Russian Chemical Reviews

August 1981

Translated from *Uspekhi Khimii*, 50, 1345 - 1375 (1981)

U.D.C. 543.42

The Applications of Quantum-chemical Methods to Spectroscopic Studies on Organic Compounds

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The ways of using quantum-chemical methods in the spectro-chemistry of organic compounds are considered and the advances in the calculation of electronic and vibrational spectra are characterised. The effectiveness of the combined application of quantum-chemical and spectroscopic methods and the possibility of using LCAO-MO methods for the interpretation of ultraviolet, infrared, and Raman spectroscopic data in the study of molecular structure in the ground and excited states are demonstrated in relation to a number of examples.
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I. INTRODUCTION

A fairly complete utilisation of the potential of molecular spectroscopy, including infrared, ultraviolet, and Raman spectroscopy, can be achieved if it is possible to establish the origin of the spectral lines (bands). Useful information about the line assignments and molecular structure can be obtained from purely empirical correlations. Different variants of the additive scheme involve wider possibilities; they relate the spectra of complex molecules to the conventional parameters attributed to individual fragments, for example, chemical bonds (force constants, "electro-optical constants" of the bonds, etc.). However, in the most interesting cases—when there is a significant interaction between the fragments of the molecule—the additive scheme is greatly complicated and the possibility of an unambiguous, non-empirical, determination of the bond parameters and their physical significance are lost.

The application of quantum-chemical methods, which are based in some way on the ideas concerning the interaction of nuclei and electrons, made it possible to proceed to better-founded calculations of line frequencies and intensities with

a considerable limitation of empirical elements. Thus it has been possible to achieve a more complete and a better-founded interpretation of the spectra and to explain on this basis the characteristic features of a series of chemical and physical properties of many compounds, to obtain additional data for the description of molecular-optical phenomena, and to make semiquantitative predictions of the spectra and of the behaviour of systems which are not readily susceptible to experiments (for example, unstable intermediates).

In view of the multiplicity and non-equivalence of the quantum-chemical methods, it is useful to characterise the specific possibilities of each, to note their advantages and disadvantages, and to assess the prospects for the development of their application in molecular spectroscopy.

II. QUANTUM-CHEMICAL METHODS FOR THE CALCULATION OF SPECTROSCOPIC PARAMETERS

In the calculations of the parameters of electronic and vibrational spectra the Hartree–Fock approximation is usually employed[1]. The many-electron wave function of the molecule is found in the form of the antisymmetrical product of the one-electron wave functions—molecular orbitals (MO) $\phi_m(\mu)$—multiplied by the spin wave functions α or β of the corresponding electron:

$$\Phi_0 = \mathscr{A}\det|\varphi_1(1)\alpha(1)\varphi_1(1')\beta(1')\ldots\varphi_n(n')\beta(n')|, \qquad (1)$$

where $2n$ is the number of electrons and μ the ordinal number of the given electron. The coefficient $\mathscr{A}$ is determined by the condition governing the normalisation of $|\Phi_0|^2$ to unity.

The molecular orbitals are sought in the form of linear combinations of atomic orbitals (LCAO)

$$\varphi_m(\mu) = \sum_i C_{mi}\chi_i(\mu), \qquad (2)$$

where the C_{mi} are the required coefficients; thus the set of atomic orbitals $\chi_i(\mu)$ constitutes the basis set for the construction of the wave function ϕ_m. The principal requirement which must be met by the basis set of atomic orbitals consists in the fact that it must represent with adequate accuracy the distribution of electron density in the molecule, i.e. the basis set must be sufficiently complete. Unfortunately it is very difficult to satisfy this condition in practice. The atomic orbitals constitute an approximate representation of the electron density in isolated atoms, but their use in calculations of the electronic wave functions of molecules leads to additional errors associated with the impossibility of reproducing certain features of the changes in electron distribution on formation of valence bonds. It is therefore necessary to expand the basis sets χ_i by including additional functions in them.

The coefficients C_{mi} in Eqn.(2) are determined by a variational procedure with minimisation of the total electronic energy of the molecule E. Roothaan[2] showed that the coefficients C_{mi} corresponding to the minimum value of E can be determined from the following equations:

$$\sum_j (F_{ij} - \varepsilon_m S_{ij})\, C_{mj} = 0, \quad \sum_{ij} C_{mi}C_{mj}S_{ij} = 1, \qquad (3)$$

where

$$F_{ij} = H_{ij} + \sum_{kl} P_{kl}\left(\langle ij|kl\rangle - \frac{1}{2}\langle ik|jl\rangle\right). \qquad (4)$$

Here the summation was carried out over all the atomic orbitals k and l in the basis set. S_{ij} is the overlap integral of the atomic orbitals i and j, ε_m the energy of the electron in the mth molecular orbital, H_{ij} the one-electron Hamiltonian, P_{kl} the matrix of the bond charges and orders, and $\langle ij/kl\rangle$ the matrix element of the Coulombic interaction of electrons in the atomic orbitals χ_i, χ_j, χ_k, and χ_l:

$$\langle ij|kl\rangle = \iint \chi_i(\mu)\chi_j(\mu)\, R^{-1}_{\mu\varkappa}\, \chi_k(\varkappa)\chi_l(\varkappa)\, d\tau_\mu d\tau_\varkappa.$$

In this expression the integration is carried out with respect to the entire space of the Cartesian coordinates and $R_{\mu\kappa}$ is the distance between the electrons μ and κ.

The self-consistent field (SCF) method is used to solve the non-linear system of Eqns.(3) and (4). The set of coefficients C_{mi}, the choice of which can be fairly arbitrary, is then used as the zeroth approximation; in semiempirical methods C_{mi} are usually calculated by a procedure similar to the extended Hückel method. The matrix F_{ij} is constructed from the zeroth-approximation coefficients determined in this way and is then used, on solving Eqn.(3), to find a new set of the C_{mi}, from which a new matrix F_{ij} is constructed, etc., until the matrix elements F_{ij} and the coefficients C_{mi} cease to vary.

In practice both semiempirical and non-empirical calculations by the LCAO-MO SCF method are used.

Among the *semiempirical* procedures, the CNDO (complete neglect of differential overlap of atomic orbitals) and INDO (incomplete neglect of differential overlap) methods are commonest[3–7]. In these methods, the wave functions are calculated only for the valence electrons and the inner shells are included in the molecular skeleton; a minimal Slater basis set is used and a part of the Coulombic interaction between the electrons is neglected. In the CNDO approximation account is taken of one- and two-centre matrix elements of the Coulombic interaction of electrons only of the type $\langle ii/kk\rangle$, while in the INDO approximation the one-centre matrix elements $\langle ij/kl\rangle$, in which the i, j, k, and l orbitals belong to a single atom, are also introduced. In order to calculate all the one-centre matrix elements, the atomic spectra are used, while the two-centre integrals are evaluated from empirical formulae reflecting the dependence of the interaction between the electrons and nuclei on the relative positions of the atomic orbitals. In the second case the parameters in the empirical formulae indicated must be determined from data not only for atoms but also for small molecules; the solution of the problem is then not unambiguous and the differences between the selection procedures are characterised by modifications of the CNDO and INDO methods. A rational selection of parameters makes it possible to diminish the disadvantages of the CNDO and INDO approximations and also of the SCF method.

The CNDO/2,[5,6] INDO[7], MINDO/2,[8,9] and MINDO/3 [10] (modified INDO approximations) are most widely used to calculate the properties of the ground states of organic molecules, while electronic absorption spectra are calculated by the CNDO/S method[11,12]. A further improvement of the semiempirical methods can be achieved in terms of the more rigorous null diatomic differential overlap (NDDO) approximation.

As regards *non-empirical* calculations, here all the matrix elements of the interaction between the electrons and nuclei are evaluated by the analytical calculations of the necessary integrals in terms of a basis set of atomic orbitals. The atomic orbitals are usually Gaussian functions, which ensure a relative simplicity of the calculations but lead to a fairly poor representation of the distribution of electron density, so that one has to use many more functions than for Slater basis sets. The OST-3GF basis set—the minimal basis set of Slater orbitals each of which can be fitted by a linear combination of three Gaussian functions, is very widely

used. In the OST-4-31GF basis set, each Slater orbital for the electrons in the inner shell is described by a linear combination of four Gaussian functions and that for valence electrons is described by a combination of three and one Gaussian functions. The use of two (instead of one) linear combinations, whose coefficients in Eqn.(2) are varied independently, makes it possible to take into account the changes in the atomic orbitals on formation of different valence bonds.

The results of the calculations depend greatly on the choice of the basis set. Generally speaking, it is desirable to expand the basis set until the attainment of the Hartree–Fock limit, whereupon its further expansion no longer alters the result. However, this can be done only for the simplest molecules, for example, for CH_4 and NH_3. For more complex molecules, it is necessary to restrict the treatment to small basis sets, but their selection introduces a considerable arbitrary element into the calculation; the treatment is not universal and different basis sets must be used for different properties of the molecule. We may also note that the employment of the Hartree–Fock approximation (the SCF method) can also introduce a large error and further refinement of the electronic wave function (allowance for electron correlation) constitutes a very complex problem.

The methods described above are most widely used in quantum-chemical calculations of molecular spectra. However, their application to complex molecules is hindered by the large amount of computer time required. At the present time calculations by non-empirical methods are in practice possible for molecules consisting of not more than 6–10 atoms (20–30 electrons); semiempirical methods of the CNDO or INDO type are applicable to molecules consisting of several tens of atoms (up to 50–100 electrons). The amount of computation for more complex objects is too great even for the most efficient computers. In recent years attempts have therefore been made again to employ combined methods based on the π-electron approximation[13]. In order to take into account σ-electrons, a special empirical quadratic function was introduced, being added to the π-electronic energy of the molecule. This function contains parameters similar to the equilibrium geometrical parameters and force constants; the parameters were chosen so that the molecular geometry can be calculated by minimising the expression for the total energy of the molecule and the force constants can be calculated by differentiating the energy with respect to the atomic coordinates. Although the scope of such calculations is in many respects limited, they make it possible to investigate the spectroscopic characteristics of very large molecules.

Calculations by non-empirical methods on molecules with heavy atoms require a very large amount of computer time. The latter can be reduced by resorting to the pseudopotential method. In this approximate method one calculates the wave functions of the outer electrons only, assuming that the latter exist in the resultant electric field of the charges of the nuclei and inner electrons; the field is introduced into the Hamiltonian in the form of an empirical potential function—the pseudopotential. Calculations by this method (see, for example, Sachs and Hinze[14] and Abarenkov[15]) are much less accurate than the usual non-empirical calculations, but a successful selection of the empirical function can lead to a significant improvement of the results.

Relativistic effects, associated primarily with the high velocity of the electrons of the inner shells (involving an increase in the mass of the electron and a lag in the Coulombic potential) and with the spin–orbital interaction, play an appreciable role in the properties of molecules with heavy atoms; the shielding of the nuclear charges by inner electrons is then altered, which influences indirectly the valence electrons. Allowance for the relativistic effects increases the amount of calculation severalfold. The relevant methods for semiempirical and non-empirical calculations in LCAO-MO SCF schemes have been described in detail in a review[16].

The SCF Xα scattered wave method, the principle of which differs fundamentally from that of the widely used LCAO-MO SCF method, has been applied in recent years to the calculation of electronic absorption spectra. In the Xα method each atom is assumed to be surrounded by a sphere (different variants either do or do not allow for the overlap of the spheres of adjacant atoms); in the space between the spheres the electronic wave function is specified by planar waves and within the spheres it is sought by solving the Schrödinger equation with an empirical potential (for further details, see the relevant review[17]). The method is usually classified as non-empirical, although the specification of the potential within the spheres surrounding the atoms is partly empirical.

The Xα method makes it possible to carry out faster calculations than by the non-empirical LCAO-MO SCF methods. It is particularly effective in the study of molecules with heavy atoms containing a large number of electrons in the inner shells, since the computation time depends in this instance only slightly on the number of electrons in the atom. However, the region of applicability of this method in spectroscopy is at present largely limited to the determination of the positions of the occupied electronic levels (which are particularly important for photoelectron and X-ray electronic spectroscopy); the electronic absorption spectra are calculated much more rarely (resorting to the extremely artificial "transition state" procedure) and only the energies of transitions averaged with respect to the multiplet (!), intermediate between singlet and triplet transitions, are usually calculated, although in principle the possibility of allowing for the multiplicity is not ruled out.

