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Charge Transfer in Complexes of the Donor - Acceptor Type

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Data on the application of physical methods for the estimation of the degree of charge transfer and the nature of charge distribution in complexes of the donor - acceptor type are examined and described systematically. The dipole moment method, infrared spectroscopy, nuclear quadrupole resonance, Mössbauer spectroscopy, X-ray electronic spectroscopy, and quantum-chemical calculations are considered.
The bibliography includes 105 references.

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I. INTRODUCTION

Numerous studies have been devoted to donor–acceptor interaction and the results have been surveyed in a number of reviews and monographs[1-9]. Interpretation of the experimental data in terms of thermodynamic parameters (equilibrium constants, enthalpy, and entropy) does not as a rule present special difficulties. Complexes of different compositions, with different initial components and with different numbers and structures of the latter, can be compared in terms of these parameters, i.e. thermodynamic parameters are to some extent universal. Interpretation of data is somewhat different as regards the structural aspect. In this case, only a comparison is made in terms of spectroscopic data and other characteristics. A general interpretation of the experimental data therefore requires the selection of universal parameters of the same type as in the study of the thermodynamics of the complexes. We believe that such parameters should be charge transfer and the nature of charge distribution in the complex. They are in fact responsible for the changes in structure and physicochemical and chemical properties on complex formation. Unfortunately the available data on charge transfer have not been arranged in an adequately systematic form.

In the present article, an attempt is made to review such estimates of the degree of charge transfer and of the nature of charge distribution in complexes of the π_σ, n_σ, π_v, and nv types. Data on charge transfer in $\pi\pi$ complexes have been adequately described in a number of communications[2,3,5,6] and are not therefore dealt with in the present review.

II. THE EFFECTIVE CHARGE

The concept of the charges of atoms in molecules is fundamental for the description of the electronic structures of chemical compounds. Naturally, complexes constitute merely a specific instance. It is therefore necessary to elucidate the definition of the charge of an atom in an individual molecule and to specify its physical significance.

The simplest and clearest description of the electronic structure of molecules involves the attribution of effective charges to atoms in the molecules†. It is understood that the very concept of the charge depends on the experimental method used to determine it. It is known that an atom in a molecule does not retain its "individuality" and the greater its loss, the less adequate is the description of the observed properties of the molecule in terms of purely atomic characteristics[12]. However, at the present state of development of theoretical chemistry one can employ with some caution the concept of the effective charge of an atom to describe the experimentally observed characteristics[13].

The model of the effective charge presupposes that the entire electronic charge of the atom can be represented by a point charge, coinciding with the nucleus. We shall assume after Mulliken that the electron density resulting from the overlapping of the wave functions of the atoms is shared between them in accordance with their non-equivalence. On the other hand, Levdin began with a basis set of atomic orbitals subjected to preliminary orthogonalisation[12]. There is then no need for assigning the overlap densities to the atoms. In principle, Levdin's definition of the effective charge reflects more satisfactorily the true charge distribution in the molecule, but so far virtually all investigations have been based on the analysis of Mulliken populations. In the present review, we shall therefore also estimate the effective atomic charges by Mulliken's method[2,14,15].

The formation of a complex of the donor–acceptor type is known to be caused by charge transfer from the donor to the acceptor[9]. We shall therefore consider charge transfer in the ground state of the complex and shall confine ourselves to an examination of the simplest wave function of the ground state (ψ_N):

$$\psi_N = a\psi_0(DA) + b\psi_1(D^+A^-). \qquad (1)$$

The coefficients a and b in Eqn. (1) characterise the fractions of the structure "without bonds" and of the structure with complete charge transfer. When the ratio b/a is small, the fraction of the state with charge transfer is likewise small and the complex is stabilised mainly by electrostatic forces (dipole–dipole, dipole–induced dipole, ion–dipole, etc.). When b/a is large, the contribution of the charge-transfer state is likewise large and the forces caused by charge transfer can appreciably exceed the usual intermolecular forces.

The coefficients a and b are related by the normalisation condition:

$$\int \psi_N^2 d\tau = 1 \quad \text{or} \quad a^2 + b^2 + 2abS_{01} = 1 \ ,$$

where S_{01} is the overlap integral of the wave functions ψ_0 and ψ_1. Here S_{01} is linked to the overlap integral S_{DA} of the wave functions of the donor (ψ_D) and acceptor (ψ_A) in the following way[9]:

$$S_{01} = \frac{\sqrt{2}\,S_{DA}}{(1 + S_{DA}^2)^{1/2}} .$$

The degree of charge transfer has been defined in different ways by different workers: b^2, $b^2/(a^2 + b^2)$, and $b^2 + abS_{01}$. It follows from estimates of Mulliken populations that the degree of charge transfer is more correctly characterised by the quantity $b^2 + abS_{01}$. For weak complexes, where $b \ll a$, different definitions of charge transfer lead to virtually identical numerical results, but for strong complexes the differences are significant. In all cases, we chose the same definition of the degree of charge transfer in terms of the quantity $\Delta = b^2 + abS_{01}$. The results presented in the Tables have been recalculated in those cases where the authors used other definitions of the degree of charge transfer.

There are many physical methods which make it possible to estimate the transferred charge in complexes and such estimates are based on Mulliken's definition of the charge. The methods include electronic absorption spectroscopy, the dipole moment method, infrared spectroscopy, nuclear quadrupole resonance (NQR), nuclear gamma-resonance (NGR) or the Mössbauer effect, X-ray electronic spectroscopy, and quantum-chemical calculations. Electronic spectroscopy permits the estimation of the coefficients a and b only for very weak complexes and we shall not therefore consider results obtained by this method.

Since the application of such different research techniques leads in essence to an adequate estimation of the degree of charge transfer, it is of interest to compare the transferred charges and the nature of their distribution in complexes, obtained by different methods for the same compounds.

III. THE DIPOLE MOMENT METHOD

One of the first methods used to investigate charge transfer in complexes was the dipole moment method. This method is very sensitive to changes in the charge distribution in the molecule, partial transfer of electron density from the donor to the acceptor resulting therefore in the generation of a very significant additional dipole moment.

