta(K'/K)] - K'Q_0(6\beta KD)^{1/2}/K + 2K'Q_0^2[1 - 2KQ_0(54\beta KD)^{-1/2}] \qquad (29)$$

This equation makes it possible to calculate the change in the activation energy ΔD for the reaction being considered with a given D, if the values are known for the vibronic constants and the changes in the electron populations in the electron rearrangement, in terms of which K', Q_0, and β are defined. Eqn. (29) can also be regarded as an empirical equation relating ΔD to the experimentally observable parameters of the molecule K, K', Q_0, and β.

For a complex molecule with many degrees of freedom, these discussions and conclusions relate to each normal coordinate, and in partiular to that along which the reaction being considered takes place (which may be a linear combination of normal coordinates). In these multidimensional cases, the equations given above can also be used to determine the change in the geometry of the molecule with change in the electronic structure.

Eqn. (29) is approximate, and has meaning only when the changes in the electronic structure relative to the original structure are not too large and have not yet led to the formation of an essentially new molecular system. These electron rearrangements take place in the above-mentioned processes of oxidation, reduction, exitation, ionisation, and coordination of a given molecule to another (in a chemical reaction, as a ligand in coordination systems, on a solid surface during adsorption in heterogeneous catalysis), etc.

The last cases, which can be combined under the general term of activation on coordination, are particularly important. Here, the values of the changes in the MO populations due to charge transfer to and from the coordination centre are fractional. Cases of the transfer of integral charges (in oxidation, reduction, ionisation, excitation, etc.) can in principle be studied by other methods (for example by calculating the total electronic structure of the initial and final systems), but the analysis of the change in the properties of a system with fractional charges can apparently be carried out only by the method examined, with the introduction of orbital vibronic constants.

The assumption that the change in the electronic structure on coordination is slight is justified in most cases; this is confirmed by spectroscopic studies, which indicate that the molecule for the most part retains its individual characteristics, which are not too greatly changed under the influence of coordination. This does not apply to such cases, as for example, the coordination of the H_2 molecule when it dissociates completely, although in these cases, the above method can also be used to determine qualitatively the direction in which the initial stage of the process takes place (for example to explain why and predict when H_2 will dissociate on coordination).

The practical application of the equations obtained requi suitable methods for determining the parameters appearing them. It follows from Eqn. (29) that the change in the activation energy of a chemical reaction with another molecule with change in the electronic structure of a given molecule, including its coordination to any coordination centre, depends on the parameters of the molecular orbital structure of the activated molecule, including the vibronic constants and the change in the MO populations Δq_i. In the general case, Δq_i are determined not only by the electronic structure of the given molecule but also by the state of the coordination centre and the coordination geometry. The latter determines which orbitals of the molecule, overlapping the orbitals of the centre, undergo the greatest change in population Δq_i.

From general considerations, confirmed by specific calculations, it follows that, apart from certain special cases, the greatest changes when simple molecules are coordinated are undergone by only two orbitals, the HOMO and the LUMO. If the change in the populations of the inner orbitals is neglected, Eqns. (24) and (25) are simplified considerably, and they can be written in the following form (the superscripts 1 and 2 refer to the HOMO and LUMO respectively):

$$F = f^{(1)}\Delta q_1 + f^{(2)}\Delta q_2, \qquad (30)$$

$$\Delta K = k^{(1)}\Delta q_1 + k^{(2)}\Delta q_2, \qquad (31)$$

$$\beta - 1 = C^{(1)}\Delta q_1 + C^{(2)}\Delta q_2. \qquad (32)$$

The force constants $k^{(1)}$ and $k^{(2)}$ introduced are combinations of the corresponding vibronic constants, and they show how the force constant will change when one electron is added to the corresponding orbital. The last equation, like the first two, describes the linear dependence of the ratio of the anharmonicity constants on the charge transfer Δq_i; the coefficients $C^{(1)}$ and $C^{(2)}$ are complex combinations of the cubic orbital vibronic constants (and orbital vibronic constants of lower degrees).

All six coefficients ($f^{(1)}$, $f^{(2)}$, $k^{(1)}$, $k^{(2)}$, $C^{(1)}$, and $C^{(2)}$) can readily be calculated if the values of F, ΔK, and β are known for any two independent electron rearrangement processes (for two pairs of values of Δq_1 and Δq_2, except the trivial case $\Delta q_1 = \Delta q_2 = 0$). These processes may be, for example, ionisation ($\Delta q_1 = -1$, $\Delta q_2 = 0$), reduction ($\Delta q_1 = 0$, $\Delta q_2 = 1$), or excitation ($\Delta q_1 = -1$, $\Delta q_2 = 1$), so long as the corresponding empirical parameters are known. For the deforming force F, Eqn. (36) gives

$$F = -K'Q_0[1 - KQ_0(6\beta KD_0)^{-1/2}] \qquad (33)$$

where K and D_0 are the constants for the non-perturbed molecule (D_0 is the dissociation energy of the molecule in the direction being considered), and K', Q_0, and β relate to the molecule which has undergone electron rearrangement.