III. THE FORCE CONSTANTS OF CHEMICAL BONDS AND INTRAMOLECULAR VIBRATION FREQUENCIES

The force constant of a chemical bond $K(i)$, equal to the second derivative of the potential energy of the molecule with respect to the increase in the length of the given bond: $(\partial^2 V/\partial q_1^2)_{q_j=\text{const.}}$, is perhaps the main characteristic of the mechanical properties of the bond. For like bonds in different molecules of a similar type, it varies within narrow limits; its semiquantitative correlations with the bond length and order and also certain relations with the dissociation energy are known. However, one should note that the usual force constants depend to some extent on the arbitrary element in the selection of the internal coordinate system in the molecule; the "independent force constants" d^2V/dq_1^2, which characterise the bond strength under the conditions where an external force is applied to only one (ith bond), are free from this disadvantage[18]. It is even more significant that the chemical bond in a polyatomic molecule cannot be, strictly speaking, characterised by a single force coefficient. For this purpose, one must introduce a whole matrix of coefficients including those related to the interaction of the given bond with all other bonds, i.e. with non-diagonal elements $K(ij) = \partial^2 V/\partial q_i \partial q_j$.[19,20] The latter determine the appearance of forces acting in the jth bonds as a result of the extension of the ith bond. The non-diagonal elements are as a rule small, but they are of primary importance for certain problems.

If the structural formula of the compound is known and the necessary set of force constants is available, it is possible to calculate fairly simply, for the conformation investigated, the frequencies ω of all the normal atomic vibrations manifested in the infrared and Raman spectra as well as vibronic absorption and secondary emission spectra, to determine the vibrational modes, and to characterise the force field in a molecule deformed in any way. These possibilities are limited in practice by the inadequacy of the information about the force constants themselves (which is particularly restricted for electronically excited states).

The total amount of information required for an exact calculation of the frequencies ω in complex molecules is extremely large and the available data must be supplemented using analogies and approximate assumptions. Under these conditions, the invocation of additional sources of information appears very important; quantum chemistry occupies a special place here, since it not only makes it possible to estimate, in principle, any force constants for both the ground and electronically excited states but it can also elucidate the origin of individual coefficients and their relation to the structure of the electron shell (unfortunately, sufficient attention has not been paid to this factor hitherto).

It is known that the solution of the converse problem—the calculation of the force coefficients from experimental frequencies ω—requires extensive and laborious preparatory work involving the synthesis of isotopic models. In many cases the solution is not unambiguous and the choice between sets of coefficients satisfying the initial system of equations is frequently based on intuition. The application of MO methods places at the disposal of the investigator independent criteria for such a choice. One can add to this that the quantum-chemical calculation of "independent force constants" does not involve any additional difficulties.

Both semiempirical and non-empirical quantum-chemical methods are used to calculate the force constants. In all cases the molecular geometry is optimised initially, i.e. the most stable form corresponding to the total energy minimum is specified; the second derivatives of the energy with respect to the Cartesian or natural coordinates (force constants) and if necessary also cubic and biquadratic terms are then found at the minimum.

The choice of the basis set has a significant influence on the results of non-empirical calculations of force constants (particularly, non-diagonal elements). Thus, when a minimal Slater basis set is used, an extremely indirect agreement with experiment is obtained. The agreement improves significantly on passing to an extended basis set (OST-4-31G, etc.), but a further extension of the latter is no longer very effective—even when the Hartree–Fock limit is reached the force constant prove to be too high by 10–20%.[21] The accuracy of the calculation of the non-diagonal elements is then much lower. Thus K(C–O, C–O′) for the CO_2 molecule was found to be too high almost by a factor of two[22]. Allowance for electron correlation improves the results[23,24], but this is virtually impossible for polyatomic molecules.

A characteristic feature of the semiempirical methods is that the deformation vibration frequencies are lower than the stretching vibration frequencies. In the CNDO/2 method the values of ω for deformation vibrations agree with experiment without the introduction of corrections, while the data for stretching modes are found to be too high. On the other hand, in the MINDO/2 method the latter are close to the experimental data, but the deformation vibration frequencies are too low. The MINDO/3 method yields results of an intermediate type; the errors are on average the same as in non-empirical calculations without allowance for electron correlation.

Since the errors are in most cases systematic, they can be greatly reduced by introducing empirically selected correcting scale factors for the determination of the types of force constant (for example, for the C–C bonds, C–C–H angles, etc.) or increments which are added to the calculated frequencies.

For calculations in terms of the MINDO/3 approximation, Dewar and Ford[25] selected a system of increments specific to stretching, deformation, and torsional vibrations of specific atomic groups or bonds; the satisfactory accuracy of the results was demonstrated in relation to a large number of examples, but the wide variety of the normal vibrational modes, which in a complex molecule include the vibrations of many bonds and angles, and the impossibility of a clear-cut separation of stretching and deformation modes limit the prospects for correcting frequencies in terms of the types of vibrations.

It appears more logical to correct the force constants and positive results have been achieved on these lines. In a non-empirical calculation of the vibrational spectra of ethylene in terms of the OST-4-31G basis set the introduction of four correcting factors (of the order of 0.75...1.0) for the diagonal force constants and of yet another correcting factor for all the non-diagonal force constants diminished the average discrepancy with 12 experimental frequencies severalfold and the latter amounted to ~7 cm^{-1}.[26] Similar results were obtained also for ethane, propane, propene, and dimethyl ether, but the corrections were chosen individually for each type of compound[27,28]. We may note that a simple determination of the frequencies from the set of coefficients $K(ij)$ obtained experimentally for other molecules of a similar type yields approximately the same accuracy in the absence of conjugation.

In the calculation of the spectra of hydrocarbons by the CNDO/2 method the following correcting factors must be introduced for the force constants[29]: 0.38 for valence bonds, 1.80 for angles in the molecular plane, and 0.62 for angles of displacement from the plane. The same corrections have been used for glyoxal and acroleine[30]. A set of scale factors for organic compounds containing N and O atoms has been recommended and tested[31]; the standard error in a series of fairly complex triazoles did not then exceed 30 cm^{-1}. We recall that the experimental error is ~±1 cm^{-1}, but the effect of the medium (solvent), which is difficult to eliminate, is an order of magnitude greater.

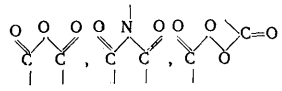
In selecting the scale factors or increments, the problem of their reproducibility in a series of different molecules naturally arises. It can be shown that it is similar to the problem of the possibility of transferring an experimental force constant, but in reality the causes of the limited universality in these two instances are completely different; in the first case such limitation arises from the significant irregularity of the errors of the selected computational method, while in the second the force field for particular test molecules has real specific features which are in themselves of extremely great interest and important for chemistry and are in addition susceptible to investigation by quantum-chemical methods.

The wide variety of procedures and correction factors reflects the subjective approach of different workers to this problem. The best results are obtained when the corrections are made specific to the maximum extent, although this inevitably reduces (and in the limit completely vitiates) the significance of the initial calculation itself.

As regards the calculations of *non-diagonal* force coefficients $K(ij)$, the latter are frequently subject to large errors and for polyatomic molecules the estimation of the accuracy of the calculations by comparison with values evaluated from experimental data is very difficult owing

to the unreliability of the latter. Practical experience with calculations has shown that semiempirical methods lead to incorrect signs of the non-diagonal coefficients characterising the interaction of the C–H bonds with adjacant valence bonds; the absolute values of these constants are low and they therefore have little effect on the frequencies, but the relative positions of the stretching vibration lines for the CH_2 and CH_3 groups depend on them. In other cases qualitatively satisfactory results were obtained. However, the non-diagonal elements were corrected by extremely arbitrary (relatively unjustified) procedures[26–31]; the correction factors were varied in the range from 0.3 to 1 (depending on the investigator who carried out the calculation and on the method used).

For non-adjacent bonds, the coefficients $K(ij)$ are extremely small and in the calculation of the frequencies ω they are therefore usually disregarded; however, in certain molecules in the presence of conjugation they proved to be fairly large, contrary to expectation. In the systems



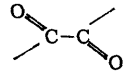
they are to a large extent responsible for the anomalously large splitting of $\omega_{C=O}$ into components corresponding to the in-phase and out-of-phase vibrations of the C=O groups[19,32]; the splitting (up to 70 cm^{-1}) and the values of $K(C=O, C=O')$ proved in this instance to be several times greater than for the system [32,33] although seemingly the opposite should have been expected.

Table 1. The force field in terms of the symmetry coordinates for the ethane molecule (K, δ, and ρ are the stretching, deformation, and torsional force constants; subscripts S and d denote the values for symmetrical degenerate vibrations).

Force constants*	Semiempirical methods		Non-empirical methods			Experiment
	CNDO/2 (Ref.29)	MINDO/2 (Ref.29)	OST-3GF (Ref.27)	OST-4-31GF (Ref.27)	large basis set (Ref.27)	
K (CC)	4.67	5.10	6.66	4.86	5.07	4.45
K_s (CH)	5.27	5.91	7.09	5.54	5.68	4.90
K_d (CH)	5.05	5.47	7.03	5.37	5.54	4.76
δ_s	0.81	0.52	0.83	0.71	0.76	0.61
δ_d	0.77	0.37	0.89	0.72	0.69	0.56
ρ	0.81	0.53	0.94	0.82	0.85	0.68
K/K_s	0.21	0.44	−0.01	0.14	0.14	0**
K/δ_s	0.28	0.36	0.34	0.39	0.39	0.35
K_s/δ_s	−0.14	−0.09	−0.11	−0.16	−0.12	−0.05

*Units—mdyn $Å^{-1}$.

**Adopted on the basis of the assumption made.

Calculation of the principal non-diagonal coefficients for acetic anhydride by the CNDO/2 method[34] confirmed the ideas concerning the interaction of two C=O groups in the vibrational process, as a result of which $K(C=O, C=O')$ for the anhydride is much greater than for a similar molecule with a methylene bridge (pentane-2,4-dione); however, calculation revealed a feature which could not be established from experimental data, namely the significance and large contribution to the splitting of $\omega_{C=O}$ by the coefficients $K(C=O, C-O)$, which are much greater than $K(C=O, C-C)$ for pentanedione.

Certain ideas concerning the accuracy of the results obtained by different computational methods and also the coefficients $K(i)$ and $K(ij)$ themselves are provided by Tables 1 and 2, which include also fairly reliable data determined from observed frequencies; the computational methods used yielded approximately equivalent results.

It follows both from the calculation and experiment (Table 2) that the non-diagonal coefficients $K(ij)$ for a molecule with conjugated NC–CN bonds are much greater than in saturated hydrocarbons. The negative sign of $K(C\equiv N, C\equiv N')$ means that the extension of one C≡N bond favours an increase in the length of another. The diagonal coefficient $K(C\equiv N)$ is in this case lower (as for the H_2N–CN and $H_2C=CH$–CN molecules[35]) than for acetonitrile by ~3% due to conjugation, while $K(C-C)$ is in fact appreciably higher.

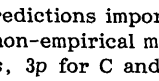
Table 2. The force constants (mdyn $Å^{-1}$) of dicyanogen and acetonitrile[35,126,127].

Force constant	Acetonitrile (experiment)	Dicyanogen				
		experimental data	INDO	MINDO/2	NMMB*	NMLB**
K (CN)	18.6	18.0	39	18	20.6	22.8
K (CC)	5.6	7.0	17.5	7.7	—	—
K (CN, C'N')	—	−0.26	−0.44	0	−0.24	−0.30
K (CN, CC)	0.15	0.42	1.8	0.7	0.14	0.09

*Calculation by a non-empirical method in terms of a moderate basis set.

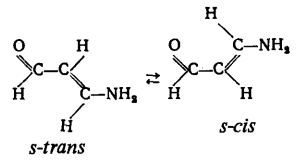
**Calculation by a non-empirical method in terms of a large basis set.

