PHYSICAL CHEMISTRY

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1962

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Abstract

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PHYSICAL CHEMISTRY

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UNUSUAL MANIFESTATIONS OF THE MUTUAL INFLUENCE OF ATOMIC GROUPS IN THE SPECTRA OF COMPLEX MOLECULES

(Presented by Academician I. V. Obreimov, 9 VI 1962)

Many examples are known of a significant influence of substituents on the stiffness of chemical bonds in atomic groups adjacent to the substituent. Changes in stiffness here are usually associated with changes in the state of the bonds (multiplicity, bond order). Intramolecular mutual influence may, however, manifest itself not only in the specificity of the force constants of bonds, i.e., of the diagonal elements K_{ii} in the matrix of second derivatives of the potential energy (U) of the molecule with respect to natural coordinates (changes in bond lengths and angles, q_i), but also in nonzero values of the off-diagonal elements,

$$K_{ij} = \frac{\partial^2 U}{\partial q_i \partial q_j}$$

(where $i \neq j$).

The off-diagonal force coefficient K_{ij} may be regarded as the coefficient of proportionality between the force (attraction or repulsion) F_j, arising between the atoms of the j-th bond upon stretching of the i-th bond, and the magnitude of the stretching of the latter; $F_j = K_{ij} q_i$ when all independent coordinates except q_i are equal to zero.

The forces F acting on the atoms of the j-th bond when $q_i \neq 0$, $q_j = 0$, generally speaking, do not coincide with the direction of this bond. The force F_j is essentially only the component of the forces F that is introduced (as is K_{ij}) for the given choice of independent coordinates; however, in some cases it can be assigned a clear physical meaning. For illustration, let us consider a model of a triatomic molecule or group XYZ (r_1, r_2, and α_0 are the equilibrium values of the bond lengths and valence angle). The force F acting on Z when $q_1 > 0$, $q_2 = 0$, may be defined as the vector sum $K_{1\alpha} r_2 q_1 = F_\alpha$ and $K_{12} q_1 = F_2$. When $K_{12} \gg K_{1\alpha} r_2$, it is quite probable that, among the causes of the appearance of the force F, redistribution (or migration) of electron density between the XY and YZ bonds has a dominant significance; when $K_{1\alpha} r_2 \gg K_{12}$, the dominant significance is probably that of forces determining the valence angle (these forces may be caused by a change in the distance between atoms X and Z and by a change in the hybridization of the valence orbitals of atom Y). The conditions $K_{1\alpha}r_2 \gg K_{12}$ are approached by the data for the CH_2 group, and the conditions $K_{12} \gg K_{1\alpha}r_2$ by the data for the nitro group (see Table 1). Redistribution of electron density between bonds in the process of nuclear vibration should promote the appearance of off-diagonal and some decrease in diagonal* force coefficients. It may manifest— also be manifested in increased values of the intensity of the corresponding infrared absorption bands (adjacent electropositive and electronegative groups in complex molecules, and other cases); then the redistribution may be provisionally called "electron migration." From this standpoint, the combination of all three of the indicated features of the spectral parameters in certain molecules with conjugated bonds deserves serious attention.

The off-diagonal coefficients K_{ij} are much smaller than the diagonal ones. However, in manifestations of the mutual influence of atomic groups in the spectra of polyatomic molecules they may sometimes play a role no less important than the specificity of K_{ii}, and may substantially affect the frequencies observed in infrared and Raman spectra. An example is the lowering of the $C = O$ frequency in passing from acetone to urea or to acetamide (CH_3CONH_2), which is associated both with a decrease in the force constant of the $C = O$ bond and with a substantial value of K_{ij} for adjacent N—C and $C = O$ bonds*. Below we shall consider cases in which certain features of the spectrum are almost entirely determined by off-diagonal coefficients.

Table 1

Compound	Bonds i and j	$K_{12} \cdot 10^6$, cm^{-2}	$K_{1\alpha} \cdot 10^6$, cm^{-2}	$K_{11} \cdot 10^6$, cm^{-2}
CH_4, $H_2C{=}CH_2$	C H H	0.05	0.36	~ 8.5
CH_3—CH_2—CH_3	C C C	< 0.05	0.43	7.0
NH_3	N H H	0.05	0.40	10.7
CH_2F_2	C F F	0.60	1.30	10.7
CH_2Br_2	C Br Br	0.25	0.80	4.8
$H_2C{=}C{=}CH_2$	C=C=C	0.15	0	15.0
Benzene	C C C	~ 1.05	~ 0.70	9.4

* In this connection, a lowered value of the force constant K_{ii} cannot yet be regarded as evidence of a lowered bond order.