Briegleb[3] obtained an expression for the dipole moments of the complex (μ_N):

$$\mu_N = a^2\mu_0 + b^2\mu_1 + abS_{01}(\mu_1 + \mu_0),$$

where $\mu_0 = \mu_D + \mu_A$ is the vector sum of the dipole moments of the non-interacting donor and acceptor for a specified configuration of the complex and μ_1 is the dipole moment of the complex with complete charge transfer. For convenience, the expression can be transformed as follows:

$$\mu_N - \mu_0 = (b^2 + abS_{01})(\mu_{DA} + \mu_D' + \mu_A' - \mu_D - \mu_A), \qquad (2)$$

† An attempt was made recently to formulate a general quantum-mechanical definition of the charge of an atom in a molecule and of bond orders[10,11]. This approach employs the technique of projection operators and electron density operators. However, despite its advantages (the generality of the procedure, the invariance of the results with respect to any orthogonal transformations, etc.), the results are difficult to interpret. For example, all the atomic charges are found to be negative, etc.[10]

where μ_{DA}, μ'_D, and μ'_A are the respective dipole moments of the donor–acceptor bond and of the components corresponding to complete charge transfer. It is seen from Eqn. (2) that the additional dipole moment $\mu_N - \mu_0$ is due to the dipole moment of the donor–acceptor bond $(b^2 + abS_{01})\mu DA$ and the changes in the dipole moments of the initial components as a result of complex formation $(b^2 + abS_{01})(\Delta\mu_D + \Delta\mu_A)$. It follows from Eqn. (2) that $b^2 + abS_{01}$, i.e. a quantity close to the Mulliken population, is a characteristic of the degree of charge transfer determined from dipole moments.

In practice, the degree of charge transfer is usually calculated in the following way: the dipole moments of the initial components are substracted from the observed dipole moment and the resulting difference is attributed to the dipole moment of the donor–acceptor bond. The latter is divided by er, where r is the distance between the directly coordinated atoms, and the transferred charge is thus obtained. It is seen from Eqn. (2) that this estimate is approximate and the calculated degree of charge transfer is closer to the true value the smaller the changes in the dipole moments of the components as a result of complex formation. This has been described in adequate detail in a monograph[9]. Here one need only mention that the dipole moment is a quantity characterising the charge distribution in the molecule of the complex as a whole, and not in its individual fragments. Because of this, the method of dipole moments cannot in principle yield the true degree of charge transfer and the difference between the true value and the value determined from the vector scheme will be greater the more effective the transfer of the influence of complex formation from the coordinating centres to other fragments of the molecules.

Table 1. The experimental dipole moments (μ) and the degrees of charge transfer ($b^2 + abS_{01}$) in the complexes $I_2.L$.[3,16,18]

Complex	μ_D, D	μ_N, D	S_{01}	$\Delta=(b^2+abS_{01})$, e
$I_2\cdot C_5H_5N$	2.21	4.50	0.1	0.25
$I_2\cdot(CH_3)_4S_2$	0	2.15	0.1	0.11
$I_2\cdot(CH_3)_2S$	1.40	3.62	0.1	0.12
$I_2\cdot(CH_3)_4CSN_2$	4.70	7.52	0.1	0.18
$I_2\cdot(CH_3)_4CON_2$	3.66	5.20	0.1	0.09
$I_2\cdot(CH_3)_4O_2$	0	1.30	0.1	0.06
$I_2\cdot(CH_3)_2SO$	3.85	5.59	0.02	0.18
$I_2\cdot(C_8H_{17})_3PO$	4.10	6.21	0.02	0.21
$I_2\cdot C_4H_9NO$	4.22	6.66	0.02	0.24
$I_2\cdot 4\text{-}CH_3C_6H_4NO$	4.73	7.43	0.02	0.26
$I_2\cdot(C_6H_5)_3AsO$	5.25	8.87	0.02	0.37

The most accurate results in studies on charge transfer should be obtained for complexes with non-polar components. In this case, the dipole moments of the donor, μ_D and μ'_D, are zero. Furthermore, for halogens μ_A is equal to zero; assuming that the charge is transferred to σ antibonding orbitals, one can assume that μ'_A is likewise zero. The additional dipole moment of the complex is then caused only by charge transfer. Thus the degree of charge transfer in the complex $I_2.C_6H_6$ found from the values of μ_N derived from two different sources[3,5] is 0.03 e or 0.08 e. The results of studies on charge transfer between the non-polar acceptor I_2 and polar donors are presented in Tables 1 and 2.

The Tables show that the degree of charge transfer varies within wide limits depending on the strength of the donor. In the complexes $TiCl_4.L$ (Table 2), the contribution of μA to the dipole moment of the complex is zero because of the square structure of $TiCl_4$ in the complexes. The main uncertainty into the calculation of the degree of charge transfer is therefore introduced by the change of the dipole moment of the donor. In the complexes $SnCl_4.L$ (Table 2), an additional error is introduced into the calculation of the transferred charge by the change in the dipole moment of the Sn–Cl bond. It is at present difficult to estimate the accuracy of the determination of the degree of charge transfer—the uncertainty in the contributions of the above factors makes it virtually impossible to make such an estimate.

Table 2. The dipole moments (μ), the degrees of charge transfer ($b^2 + abS_{01}$), and the heats of formation of donor–acceptor bonds (ΔH) for complexes of the $n\sigma$ and $n\nu$ types[9].

Complex	μ_N, D	μ_D, D	μ_{DA}, D	r_{DA}, Å	$\Delta=b^2+abS_{01}$, e	$-\Delta H$, kcal mole^{-1}
$I_2\cdot(C_2H_5)_2O$	1.90	1.21	1.4	2.60	0.11	4.3
$I_2\cdot C_5H_{11}O$	2.82	1.63	1.8	2.60	0.14	4.9
$I_2\cdot C_4H_8O$	3.00	1.70	2.0	2.60	0.16	5.3
$I_2\cdot(C_6H_5)_2S$	1.99	1.56	0.4	2.78	0.03	0.3
$I_2\cdot(C_2H_5)_2S$	3.64	1.44	2.0	2.78	0.15	4.6
$I_2\cdot(C_6H_5CH_2)_2S$	3.78	1.38	2.2	2.78	0.16	4.8
$I_2\cdot(i\text{-}C_8H_{17})_2S$	4.72	1.63	3.1	2.78	0.23	7.4
$I_2\cdot(i\text{-}C_7H_{15})_2S$	4.90	1.63	3.4	2.78	0.25	8.1
$I_2\cdot(C_2H_5)_2S$	4.62	1.60	3.1	2.78	0.23	7.8
$I_2\cdot(C_3H_7)_2S$	4.90	1.55	3.4	2.78	0.25	8.1
$I_2\cdot(C_4H_9)_2S$	5.00	1.57	3.6	2.78	0.27	7.6
$I_2\cdot(C_5H_{11})_2S$	5.34	1.58	3.8	2.78	0.28	7.0
$I_2\cdot(C_8H_{17})_2S$	5.07	1.58	3.5	2.78	0.26	7.4
$I_2\cdot C_4H_8S$	5.49	1.87	3.9	2.78	0.29	10.0
$I_2\cdot(C_6H_{11})_2S$	5.44	1.60	4.0	2.78	0.30	10.5
$I_2\cdot(C_6H_5CH_2)_3N$	2.80	0.65	1.1	2.30	0.10	2.3
$I_2\cdot C_5H_5N$	5.70	2.02	2.7	2.30	0.24	7.5
$I_2\cdot C_9H_7N$	5.70	2.25	2.5	2.30	0.23	7.1
$I_2\cdot C_4H_9NH_2$	6.07	1.40	3.4	2.30	0.31	8.4
$SnCl_4\cdot C_6H_5SC_2H_5$	4.20	1.48	0.9	2.27	0.07	2.0
$SnCl_4\cdot(C_6H_5CH_2)_2S$	4.77	1.38	1.5	2.27	0.12	3.8
$SnCl_4\cdot(C_3H_7)_2S$	6.49	1.55	3.3	2.27	0.27	12.9
$SnCl_4\cdot(C_4H_9)_2S$	6.71	1.57	3.5	2.56	0.28	12.6
$SnCl_4\cdot(C_8H_{17})_2S$	6.79	1.58	3.6	2.56	0.29	11.9
$SnCl_4\cdot(i\text{-}C_8H_{17})_2S$	3.76	1.63	0.4	2.56	0.03	0.4
$SnCl_4\cdot CH_3CN$	7.63	3.40	1.2	2.20	0.11	7.0
$SnCl_4\cdot C_6H_5CN$	8.40	3.90	1.5	2.20	0.14	6.1
$TiCl_4\cdot C_6H_5CN$	7.08	3.90	3.1	2.13	0.50	11.5
$TiCl_4\cdot(C_4H_9)_2O$	3.67	1.22	2.5	2.18	0.24	6.0
$TiCl_4\cdot(C_8H_{17})_2O$	3.83	1.22	2.6	2.18	0.25	6.3
$TiCl_4\cdot C_5H_{11}O$	4.52	1.87	3.1	2.18	0.30	12.0
$TiCl_4\cdot C_4H_8S$	4.54	1.71	4.1	2.47	0.34	12.0
$TiCl_4\cdot(C_2H_5)_2S$	4.66	1.58	4.3	2.47	0.36	11.5
$BF_3\cdot(CH_3)_2O$	4.35	1.25	1.7	1.54	0.23	13.7
$BF_3\cdot C_4H_8O$	5.68	1.70	2.6	1.54	0.35	18.8