In individual studies attempts were made to investigate the accompanying molecular forms which cannot be isolated from the equilibrium system. In the communication quoted above[30] interesting data are presented for the semiempirical calculation of the spectra of the *s-cis*-conformers of butadiene and glyoxal, for which limited and unreliable information was available. According to the results[30,33], the force constants of the double bonds in the *s-cis*- and *s-trans*-conformers are virtually the same, but $K(C-C)$ for *cis*-glyoxal is appreciably smaller than for the *trans*-isomer, as a result of which ω_{C-C} is lower by 100–200 cm^{-1}. The interaction coefficients of the double bonds are in all cases small, but the symmetric vibration frequency of the double bonds in the *s-cis*-form (in contrast to the *s-trans*-form) should be lower than the antisymmetric frequency.

Detailed information has been obtained for the rotational isomers of formic acid[33]. The spectrum of the *s-cis*-conformer  was unknown and the calculation yielded predictions important for experiment. The application of a non-empirical method with a fairly large basis set (9*s*, 5*p*/5*s*, 3*p* for C and O) yielded the following force constants for the *s-cis*-conformer (*s-trans*-conformer): $K(C=O) = 14.6$ (14.1) mdyn $Å^{-1}$; $K(C-O) = 6.9$ (7.2) mdyn $Å^{-1}$; $K(O-H) = 8.8$ (7.9) mdyn $Å^{-1}$; $K(C=O, C-O) =$ 1.9 (1.3) mdyn $Å^{-1}$. In conformity with the differences between bond strengths in the *s-cis*-form, $\omega_{C=O}$ should be higher by 50 cm^{-1} and ω_{O-H} should be higher by 200 cm^{-1}. The data obtained make it possible to estimate the zero-point vibration energy and to revise the calculations of the

heats of chemical reations; on the other hand they enable one to supplement the available information about the interrelations between the $K(i)$ and the chemical bond lengths.

In the infrared spectra of certain aminocarbonyl compounds with conjugated C=C and C=O bonds, a third band, whose origin is obscure, appears in the region of 1610 cm^{-1} in addition to the bands at ~1650 cm^{-1} ($\omega_{C=O}$) and ~1570 cm^{-1} ($\omega_{C=C}$) usually observed. Calculations of the spectrum of animopropenyl[36] showed that the band is associated with the second rotational isomer and at the same time that $K(C=O)$ increases in *cis–trans*-isomerisation:



(15.0 mdyn $Å^{-1}$ for the *s-cis*-isomer and 16.1 mdyn $Å^{-1}$ for the *s-trans*-isomer), while the C=C bond changes little (36); unfortunately the authors did not estimate K(C–C) and K(C=C, C=O).

The non-empirical calculation of the force constants for methylamine and a series of other simple molecules[37–39] permitted the assignment of certain lines concerning which contradictory view had been expressed or at least to reject the earlier explanations; for example it was established that the 777 cm^{-1} band in the spectrum of HNCO refers to an out-of-plane vibration, while in the hydroxylamine spectrum the torsional vibration band should be in the region of ~1300 cm^{-1}.

The estimates of the strengths of bonds involving the metal atom in salts in the absence of intermolecular interaction are of interest. According to calculated data[40], the coefficient K(Li–C) for an isolated LiCN molecule should be lower by a factor of 3–4 than for the bonds with the cyano-group in the H–CN, Cl–CN, and H_3C–CN molecules.

According to Schlegel et al.[21], the force constants differ significantly for the C–H bonds oriented in different ways relative to the unshared electron pair of the neighbouring heteroatom. Predictions of the spectrum of vinylborane, which is virtually impossible to determine experimentally, have been made on the basis of the calculated force constants and frequencies[41].

During recent years attempts were made to use quantum-chemical calculations of vibrational frequencies for the evaluation of the partition functions and for the determination from the latter of the entropy contribution to the free energy. The spectra of stable molecules can be most simply determined experimentally, but quantum-chemical methods are applicable also to unstable compounds and to transition states (see, for example, Yoshioka et al.[43]); at the same time they can yield information about the frequencies of unobserved transitions. Thus the entropy contribution to the activation energy can be estimated from calculated frequencies and extremely fine kinetic effects can be interpreted. The first studies showed that the accuracy of the method is entirely sufficient for this purpose; thus data have been obtained for the primary kinetic isotope effect in the reaction $CH_2=CH-CH_2COOH \rightarrow CH_3CH=CH_2 + CO_2$, which agreed well with experiment[25].

In connection with the foregoing, it must be emphasised that the results of quantum-chemical calculations cannot as yet characterise the force field and the frequencies ω with an accuracy equal to that of the experimental determination, but they are extremely useful for line assignments and the combination of calculated and experimental data leads to a more complete and reliable description of the spectrum. The calculated *relative* values are more reliable and can assist in interpreting the comparatively small differences between the frequencies of similar molecules, which cannot always be done by other methods.

By combining quantum-chemical methods with the usual methods involving calculation from experimental frequencies, it is possible to achieve a significant refinement of the force field (see the examples in the literature[42,44,55]).

IV. THE INTENSITIES OF INFRARED ABSORPTION BANDS

The integral intensity of a fundamental infrared absorption band is known to be proportional to the square of the derivative of the molecular dipole moment $\partial\mu/\partial Q$. The origin of the dependence of the dipole moment on Q is associated both with the displacement of the atoms carrying a charge and with the changes in the charges themselves (or in the populations of the atomic orbitals).

In order to calculate the intensity, it is sufficient to evaluate the dipole moments for the equilibrium and non-equilibrium values of Q, which does not present significant technical difficulties, although it does require the knowledge of the vibrational mode. Among the semiempirical methods, best agreement with experiment is achieved with the aid of the CNDO/2 method and a somewhat worse agreement is obtained using the MINDO/3 and INDO methods. An important feature of the quantum-chemical methods is the possibility of determining the signs of the derivatives of the dipole moment. If the derivatives are fairly large, their signs are found to be the same whatever the method, including the non-empirical methods, and they can be regarded as more or less reliable; the differences in sign have been obtained only for certain deformation vibrations of the C–H bonds.

Table 3. Derivatives of the dipole moments with respect to symmetry coordinates (D $Å^{-1}$).

Symmetry coordinate	CNDO/2 (Ref.45)	CNDO/2 (Ref.125)	MINDO/3 (Ref.45)	NMLB* (Ref.125)	Experimental
		CH_4			
S_3 (stretch)	−0.625	−0.74	−1.39	−0.97	0.704
S_4 (deformation)	0.24	−0.34	0.29	0.33	0.387
		C_2H_4			
S_7 (deformation)	2.37	1.50	0.59	2.35	1.805
S_8 (stretch)	−1.23	−1.17	−2.03	−0.91	0.725
S_{10} (deformation)	−0.392	−0.33	0.05	−0.05	0.350
S_{11} (stretch)	0.859	0.69	0.94	0.79	0.605
S_{12} (deformation)	0.043	0.08	−0.13	0.30	0.269

*Calculation by a non-empirical method in terms of a large basis set.

The results of calculations by different methods for methane and ethylene (Table 3) and other compounds[45–50] have shown that the quantum-chemical methods make it possible to obtain a semi-quantitative agreement with experiment and to determine which lines should be intense, which should be weak, and which should not be observed at all. Such data are sufficient for the solution of many spectrochemical problems. The differences between the intensities of lines associated with isotypical vibrations can

be calculated with a high degree of accuracy for a series of molecules with similar structures. Thus a fairly satisfactory correlation with experiment has been obtained for the C=C stretching vibration bands in the spectra of different ethylene derivatives $H_2C=CHX$, although the intensities differed in this instance by a factor of 5–10;[51] here it would be appropriate to take the next step and to give a well-founded explanation of the higher intensity of the bands of molecules containing electron-donating groups X.

The simplest but as yet insufficiently tested procedure for increasing the accuracy of the calculation of the line intensities involves the selection of scale factors or increments. This method has been used to find derivatives of the dipole moments of acetylene, ethylene, and ethane. In calculations by the non-empirical method in terms of a minimal basis set the derivatives were found to be too low to approximately the same extent; their multiplication by 1.2 led to quite acceptable results and to an adequate agreement with experiment[52].

Problems of increasing the accuracy of the calculation of the vibrational mode for the atoms and of extending the basis set for the calculation of the wave functions by including polarising orbitals in the set (p orbitals for the H atom and d orbitals for the C and O atoms) and also of allowing for electron correlation stand in the way towards a more rigorous and accurate calculation of the infrared band intensities (without introducing corrections)[53].

V. PROCEDURES FOR THE INVESTIGATION OF THE STRUCTURES OF MOLECULES IN ELECTRONICALLY EXCITED STATES

The available information about the electronic structures and properties of organic molecules in excited states is extremely scanty. Such substances are comparatively unsusceptible to experimental study and the possibility of resorting to quantum-chemical methods is very important. It is noteworthy that the study of excited states is very important not only for the characterisation of the optical properties of molecules but also for understanding the characteristics and mechanisms of many chemical (primarily photochemical) reactions.

The Hartree–Fock approximation for molecules with closed shells, described in Section II, makes it possible to calculate the electronic wave function of the ground state Φ_0. In the study of electronically excited states, certain modifications must be introduced into the computational scheme. The simplest modification is the approximation of virtual orbitals[54], in which all the one-electron molecular orbitals are calculated by the standard Hartree–Fock method for the ground state, each occupied molecular orbital containing a pair of electrons with opposed spins. After the calculation of the coefficients (adjusted for self-consistency) of the expansion of the molecular orbitals with respect to atomic orbitals the energy of the molecular orbital, and the total molecular energy, one of the electrons is "transferred" from the occupied to the vacant orbital. The energy of this transition ($m \to r$) is calculated as the difference between the energies of the electron in these orbitals, since all the remaining molecular orbitals are assumed to be unaltered (which can be regarded as a fairly rough approximation).

In order to take into account the changes in the molecular orbitals of electronic excitation, we shall make use of the method of configuration interaction (CI). In this method the wave functions $\Phi_{m \to r}$ of excited singlet states, calculated in terms of the approximation of virtual orbitals

$$\Phi_{m\to r} = \text{const} \cdot \det|\varphi_1(1)\alpha(1)\varphi_1(1')\beta(1')\ldots\varphi_{m-1}(m-1)\times \cdot\times\alpha(m-1)\varphi_{m-1}(m-1)'\beta(m-1)'\varphi_m(m')\beta(m')\ldots \ldots\varphi_n(n)\alpha(n)\varphi_n(n')\beta(n')\varphi_r(r)\alpha(r)|$$

constitute the basis set. Linear combinations of these functions

$$\Psi_{q\to t} = \sum_{mr} C_{mr}^{qt}\Phi_{m\to r}$$

give rise to more accurate wave functions of the excited states. The subscripts and superscripts m, r, q, and t can vary from 1 to N, where N is the number of atomic orbitals in the basis set adopted. The coefficients C_{mr}^{qt} are determined by the diagonalisation of the matrix made up of the elements $\langle\Phi_{m\to r}|H|\Phi_{m'\to r'}\rangle$. The functions $\Phi_{m\to r}$ are of the one-determinant type, while the functions $\Psi_{q\to t}$, with CI, are of the multideterminant type. However, for the majority of excited states the main contribution to $\Psi_{q\to t}$ comes from only a single one-determinant function $\Phi_{m\to r}$, while others introduce only a small correction reflecting the changes in the molecular orbital on excitation.

Other methods widely used to study the geometry and electronic structure of molecules in the excited state are the restricted and unrestricted Hartree–Fock methods for open shells and the Dewar half-electron method.

In calculations by the restricted Hartree–Fock method on systems with open shells equations of types (3) and (4) include non-diagonal Lagrange coefficients[2], and their solution is more complex than for systems with closed shells. However, entirely acceptable procedures have been proposed for their solution[56–59], which made it possible to apply the method on a fairly large scale in non-empirical calculations of the geometry of excited states.

When the unrestricted Hartree–Fock method is used, two different sets of linear combinations of atomic orbitals, corresponding to electrons of different spins, are introduced for each electron pair. Each electronic state is described by a specific set of coefficients defining the electron population of the molecular orbitals. The coefficients of the expansion of MO and AO are determined from the system of equations obtained by Pople and Nesbet[60]. The principal deficiency of the method consists in the fact that the wave function obtained does not, strictly speaking, represent the eigenfunction of the square of the spin operator and is an inaccurate solution, which can be improved only by introducing an additional laborious procedure.