The force constants K and K' are readily found from the corresponding vibration frequencies. It is more difficult to determine the deformation of the molecule Q_0 in the direction Q; direct X-ray diffraction data are not always available. For simple electron rearrangements such as ionisation or excitation, Q_0 can be determined from spectroscopic data. In a number of cases, particularly for simple molecules, Q_0 can be determined from the known value of K', using empirical relationships between them (see for example Ref. 26). In this case the theory becomes one-parameter; [23,24] all the quantities are determined by one parameter, namely the change in the corresponding vibration frequency in the coordinated state. This version is best in the parametrisation of the theory being considered, since in the experimental

determination of Q_0, for example by X-ray diffraction, the formation of the lattice may influence its numerical value, with a significant effect on the results (the value of Q_0 must be known with a relatively high accuracy).

Knowing the coefficients in Eqns.(30)–(32), it is possible to use the charge transfer to determine the deforming force and the changes in the force constant and the anharmonicity constant in the direction of the chemical reaction, and then to use Eqn.(29) to estimate the change ΔD as a function of D. On the other hand, if F and ΔK are known for the perturbed molecule, it is possible to determine Δq_1 and Δq_2 for the HOMO and LUMO.

As already noted, Eqn.(29) can also be used as an empirical relationship between ΔD and D:

$$\Delta D = aD + bD^{1/4} + c + dD^{-1/4} \qquad (34)$$

where the coefficients a, b, c, and d are determined from the known empirical parameters K, K', and Q_0, and β. Frequently, the value of D, that is the activation energy of the reaction being considered in the absence of a catalyst, is unknown. In these cases it is possible, by constructing the $\Delta D = f(D)$ curves for each coordination centre (or any other source of electron rearrangement), to compare them with one another and to determine the relative efficiency of different centres (or sources) for each value of D.

Specific examples can be considered. The electronic structure and spectroscopic parameters of the CO molecule have been well studied, so that it is comparatively easy to determine its fundamental vibronic constants and force constants. Its HOMO is the 5σ orbital, and the LUMO the 2π orbital. Knowing from experimental data the values of K for the original CO molecule and the values of K', β, and Q_0 for the ionised molecule CO^+ [25,27] ($\Delta q_1 = -1$, $\Delta q_2 = 0$) and for the excited state of CO ($5\sigma^2 2\pi^0 \rightarrow 5\sigma^1 2\pi^1$ transition; $\Delta q_1 = -1$, $\Delta q_2 = 1$), [26,28] it is possible to obtain from Eqns. (30)–(32) the following values (for the configurations $5\sigma^1 2\pi^1$, the average values for the two terms $A\,^1\Pi$ and $a\,^3\Pi$ were used):

$$\begin{array}{ll} f^{(1)} = -4.54\cdot10^{-4}\ \text{dyn} & f^{(2)} = -12.1\cdot10^{-4}\ \text{dyn} \\ k^{(1)} = -0.080\cdot10^{6}\ \text{dyn cm}^{-1} & k^{(2)} = -0.83\cdot10^{6}\ \text{dyn cm}^{-1} \\ C^{(1)} = 0.134 & C^{(2)} = 0.0104 \end{array} \qquad (35)$$

The values of both the vibronic constants and the force constants show that both orbitals (5σ and 2π) are antibonding, the latter being much more antibonding than the former. Unlike the qualitative picture of the nature of the corresponding orbital (antibonding or bonding), which can often (but not always) be obtained without using the vibronic approach, the latter, as can be seen from the figures obtained, makes it possible to determine quantitatively the degree of participation of the corresponding orbital in the deforming force and the force constant.

Knowing the constants (35), it is possible to analyse the behaviour of the carbon monoxide molecule in any other situation, in particular when coordinated. If the charge transfer Δq_1 and Δq_2 resulting from coordination is known, it is possible to determine the values of F, β, and ΔK, and hence ΔD (for a given D), and conversely. The values of these constants show that the negative (antibonding, and hence decreasing the activation energy) force F and the negative ΔK (acting in the same direction) will be greater, the greater the positive values of Δq_1 and Δq_2, that is the greater the increase in the populations of the HOMO and LUMO. Since the HOMO is completely occupied by electrons, however, Δq_1 may be either zero or negative. Thus the activation of CO will be greater, the greater Δq_2 and the smaller the absolute magnitude of the negative Δq_1, so that, for example, for linear coordination the catalyst of the corresponding reactions will be more effective, the stronger its π-donor properties and the weaker its σ-acceptor properties.

The linear coordination of CO to a nickel atom on an NiO surface can be considered. Experimental data for this system give the value $K' = 1.710 \times 10^6$ dyn cm^{-1}, [27] and the relationship between K' and Q_0, [25] namely $K' = (1.7957 - 8.2926\, Q_0\ [\text{Å}]) \times 10^6$ dyn cm^{-1}, can be used to obtain $Q_0 = 0.0126$ Å, $F = -2.119 \times 10^{-4}$ dyn, and $\Delta K = K' - K = -0.192 \times 10^6$ dyn cm^{-1}; Eqns.(30)–(32) then give $\Delta q_1 \cong -0.32$, $\Delta q_2 \cong +0.26$, and $\beta = 0.93$. This gives the details of the mechanism of the activation of CO on nickel oxide: coordination is accompanied by the transfer of an electron charge of ~0.3 e to the metal from the weakly antibonding 5σ orbital of CO, and by approximately the same transfer of charge from nickel to the strongly antibonding 2π orbital of CO.