The method involving the estimation of charge transfer from the enthalpies of complex formation ($-\Delta H$) may be regarded as a "derivative" of the dipole moment method. The linear relation $-\Delta H = 35.3\ \mu_{DA}/er_{DA}$ makes it possible to determine the transferred charge from the known value of ΔH (Table 2). For small and moderate charge transfers, this equation yields fully acceptable results. However, for large values of $-\Delta H$ and μ_{DA}, the coefficient of the relation between $-\Delta H$ and μ_{DA} will be different and cannot be used to determine the degree of charge transfer. For example, in the study of complexes of SO_3 with ethers[18], the coefficient μ_{DA}/er_{DA} proved to be 79.96.

IV. INFRARED SPECTROSCOPY

Infrared spectroscopy is one of the main methods used to estimate the degree of charge transfer. The degree of charge transfer can be estimated from the changes in the force constants of the halogen–halogen bonds for σ acceptors, and metal–halogen bonds for v acceptors with the aid of the force constants of the donor–acceptor bonds and from the relative changes in the stretching vibration frequencies on complex formation. One should note that the most correct values should be obtained using force constants, since in this case there is no reduced mass effect. However, owing to the difficulties in the calculation of the force constants of bonds, estimates of the degree of charge transfer from changes in the frequencies of the stretching vibrations have become most common, and in almost all studies of this kind complexes of σ acceptors are considered. The formation of complexes by v acceptors as a rule leads to a decrease of the stretching vibration frequencies of the metal–halogen bonds, but the degree of charge transfer cannot be estimated unambiguously from the relative shift of these frequencies, since the formation of complexes by v acceptors entails a change in the hybridisation of the central atom and hence a change in the parameters of the metal–halogen bonds (the amount of ionic character, the amount of double bond character, etc.), which must naturally be reflected in their frequencies.

Table 3. The degree of charge transfer in complexes of σ acceptors according to infrared spectroscopic data*.

Complex	Δ_1, e	Δ_2, e	Δ_3, e	Complex	Δ_1, e	Δ_2, e	Δ_3, e
$Cl_2 \cdot C_6H_6$	—	0.08	0.06	$ICl \cdot (C_6H_5)_3$	—	0.17	0.11
$Br_2 \cdot C_6H_6$	—	0.13	0.09	$ICl \cdot CH_3CN$	—	0.24	0.15
$Br_2 \cdot CH_3C_6H_5$	—	0.15	0.10	$ICl \cdot C_5H_5N$	0.46	0.64	0.42
$Br_2 \cdot ClC_6H_5$	—	0.09	0.07	$ICl \cdot 3\text{-}CH_3C_5H_4N$	0.41	0.69	0.39
$Br_2 \cdot C_6H_5COC_6H_5$	—	0.08	0.06	$ICl \cdot 4\text{-}CH_3C_5H_4N$	0.46	0.77	0.43
$Br_2 \cdot C_6H_5C_6H_5$	—	0.08	0.06	$ICl.2,6\text{-}(CH_3)_2C_5H_3N$	0.44	0.77	0.43
$Br_2 \cdot C_5H_5N$	0.36	0.76	0.42	$ICl.2,3\text{-}(CH_3)_2C_5H_3N$	0.46	0.81	0.45
$Br_2 \cdot CH_3CN$	—	0.08	0.06	$ICl.2,4\text{-}(CH_3)_2C_5H_3N$	0.52	0.90	0.50
$Br_2 \cdot (C_2H_5)_3N$	—	0.78	0.44	$ICl \cdot (CH_3)_3N$	—	0.92	0.51
$I_2 \cdot C_6H_6$	—	0.09	0.07	$ICl \cdot Cl_2CHSCH_3$	—	0.41	0.24
$I_2 \cdot CH_3C_6H_5$	—	0.11	0.08	$ICl \cdot ClCH_2SCH_3$	—	0.47	0.27
$I_2 \cdot 1,2\text{-}(CH_3)_2C_6H_4$	—	0.13	0.09	$ICl \cdot (C_6H_5)_2S$	—	0.56	0.32
$I_2 \cdot C_5H_5N$	0.21	0.53	0.24	$ICl \cdot CH_3SC_6H_5$	—	0.71	0.40
$I_2 \cdot 2\text{-}CH_3C_5H_4N$	--	0.39	0.23	$ICl \cdot (CH_3)_2S$	—	0.99	0.55
$I_2 \cdot 4\text{-}CH_3C_5H_4N$	—	0.39	0.23	$ICl \cdot CH_3SC_2H_5$	0.53	0.92	0.51
$I_2 \cdot (CH_3)_3N$	0.43	0.51	0.30	$ICl \cdot (C_2H_5)_2S$	0.53	0.92	0.51
$I_2 \cdot (C_2H_5)_3N$	—	0.31	0.18	$IBr \cdot C_6H_6$	0.09	0.11	0.08
$I_2 \cdot CH_3CN$	—	0.08	0.06	$IBr \cdot CH_3C_6H_5$	0.10	0.15	0.10
$I_2 \cdot Cl_2CHSCH_3$	—	0.15	0.10	$IBr \cdot 1,2\text{-}(CH_3)_2C_6H_4$	0.10	0.15	0.10
$I_2 \cdot ClCH_2SCH_3$	—	0.36	0.21	$IBr \cdot CH_3CN$	0.12	0.17	0.11
$I_2 \cdot (C_6H_5)_2S$	—	0.39	0.23	$IBr \cdot C_5H_5N$	0.36	0.57	0.35
$I_2 \cdot CH_3SC_6H_5$	—	0.43	0.25	$IBr \cdot (CH_3)_3N$	—	0.61	0.34
$I_2 \cdot (CH_3)_2S$	0.30	0.54	0.31	$IBr \cdot (C_2H_5)_3N$	—	0.60	0.34
$I_2 \cdot CH_3SC_2H_5$	0.30	0.54	0.31	$IBr \cdot Cl_2CHSCH_3$	—	0.39	0.23
$I_2 \cdot (C_2H_5)_2S$	0.33	0.52	0.30	$IBr \cdot ClCH_2SCH_3$	—	0.49	0.28
$I_2 \cdot (t\text{-}C_4H_9)_2S$	—	0.56	0.32	$IBr \cdot (C_6H_5)_2S$	—	0.58	0.33
$ICl \cdot C_6H_6$	—	0.19	0.12	$IBr \cdot CH_3SC_6H_5$	—	0.94	0.52
$ICl \cdot CH_3C_6H_5$	—	0.19	0.12	$IBr \cdot (CH_3)_2S$	—	0.86	0.48
				$IBr \cdot CH_3SC_2H_5$	—	0.90	0.50