Compound	Bonds i and j	$K_{12} \cdot 10^6$, cm^{-2}	$K_{1\alpha} \cdot 10^6$, cm^{-2}	$K_{11} \cdot 10^6$, cm^{-2}
CH_3NO_2	N O O	1.6	0.60	14.0
CO_2	O=C=O	2.0	0	24.4

Table 1 gives values of K_{ij} for some adjacent bonds of the same type (literature data).

As can be seen, K_{ij} depend on the nature of the chemical bonds and vary over wide limits. They are considerably larger for bonds whose character is intermediate between single and double, or between covalent and ionic. Apparently, in these cases the state of the bonds (characterized, in particular, by their order and degree of ionicity) is more labile, i.e., depends substantially on the nuclear coordinates.

The intramolecular influence of one group of atoms on the stiffness of bonds in another group rapidly weakens as the number of intermediate links increases (even if they constitute a system of conjugated π-bonds) ([1]). The coefficients K_{ij}, generally speaking, should also decrease when intermediate links are introduced between the bonds i and j. For nonadjacent bonds they are, as a rule, taken to be zero. However, this is not always justified.

Let us consider symmetric molecules containing two identical groups of atoms, and two frequencies—of the symmetric (ω_s) and antisymmetric (ω_{as}) vibrations of these two groups. The magnitude of the splitting ($\omega_s - \omega_{as} = \Delta\omega$) depends to a significant extent on the mechanical parameters of the intermediate links. In molecules in which multiple bonds are separated by less stiff single—

···by single C–C bonds, $\Delta\omega$ falls rapidly with an increase in the number of intervening bonds. Table 2 illustrates this with the example of the $C = O$ frequencies of dicarbonyl compounds (according to literature data).

Quite different relationships occur when there is an oxygen or nitrogen bridge between the carbonyl groups. In carboxylic acid anhydrides, despite the larger number of intervening links, the splitting of the $C = O$ frequency is much greater than in diacetyl; thus, for succinic anhydride (I) $\Delta\omega = 77$ cm^{-1}, while for N-methylsuccinimide (II) $\omega_s = 1748$ cm^{-1}, $\omega_{as} = 1715$ cm^{-1}, $\Delta\omega = 69$ cm^{-1} (the assignment of the bands is indirectly proved by the fact that the 1715 cm^{-1} band is very intense in the infrared spectrum, whereas the 1784 cm^{-1} band is very intense in the Raman spectrum). Frequency calculations show that the

* A large value of K_{ij} here could already have been expected from the fact that the mutual influence in the N—$C = O$ system is appreciably reflected in interatomic distances, r_0 (see X-ray data). In some cases the reverse reasoning is also possible: from K_{ij}, about peculiarities of r_0.

large splitting in such compounds cannot be explained by a simple mechanical interaction of the vibrating groups, as was done, for example, by Bellamy (^{2}).

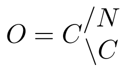
Table 2

Compound	Structure of the main chain	ω_s, cm^{-1}	ω_{as}, cm^{-1}	$\Delta\omega$, cm^{-1}
Carbon dioxide	$O = C = O$	1336	2350	−1104
Dimethyl oxalate	$O = C—C = O$	1776	1770	6
Diacetyl	$O = C—C = O$	1725	1718	7
Dimethyl acetylacetone	$O = C—C—C = O$	1710	1710	0
Acetonylacetone	$O = C—C—C—C = O$	1707	1707	0
Acetone	$C = O$	1710	–	–

Nor does the ratio of the intensities of the two lines (A_s and A_{as}) in the infrared spectra find an explanation within the framework of a simple additive scheme. Let μ denote the dipole moment of the molecule, and $Q_{C=O}$ the normal coordinate of the "$C = O$ vibration." If the vector

$$\frac{\partial\mu}{\partial Q_{C=O}} = \mu'$$

in the bond system



$$O = C\begin{matrix}/N \\ \backslash C\end{matrix}$$

for example, in acetamide and N-methylpyrrolidone (III) molecules (the notation in the subscripts is mp), were directed along the $C = O$ bond, then in methylsuccinimide, at the observed angle of 136° between the two $C = O$ bonds, A_s would be $\sim 0.3A_{\mathrm{mp}}$, and A_{as} about $1.7A_{\mathrm{mp}}$. In reality, however, $A_s \ll 0.3A_{\mathrm{mp}}$, and $A_{as} > 1.7A_{\mathrm{mp}}$.