The Dewar half-electron method[61] is based on the standard Roothaan equations for molecules with closed shells (where there are two electrons in each molecular orbital) but with an altered number of electrons in two molecular orbitals in the calculation of the bond charge and order matrix P_{ij}. This description of the excited state with retention of Eqn.(4) for F_{ij} implies in essence that the molecular orbitals, occupied by a single electron in the standard Roothaan method, are populated by two "halves" of an electron with opposed spins. F_{ij} then incorporates the matrix elements of the Coulombic interaction of the electron halves and the exchange interaction between the unpaired electrons is incorrectly taken into account. The necessary corrections for this can be introduced into the final total energies, retaining the standard Roothaan expressions for F_{ij}. In this case the usual programs for molecules with closed shells are less altered on passing to the study of excited states. In the determination of the coefficients for the expansion of the molecular orbitals with respect to the basis set of atomic

orbitals one then minimises an inaccurate expression for the total energy, but the associated errors are small and do not have a significant influence on the results of the calculation.

The advantages and disadvantages of each of the above methods have not yet been adequately investigated, but they are apparently entirely suitable for calculations of the geometries and electronic structures of excited molecules. Examples of calculations of the geometries of excited singlet states are presented in Table 4. It is noteworthy that Table 4 lists the absolute geometrical parameters, whereas for spectroscopic purposes their changes on excitation are mainly required; the latter are reproduced much less accurately by quantum-chemical methods. For other examples, see the literature[62-68]. From the standpoint of computer time, the Dewar half-electron method[68] is the most economical among those enumerated above and can be recommended for calculations on large molecules.

Table 4. The geometry of molecules in the lowest electronically excited state[61,65].

Parameter*	CNDO/2 (virtual MO)	CNDO/2 with allowance for CI	OST-4G with allowance for CI	OST-4-31G with allowance for CI	MINDO/3 in combination with RHFM**	MINDO/3 ***	Experimental
			HCN				
R_{CN}, A	1.30	1.30	1.37	1.30	—	—	1.30
H-C-N angle, deg	129	127	112	127	—	—	125
			H_2CO				
R_{CO}, A	1.28	1.28	1.31	1.27	1.26	1.25	1.32
α, deg	0	31	28	15	38	29	31
			HC≡CH				
R_{CC}, A	1.34	1.33	1.37	1.37	1.35	1.35	1.39
H-C-C angle, deg	137	136	121	125	124	124	120

*Here R is the interatomic distance and α the angle between the C=O bond and the CHC plane.

**Restricted Hartree–Fock method.

***In combination with the "half-electron" method.

VI. QUANTUM-CHEMICAL CALCULATIONS OF THE FREQUENCIES AND PROBABILITIES OF ELECTRONIC TRANSITIONS

The quantum-chemical calculations of the geometry and of the distribution of electron density for excited states, examined above, can be regarded as successful, since even semiquantitative results are extremely useful. However, for the calculation of electronic absorption spectra, it is necessary to have more accurate wave functions and, despite their laborious nature, variants taking into account the configuration interaction are used nowadays for this purpose.

Calculations in terms of the CNDO/S valence approximation with allowance for CI are most widely used to investigate the electronic absorption spectra of molecules containing systems of conjugated π-bonds[11,12]. Several modifications of the method have been proposed, differing slightly from one another in the choice of the empirical parameters but leading to fairly similar final results. The errors in practical calculations of the energies of $\pi \rightarrow \pi^*$ electronic transitions do not exceed several tenths of electron-volts even for fairly complex molecules (Table 5). The accuracy is lower for the $n \rightarrow \pi^*$ transitions and the energies obtained are in most cases too low. The latter is apparently associated with the use of the CNDO approximation in which no account is taken of a series of interaction integrals between electrons making a significant contribution to the energy of the $n \rightarrow \pi^*$ transitions. The singlet–triplet splitting for n, π^* excited states is then found to be zero, although in reality for certain compounds it reaches 1 eV.

Table 5. Calculation of the electronic absorption spectra by the CNDO/S method[11,12].

Transition	Transition energy, eV		Oscillator strength	
	calc.	expt.	calc.	expt.
		Benzene		
$^1B_{2u}$ $(\pi \rightarrow \pi^*)$	4.8	4.9	0	0.002
$^1B_{1u}$ $(\pi \rightarrow \pi^*)$	6.1	5.9	0	0.1
$^1E_{1u}$ $(\pi \rightarrow \pi^*)$	6.9	6.7	1.2	0.7
		Chlorobenzene		
B_1 $(\pi \leftarrow \pi^*)$	4.8	4.8	0	0.005
A_1 $(\pi \rightarrow \pi^*)$	6.0	6.0	—	0.2
B_1 $(\pi \rightarrow \pi^*)$	6.7	6.7	0.3	0.47
A_1 $(\pi \rightarrow \pi^*)$	6.8	6.9	1.7	0.73
		Pyridine		
$^1B_2$ $(n \rightarrow \pi^*)$	4.4	4.3	0.006	0.003
$^1B_1$ $(\pi \rightarrow \pi^*)$	5.0	4.8	0.06	0.04
$^1A_1$ $(\pi \rightarrow \pi^*)$	6.2	6.2	0.08	0.20
$^1B_1$ $(\pi \rightarrow \pi^*)$	7.2	7.0	0.8	1.3

Semiempirical methods have been little used for the calculation of the energies of $\sigma \rightarrow \sigma^*$ transitions; the accuracy obtained using the existing parametrisations should be low and one may expect qualitative rather than quantitative results. One should remember that in semiempirical methods one normally employs a minimal basis set and this precludes the calculation of the parameters of the Rydberg transitions (to orbitals with large quantum numbers), which usually occur in the region of $\sigma \rightarrow \sigma^*$ electronic transitions and can be mixed with them.

In calculations on the excited states and electronic absorption spectra by non-empirical methods one has to have much larger basis sets than for the calculation of the properties of the molecular ground state. The attempts to select small basis sets have led to agreement with experiment only for individual electronic transitions in a limited range of compounds. This is because the change in the distribution of electron density on excitation is not reproduced with the necessary accuracy by a simple alteration of the population of the molecular orbitals or even by a transition to their linear combinations. In other words, the basis set of atomic orbitals selected for the ground state is unsatisfactory for the excited state. On excitation, the electron cloud usually expands and this has a marked influence on the matrix elements for the interaction of electrons and nuclei. In order that the wave function expanded in terms of the basis set of atomic orbitals (i.e. represented by a linear combination of atomic orbitals) should reproduce this expansion, the basis set must be modified—the orbital exponents must be altered somewhat or additional diffuse orbitals must be included. The nature of the expansion of the electron cloud is specific to each $0 \rightarrow e$ electronic transition and the only rational method of improving the basis set involves an increase of the number of atomic orbitals.

The introduction of very large basis sets and allowance for the contributions of all singly and doubly excited configurations greatly extend the scope of the calculation and make it possible to evaluate the energies of electronic transitions to within 0.2–0.5 eV. However, at the present time this is possible only for small molecules, since the difficulty of the calculations increases very rapidly with increase of the number of atoms. The results of such calculations of the spectra of ethylene, butadiene, benzene, and certain other compounds with simple molecules have been published in a review[69].

Non-empirical methods are most widely applied in calculations on Rydberg transitions[69–72]. For simple molecules, it has been possible to calculate, in good agreement with experiment (±0.1 eV), the positions of the absorption bands, but their assignments are not always reliable, since the Rydberg bands are very close to one another (even in triatomic–penta-atomic molecules up to 10 transitions may be located in the region of 7–8 eV). The non-empirical methods lead to appreciably high energies of the lowest $\pi \rightarrow \pi^*$ transitions (error up to 1 eV).

In practice calculations of the electronic absorption spectra of organic compounds extend over a region of not more than 8–10 eV. For a more remote region, the difficulty of the calculations increases greatly owing to the necessity to take into account highly excited configurations.

The oscillator strengths of the electronic transitions are calculated less accurately in all the methods than the transition energies and the results can differ severalfold from the experimental data. The requirements for the accuracy of the wavefunctions are then particularly stringent and the small errors associated with the selection of the basis set can be markedly reflected in the results; in practice it is necessary to take into account the contributions of a still greater number of excited configurations. However, the oscillator strengths of the observed $0 \rightarrow e$ transitions can differ by several orders of magnitude; under these conditions, even semiquantitative estimates are sufficient for the prediction of the overall form of the absorption spectrum and for the interpretation of the individual bands.

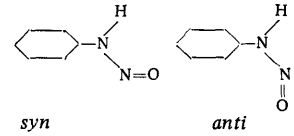
The results of the calculation can usually be compared with experiment only for a few (long-wavelength) electronic transitions. The majority of transitions are located in a region difficult to investigate experimentally (<1500 Å) and the lack of experimental data for such transitions hinders the direct estimation of the accuracy of the computational methods. However, indirect procedures can be used for this purpose. The electronic polarisability can be evaluated from the oscillator strengths and frequencies ν_e of the $0 \rightarrow e$ transitions calculated by a quantum-chemical method and the results can be compared with experimental data. Polarisability calculations have been carried out for many types of molecules[70–75] and for the majority of these a sufficient agreement with experiment has been obtained, which shows indirectly a satisfactory accuracy of the calculation of the parameters of the absorption bands over a wide range of the spectrum.

When the results of the calculation of oscillator strengths are used to infer the structure of complex molecules, one must not underestimate their approximate nature. In this connection mention should be made of calculations for 4-nitro-*N*-benzylideneaniline[76]; within the framework of the comparison made, the results correspond to the arrangement of the two benzene rings in perpendicular planes, which is extremely unlikely. Examples of the application of calculations of oscillator strengths, dipolar and quadrupolar polarisabilities, and hyperpolarisability have been described[77–82].

VII. THE APPLICATIONS OF QUANTUM-CHEMICAL CALCULATIONS TO THE EXCITED STATES OF ORGANIC MOLECULES

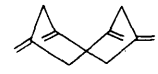
The quantum-chemical calculations of the electronic structures and geometries of electronically excited molecules are widely used to interpret experimental data and to assign ultraviolet absorption bands, to establish a relation between absorption spectra and the structure of the molecule and its conformation, and also to investigate the reactivities of electronically excited molecules in photochemical processes[83–90].

We shall consider several examples. In the absorption spectra of certain organic compounds the characteristic long-wavelength bands were previously tentatively assigned to charge-transfer transitions but this could be proved and the contribution of charge transfer could be estimated only by quantum-chemical calculations. In particular, it has been established for *N*-alkyl-*N*-nitrosoaniline and its alkyl derivatives[83] that excitation in the first (long-wavelength) absorption band leads to an electronic transition in the benzene ring (^1L_b), while excitation in the second band leads to an electronic transition mainly in the NNO group; the absorption of light whose frequency corresponds to the third band gives rise to an electron density distribution with transfer of more than half of the electronic charge from the NNO group to the benzene ring, while absorption in the fourth band modifies the wave functions in the region of the benzene ring (^1L_a). It follows from the calculation that the charge-transfer band should be observed experimentally only for the *anti*-isomer, while for the *syn*-isomer it should be close to the more intense ^1L_a band and should be masked by the latter:



syn *anti*

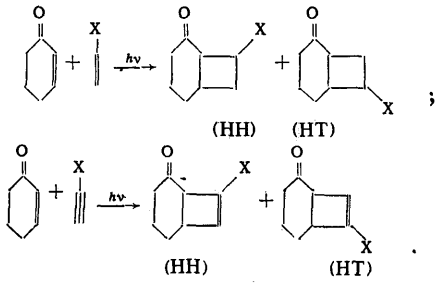
The experiments have shown that certain non-conjugated polyene compounds (adamantane derivatives) with a fixed relative orientation of two double bonds of the type



have an intense absorption band at ~230 nm (while for monoolefins the first intense band is located in the region <200 nm). Non-empirical calculations have led Braverman et al.[84] to the conclusion that this band is due to the electronic transition between the components of the split π and π^* levels, caused by the mutual influence of the double bonds through space. This influence also leads to the stabilisation of the excited state, while interaction via methylene bridges (with participation of the σ orbitals of the C–H bonds) affects the energies of the highest occupied orbitals and the symmetries of the molecular wave functions; the latter explains the high intensity of the absorption band. A simpler system with two weakly interacting C=C bonds (norbornadiene) has been investigated[85]; the contributions of charge transfer were estimated for each excitation level and the influence of hyperconjugation involving the bridging atoms on the $^1A_1 \rightarrow {}^1B_2$ transition was noted.