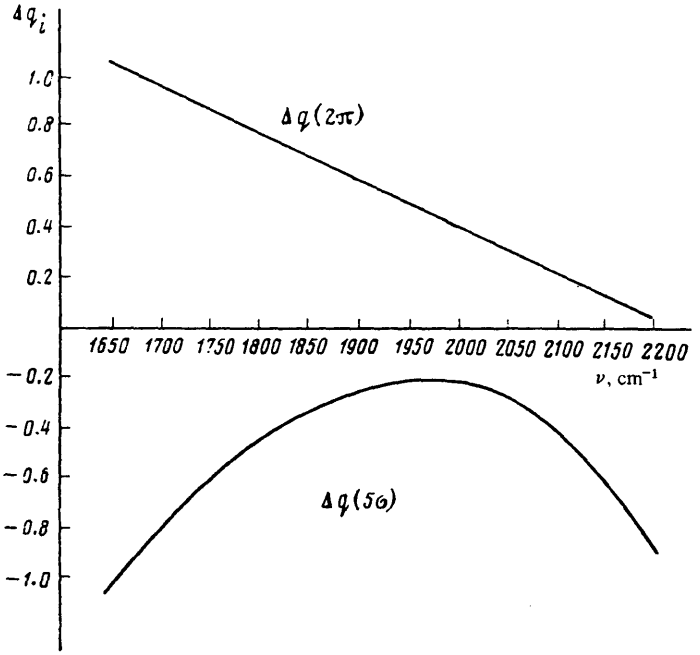


Figure 4. Dependence of the charge transfer $\Delta q(5\sigma)$ and $\Delta q(2\pi)$ to the CO molecule on its vibrational frequency in the coordinated state in the one-parameter two-level theory of vibronic activation on coordination. [23,24]

The relationship between K' and Q_0 given above can be used to obtain a correlation diagram relating the vibration frequency of CO and the transfer of charge from the 5σ HOMO to the active centre ($-\Delta q_1$) and from the latter to the 2π LUMO (Δq_2) on coordination, [23,24] shown in Fig.4. It may be noted, however, that the empirical relationship $K' = f(Q_0)$ was obtained for the range where the charge transfer and the change in the CO vibration frequency are not too small. With allowance for the correlation between K' and Q_0, the vibronic theory of activation becomes one-parameter, that is all the results depend on one parameter, namely the value of the vibration frequency of CO in the coordinated state (or K').

In this approximation, the change in the reactivity of CO on the NiO surface, obtained from Eqn.(29), gives the following relationship (values of D and ΔD in kcal mole^{-1}):

$$\Delta D = -0.17D - 1.40D^{1/4} + 0.78 - 0.15D^{-1/4} \cdot \qquad (36)$$

The $\Delta D = f(D)$ curve for this case, together with other analogous curves obtained for a number of coordination centres which activate CO, is given in Fig.5.[22]

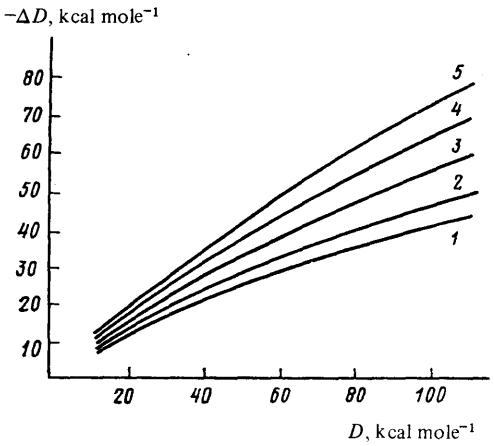


Figure 5. $\Delta D = f(D)$ relationships for the activation of the CO molecule on coordination to various systems, constructed from vibronic theory for the systems: *1*) Pd–Co, *2*) Ni–Co, *3*) $Fe(CO)_5$, *4*) $V(CO)_5$, 5) $Mn(CO)_5$.

To estimate the efficiency of Eqn.(36) it is necessary to obtain the numerical values of ΔD for a known D and to compare them with the experimental values. If it is assumed that the activation energy of the reaction $CO + O_2 \rightarrow CO_2 + O$ in a flame (D = 48 kcal mole^{-1})[29] corresponds to the activation of CO, then for linear coordination on a nickel oxide surface, according to Eqn.(36), the activation energy decreases by $\Delta D \cong -17$ kcal mole^{-1} and becomes equal to $D' = D + \Delta D \cong 31$ kcal mole^{-1}, in good qualitative agreement with the experimental data for this reaction on a nickel catalyst, for which (in an excess of CO) D_{expt} = 25.4 kcal mole^{-1}.[30]

Interesting results have been obtained in a study of the vibronic activation of CO on transition metal clusters.[23] It has been found, in particular, that CO molecules coordinated simultaneously to two (in $Co_2(CO)_8$) and more particularly to three (in $Rh_6(CO)_{16}$) metal atoms are activated to a much greater extent than when coordinated to one atom. On the other hand, in $Mn_2(CO)_{10}$ the axial CO groups are activated to a much greater extent than the equatorial groups.