To explain this, let us note that $A_{C=O}$ in acetamide and methylpyrrolidone is 2–3 times greater than in acetone. Here a substantial electron migration during the "$C = O$ vibration" from the N atom to the O atom and back is quite probable. If it made the dominant contribution to the real value of μ', then the structural formula of dinitrodiphenylamine

Figure 1: structural formula of dinitrodiphenylamine

direction of this vector in methylpyrrolidone would be closer to the direction $N \ldots O$ than to the direction of the $C = O$ bond. Then in succinimide, in which the angle $O \ldots N \ldots O$ is close to 180°, the sum of two such vectors (μ_p' and μ_l'), conventionally assigned to the "right" and "left" halves of the molecule, would be close to zero, whereas their difference, on the contrary, would be considerably greater than at an angle of 136°; under these conditions A_s would be close to zero, and A_{as} to $2A_{\mathrm{mp}}$ (or would even exceed this value owing to the contributions of $\frac{\partial \mu_p}{\partial q_l}$ and $\frac{\partial \mu_l}{\partial q_p}$). This is in fact what is observed.

A calculation of the $C = O$ frequencies of methylsuccinimide with allowance for K_{ij} for all adjacent coordinates (but without allowance for the participation of hydrogen atoms) led to the values

$\omega_s = 1779$ cm^{-1}, $\omega_{as} = 1766$ cm^{-1}.* Calculation of the coefficient K_{ij} for taking into account the interaction of both C=O groups, which leads to the corresponding experiment $\Delta\omega = 69$ cm^{-1}, gives the value $0.65 \cdot 10^{-6}$ cm^{-2}. Thus, the main reason for the strong splitting of the C=O frequency in methylsuccinimide (and in other similar symmetrical molecules with a nitrogen or oxygen bridge) is apparently the anomalously large value of the indicated off-diagonal element, which determines the interaction of chemical bonds remote from one another.

Still more unusual may appear the data for dinitrodiphenylamine (IV). Let us consider the stretching vibrations of the nitro groups (symmetric with respect to the symmetry elements of the nitro groups): the in-phase vibration of both nitro groups

(IV)

(the very intense line in the Raman spectrum, 1342 cm^{-1}) and the out-of-phase vibration (the very intense band in the IR spectrum, ~ 1320 cm^{-1}). The magnitude of the splitting determines the value $K_{ij} =\sim 0.1 \cdot 10^{-6}$ cm^{-2}. With 10 intermediate links between the nitro groups (bonds i and j), this quantity is quite unusual; it shows that the force field in one group of atoms of a complex molecule can depend substantially on the coordinates of atoms in another, very remote group. Somewhat simplifying and schematizing the actual relationships, one may imagine that in the equilibrium configuration of molecule IV there is a substantial displacement of an electron from the N atom of the amino group toward the O atoms of both nitro groups (as in the structurally simpler molecule n-nitroaniline, which, as is known, has a very large dipole moment). In the out-of-phase vibration of the nitro groups, at a certain phase of the vibration the displacement of the electron toward one nitro group decreases, while the displacement toward the other increases; both aspects of this phenomenon should reinforce one another and contribute to some decrease in the potential energy of the deformed molecule (in the in-phase vibration the situation is the opposite).

The features of the spectrum of dinitrodiphenylamine described here are practically absent in similar compounds in which, instead of the bridge –NH–, there is the bridge $-CH_2-$.

The calculation and study of the off-diagonal elements K_{ij} leads to a more correct and complete interpretation of spectra and broadens the possibilities for studying the mutual influence of atoms and its nature. It may also help in elucidating the mechanism of transmission of the influence of external actions on a molecule along a chain of chemical bonds (for example, in studying the influence of steric hindrances and strains, the influence of a solvation shell or catalyst on structural elements of the molecule remote from them, and in studying the process of excitation of vibrations during collisions of molecules).

Received
8 VI 1962

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[*] K_{ii} and K_{ij} were estimated by analogy with other known molecules of suitable structure. In addition, by Mayants' method (3), the possible error in the calculation of $\Delta\omega$, caused by the possible inaccuracy of all the values of K_{ii} and K_{ij} used, was estimated.

Note: Figure translations are in progress. See original paper for figures.

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