*The degrees of charge transfer Δ_1, Δ_2, and Δ_3 have been calculated by Eqns. (4), (3), and (5) respectively.

In complexes formed by halogens, the stretching vibration frequencies of the halogen–halogen (X–X′) bonds are also reduced[19–28]. Mulliken[2] links such changes to the degree of charge transfer by the relation

$$\Delta = b^2 + abS_{01} \simeq \frac{8}{3} \cdot \frac{\Delta\nu}{\nu_1}, \qquad (3)$$

where $\Delta\nu = \nu_1 - \nu_0$ is the difference between the vibration frequencies of the X–X′ bond in the free halogen molecule and in the molecule bound in the complex. The third column of Table 3 lists the degrees of charge transfer Δ_2 obtained from the literature data using Eqn. (3). In order to estimate $b^2 + abS_{01}$, one can also use the change in the stretching vibration frequencies of the bonds of the donor molecules. However, in this case the coefficient of $\Delta\nu/\nu_1$ is unknown. Furthermore, complex formation results in changes in the stretching vibration frequencies of many bonds in donor molecules and it is impossible to select a single vibration as a criterion for the estimation of the degree of charge transfer.

As mentioned above, the most accurate degrees of charge transfer are obtained when the force constants $f_{X\text{-}X'}$ of the halogen–halogen bonds are used. Thus, following Mulliken[2], many workers employ $f_{X\text{-}X'}$ to estimate the contribution of the dative structure to the electronic ground state of the complexes[19,22,29,30]. The relation for the estimation of the degree of charge transfer can then be represented in the form

$$\Delta = b^2 + abS_{01} = \frac{f^0_{X\text{-}X'} - f_{X\text{-}X'}}{f^0_{X\text{-}X'}}, \qquad (4)$$

where $f^0_{X\text{-}X'}$ and $f_{X\text{-}X'}$ are the force constants of the halogen–halogen bond in the free halogen molecule and in the complex. The second column of Table 3 lists the degrees of charge transfer Δ_1 calculated by Eqn. (4) from the literature data both by Person and coworkers[22,23] and in some cases by the present authors. Comparison of the transferred charges obtained from Eqns. (3) and (4) shows that the agreement between them is poor. Bearing in mind that Eqn. (4) gives a better estimate of the degree of charge transfer than Eqn. (3), we attempted to find another coefficient of $\Delta\nu/\nu_1$ in Eqn. (3) from the correlation between $\Delta\nu/\nu_1$ and $(f^0_{X\text{-}X'} - f_{X\text{-}X'})/f^0_{X\text{-}X'}$. The degrees of charge transfer in halogen complexes were determined from the resulting relation:

$$\Delta = b^2 + abS_{01} \simeq 1.42\,\Delta\nu/\nu_1 + 0.02 \quad . \qquad (5)$$

The fourth column of Table 3 shows that the degree of charge transfer Δ_3 calculated by Eqn. (5) is closer to the values obtained from the ratio of the bond force constants and, furthermore, that Eqn. (5) holds satisfactorily for different types of complexes—both $\pi\sigma$ and $n\sigma$.

Analogous results are also obtained in the study of complexes of chlorine and olefins. The degrees of charge transfer have been calculated[31] by Eqn. (3). However, the results (based on the donor properties of olefins) appear to be too high, since the transferred charges are the same as in the stronger $n\sigma$ complexes of iodine and amines. On the other hand, the estimates by Eqn. (5) lead to more acceptable values (Table 4).

The degree of charge transfer can also be estimated from the force constants f_{DA} of the donor–acceptor bonds. Here one usually begins with the hypothesis that f_{DA} is determined solely by the contribution of the dative structure[9]:

$$\Delta = b^2 + abS_{01} \simeq f_{DA}/f^0_{DA}, \qquad (6)$$

where f^0_{DA} is the force constant of the donor–acceptor bond in the purely dative structure. The simultaneous application of Eqns. (4) and (6) leads to the expression[9]

$$f^0_{DA} = \frac{f_{DA} f^0_{X\text{-}X'}}{f^0_{X\text{-}X'} - f_{X\text{-}X'}}. \qquad (7)$$

f^0_{DA} calculated by Eqn. (7) from the experimental values of f_{DA} and $f^0_{X\text{-}X'}$ for halogen complexes[22] proved to be 2.5×10^5 dyn cm^{-1}, i.e. close to the values of f_{DA} for the most stable donor–acceptor complexes of Group III metal halides, where the contribution of the structure with charge transfer plays the dominant role. An estimate of the transferred charge[9] showed that it amounts to (0.4–0.8) *e* for complexes of aluminium halides[29] and (0.2–0.4) *e* for complexes of iodine with various donors[22].

Table 4. The degrees of charge transfer in the $\pi\sigma$ complexes of Cl_2 with olefins[31]*.