No less interesting results can be obtained in the study of photochemical reactivity. Thus the stereospecificity of the photochemical addition of acetylene and ethylene derivatives (HC≡CX and $H_2C=CHX$) to α,β-unsaturated

ketones has been considered[86]. Experimental studies on the reaction led to unusual results; it was found that certain acetylene and ethylene derivatives form products in which the carbonyl group of the ketone and the substituent X are directed to one side ("head to head", HH), while in others, i.e. in the presence of a second substituent X, they are directed to different sides ("head to tail", HT); in the third case the stereospecificity vanishes; examples of the reaction mechanisms are given below:



According to the results of the calculations the ground and excited (triplet) states by the CNDO/2 method, the above difference can be accounted for by the fact that the stereospecificity of the reaction of ethylene derivatives is due mainly to the interaction between the π-electron orbitals of the C=C bonds of the reacting molecules, while in the case of acetylene derivatives it is caused by the dipole–dipole interaction. The absence of stereospecificity in the addition of acetylene derivatives containing only the highly polar CHO and COOH substituents is associated with the fact that the component of the dipole moment perpendicular to the direction of the C ≡ C bond predominates in these derivatives[86].

Interesting data concerning the changes in molecular geometry on electronic excitation have been obtained with the aid of non-empirical methods (Fig.1). It is at present impossible to obtain such information in other ways. In another investigation[89] it has been shown that all the bond lengths in the pyrazine ring increase as a result of the $\pi \rightarrow \pi_1^*$ electronic transition, while in the $n \rightarrow \pi_1^*$ transition the C–C bonds become shorter.

The use of quantum-chemical methods in the study of optical activity is particularly appropriate for molecules with conjugated or highly interacting bonds where the approximation of weakly bound subsystems (molecular fragments) is unsuitable. As an example, we may note the calculations of the rotatory power of the $n \rightarrow \pi^*$ electronic transitions in dioxan-1,4-dione and its methyl derivatives, as a result of which it was possible to estimate separately the contributions of the asymmetric substitution in the ring and of the dissymmetry (chirality) of the ring itself in each conformer[87].

VIII. THE INTENSITIES OF THE COMPONENTS OF VIBRONIC TRANSITIONS

The calculation of the intensities of the components of the vibrational structure is of primary important for the characterisation of the overall form of the bands in the electronic absorption and fluorescence spectra and also for the calculation of the Raman line intensities.

In specific calculations it is usually assumed that, in the overall wave function of a molecule, it is possible to distinguish the electronic and vibrational components Ψ_e and $\prod_a u(Q_a)$. The transition moment $00 \rightarrow ev$ involving a change in the electronic and vibrational states can then be represented by the following expression of:

$$\mathbf{M}^{00\rightarrow ev} = \int \ldots \int \prod_a u_{00}(Q_a)\, M^{0e} u_{ev}(Q_a)\, \mathrm{d}Q_i, \qquad (7)$$

in which the integration is carried out with respect to all the Q_a, M^{0e} is the moment of the $0 \rightarrow e$ transition determined by the function Ψ_0 and Ψ_e, and u_{00} and u_{ev} are the nuclear wave functions of the initial (00) and final (ev) states. In principle, M^{0e} is a function of the normal nuclear coordinates; M^{0e} can be expanded in series in powers of Q, retaining only its first terms in view of the rapid convergence of the series. The dependence of M^{0e} on the coordinates Q_{as} of the antisymmetric atomic vibrations largely determines the distribution of intensities in the series of components $\nu_{e0} + n\nu_{as}$ of the absorption band. However, for symmetrical modes, this type of dependence is of secondary importance and is frequently disregarded; the calculation of the intensities of the components of vibronic transitions then requires the calculation of M^{0e}, the molecular geometry, the frequencies and modes of the atomic vibrations, and the nuclear wave functions for the ground and excited states.

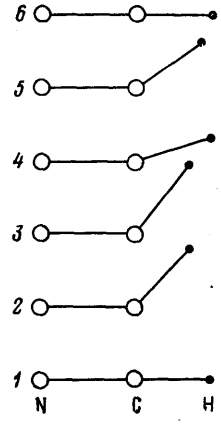


Figure 1. The geometry of the HCN molecule in the ground and excited states (the energies of the states are given in brackets in eV): *1*) ground state (0.0); *2*) $^1A''$ (6.48); *3*) $2^1A'$ (6.78); *4*) $2^1A''$ (7.52); *5*) $3^1A'$ (7.85); *6*) $3^1A''$ (8.97).[80]

Calculations of the intensity taking into account the $M^{0e}(Q)$ relation and, if necessary, the differences between the potential energy curves for the molecule in the ground and excited electronic states, carried out by non-empirical methods for formaldehyde and other molecules[91–94] and by semiempirical methods for benzene, naphthalene, benzoperylene, formaldehyde, and benzaldehyde[95–100], led to a fairly satisfactory agreement with experimental data (Table 6). The results made it possible to interpret certain vibronic bands in the absorption spectra; in particular, it has been shown[92] that the electronic transition $n \rightarrow \pi^*$ in the N_2H_2 molecule is combined with the excitation not only of the fully symmetrical modes but also of the antisymmetric stretching vibration of the N–H bonds, giving rise to a whole series of the corresponding components in the vibrational structure of the absorption band.

According to Herzberg and Teller, the $M^{0e}(Q)$ relation can be expressed in terms of a set of coefficients h_{es}, which determine the mixing of the wave functions Ψ for different electronic states (e and s) as the normal coordinate Q is varied. In this connection, some workers arrived at the erroneous idea that a simple quantum-chemical calculation of the probability of vibronic transitions in terms of mixing coefficients is possible. However, such calculation requires the evaluation of the overlap integrals of the multideterminant electronic wave function of the excited state of a deformed molecule (i.e. for $Q \neq 0$) and the wave functions of all other states corresponding to the equilibrium positions of the atoms in the ground state ($Q = 0$). The exact evaluation of these integrals is difficult owing to the incompleteness of the sets of atomic orbitals used in practice, so that the molecular orbitals corresponding to $Q = 0$ and $Q \neq 0$ are constructed in terms of different basis sets (displaced relative to one another). Under these conditions, it is generally speaking impossible to expand the function Ψ of a deformed molecule in terms of the atomic orbitals corresponding to the equilibrium molecular geometry. In order to calculate the coefficients h_{es}, it is therefore necessary to introduce a series of approximate assumptions[95]. On the other hand, direct calculation of the derivatives $\partial M^{0e}/\partial Q$ does not require the introduction of additional assumptions and is fairly easy[97].

Table 6. Calculation of the oscillator strengths of vibronic transitions ($00 \rightarrow ev$) corresponding to four vibrational modes in benzene by the CNDO/S method (the results of calculations with the aid of the Herzberg–Teller expansion described by Roche and Jaffe[95] are indicated in brackets).

ω, cm^{-1}	$^1B_{2u}$ transition			$^1B_{1u}$ transition		
	calc. (Ref.97)	calc. (Ref.99)	expt.	calc. (Ref.97)	calc. (Ref.99)	expt.
606	$5\cdot10^{-4}$	$8\cdot10^{-4}$	$1.4\cdot10^{-3}$	$1.6\cdot10^{-2}$	$1.3\cdot10^{-2}$	$1.9\cdot10^{-2}$
1595	$2.5\cdot10^{-4}$	$8\cdot10^{-5}$	10^{-4}	$6.8\cdot10^{-2}$	$1.4\cdot10^{-1}$	$7.5\cdot10^{-3}$
3047	$8\cdot10^{-6}$	$6\cdot10^{-5}$	0	$7\cdot10^{-4}$	10^{-3}	0
1177	$4\cdot10^{-5}$	$2\cdot10^{-6}$	0	$6\cdot10^{-3}$	$1.2\cdot10^{-2}$	0
Overall oscillator strengths						
	$8\cdot10^{-4}$	$9\cdot10^{-4}$ ($9\cdot10^{-4}$)	10^{-3}	$9\cdot10^{-2}$	$2\cdot10^{-1}$ ($2\cdot10^{-1}$)	$9\cdot10^{-2}$

IX. CALCULATION OF LINE INTENSITIES IN RAMAN SPECTRA UNDER CONDITIONS REMOTE FROM AND CLOSE TO RESONANCE

The intensity of the Raman lines and the line excitation spectra (the dependence of the intensity on the frequency of the exciting light ν) can be calculated subject to greater or smaller limitations, using the classical, semi-classical, or quantum theories. In the "polarisability theory" designed for cases very remote from resonance the line intensity I_a is determined by the set of derivatives of the components of the molecular electronic polarisability tensor α with respect to the coordinate Q_a. The polarisability theory treats α as a single-valued function of Q (and corresponds to ideas concerning a molecule with stationary nuclei in any specified positions Q) but it does not define the origin of the $\alpha(Q)$ relation. The latter is described within the framework of the semiclassical theory[101] as a consequence of the dependence on Q of (a) the Cartesian components $M^{0e}(Q)$ of the dipole moment of the electronic transition $0 \rightarrow e$ made up of the electronic wave functions $\Psi(Q)$ and (b) the frequency ν_e. The contributions of all the electronic excitation levels e are then added together (cf. the book of Tang and Albrecht[102] where incorrect information is given on this subject).

The origin of the $M^{0e}(Q)$ relation in the vibronic theory of Tang and Albrecht[102] is inferred by considering the matrix of the coefficients h_{es}, which describes the mixing of the electronic wave functions of the levels e and s when the nuclei are displaced from the equilibrium positions (see below). In the simplest case

$$M^{0e}(Q) \simeq M^{0e}(0) + Q \sum_{s \neq e} \frac{h_{es} M^{0s}(0)}{E_e(0) - E_s(0)},$$

where $E_e(0)$ and $E_s(0)$ are the molecular energies in the states e and s for $Q = 0$.[103]

All the Cartesian components ($\rho\sigma$) of the polarisability tensor for any positions of the atomic nuclei can be calculated in terms of the adiabatic approximation of the second order perturbation theory by the formula

$$\alpha_{\rho\sigma}(Q) = \frac{1}{h} \sum_e \left[\frac{M_\sigma^{0e} M_\rho^{e0}}{\nu_e - \nu} + \frac{M_\rho^{0e} M_\sigma^{e0}}{\nu_e + \nu} \right]. \quad (8)$$

The introduction of the dependence of M^{0e} and ν_e on Q compensates to some extent the lack of summation of the contributions of the individual vibrational sublevels ev. The wave functions Ψ necessary for the calculation of the polarisability are determined by quantum-chemical methods; the derivatives with respect to Q are usually found by numerical differentiation.

Calculations of the Raman line intensity by Eqn.(8), which reflect in some form the factors of the semiclassical theory $\nu_e(Q)$ and $M^{0e}(Q)$, have been carried out for many simple molecules (H_2, Cl_2, methane, ethane, ethylene, acetylene, dimethyl ether, etc.). Analysis of the results obtained by different LCAO-MO SCF methods[26,29,70,104–110] showed that for polyatomic molecules they reproduce the distribution of intensities in a manner which is qualitatively correct but extremely approximate, and that non-empirical methods in terms of basis sets of moderate size of the type of OST-4-31GF do not result in a perceptible increase of accuracy compared with semiempirical methods.

More accurate but more laborious non-empirical calculations, using extended basis sets with polarisable orbitals and taking into account electronic correlation, have led to a very satisfactory agreement with experiment for the simplest molecules[111,112]; thus the derivatives of the polarisability of the hydrogen molecule[111] are $\alpha'_\parallel = 1.78$ and $\alpha'_\perp = 0.83$, while the corresponding experimental values are 1.69 and 0.85 respectively. The closeness to the experimental data is not surprising, since virtually exact wave functions were obtained in the relevant investigation[111]; unfortunately such calculations are virtually impossible for complex molecules.

Studies on the simplest hydrocarbons (methane and ethylene) by CNDO/2 methods resorting to the vibronic theory[113,114] led to the conclusion that the $\nu_e(Q)$ relation predominates for lines associated with symmetrical vibrations and also that the mixing of the electronic wave functions Ψ_e with the function Ψ_0 of the ground state (which is usually neglected) makes a significant contribution. However, the polarisability derivatives obtained are in poor agreement with experimental data and at the same time differ markedly from the results of the calculation within the framework of the polarisability theory. The

discrepancies with experiment are to a large extent associated with the insufficiency of information about the highest levels e and with the approximate nature of the calculation of the coefficients h_{es} from the formula of Murrell and Pople[95,115].