The N_2 molecule, which is isoelectronic with CO, also has a 5σ HOMO and a 2π LUMO. The experimental data for N_2^+ and the excited states $a\,^1\Pi g$ and $B\,^3\Pi_g$[31] (the latter correspond to the excitation $5\sigma^2 \rightarrow 5\sigma^1 2\pi^1$ with $\Delta q_1 = -1$ and $\Delta q_2 = 1$) give from Eqns.(30)–(32) the following values for the vibronic parameters:[7–10]

$$\begin{aligned} f^{(1)} &= 3.51 \cdot 10^{-4} \text{ dyn} \\ k^{(1)} &= 0.286 \cdot 10^{6} \text{ dyn cm}^{-1} \\ C^{(1)} &= 0.112 \\ f^{(2)} &= -8.18 \cdot 10^{-11} \text{ dyn} \\ k^{(2)} &= -0.785 \cdot 10^{6} \text{ dyn cm}^{-1} \\ C^{(2)} &= 0.127 \end{aligned} \qquad (37)$$

It can be seen that the highest occupied 5σ orbital of the N_2 molecule, unlike that of CO, is bonding, but the 2π LUMO, as in CO, is antibonding. Thus in contrast to CO, for the activation of N_2 the coordination centre for longitudinal linear coordination should be a good π-acceptor and π-donor. In principle, an analogous effect brings about charge transfer to the coordination centre through the π-bond, which in the case of linear coordination may take place from the deeper-lying π_u orbital. For transverse coordination this transfer can take place only from the antibonding σ_u orbital. This explains the differences in the activation of N_2 with respect to the coordination geometry (see Refs.7–9 for more details). Estimates of the orbital vibronic constants are also given in Ref.32.

The Table gives examples of calculations of the changes in activation energy and charge transfer for a number of specific cases of the coordination of an N_2 molecule to transition metal complexes.[3,10] The vibrational frequencies of coordinated N_2 were taken from Ref.33, and the values of Q_0 were estimated from the empirical equation (ν' in cm^{-1}):

$$Q_0, \text{ Å} = 0.9482 - 0.7105(\nu' \cdot 10^{-3}) + 0.1302(\nu' \cdot 10^{-3})^2 \qquad (38)$$

The Table shows particularly, that as expected in the general case, the greatest contribution to ΔD on coordination is due to the linear vibronic effect, that is to the production of the deforming force (terms with coefficients b and c in Eqn.(34)), that the softening influence (the quadratic term with coefficient a) makes a smaller contribution, and that the anharmonicity terms (with coefficient d) make a very small contribution.

Semi-empirical estimates of the charge transfer to the HOMO Δq_1 and LUMO Δq_2 and the lowering of the activation energy $\Delta D = aD + bD^{1/2} + c + dD^{-1/2}$ of the N_2 molecule on coordination (one-parameter approximation).

Coordination system	ν', cm^{-1}	$10^{-6}K'$, dyn cm^{-1}	$10^{-6}\Delta K$, dyn cm^{-1}	r_0, Å	$10^4 F$, dyn	Δq_1	Δq_2	a	b	c	d
$[RuH_2(N_2)(PPh)_3]$	2147	1.900	−0.394	0.0229	−4.19	−0.16	0.44	−0.14	−2.72	2.87	−0.01
$[\{Ru(NH_3)_5\}_2N_2]^{4+}$	2100	1.821	−0.479	0.0303	−5.25	−0.57	0.41	−0.21	−3.37	4.81	−2.28
$[Os(NH_3)_5N_2]Br_2$	2028	1.695	−0.599	0.0428	−6.77	−1.00	0.40	−0.31	−4.32	8.94	−6.17
$[(tol)(PPh_3)_2Mo-N_2-Fe(C_5H_5)(dmpl)]^+$	1930	1.536	−0.758	0.0619	−8.54	−1.21	0.52	−0.37	−5.62	16.9	−17.0

Note: tol = toluene, dmpl = $Me_2PCH_2CH_2PMe_2$, $\Delta K = K' - K$.

Analogous estimates of the activation on coordination have been carried out for a number of other small molecules, including NO, O_2, C_2H_4, C_3H_8, etc.[3,10]

V. ELECTRON-CONFORMATIONAL INTERACTIONS. APPLICATIONS TO METALLOPORPHYRINS AND HAEM-CONTAINING PROTEINS

In the previous section it was shown how a change in the electronic structure of a molecular system leads via vibronic coupling to the production of a force which deforms the core of the molecule in a definite direction, to a change in the force constant, which "softens" this system (or makes it "harder"), to a change in the anharmonicity constants, etc. These changes alter the form of the adiabatic potential, including its behaviour at large distances, that is the reactivity of the system. The change in reactivity has an influence, however, in the interaction of the given system with another system, with which it undergoes a chemical reaction. Under different conditions (in the absence of this interaction), other effects, resulting from the above changes in the parameters of the system, are more significant.

In particular, a direct result of the production of a non-zero deforming force

$$F_{\bar{\Gamma}} = \sum_i \Delta q_i f^i_{\bar{\Gamma}}$$

(Eqn.(24)) is a change in the spatial configuration (geometry) of the system in the direction $Q_{\bar{\Gamma}}$. The latter is determined by the symmetry of the molecular orbitals i, for which the orbital vibronic constant $f^i_{\bar{\Gamma}}$ and the changes in the populations Δq_i are non-zero. The representations $\bar{\Gamma}$ for which $f^i_{\bar{\Gamma}}$ is non-zero, as already noted, are found directly. If the ith MO is non-degenerate, then $\bar{\Gamma} = \bar{\Gamma}_i \times \bar{\Gamma}_i = A_1$, that is the direction $Q_{\bar{\Gamma}}$ can only be totally symmetric. In other words, a change in the population of the non-degenerate molecular orbitals changes only the interatomic distances, without changing the symmetry of the system (without distorting it). If however the orbital state Γ_i is degenerate, then $\bar{\Gamma} = [\Gamma_i \times \Gamma_i]$ contains both totally symmetric and non-totally-symmetric representations, so that the presence of electrons in these orbitals leads to distortion of the system; the direction of the distortion coincides with the direction of the distortion in the Jahn–Teller effect.[2]