Complex	$\nu^c_{Cl\text{-}Cl'}$, cm^{-1}	$\Delta\nu/\nu_1$	Δ_1, *e*	Δ_2, *e*
$Cl_2\cdot H_2C{=}CH_2$	520	0.039	0.07	0.10
$Cl_2\cdot H_2C{=}CHCl$	526	0.031	0.06	0.08
$Cl_2\cdot H_2CCH{=}CH_2$	500	0.076	0.13	0.20
$Cl_2\cdot CH_3CH_2CH{=}CH_2$	500	0.076	0.13	0.20
$Cl_2\cdot H_2C{=}CH(CH_2)_4CH_3$	500	0.076	0.13	0.20
$Cl_2\cdot (CH_3)_2C{=}CH_2$	495	0.085	0.14	0.23
$Cl_2\cdot (CH_3)_2C{=}CHCH_3$	480	0.113	0.18	0.30
$Cl_2\cdot H_2C{=}CHCH_2Cl$	518	0.042	0.08	0.11

* Δ_1 and Δ_2 are the degrees of charge transfer calculated by Eqns. (5) and (3) and $\nu^c_{Cl\text{-}Cl}$ is the stretching vibration wavenumber of the Cl–Cl bond in the complex.

Interesting results were obtained for complexes of *v* acceptors[32]. The authors calculated the force constants of the metal–halogen bonds in the complexes $BX_3.NCCH_3$ (X = F, Cl, or Br). Table 5 presents the force constants of the metal–halogen bonds calculated using symmetrical (*A*) and asymmetric (*E*) vibrations and it also includes the degrees of charge transfers obtained by the authors. One should note that the large differences between the degrees of charge transfer in the complex $BF_3.NCCH_3$ calculated from the force constants of the symmetrical and asymmetric vibrations cast doubt on the validity of the calculation of the force constants in this case.

Table 5. The degrees of charge transfer in the complexes of BX_3 with CH_3CN. [32]

Compound	Force constant, mdyn A^{-1}		$\Delta = b^2 + abS_{ss}$, *e*	
	A	*E*	*A*	*E*
BF_3	8.82	7.82	—	—
$BF_3\cdot NCCH_3$	6.49	3.85	0.26	0.51
BCl_3	4.63	4.19	—	—
$BCl_3\cdot NCCH_3$	3.32	3.24	0.28	0.23
BBr_3	3.64	2.80	—	—
$BBr_3\cdot NCCH_3$	2.94	2.45	0.19	0.12

V. NUCLEAR QUADRUPOLE RESONANCE AND MÖSSBAUER SPECTROSCOPY

Nuclear quadrupole resonance (NQR) began to be used in the study of charge transfer comparatively recently. The method makes it possible to estimate the degree of charge transfer in complexes and the nature of charge distribution in the components. The changes in the quadrupole interaction constants (QIC) or the electric field gradient (EFG) on complex formation are directly related to the changes in electron density at all the atoms of the interacting molecules. As a result of this, the extent of the change in the charges of the quadrupole nuclei can be estimated from the changes in the QIC (or EFG). For atoms whose nuclei do not have a quadrupole moment in the ground state, one can employ the Mössbauer method. Mössbauer spectra also make it possible to obtain the values of the QIC and in addition the isomeric shifts δ, which is related to the population of the *s* orbitals of the atom investigated. However, the population of the *s* orbitals is difficult to estimate quantitatively from the isomeric shift, since the shielding of the *s* electrons by *p* and *d* electrons exerts a major influence on δ.

Relations between the EFG (Δq_A), on the one hand, and the degree of charge transfer b^2 and the nature of charge distribution c^2_{At} in the acceptor molecule on the other have been obtained[33] using the Mulliken theory:

$$\Delta q_A = \frac{b^2}{1+S^2_{DA}}\sum_t c^2_{At}q_t, \qquad (8)$$

where S_{DA} is the overlap integral of the wave functions ψ_D and ψ_A, c^2_{At} the electron density of the *t* atomic orbital of the electron-accepting molecular orbital, and q_t the contribution to the EFG at the given nucleus of the acceptor molecule due to a single electron in this atomic orbital.

For diatomic halogens and interhalogen compounds, Eqn. (8) simplifies:

$$\frac{\Delta\nu}{\nu}\simeq\frac{\Delta q_{zz}}{q_z}=-\frac{b^2}{2(1-S^2_{DA})}, \qquad (9)$$

where Δq_{ZZ} is the change in the EFG on complex formation and $\Delta\nu$ the change in the NQR frequency of the halogen atom. It is seen from Eqn. (9) that Δq_{ZZ} is directly proportional to the degree of charge transfer. An increase in σ-electron density in the molecule leads to an increase of the population of the p_Z orbital of the halogen atom, which decreases the EFG and the NQR frequency. One should note that in this approximation account is taken of the change in the charge only of the molecule, disregarding the overlap integral of the wave functions of the donor and the acceptor.

For the more involved complexes of *v* acceptors, it is impossible to obtain an analytical expression giving an estimate of the degree of charge transfer. Quantitative estimates of this kind can be made only with the aid of specific calculations.

We shall examine certain quantitative results for complexes of halogens and interhalogen compounds. Complexes of bromine with π and *n* donors have been most fully investigated[34–37]. The observed low-frequency shifts are small and lie in the range 0.01–0.04%. Table 6 presents the NQR frequencies of ^{81}Br and the degrees of charge transfer calculated by Eqn. (9). Complexes of chlorine with π and *n* donors have been less thoroughly studied[38]. In these complexes, low-frequency shifts are also observed and the degrees of charge transfer can be estimated by Eqn. (9) (Table 6). The degree of charge transfer for complexes of both Br_2 and Cl_2 is evidently insignificant and agrees well with the results obtained by other methods[9].

The complexes of halogens and interhalogen compounds (I_2, Br_2, ICl, and IBr) with certain nitrogen-containing donors are extremely involved and interesting objects

for the study of the transferred charge and particularly of its distribution in the acceptor molecule. The NQR spectra of these complexes show that the QIC of the central halogen atoms are greater than the QIC of the same atoms in the individual molecules. To explain this, it has been suggested[39,40] that the acceptor molecules behave as v acceptors in the stable complexes of halogens and interhalogen compounds with nitrogen-containing donors. Here the central iodine atom is sp^3d-hybridised, three orbitals are occupied by the lone electron pairs, one is involved in the formation of a covalent bond with another halogen atom, and one is involved in intermolecular interaction.

Table 6. The parameters of the NQR spectra and the degrees of charge transfer in bromine and chlorine complexes.