Regardless of the foregoing, one may state in a more general form that the application of the vibronic theory in the quantum-chemical calculations of Raman line intensities is undesirable, since the $M^{0e}(Q)$ relation can be calculated directly and much more readily and accurately without introducing the h_{es} matrix and without any additional approximations by evaluating analytically or numerically all the necessary integrals in Eqn.(8); this does not require information about all the levels s, which can be mixed with the level e. However, the calculation of h_{es} is necessary if it is required to elucidate the origin of the $M^{0e}(Q)$ relation.

Thus, in order to calculate the intensity, it is sufficient to carry out independent calculations of M^{0e} and ν_e for several values of Q and to estimate from these data their derivatives with respect to Q and then calculate the derivatives of the polarisability from the formula of the semiclassical theory. Similar calculations for ethylene in the CNDO/S valence approximation with allowance for the contributions of all the singly excited configurations[109] led to estimates of the form of the Raman line excitation spectra and by no means fully confirmed the conclusions of the study quoted above[114]; it follows from the calculations of Burshtein and Shorygin[109] that, following Raman excitation in the visible part of the spectrum, the $M^{0e}(Q)$ relation predominates for all the C–H lines, while the $\nu_e(Q)$ relation predominates for the C=C line. The main contribution for the C=C line comes from the long-wavelength electronic transitions $\pi \rightarrow \pi_1^*$, while for other lines the transitions in the region of ~1000 Å, localised predominantly at the C–H bonds, are the most significant.

Calculations of polarisability for several values of Q for each molecule require a large amount of computer time. To reduce it, it has been suggested that one calculates the derivatives with respect to the external electric field strength of the gradient (with respect to Q) of the potential energy of the molecule present in this field; these derivatives are found only for the equilibrium geometry of the molecule[116].

We may note that the calculation of the derivatives is generally speaking not obligatory; one can resort to the relation $2\alpha_{01} \cong \alpha(Q_0) - \alpha(-Q_0)$, which leads to a somewhat greater accuracy and requires the calculation of α for only two values of $Q = \pm Q_0$, where Q_0 is the zero point amplitude[117].

The use of a minimal basis set in calculations of the polarisability and intensity is fairly problematical. Some investigators[110] insist on introducing extended basis sets of atomic orbitals with inclusion of polarising atomic orbitals (2p and 3p for hydrogen atoms and d for atoms of elements in the Second and Third Periods) and diffuse orbitals. One must agree with this if one is dealing with non-empirical calculations; however, when semiempirical methods are employed, a rational selection of the parameters determining the interaction of the nuclei and electrons makes it possible to compensate to a large extent for the incompleteness of the basis set, because ultimately one needs to determine not the atomic wave functions themselves but the matrix elements calculated using these functions. Whereas in the non-empirical methods of calculation the selection of the basis set to a large extent determines the set and magnitudes of the matrix elements for the interactions of the electrons and nuclei, in semiempirical methods the selection of the basis set is less significant in this respect and the extension of the basis set is associated with a certain arbitrary element in the choice of the parameters for atomic orbitals with large quantum numbers (polarising orbitals) and at the same time does not lead to an appreciable improvement of the results; for these reasons, it is not desirable.

Instead of introducing polarising functions into the computational scheme, it is possible to introduce at some stage corrections in the form of atomic increments[75]. In principle, it is thus possible to correct, for example, the matrix elements of the interaction, but it is simpler to select polarisability increments. The latter are most significant for hydrogen atoms and they can be determined in this instance from experimental data for the H_2 molecule. In calculations using the minimal basis set (without corrections) the perpendicular components of the polarisability of H_2 and its derivative are found to be zero and their true values, determined experimentally, are used as the increments.

The principal difficulty in the calculation of the polarisability by Eqn.(8) consists in the need to calculate the parameters of all the electronically excited states—the energies, the wave functions Ψ_e, and the matrix elements M^{0e}. This difficulty can be in many instances obviated by resorting to the finite perturbation theory[104–106] or by using a variational procedure[118,119], for which it is sufficient to know the wave function Ψ_0 of the ground state. Bearing in mind that calculations by the LCAO-MO method are more accurate for Ψ_0 than for Ψ_e, under certain conditions it is possible to count on a higher accuracy of the determination of the polarisability[120].

Only the tensor of the *static* electronic polarisability can be calculated by the finite field methods in the perturbation theory. To evaluate this tensor, an electric field is introduced into the electronic Hamiltonian of the molecule. In the CNDO valence approximation it is sufficient for this purpose to add to the diagonal elements of the Fock matrix terms of the type $-eE_x x_a$ and to the non-diagonal elements of the type $-eE_x\langle s_a|z|p_{xa}\rangle$, where E is the electric field strength and s_a and p_{xa} are atomic orbitals of the s and p type of the atom a. Having calculated in this way all the Cartesian components of the dipole moment of the molecule in the ground state with (μ^*) and without (μ^0) an external field, we obtain the following expression for the specified positions of the atoms:

$$\alpha_{\rho\sigma}(Q) = (\mu_\rho^* - \mu_\rho^0)/E_\sigma.$$

The Raman line intensities for methane, ethylene, tetrachloroethylene, and other simple molecules were calculated from the polarisabilities and their derivatives found by this procedure. The calculations of μ were performed within the framework of the extended Hückel method, by the CNDO/2 and INDO methods, and also by non-empirical methods in terms of very large Gaussian basis sets with polarising functions[104–106,116].

The applications of the finite perturbation theory are not associated with cumbersome calculations and they can therefore be extended to more complex polyatomic organic molecules. The results for cyclopropenone are compared with experimental data in Fig.2.

It must be emphasised that static polarisability data can be used only when the frequency of the exciting light is very remote from ν_e; the Raman intensities calculated directly via derivatives of the static polarisability have generally speaking no physical significance although they can differ only slightly from values found for low frequencies of the exciting light ($\nu \ll \nu_e$). The latter factor justifies the application of the finite field method

in the study of the spectra of saturated hydrocarbons and certain other compounds without conjugated bonds and having absorption bands only in the far ultraviolet.

The variational method, which can be regarded as an alternative to the method of perturbation theory, makes it possible, at least under conditions remote from resonance, when $\nu \ll \nu_e$, to calculate the molecular dynamic electronic polarisability tensor without evaluating the contribution of each excited state[119,120]. Some information about these states is then introduced in the form of the wave functions of the singly and doubly excited configurations.

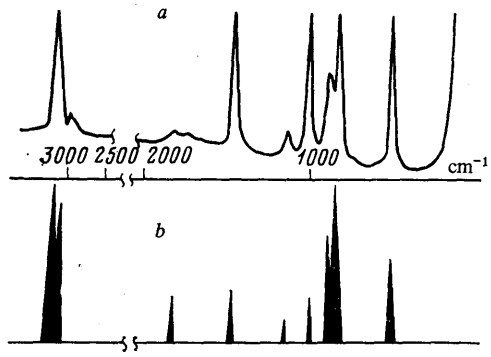


Figure 2. Raman spectra of cyclopropenone: *a*) experiment; *b*) calculation by the CNDO/2 method[105].

Within the framework of the method indicated, the sums of the first and second components of the binomial terms in Eqn.(8) are calculated by the variational procedure. Thus, in order to find the $\sigma\sigma$ component, the following expression is minimised in the first place at a specified frequency ν:

$$B_{\sigma\sigma}(Q, \nu) = \langle f|H - E_0 - h\nu|f\rangle + 2\langle\psi_0|\mu_\sigma|f\rangle, \qquad (9)$$

where f is the function to be varied, which is sought in the form of a linear combination of the wave functions of all the singly excited configurations, μ_σ the σ component of the dipole moment operator, H the electronic Hamiltonian, and E_0 and Ψ_0 are the energy and electronic wave function of the ground state, which are found by the usual quantum-chemical methods. At the minimum $f = f_0$ and $B_{\sigma\sigma}(Q, \nu)$ is close to the sum in Eqn.(8) being sought. Next the expression

$$\langle g|H - E_0|g\rangle + 2\langle g|\mu_\sigma|f_0\rangle, \qquad (10)$$

is minimised and g_0 for the function g being varied is found in the form of a linear combination of doubly excited configurations. Then

$$\frac{1}{h}\sum_e \frac{M_\sigma^{0e} M_\sigma^{e0}}{\nu_e - \nu} = B_{\sigma\sigma}(Q,\nu) + 2\langle g_0|H - E_0|\varphi_0\rangle, \qquad (11)$$

where $B_{\sigma\sigma}(Q, \nu)$ is calculated by Eqn.(9) with $f = f_0$.

Similar calculations (in each case for several values of the coordinate Q) by the CNDO/2 method enabled Svendsen and Tangaa[121] to calculate the first and second derivatives of the polarisabilities of methane, ethane, ethylene, and acetylene. An entirely satisfactory accuracy was achieved and the second order correction determined by Eqn.(10) proved to be small (≤10–20%). In addition, data were obtained for ethylene at several exciting light frequencies ν, which indicate, in conformity with the conclusions of the semiclassical theory, a faster increase of the intensity of the overtone with increase of ν; however, in the region of the resonance the calculations are merely conventional.

Selective allowance for the excited configurations in terms of the symmetry type led the authors[121] to estimates of the contributions of σ and π electrons; according to these estimates, the latter determine the polarisability of the ethylene molecule to the extent of 2/3, the derivative with respect to the symmetry coordinate of C–H to the extent of 12%, and the derivative with respect to the C=C coordinate to the extent of 95%.

The Raman line intensity corresponding to the vibrational transition $0 \to f$ is proportional to $\sum_{\rho\sigma} |(\alpha_{\rho\sigma})_{0f}|^2$ according to the quantum theory, where $(\alpha_{\rho\sigma})_{0f}$ is the Cartesian component of the electronic polarisability tensor.

When account is taken of the contributions of the sublevels ev, one can write the following equality for each tensor component:

$$(\alpha_{\rho\sigma})_{0f} = \text{const} \sum_{ev} \left[\frac{\langle 0|M_\rho^{0e}|v\rangle\langle v|M_\rho^{e0}|f\rangle}{\nu_{ev} - \nu} + \frac{\langle 0|M_\sigma^{e}|v\rangle\langle v|M_\rho^{e0}|f\rangle}{\nu_{ev} + \nu} \right], \qquad (12)$$

where 0, ν, and f are the quantum numbers of the vibrational sublevels of the ground, intermediate, and final states, M_σ^{0e} and M_ρ^{0e} are the Cartesian components of the vector of the dipole moment of the electronic transition $0 \to e$, ν_{ev} the frequency of the $00 \to ev$ transition, and ν the frequency of the incident light, which generally speaking should occur in a region far from or close to resonance with the frequency ν_{ev}. M_σ^{0e} and M_ρ^{0e} are usually regarded as functions of Q; the use of corrected quantities of the type of M^{0ev} is an alternative.

If there are many effective intermediate levels ev, it is more convenient to replace Eqn.(12) by the evaluation of the integral $\langle 00|G|0f\rangle$, where G is a Green function in which the functions Ψ_e and summation with respect to ev are used; thus one carries out initially the summation and then integration with respect to the coordinates of the electrons and nuclei[122].

The relation between the quantum and simple classical theories as regards the non-resonance Raman lines of the fundamental band can be determined by the direct proportionality between the matrix element $(\alpha_{\sigma\sigma})_{01}$ and the derivative $\partial\alpha_{\sigma\sigma}(Q)/\partial Q$. In certain investigations (including those quoted above[113,114]) the quantity $(\alpha_{\rho\sigma})_{0f}$ is set equal to the sum of the contributions of the derivatives of the polarisability with respect to all the normal coordinates Q (or the sum of the corresponding matrix elements of the polarisability), which, however, lacks any justification.

It is noteworthy that in a more sophisticated version of the classical theory the polarisability is not a single-valued function of Q and is replaced by the more general transmission function $\mathcal{K}(\nu, t)$, where t is the time; the latter includes an expression similar to Eqn.(12) with the corresponding decay constants[123].

Eqn.(12) describes the response of a system in a fixed initial position i. If a statistical description of a mixed *ensemble* of molecules and of its time variation is required, one can go over to the use of the density matrix ρ. The intensity of the secondary emission is then proportional to $\sum_i \rho_{ii} |\alpha_{if}|^2$, where the square of the modulus is averaged with respect to the *ensemble*.