If the change in the electronic structure changes the populations Δq_i of not one but several MO, and the directions of the deformation of the core, determined by the coordinate $Q_{\bar{\Gamma}}$, are different for these orbitals, then the total distortion will be equal to their vector sum. To determine the latter it is also necessary to know the magnitude of the distortion $Q_{0\bar{\Gamma}}$ in each of the directions $Q_{\bar{\Gamma}}$. In the approximation linear with respect to the vibronic interaction, it is determined directly from the relationship

$$Q_{0\bar{\Gamma}} = F_{\bar{\Gamma}}/K_{\bar{\Gamma}} \qquad (39)$$

where $K_{\bar{\Gamma}}$ is the force constant in the direction $Q_{\bar{\Gamma}}$. With allowance for the change in the latter and the anharmonicity constant as a result of the change in the electronic structure, the expression for $Q_{0\bar{\Gamma}}$ becomes more complex, and takes the form given in Eqns.(27). Substituting the expression for $F_{\bar{\Gamma}}$ in Eqn.(39) gives

$$Q_{0\bar{\Gamma}} = \sum_i \Delta q_i f^i_{\bar{\Gamma}}/K_{\bar{\Gamma}} \ , \qquad (40)$$

From this it can be seen that in the directions $Q_{\bar{\Gamma}}$ for which $f^i_{\bar{\Gamma}}$ is small and the hardness of the molecule is high ($K_{\bar{\Gamma}}$ large), $Q_{0\Gamma}$ is small. In other words, a contribution to the distortion of the molecule in the given direction is made only by those orbitals for which the vibronic constant is sufficiently high, which is the case when the orbital being considered is sufficiently effectively involved in the bonding (antibonding) system in the given direction. On the other hand, appreciable distortions may take place in those directions in which the system is sufficiently "soft" (that is $K_{\bar{\Gamma}}$ is small). Similarly, Eqn.(25) makes it possible to estimate the softening or hardening (in the sense of the change in the force constant and the vibrational frequency) of the system in the direction $Q_{\bar{\Gamma}}$.

In simple cases these effects are qualitatively completely understandable from general considerations, but the above equations give quantitative estimates for these effects in the general case, and make it possible to predict them.

The change in the configuration of a molecule and its hardness with change in its electronic structure is directly related to the so-called electron-conformational interactions. The latter essentially coincide with the vibronic interactions, and the apparatus developed above can be used directly to analyse electron-conformational effects. Most frequently, electron-conformational transitions in which the appearance or disappearance of one electron leads to a change in the conformation of the system are considered. In this formulation, the problem is solved approximately using the above scheme, in which the additional population of the ith orbital ($\Delta q_i = 1$) with $f^i_{\bar{\Gamma}} \neq 0$ leads to fairly strong distortion of the system in the direction $Q_{\bar{\Gamma}}$, particularly if the value of $K_{\bar{\Gamma}}$ in this direction is small. For large systems, the appearance of an electron in a given position, usually in the active centre, leads to a local distortion $Q_{0\bar{\Gamma}}$ which initiates a conformational transformation of the system as a whole (the so-called trigger mechanism).

The electron-conformational transitions in biological systems are of particular interest. For example, in haemoglobin the displacement of the iron atom from the haem plane in the deoxy-form and its return on oxygenation, according to Perutz,[34,35] initiates a conformational $T \rightarrow R$ transition. This transition is determined by the cooperative properties of the four active iron centres in haemoglobin, and leads to the unusual S-shaped kinetic curve for the oxygenation (the "trigger" mechanism of the oxygenation of haemoglobin). The analogous haem-centres in various proteins have a wide range of functions, from electron transfer to the oxidation of saturated hydrocarbons, and all of these functions are related in some form or other to electron-conformational interactions. As noted above, the distortions of the molecular system due to electron rearrangement (Eqn.(40)), like the Jahn–Teller effect and pseudo-effect, are greater, the softer the system (that is the smaller $K_{\bar{\Gamma}}$) in the direction $Q_{\bar{\Gamma}}$ being considered.

A distinguishing feature of biological systems is that, because of the large number of atoms present, there are soft modes which give the vibronic effects a high efficiency. On the other hand, because of the large dimensions, the initial ("trigger") electron rearrangement generally takes place locally in an active centre, initiating the conformational transition of the system as a whole.