Complex	ν^*, MHz	b^*, e	Complex	ν^*, MHz	b^*, e
Br_2	319.54	—	$Cl_2 \cdot C_6H_5NO_2$	54.510	
$Br_2 \cdot CH_3COCH_3$	318.34	0.01		53.675	0.02
$Br_2 \cdot C_6H_5COC_2H_5$	317.18	0.02		53.050	
$Br_2 \cdot CH_3COOOCH_3$	318.01	0.02	$Cl_2 \cdot C_6H_6$	53.463	0.03
$Br_2 \cdot C_4H_8O_2$	314.99	0 04	$Cl_2 \cdot C_6H_5CH_3$	53.730	
$Br_2 \cdot HCOOC_2H_5$	318.78	0.01		53.595	0.03
$Br_2 \cdot 2CH_3OH$	317.95			53.338	
	315.98	0.03		53.128	
$Br_2 \cdot C_6H_5Br$	317.85	0.02	$Cl_2 \cdot 1,2\text{-}(CH_3)_2C_6H_4$	53.863	
Cl_2	54.247	—		53.530	0.02
$Cl_2 \cdot C_4H_8O_2$	53.257	0.04		53.400	
$Cl_2 \cdot O(C_2H_5)_2$	53.573	0.02	$Cl_2 \cdot 1,4\text{-}(CH_3)_2C_6H_4$	53.533	0.03

* The ^{81}Br and ^{38}Cl wavenumbers respectively are quoted.

The application of the Dailey–Townes theory shows that the degree of charge transfer is in this case 40–50%, which agrees well with infrared spectroscopic and dipole moment data. The authors[41,42] observed only one NQR frequency for the central iodine atom in complexes with nitrogen-containing ligands. Owing to the inadequacy of the experimental data, it was assumed[39] that the amount of ionic character of the iodine–halogen bond does not change on complex formation. On the other hand, the frequencies of the terminal halogen atoms were also observed in the NQR spectra of the complexes $ICl.C_5H_5N$ and $ICl.4\text{-}CH_3C_5H_4N$, [43] as well as the complexes of ICl, IBr, and Br_2 with $3,5\text{-}Br_2C_5H_3N$.[41] The appreciable decrease of these frequencies on complex formation indicates a significant change in the amount of ionic character of the halogen–halogen bonds. Taking this into account, the authors[43,44] estimated the charge distribution in the complexes (Table 7). It was found that there is always a positive charge on the central halogen atom. The study of the NQR spectra[45,46] and calculation by the CNDO method without taking into account the d orbitals[47] of the trihalide ions also lead to a positive charge on the central halogen atom. The charge distributions in such ions, calculated by Harada et al.[45] and Gabes et al.[46], are presented in Table 7.

Such charge distribution can be explained within the framework of a three-centre delocalised σ orbital. The simplest wave function of the ground state of stable $n\sigma$ amine–halogen complexes (NX_2) can be formulated as follows:

$$\psi_N = a\psi(N, X_2) + b\psi(N^+ - X_2^-).$$

When account is taken of the polarisation of the acceptor molecule, we obtain

$$\psi_N = a\psi(N, X_2) + b_1\psi(N^+XX^-) + c\psi(N^+X^-X) + d\psi(NX^+X^-). \quad (10)$$

The positive charge on the central halogen atom indicates the considerable importance of the polarisation term $d\psi(NX^+X^-)$ in Eqn. (10). In stable $n\sigma$ complexes and trihalide ions, the polarisation of the acceptor molecule apparently plays a significant role.

Table 7. The charge distribution in complexes of the $n\sigma$ type and trihalide ions.

Compound	Charge on halogen atom, e		Total charge, e	Compound	Charge on halogen atom, e		Total charge, e
	central	terminal			central	terminal	
$(CH_3)_4NI_3$	+0.08	—0.50	—0.92	$CsICl_2$	+0.35	—0.64	—0.93
$(C_2H_5)_4NI_3$	+0.07	—0,50	—0.93	$KICl_2$	+0.28	—0.66	—1.04
$(n\text{-}C_4H_9)_4NI_3$	+0.08	—0.50	—0.92	$(CH_3)_4NIBr_2$	+0.18	—0.58	—0.98
$(n\text{-}C_3H_7)_4NI_3$	+0.05	—0.55	—1.05	$(C_4H_9)_4NIBr_2$	+0.21	—0.60	—0.98
$(CH_3)_2NH_2I_3$	+0.08	—0.51	—0.94	$CsBr_2$	+0.06	—0.52	—0.98
$(n\text{-}C_3H_7)_2NH_2I_3$	+0.08	—0.51	—0.94	$(C_4H_9)_4Br_3$	+0.01	—0.52	—1.04
TlI_3	+0.03	—0.54	—1.06	$Br_3\cdot 3,5\text{-}Br_2C_5H_3N$	+0.10	—0.30	—0.20
CsI_3	+0.08	—0.49	—0.90	$IBr\cdot 3,5\text{-}Br_2C_5H_3N$	+0.30	—0.55	—0.25
NH_3I_3	+0.07	—0.48	—0.88	$ICl\cdot 3,5\text{-}Br_2C_5H_3N$	+0.35	—0.65	—0.30
RbI_3	+0.08	—0.48	—0.89	$ICl\cdot C_5H_5N$	+0.35	—0.61	—0.26

Comparison of the transferred charges calculated using the sp^3d hybridisation of the central atom and three-centre orbitals shows that the degrees of charge transfer in the complexes are similar in the two cases. However, treatment of the problem from different standpoints leads to differences in charge distribution in the acceptors.

The application of the Mössbauer method for the estimation of charge transfer in iodine complexes has been demonstrated[48]. The authors studied the complex $I_2.C_6H_6$. The employment of the dependence of the isomeric shift of ^{127}I on the number of vacancies in the $5p$ shell led to a degree of charge transfer of 26%. This value is not confirmed by data obtained by other methods, including the NQR method[41]. Presumably a relation of this kind does not permit a correct estimate of the degree of charge transfer.

As mentioned previously, a single relation, similar to Eqn. (8), linking the change in the EFG to the degree of charge transfer, cannot be obtained for complexes of v acceptors. The formation of complexes by v acceptors leads in most cases to a complete rearrangement of the entire electronic system of the molecule and to the formation of one or several additional vacant orbitals. Such rearrangement leads also to a change in the parameters of the metal–halogen bonds (amount of ionic character, amount of double bond character, etc.). In most cases a detailed analysis of the changes in the EFG is therefore possible only on the basis of a detailed calculation for each specific complex. If it is possible to obtain the QIC for all the acceptor atoms, the calculation of charge transfer for a complex with a known geometry can be performed on the basis of the Dailey–Townes theory. Otherwise, one can only consider qualitative changes in the degree of charge transfer within the limits of a series of complexes.

Interesting results have now been obtained for complexes of Group III, IV, and V metal halides. Much attention has been devoted[49-52] to the study of the octahedral complexes $SbCl_5.L$. The known geometry of the complexes[51] made it possible to carry out calculations by the molecular orbital method. It was shown that the electron density at the equatorial chlorine atoms should be smaller than at the axial atom. Indeed, such electron density distribution has been observed in the complexes of $SbCl_5$ with methyl and ethyl alcohols, acetonitrile, and dimethylformamide. On the other hand, in the remaining complexes the steric influence of the donor molecules on the quadrupole frequencies of the equatorial chlorine atoms is pronounced and the NQR frequencies of chlorine cannot be assigned to the axial and equatorial atoms. However, the employment of average frequency shifts on complex formation makes it possible to estimate the degree of charge transfer Δ and the charge distribution in all $SbCl_5.L$ complexes. Table 8 presents data for all the $SbCl_5.L$ complexes investigated[51,52] with $e^2Qq^{Sb}_{am} = 1300$ MHz [53] and a positive sign of the EFG at the antimony atom[54,55]; Δ_{Sb} is the change of the charge of the antimony atom on complex formation and Δ_{Cl} the corresponding change for all the chlorine atoms. Table 8 shows that complex formation results in a significant increase of electron density at the chlorine atoms of the acceptor molecule and in a slight decrease of the electron density at the antimony atom.