The matrix elements $(\alpha_{\rho\sigma})_{0f}$ are calculated in the same way as in the calculation of the vibrational structure of the electronic transition $00 \rightarrow ev$ (see Section VIII) and requires information about the frequencies and modes of the atomic vibrations and the molecular geometry for the ground and all the excited states. The determination of these parameters is very laborious and is virtually impossible for complex molecules. For resonance Raman excitation, the treatment may be restricted to the contribution of a single electronic level e in Eqn.(12), but decay constants must be introduced.

If the linear term of the expansion of Ψ_e in series in terms of powers of Q by the Herzberg–Teller method is used for the calculation of the matrix elements $\langle 0|M^{0e}(Q)|v\rangle$ in Eqn.(12) or of M^{0e} in Eqn.(8), then we go over to the vibronic theory of Tang and Albrecht[102]. Specific calculations have not been made by Eqn.(12) within the framework of this theory and calculations by Eqn.(8) have already been described above.

The intensity of the Raman lines and the excitation spectra of these lines in the pre-resonance and resonance regions for butadiene and certain polyenes have been calculated[124] by Eqn.(12) but with allowance for only one first excited state π, π_1^*. In order to reduce the amount of computer time, the authors[124] used the approximate combined method proposed by Warshel and Karplus (see Section II) and obtained good results. They concluded that in the region of resonance the dominant Raman mechanism involves a process which, in terms of the semiclassical theory, is referred to as the modulation of the electronic transition frequency and is determined by the derivatives of ν_e.

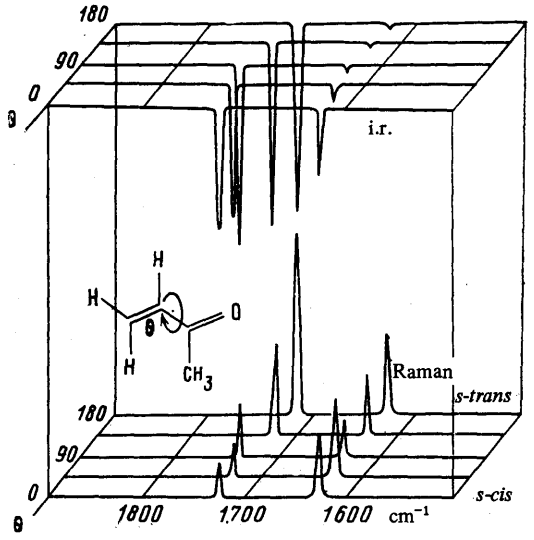


Figure 3. The line intensities associated with the stretching vibrations of the C=C and C=O bonds in the infrared and Raman spectra of methyl vinyl ketone, calculated by the CNDO/2 method[129] as a function of the angle θ of internal rotation about the central C–C bond.

The changes in the intensities of the Raman and infrared lines as well as the spectroscopic features of the conjugation of the C=C and C=O double bonds with a smooth variation of the angle of rotation θ about the C–C bond have been calculated[129] by the CNDO/2 method; the results are presented in Fig.3 (taking into account the data of other workers). The susceptibility of systems with any specified angle θ to calculation greatly extends the scope of the experiments. Other examples of calculations of the intensity have also been published[130–134].

The data presented above demonstrate the wide variety of methods used to calculate the Raman line intensities. Comparison of the results for ethylene obtained by different procedures (Table 7) shows that in most cases a satisfactory agreement with experiment was achieved; discrepancies with experiment by a factor of 2–4 have been noted for individual lines, but this accuracy is sufficient for the qualitative analysis of experimental data. In comparisons of this kind, one should bear in mind that the results of the calculation may vary by a factor of 2–3 owing to the inaccuracy of the atomic vibrational modes on which they are based.

Table 7. The relative Raman line intensities for ethylene on excitation under conditions remote from resonance in the visible region.

Type of vibration	ω, cm⁻¹	Finite perturbation theory with Φ obtained by different methods			Calculation of the partition function with respect to all excited states with Φ obtained by different methods			Vibronic theory	Experiment
		CNDO/2 (Ref.106)	non-emp. (Ref.116)*	CNDO/2 (Ref.128)	CNDO/2 (Ref.114)	CNDO/S (Ref.109)	non-emp. (Ref.26)**	CNDO/2 (Ref.114)	
A_{1g}	3026	1	1	1	1	1	1	1	1
A_{1g}	1630	0.1	0.24	0.2	0.12	0.30	0.18	0.53	0.30
A_{1g}	1342	1.36	1.35	1.65	1.04	0.60	0.46	0.62	0.53
B_{1g}	3103	0.59	0.92	0.98	0.57	0.97	0.38	0	0.2
B_{1g}	1220	0.03	0	0	0	0.01	0	0	0

*Non-empirical calculation in terms of a biexponential basis set with polarising functions.

**Non-empirical calculation in terms of the OST-4-31G basis set.

X. CONCLUSION

The susceptibility of the electronic wave functions and of the energy of excited molecules to calculation in terms of LCAO schemes permits the invocation of molecular orbital methods in the study of virtualiy any molecular-orbital phenomena; among them, one can note also those which have begun to be investigated only in recent years, for example, the Raman-induced Kerr effect, the Raman-optical activity, simultaneous electronic (or vibrational) transitions in components of the mixture, the beats in the secondary emission of light by molecules associated with the interference of electronic states, non-linear optical phenomena, the manifestation of the anharmonic interaction of the modes and of non-adiabatic conditions, etc.

In principle, one can predict the overall form (and interpret) the absorption and emission spectra of simple molecules, complexes, ions, radicals, and molecular crystals and to infer the dependence of the spectra on the conformation, on the initial electronic state, or on additional perturbations. At the same time it is possible to refine and supplement the available information about the force field, to determine the signs of the derivatives of the polarisability and the dipole moment, to estimate

the frequencies of the unobserved transitions, to characterise the potential energy curves for excited states, etc.

The accuracy of the calculations of the spectral parameters is at present much lower than the experimental accuracy but is sufficient for the solution of many spectrochemical problems; the combination of calculated and experimental data leads to a more complete and reliable description of the spectrum.

The use of quantum-chemical methods makes it possible to increase the amount of information derivable from spectroscopic studies, to discover the principles underlying the empirical relations between the spectra and various physical and chemical properties of molecules, and to elucidate the nature of the interaction between the atomic groups in complex molecules on the basis of the idea of the interaction of electrons and nuclei.

Further advances in the application of quantum-chemical methods to spectroscopy will be evidently closely related to progress in computer techniques. The development of fast computers will extend the scope for taking into account more fully the electron correlation (particularly as a result of the inclusion of highly excited configurations in the SCF method) and will permit the abandonment of many simplifications, for example,the appreciable limitation of the size of sets of basis functions and the neglect of the contributions of the *d* and *f* atomic orbitals of the elements in the first two Periods, the empirical selection of certain parameters, the restriction to models simulating a small fragment (for example, an active centre) of a complex molecule, etc. On the other hand, one can count on considerable progress in the study of molecular systems and processes as a function of time.

It is noteworthy that compounds both with and without heavy atoms are being successfully studied in experimental spectrochemistry. The compounds with heavy atoms are not susceptible to investigation by the majority of quantum-chemical methods. The accumulation of experience in the parametrisation of such systems will undoubtedly diminish the gap between the scopes of the experimental and theoretical methods. At the same time, one may expect further successes in the development of ways of taking into account relativistic effects, which in certain systems can appreciably alter the disposition of electronic levels, the transition probabilities, and the frequencies ω; the influence of these effects increases very rapidly with increase of the effective nuclear charge and can therefore prove comparable to, for example, the result of the Coulombic interaction and can be much greater than the influence of the usual conjugation of double bonds.

Progress in the development of computational methods is closely related to the endeavour to develop more universal and more accurate but sufficiently compact versions and, on the other hand, to limit the elements of subjectivity and uncertainty, which are expressed, for example, in the selection of a variant of the computational method leading to the best result in the solution of a specific problem, in the adaptation of parameters, and in the introduction of corrections specific to a particular type. As a result of these features, the application of even non-empirical methods proved to be far from free from empirical characteristics.

The alternatives to the LCAO approximation, which resemble the usual schemes as regards their conventional aspect, are of great interest, but hitherto fairly modest advances have been made on these lines, being limited by the imperfection of the proposed schemes and the large amount of computer time required.

Bearing in mind all the data described here, one can say in conclusion that the combination of the methods of experimental spectroscopy and quantum chemistry will greatly increase the effectiveness of the studies of molecular structures and the mechanisms of chemical processes and will extend the scope of practical chemical applications of spectroscopy.

REFERENCES

1. M.J.S.Dewar, "The Molecular Orbital Theory of Organic Chemistry" (Translated into Russian), Moscow, 1972, Chapter 2.
2. C.C.Roothaan, Rev.Mod.Phys., 1951, **23**, 69; 1960, **32**, 179.
3. J.A.Pople, D.P.Santry, and G.A.Segal, J.Chem. Phys., 1965, **43**, 129.
4. J.A.Pople and G.A.Segal, J.Chem.Phys., 1965, **43**, 136.
5. J.A.Pople and G.A.Segal, J.Chem.Phys., 1966, **44**, 3289.
6. D.P.Santry and G.A.Segal, J.Chem.Phys., 1967, **47**, 158.
7. J.A.Pople, D.L.Beverige, and P.A.Dobosh, J.Chem.Phys., 1967, **47**, 2026.
8. M.Dewar and E.Haselbach, J.Amer.Chem.Soc., 1970, **92**, 590.
9. N.Bodor, M.Dewar, A.Harget, and E.Haselbach, J.Amer.Chem.Soc., 1970, **92**, 3855.
10. R.C.Bingham, M.Dewar, and D.H.Lo, J.Amer. Chem.Soc., 1975, **97**, 1285.
11. J.Del Bene and H.H.Jaffe, J.Chem.Phys., 1968, **48**, 1807.
12. G.Kuehnlenz and H.H.Jaffe, J.Chem.Phys., 1973, **58**, 2238.
13. A.Warshel and M.Karplus, J.Amer.Chem.Soc., 1972, **94**, 5612; 1974, **96**, 5677.
14. E.S.Sachs and J.Hinze, J.Chem.Phys., 1975, **62**, 3393.
15. I.V.Abarenkov, "Metody Kvantovoi Khimii" (Quantum-Chemical Methods), Chernogolovka, 1979, p.125.
16. P.Pyykkö, in "Advances in Quantum Chemistry" (Edited by P.O.Löwdin), Acad.Press, New York, 1978, Vol.11, p.354.
17. K.H.Johnson, Ann.Rev.Phys.Chem., 1975, **26**, 39.
18. P.P.Shorygin and E.M.Popov, Zhur.Fiz.Khim., 1964, **38**, 1429 [Russ.J.Phys.Chem., 1964(6)].
19. P.P.Shorygin and E.M.Popov, Dokl.Akad.Nauk SSSR, 1962, **146**, 1132.
20. P.P.Shorygin, Optika i Spektrosk., 1966, **21**, 381.
21. H.B.Schlegel, S.Wolfe, and F.Bernardi, J.Chem. Phys., 1975, **63**, 3632; 1977, **67**, 4181, 4194.
22. J.Pacansky, U.Wahlgren, and P.S.Bagus, Theor. Chim.Acta, 1976, **41**, 301.
23. U.Wahlgren, J.Pacansky, and P.S.Bagus, J.Chem. Phys., 1975, **63**, 2874.
24. T.-K.Ha, C.E.Blom, and H.Günthard, Chem.Phys. Letters, 1980, **70**, 473.
25. M.J.Dewar and G.P.Ford. J.Amer.Chem.Soc., 1977, **99**, 1685, 7823, 8343.
26. C.E.Blom and C.Altona, Mol.Phys., 1977, **34**, 177, 557.
27. C.E.Blom and C.Altona, Mol.Phys., 1976, **31**, 1359, 1377.
28. C.E.Blom, L.P.Otto, and C.Altona, Mol.Phys., 1976, **32**, 1137.