The electron-conformational and other vibronic effects in metalloporphyrins and haem-containing proteins[36–43] can be considered as examples illustrating these ideas. In addition to their independent interest for biology, these examples are of general importance, since the behaviour of the active

centre in them reflects the general situation arising in many coordination and organometallic compounds similar to metalloporphyrins. A distinguishing feature of these systems is the presence of close energy levels of the *d* electrons of the metal and the π-system of the porphyrin ring (or other similar ligands). If for example (as in metalloporphyrins) these states mix as a result of nuclear displacements of type A_{2u}, which move the metal atom from the plane of the porphyrin ring (Fig.6), then when it is sufficiently strong, this vibronic mixing softens the system or even makes it unstable with respect to this displacement of the metal from the plane (Jahn–Teller pseudo-effect). The explanation for the displacement of the metal atom from the plane of the porphyrin ring is that this displacement leads to the formation of additional metal–ligand π-bonds (for the metal atom situated in the plane of the porphyrin ring, the overlap of the corresponding orbitals is equal to zero), whose contribution to the bond energy is greater than the decrease in the strength of the corresponding σ-bonds.

As a result of the Jahn–Teller pseudo-effect, the force constant K for displacements in the direction Q, as noted above, decreases by F^2/Δ, where $F = \langle 1|(\partial V/\partial Q)_0|2\rangle$ is the corresponding vibronic constant; if $(F^2/\Delta) > K$, the system becomes unstable with respect to Q-displacements. For the metalloporphyrins with D_{4h} symmetry being considered, the Q-displacement of the metal atom from the plane of the porphyrin ring relates to the A_{2u} representation (Fig.6). This means that in order to have $F \neq 0$, the product of the representations of the mixing states 1 and 2 must contain the representation A_{2u}.

Fig.7 gives the highest occupied and lowest unoccupied energy levels of the molecular orbitals of a number of metalloporphyrins of Mn, Fe, Co, Ni, Cu and Zn, and (for comparison) manganese phthalocyanine (MnPc), obtained from a calculation for the planar configuration.[44,45] Figs.5 and 6 show that, for example, for FeP the ground state is ^3E_g, so that the excited state, which is displaced with it for A_{2u} displacements, should have ^3E_u symmetry ($E_g \times A_{2u} = E_u$); for MnP, MnPc, and CoP, the corresponding excited states are $^4A_{2g}$, ^4E_g, and $^2A_{2u}$. They can all be obtained by one-electron excitation from the $a_{2u}(\pi)$-level of (mainly) the porphyrin ring into the unoccupied $a_{1g}(d_{z^2})$-level of (mainly) the metal; here, $2\Delta \cong \varepsilon(a_{1g}) - \varepsilon(a_{2u})$ is comparatively small. For other metalloporphyrins, NiP, CuP, and ZnP, this a_{1g} orbital is occupied by electrons (Fig.7), and the next MO with the same symmetry are very high above it (not shown in Fig.7). Thus the last three metalloporphyrins show practically no Jahn–Teller pseudo-effect with respect to displacement of the metal atom from the plane, whereas the effect can appear in other systems.

To estimate this possibility, it may be noted that the calculated values of 2Δ in the series MnP, FeP, CoP, and MnPC are 0.15, 0.2, 0.6, and 1.0 eV respectively.[44,45] The vibronic constant estimated[38] for FeP is $F \cong 10^{-4}$ dyn (for other metalloporphyrins, calculations for the same states give values of F of the same order of magnitude), and the force constant of the A_{2u} displacement is $K \cong 10^4$ dyn cm^{-1} Thus $(F^2/K) \cong 0.1$ eV, that is F^2/K and Δ are of the same order of magnitude, so that the ground state is softened considerably as a result of the Jahn–Teller pseudo-effect. The porphyrins MnP and FeP ($\Delta \cong 0.08$ eV and 0.1 eV) may be unstable, since for them $\Delta < F^2/K$, whereas for CoP and MnPc ($\Delta \cong 0.3$ and 0.5), the position of the metal is softened, although it is stable. These results are in complete qualitative agreement with experimental data.[46,47]

Thus the observed displacement of the iron atom from the plane in the deoxy-form of haemoglobin (and in other analogous systems) is satisfactorily explained in terms of the Jahn–Teller pseudo-effect (the existence of a bond with the imidazole residue (Fig.6) does not lead to qualitative changes, since the energy levels a_{1g} and a_{2u} do not move apart to a significant extent;[48] see Refs.41–43 for more details). It is of interest to explain from the same viewpoint the return of the iron atom to the haem plane on oxygenation, initiating the above-mentioned conformational $T \rightarrow R$ transition. Fig.8 gives the MO energy levels for planar FeP, the deoxy-form of haemoglobin (Hb), and the changes in these levels when O_2 and CO are coordinated.[44,48] It can be seen that the comparatively small difference $2\Delta = \varepsilon(a_{1g}) - \varepsilon(a_{2u})$, which ensures softening and instability in the first two systems, including the deoxy-form of haemoglobin, increases sharply when O_2 or CO are added ($2\Delta \cong 3$ eV for HbO_2 and $2\Delta \cong 4$ eV