Table 8. The degrees of charge transfer in the complexes $SbCl_5.L$.

Complex	Δ, *e*	Δ_{Sb}, *e*	Δ_{Cl}, *e*	Complex	Δ, *e*	Δ_{Sb}, *e*	Δ_{Cl}, *e*
$SbCl_5 \cdot POCl_3$	0.26	—0.04	0.30	$SbCl_5 \cdot CH_3OH$	0.29	—0.11	0.40
$SbCl_5 \cdot CH_3CN$	0.23	—0.09	0.32	$SbCl_5 \cdot C_2H_5OH$	0.28	—0.11	0.39
$SbCl_5 \cdot C_6H_5CN$	0.24	—0.09	0.33	$SbCl_5 \cdot (CH_2Cl)_2O$	0.25	+0.02	0.23
$SbCl_5 \cdot ClCN$	0.20	—0.12	0.32	$SbCl_5 \cdot (CH_2)_4O_2$	0.28	—0.11	0.39

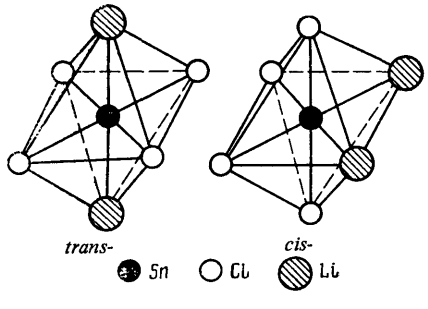


Figure 1. The *cis-trans* isomerism in the octahedral complexes $SnCl_4.L_2$.

Among the complexes of Group IV elements, very vigorous studies are being made on the octahedral complexes $SnCl_4.L_2$ (Fig. 1) both by the NQR method[42,56-59] and by Mössbauer spectroscopy[60-63]. One should note that, whereas the degree of charge transfer in the complexes $SbCl_5.L$ was estimated from the known QIC of the antimony atom obtained from the NQR spectra, in the complexes $SnCl_4.L_2$ the degree of charge transfer was calculated using the quadrupole splitting by the tin atom observed in the Mössbauer spectra[64,65]. Table 9 presents the calculation of the degree of charge transfer in all the $SnCl_4.L_2$ complexes investigated hitherto, taking into account the sign of the EFG at the tin atom[60]. As in the complexes $SbCl_5.L$, there is a significant increase of electron density at the chlorine atom in the acceptor. However, in contrast to the complexes $SbCl_5.L$, there is a fairly considerable increase of the positive charge of the tin atoms in almost all the complexes $SnCl_4.L_2$. It is also important to note[64] (Table 10) that, as expected from calculations by the molecular orbital method[56], in complexes having a *cis*-structure, the electron density at the axial chlorine atoms is smaller than at the equatorial atoms. Such redistribution of electron density is consistent with the concept of the mutual influence of ligands in complexes of non-transition elements[66].

Table 9. The degrees of charge transfer in the complexes $SnCl_4.L_2$.

Complex	Δ, *e*	Δ_{Sn}, *e*	Δ_{Cl}, *e*
$SnCl_4 \cdot 2CH_3OH$	0.37	—0.08	0.45
$SnCl_4 \cdot 2C_2H_5OH$	0.39	—0.05	0.44
$SnCl_4 \cdot 2(CH_2)_4O_2$	0.27	—0.13	0.40
$SnCl_4 \cdot 2(CH_2)_4O$	0.23	—0.21	0.44
$SnCl_4 \cdot 2(C_2H_5)_2O$	0.27	—0.13	0.40
$SnCl_4 \cdot 2CH_3CN$	0.34	0	0.34
$SnCl_4 \cdot 2C_6H_5CN$	0.40	0	0.40
$SnCl_4 \cdot 2HCON(CH_3)_2$	0.35	—0.21	0.56
$SnCl_4 \cdot 2(CH_3)_2SO$	0.46	—0.05	0.51
$SnCl_4 \cdot 2[3\text{-}CH_3C_5H_4N]$	0.38	—0.18	0.56
$SnCl_4 \cdot 2(i\text{-}C_3H_7)_3PO(SCH_3)$	0.34	—0.18	0.52
$SnCl_4 \cdot 2(i\text{-}C_3H_7O)_2PO(SCH_3)$	0.23	—0.24	0.47

Table 10. The charge distribution in the *cis*-complexes $SnCl_4.L_2$.

Complex	Δ^{ax}_{Cl}, *e*	Δ^{eq}_{Cl}, *e*	Δ_{Cl}, *e*
$SnCl_4 \cdot 2CH_3OH$	0.17	0.28	0.45
$SnCl_4 \cdot 2C_2H_5OH$	0.16	0.28	0.44
$SnCl_4 \cdot 2(CH_3)_2CO$	0.17	0.23	0.40
$SnCl_4 \cdot 2CH_3CN$	0.15	0.19	0.34
$SnCl_4 \cdot 2POCl_3$	0.14	0.20	0.34
$SnCl_4 \cdot 2CH_3OCH_2Cl$	0.10	0.18	0.28
$SnCl_4 \cdot 2(CH_3)_2SO$	0.24	0.27	0.51

Calculation for the complex of $SnBr_4$ with hexamethylphosphoramide from the data of Petrosyan et al.[67] and Philip et al.[68] yielded a transferred charge of 0.37 *e*. The nature of the change in the charge on the acceptor atoms proved to be the same as in the complexes $SnCl_4.L_2$. The negative charge on the bromine atoms increases by 0.60 *e* while the positive charge on the tin atom increases by 0.23 *e*.

The study of the complexes $SbCl_5.L$ and $SnCl_4.L_2$ using the Mössbauer effect[54,55,60-63] should yield information about the populations of the 5*s* and 5*p* orbitals of the antimony and tin atoms. Fig. 2 presents the relation between the isomeric shift δ and the QIC of ^{121}Sb in certain complexes $SbCl_5$. RCN.[54] An increase of the isomeric shift leads to an increase of the QIC. The parallel

variation of δ and QIC for ^{119m}Sn is also observed for the complexes $SnCl_4.L_2$. The relation may be caused both by a decrease of the population of the 5*s* orbitals by an increase of the shielding of the 5*p* orbitals[69]. It is therefore impossible to discover unambiguously for both types of complexes, on the basis of the Mössbauer spectra, how the populations of the orbitals of the antimony and tin atoms change on complex formation.