29. K.Kozmutza and P.Pulay, Theor.Chim.Acta, 1975, **37**, 67.
30. Yu.N.Panchenko, P.Pulay, and F.Török, J.Mol. Struct., 1976, **34**, 283.
31. A.Grofcsik, J.Mol.Struct., 1979, **56**, 277.
32. E.M.Popov, A.Kh.Khomenko, and P.P.Shorygin, Izv.Akad.Nauk SSSR, Ser.Khim., 1965, 51.
33. C.W.Bock, P.George, and M.Trachtman, J.Mol. Spectr., 1979, **78**, 248; 1980, **80**, 1131.
34. N.B.Colthup and M.K.Orloff, Spectrochim.Acta, 1974, **30a**, 425.
35. I.N.Juchnovski, J.S.Dimitrova, and J.Kaneti, Izv.B'ly.Akad.Nauk, 1979, **12**, 97.
36. S.A.Kucharski and L.Czuchajowski, Z.phys. Chem., 1980, **261**, 796.
37. P.Pulay and F.Török, J.Mol.Struct., 1975, **29**, 239.
38. P.Botschwina, E.Nachbaur, and B.M.Rode, Chem. Phys.Letters, 1976, **41**, 486.
39. Y.Hamada, M.Tsuboi, and H.Umeyama, Bull.Chem. Soc.Japan, 1980, **53**, 48.
40. A.Schmiedekamp, C.W.Bock, and P.George, J.Mol. Struct., 1980, **67**, 107.
41. M.J.Dewar and M.L.McKee, J.Mol.Struct., 1980, **68**, 105.
42. E.Marmar, C.Pouchan, and M.Chaillet, J.chim. phys.et phys.chim.biol., 1979, **76**, 1125.
43. Y.Yoshioka, J.D.Goddard, and H.F.Schaefer, J.Chem.Phys., 1981, **74**, 1855.
44. P.Botschwina, H.Haertner, and W.Sawodny, Chem.Phys.Letters, 1980, **74**, 156.
45. T.P.Lewis and I.W.Levin, Theor.Chim.Acta, 1970, **19**, 55.
46. H.H.Seydewitz and E.D.Schmid, J.Chem.Phys., 1973, **58**, 3486.
47. W.M.Smit and T.van Dam, J.Chem.Phys., 1980, **72**, 3658.
48. Y.Sugawara, Y.Hamada, and A.Y.Hirakawa, Chem.Phys., 1980, **50**, 105.
49. H.Werner and E.Reinsch, Chem.Phys.Letters, 1981, **78**, 311.
50. J.Bunnell, B.Crafford, and T.Ford, J.Mol.Struct., 1980, **61**, 383.
51. R.T.C.Brownlee, J.Munday, R.D.Topsom, and A.R.Katritzky, J.Chem.Soc., Faraday Trans.II, 1973, **69**, 349.
52. G.Jalsovszky and P.Pulay, Kem.közl., 1976, **46**, 430.
53. B.Liu, K.M.Sando, C.S.North, H.B.Friedrich, and D.M.Chipman, J.Chem.Phys., 1978, **69**, 1425.
54. H.W.Kroto and D.P.Santry, J.Chem.Phys., 1967, **47**, 792.
55. P.Pulay, G.Fogarasi, and J.Boggs, J.Chem.Phys., 1981, **74**, 3999.
56. S.Huzinaga, Phys.Rev., 1960, **120**, 866; 1961, **122**, 131.
57. S.Huzinaga, J.Chem.Phys., 1969, **51**, 3971.
58. K.Hirao and H.Nakatsiyi, J.Chem.Phys., 1973, **59**, 1457.
59. K.Hirao, J.Chem.Phys., 1974, **60**, 3215.
60. J.A.Pople and R.H.Nesbet, J.Chem.Phys., 1954, **22**, 571.
61. M.J.Dewar, J.A.Hashmall, and C.G.Venier, J.Amer. Chem.Soc., 1968, **90**, 1953.
62. J.Langlet and J.P.Malrieu, Theor.Chim.Acta, 1974, **33**, 307.
63. G.H.Kirby and K.Miller, J.Mol.Struct., 1971, **8**, 373.
64. F.Fratęv, J.Mol.Struct., 1976, **30**, 217.
65. P.Zahradnik and J.Leška, Chem.Phys.Letters, 1976, **41**, 293.
66. P.Zahradnik and J.Leška, Coll.Czech.Comm., 1977, **42**, 2060.
67. K.Gustav and J.Sühnel, Z.Chem., 1980, **20**, 283.
68. M.J.Dewar and S.Olivella, J.Chem.Soc., Faraday Trans.II, 1979, **75**, 829.
69. S.D.Peyerimhoff and R.J.Buenker, in "Advances in Quantum Chemistry" (Edited by P.O.Löwdin), Acad.Press, New York, 1975, Vol.9, p.69.
70. T.C.Jao, N.H.F.Beebe, W.B.Person, and J.R.Sabin, Chem.Phys.Letters, 1974, **26**, 474.
71. I.C.John, G.B.Bacskay, and N.S.Hush, Chem. Phys., 1980, **51**, 49.
72. N.P.Borisova and L.P.Bokacheva, Vestnik Leningrad.Univ., Fiz., Khim., 1974, No.4, 36.
73. J.Römelt, S.D.Peyerimhoff, and R.Buenker, J.Chem.Phys., 1981, **54**, 147.
74. M.J.Dewar, R.S.Haddon, and S.H.Suck, Chem. Comm., 1974, 611.
75. K.Ya.Burshtein, P.P.Shorygin, and N.A.Anikin, Optika i Spektrosk., 1978, **44**, 913.
76. R.Akaba, K.Tokumaru, and T.Kobayashi, Bull. Chem.Soc.Japan, 1980, **53**, 1993.
77. I.Baraldi and M.C.Bruni, Gazzetta, 1979, **109**, 595.
78. M.Nascimento and W.Goddard, Chem.Phys., 1980, **53**, 251, 265.
79. V.A.Godik, G.G.Konoplev, A.N.Rodionov, and D.M.Shigorin, Zhur.Fiz.Khim., 1980, **54**, 3004 [Russ.J.Phys.Chem., 1980(12)].
80. G.M.Schwenzer, S.V.O'Neil, H.F.Schaefer III, C.P.Baskin, and C.F.Bender, J.Chem.Phys., 1974, **60**, 2787.
81. J.A.Hudis and R.Ditchfield, Chem.Phys.Letters, 1981, **77**, 202.
82. O.Zamani-Khamiri, E.F.McIntyre, and H.F.Hameka, J.Chem.Phys., 1980, **72**, 5906.
83. J.T.D'Agostino and H.H.Jaffe, J.Amer.Chem.Soc., 1969, **91**, 3383.
84. S.Braverman, D.Cohen, D.Reisman, and H.Basch, J.Amer.Chem.Soc., 1980, **102**, 6556.
85. D.A.Lightner, J.K.Gawronski, and T.D.Bouman, J.Amer.Chem.Soc., 1980, **102**, 5749.
86. K.Ja.Burshtein and E.P.Serebryakov, Tetrahedron, 1978, **31**, 3233.
87. F.S.Richardson and N.Cox, J.Chem.Soc., Perkin Trans.II, 1975, 1240.
88. R.L.Martin, J.Chem.Phys., 1981, **74**, 1852.
89. S.K.Srivastava and P.C.Mishra, J.Mol.Struct., 1980, **68**, 183.
90. Yu.A.Tishchenko, L.V.Orlovskaya, and V.I.Danilova, Izv.Vys.Ucheb.Zaved., Fizika, 1980, **23**, No.3, 132.
91. R.J.Buenker, S.D.Peyerimhoff, and M.Peric, Chem.Phys.Letters, 1976, **42**, 383.
92. M.Peric, R.J.Buenker, and S.D.Peyerimhoff, Canad.J.Chem., 1977, **55**, 1533.
93. M.Peric, R.J.Buenker, and S.D.Peyerimhoff, Canad.J.Chem., 1977, **55**, 3664.
94. F.Pauzat, B.Levy, and Ph.Millie, Mol.Phys., 1980, **39**, 375.
95. M.Roche and H.H.Jaffe, J.Chem.Phys., 1974, **60**, 1193.
96. V.I.Khaustova and V.I.Danilova, Izv.Vys.Ucheb. Zaved., Fizika, 1978, No.5, 122.
97. L.Ziegler and A.C.Albrecht, J.Chem.Phys., 1974, **60**, 3558.
98. S.J.Strickler, J.Phys.Chem., 1976, **80**, 2149.
99. K.Ohno, Chem.Phys.Letters, 1979, **64**, 560.

100. M.F.Lafore–Merienne and H.P.Trommsdorff, J.Chem.Phys., 1976, **64**, 3791.
101. P.P.Shorygin, Uspekhi Khim., 1978, **47**, 1697 [Russ.Chem.Rev., 1978(10)].
102. J.Tang and A.C.Albrecht, "Raman Spectroscopy", Plenum Press, New York, 1970, Vol.2, p.33.
103. L.L.Krushinskii and P.P.Shorygin, Optika i Spektrosk., 1965, **19**, 562.
104. N.S.Hush and M.L.Williams, Theor.Chim.Acta, 1972, **26**, 141.
105. P.Bleckmann, Z.Naturforsch., 1974, **29a**, 1485.
106. P.Bleckmann and W.Wiegeler, J.Mol.Struct., 1977, **42**, 227.
107. H.Yamada, Kwansei Gakuin University Annual Studies, 1972, **21**, 95.
108. H.Shinoda and T.Miyazaki, Chem.Letters, 1973, 563.
109. K.Ya.Burshtein and P.P.Shorygin, "Teoreticheskaya Spektroskopiya" (Theoretical Spectroscopy), Izd. Akad.Nauk SSSR, Moscow, 1977, p.47.
110. E.N.Svendsen, J.Mol.Struct., 1978, **50**, 195.
111. W.Kolos and L.Wolniewicz, J.Chem.Phys., 1967, **46**, 1426.
112. J.Tang and A.Albrecht, J.Chem.Phys., 1968, **49**, 1144.
113. H.Shinoda, Bull.Chem.Soc.Japan, 1975, **48**, 1777.
114. H.Shinoda, Bull.Chem.Soc.Japan, 1976, **49**, 1267.
115. J.N.Murrell and J.A.Pople, Proc.Phys.Soc., 1956, **A69**, 245.
116. A.Komornicki and J.W.McIver, J.Chem.Phys., 1979, **70**, 2014.
117. P.P.Shorygin, Pure Appl.Chem., 1962, **4**, 87.
118. H.F.Hameka and E.N.Svendsen, Int.J.Quantum Chem., 1977, 11, 129.
119. E.N.Svendsen and T.Stroyer-Hansen, Theor. Chim.Acta, 1977, **45**, 53.
120. E.N.Svendsen, T.Stroyer-Hansen, and J.Tangaa, J.Mol.Spectr., 1979, **77**, 244.
121. E.N.Svendsen and J.Tangaa, J.Raman Spectr., 1978, **7**, 268.
122. S.I.Vetchinkin, I.M.Umanskii, V.L.Bakhrakh, and A.D.Stepukhovich, Optika i Spektrosk., 1980, **48**, 49.
123. P.P.Shorygin and L.L.Krushinskii, Optika i Spektrosk., 1964, **17**, 551.
124. A.Warshel and P.Dauber, J.Chem.Phys., 1977, **66**, 5477.
125. G.Jalsovszky and P.Pulay, J.Mol.Struct., 1975, **26**, 277.
126. P.Pulay, A.Ruoff, and W.Sawodny, Mol.Phys., 1975, **30**, 1123.
127. B.Nelander and G.Ribbegard, J.Mol.Struct., 1974, **20**, 325.
128. M.Spiekermann, D.Bougeard, H.-J.Oelichmann, and B.Schrader, Theor.Chim.Acta, 1980, **54**, 301.
129. B.Schrader, D.Bougeard, and W.Niggemann, "Computational Methods in Chemistry", Plenum Press, New York, 1979.
130. E.N.Svendsen, Dissertation, Department of Chemistry, Odense University, Odense, Denmark, 1980.
131. W.Wiegeler and P.Bleckmann, J.Mol.Struct., 1980, **66**, 273.
132. F.S.Lur'e and Yu.L.Frolov, Symposium, "9-i Mezhdunarodnyi Simpozium po Khimii Soedinenii Sery, Riga, 1980" (The 9th Internal Symposium on the Chemistry of Sulphur Compounds, Riga, 1980), p.244.
133. J.Sadley, Pol.J.Chem., 1980, **54**, 991.
134. E.D.Schmid and R.D.Topson, J.Amer.Chem.Soc., 1981, **103**, 1628.

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