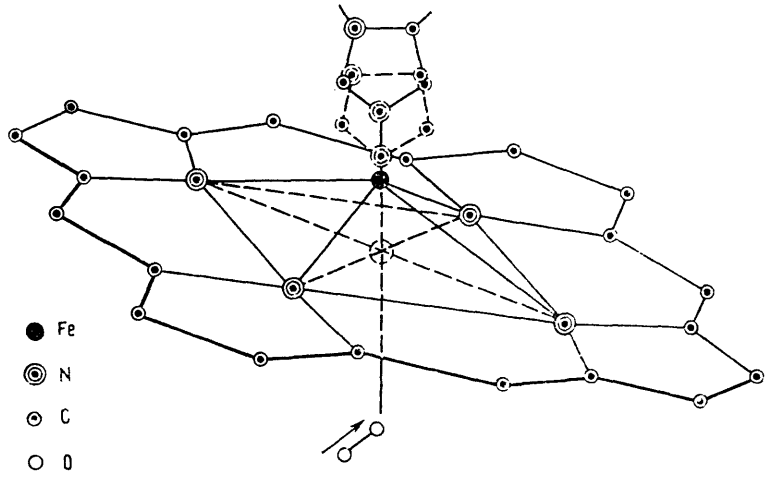


Figure 6. The structure of metalloporphyrins and the corresponding fragments of haem-containing proteins. The two positions of the iron atom together with the imidazole group of histidine correspond to the deoxy-form (continuous lines) and the oxygenated configuration (broken lines).

for HbCO). The increase in Δ removes completely the Jahn–Teller pseudo-effect, and the position of the iron atom becomes stable in the haem plane; this leads to the above-mentioned $T \rightarrow R$ conformational transition in the system (the trigger mechanism of the oxygenation of haemoglobin). At the same time, the increase in Δ may (and does, see Fig. 8) lead to a change in the spin state from $S = 2$ to $S = 0$, which is extremely typical of the compounds of iron and various other transition metals, and is known as "cross-over" (the conversion of the high-spin to the low-spin state takes place when $\Delta > \Pi$, where Π is the binding energy of the electrons in the corresponding orbitals.[1] This question is examined in more detail in Refs. 41–43.

It may be noted that since the geometry and multiplicity of metalloporphyrins depends on the interaction of the $a_{2u}(\pi)$-orbital, which is sensitive to the introduction of substituents at the periphery of the ring, with the $a_{1g}(d_{z^2})$ orbital, which is affected by the axial ligands of the metalloporphyrin, the properties of these systems may depend markedly on the protein environment in haem proteins, as in fact observed.

It has been found that not only the displacement of the metal from the plane and its return with change in the electronic structure, but also the geometry of the coordination of small ligands (NO, O_2, CO, etc.) and the unusual quantum yield of photolysis, which depends markedly on this geometry, are explained by vibronic effects, critically dependent on the electronic structure.[39–43] Overall, the approach is of course general in character and can be applied to any molecular formations in chemistry and biology.[3]

The chemical aspects of the concept of vibronic interactions examined above make it possible to reach a number of conclusions of general importance for present-day chemistry. The concept of vibronic interactions involves taking more detailed account (compared with the adiabatic approximation) of the effect of the electrons on the nuclear configuration and its dynamics, resulting from the vibronic mixing of the electronic states by the nuclear displacements. The orbital vibronic constants introduced provide a new and more complete (extended into the dynamic range) description of the electronic structure of molecules in the molecular orbital approximation. The new description makes it possible to predict changes in the nuclear configuration and its dynamics with change (perturbation) in the electronic structure.

It follows from vibronic theory that the only source of dynamic instability in molecular systems is the vibronic mixing of the ground state with one (or possibly several) excited states. This conclusion opens up extensive possibilities for explaining and predicting the stereochemistry and crystal chemistry of chemical compounds, and also for analysing the origin and studying the intermediate states of chemical reactions.

It has been shown that vibronic effects lead to a lowering of the barriers to reaction with other molecules in definite directions, that is to an increase in reactivity for certain reaction mechanisms. The knowledge of the mechanism for the production of instability and reactivity has been used to develop a theory of the process by which reactivity is induced under the influence of another molecular system, that is the theory of chemical activation on coordination. The

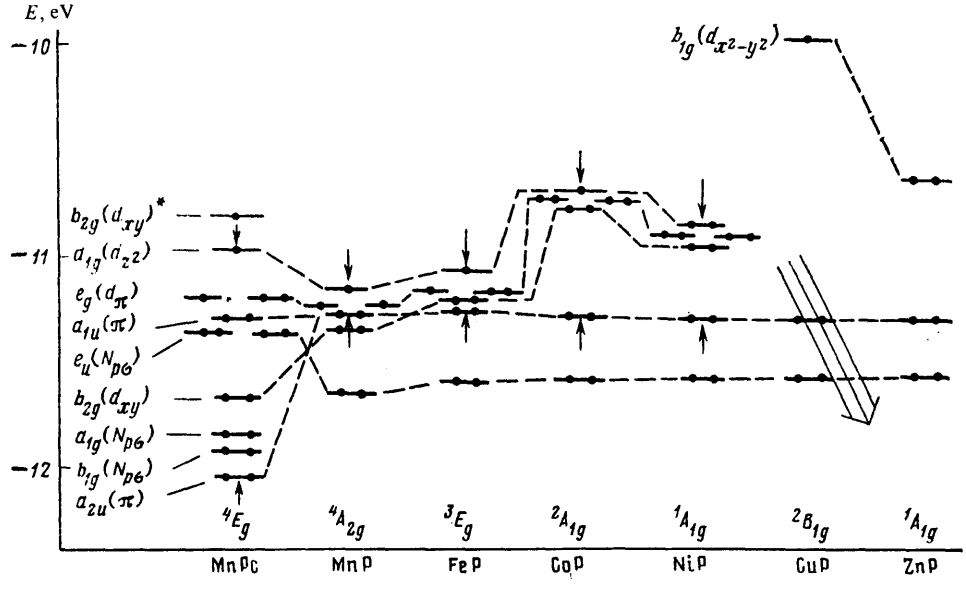


Figure 7. Energy levels of some HOMO and LUMO for metalloporphyrins and manganese phthalocyanine (MnPc); the ground terms of the systems in the configuration with the metal in the plane of the porphyrin (phthalocyanine) ring are indicated. The arrows indicate the energy gaps 2Δ between the ground and lowest excited states, which are mixed in the A_{2u} displacements of the metal.

orbital vibronic constants have been used to develop a semi-empirical two-level version of the theory, which makes possible an approximate prediction of chemical activation (lowering the activation energy of the reaction) on coordination to a given catalyst active centre.

In addition, vibronic effects form the basis of electron-conformational transformations in chemistry and biology, as has been demonstrated for specific examples, namely metalloporphyrins and haem-containing proteins.

Each of these conclusions (except the first) requires further development in detail, and the applied aspects, with some development, may each become a starting point for a new direction in this field of study. This confirms the conceptual character of the new approach to the structure–property problem briefly presented in the present review.

In general, as already noted, the concept of the mixing of electronic states as a result of nuclear displacements (produced by abandoning the separate description of the movements of the electrons and the nuclei in the simple adiabatic approximation) introduces new elements into the chemist's way of thinking, making it possible to avoid restricting stereotypes. In the new understanding, in particular, the ground and excited states of a molecule for a given configuration of the nuclei, strictly speaking, no

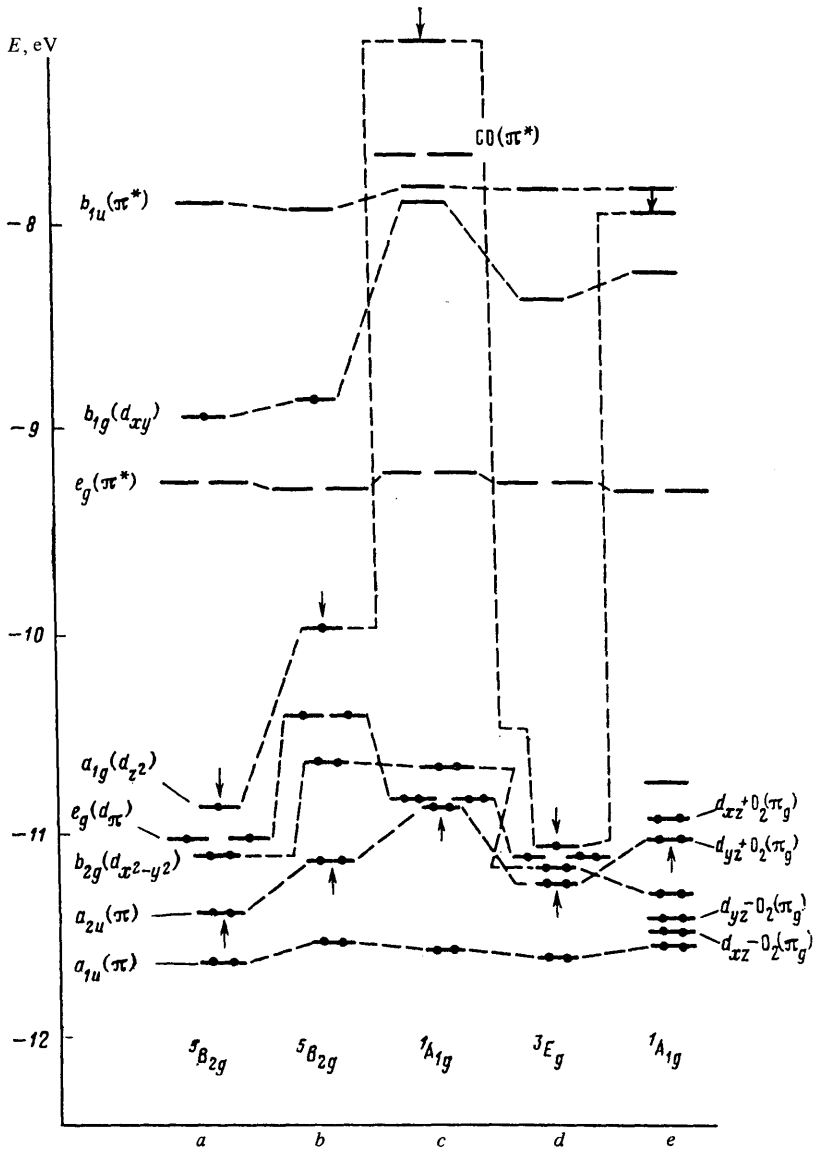


Figure 8. Energy levels of some HOMO and LUMO: *a*) FeP in the configuration with the Fe atom displaced from the porphyrin plane by $\Delta R = 0.49$ Å; *b*) the deoxy-form of haemoglobin with $\Delta R = 0.62$ Å; *c*) Hb–CO system; *d*) planar FeP, that is $\Delta R = 0$; *e*) Hb–O_2 system. The ground term and (arrows) the gap 2Δ between the states mixed in the displacement of the iron atom from the plane of the porphyrin ring are indicated.

longer exist as independent concepts; they may be mixed considerably when allowance is made for the displacements of the nuclei. In other words, the excited electronic states of the molecular configuration being considered may determine its properties in the ground state to the same extent as the ground electronic state in this configuration.

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