Among complexes of Group III elements, Tong made a detailed study of the complexes of $GaCl_3$ with a number of *n* donors[70]. The lack of specific data for NQR frequencies precludes the calculation of the degrees of charge transfer in these complexes. However, the relation between the ^{35}Cl and ^{69}Ga NQR frequencies permitted the estimation of the charge distribution in these complexes. It has been shown[39] that 2/7 of the transferred charge is located at the gallium atom and 5/7 is distributed between the three chlorine atoms.

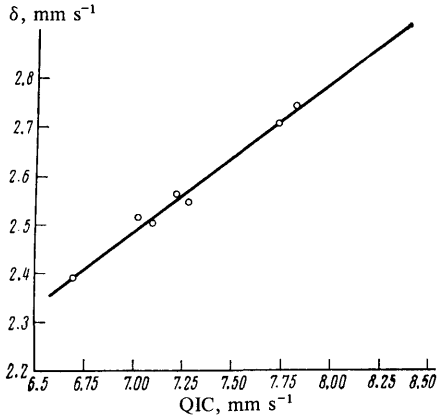


Figure 2. Relation between δ and the ^{121}Sb QIC in the complexes $SbCl_5.RCN$.

The complexes of antimony and arsenic trihalides with aromatic bases have been very widely investigated[71-75]. The attempt to estimate the degrees of charge transfer in these complexes undertaken by the present authors[75] was unsuccessful owing to the incorrect selection of the sign of the EFG at the nucleus of the antimony atom[76,77]. This failure is probably associated with the lack of the exact knowledge of the hybridisation of the antimony and arsenic atoms in these complexes.

A Mössbauer study of the complexes $n SbHal_3.Ar$ [76,77] yielded additional information about charge transfer in them. The authors believe that the population of the 5*s* orbitals of the antimony atom varies insignificantly owing to the slight change of the isomeric shift. The use of the relation between the isomeric shift and the population of the 5*p* orbitals of the antimony atom[78] made it possible to estimate the latter[76] (Table 11). However, as shown previously, the decrease of the isomeric shift is caused both by the decrease of the population of the 5*s* orbitals of antimony and by the increase of the shielding of the 5*p* orbitals[69]. The results presented in Table 11 are therefore to some extent controversial.

A study was made of the change in the charge on the acceptor atoms in all the complexes. There is no doubt that the changes in the charge on the donor atoms are of considerable interest. Unfortunately, there have been virtually no NQR studies on these lines. Only two investigations may be noted. Negita et al.[79] studied the complexes of acetonitrile with chlorine and bromine. The observation of NQR signals due to the nitrogen and halogen nuclei made it possible to estimate the degree of charge transfer in these complexes both from the NQR spectrum of the donor and from the spectrum of the acceptor (Table 12). The authors' explanation of the difference between the transferred charges calculated from the ^{14}N and ^{81}Br QIC is that part of the charge is transferred from the CH_3CN molecule via the d_z^2 orbitals of the bromine atom, which make a much smaller contribution to the EFG than the p_z orbitals.

Table 11. The degrees of charge transfer in the complexes $n SbCl_3.Ar$ from Mössbauer spectroscopic data[76]*.

Complex	n_p	Δ, *e*	$\lvert\psi(0)\rvert^2/a_0^3$
$SbCl_3$	1.35	—	33.0
$2SbCl_3 \cdot C_6H_6$	1.57	0.22	32.5
$2SbCl_3 \cdot C_6H_5CH_3$	1.47	0.12	32.9
$2SbCl_3 \cdot 1,4\text{-}(CH_3)_2C_6H_4$	1.53	0.18	32.6
$SbCl_3 \cdot 1,3,5\text{-}(CH_3)_3C_6H_3$	1.60	0.25	32.3
$2SbCl_3 \cdot C_6H_5OCH_3$	1.53	0.18	32.6
$SbCl_3 \cdot C_6H_5C_2H_5$	1.30	—	33.1
$2SbCl_3 \cdot C_6H_5C_6H_5$	1.35	—	33.0
$2SbCl_3 \cdot C_{10}H_8$	1.50	0.15	32.8

*n_b is the number of vacancies in the 5*p* shell of the antimony atom, Δ the degree of charge transfer, and $\lvert\psi(0)\rvert^2/a_0^3$ the overall electron density of the antimony nucleus.

Table 12. The degrees of charge transfer in the complexes $2CH_3CN.Hal_2$.

Complex	Change in charge, *e*	
	on nitrogen	on halogen
$2CH_3CN \cdot Cl_2$	+0.028	—0.021
$2CH_3CN \cdot Br_2$	+0.029	—0.00

The charge distribution in the complexes $AlBr_3.SbBr_3$ and $AlBr_3.BiBr_3$ has been investigated[80]. The transferred charge Δ was calculated from the QIC of the antimony, bismuth, and bromine atoms forming part of the donor molecules. The change in the charge on the aluminium atom in consequence of complex formation was estimated relative to the Al_2Br_6 dimer from the change in the QIC of the bromine atoms. The results (Table 13) showed that the charge in the donor molecules is transferred directly from the lone pair of the central atom and hardly involves the halogen atoms of the donor.

Thus the application of the NQR and Mössbauer methods to the calculation of the degree of charge transfer and of charge distribution in the complexes leads to very interesting results. The degree of charge transfer is satisfactorily correlated with data obtained by other methods. The most important factor is that NQR and the Mössbauer effect made it possible to obtain the distribution of the transferred charge, in contrast to the other methods described previously. One can now assume that both in complexes of the $n\sigma$ type and in complexes of v acceptors, the polarisation of the valence shells of the central complex-forming atom apparently plays a significant role. Furthermore, in v-acceptor molecules, the changes in atomic charges on complex formation are associated with the changes in the hybridisation of the central atom.

Table 13. The degrees of charge transfer in the complexes $AlBr_3.L$.

Complex	Δ, e	$\Delta_{Sb\,(Bi)}$, e	Δ'_{Br}, e	Δ_{Al}, e	Δ_{Br}, e
$AlBr_3 \cdot SbBr_3'$	0.20	−0.15	−0.05	−0.08	0.28
$AlBr_3 \cdot BiBr_3'$	0.27	−0.29	0.02	−0.05	0.32

VI. X-RAY ELECTRONIC SPECTROSCOPY

X-Ray electronic spectroscopy of complexes has been developing very vigorously recently. The application of X-ray electronic spectra in the study of donor–acceptor interaction is based on the parallel variation of the effective charges of the atoms investigated and of the shift of the X-ray electronic lines. One can therefore infer the changes in the electron densities at the atoms from the changes in the energy of the binding of electrons (E_b).

Using the electrostatic potential model[81], the shift of the internal energy level can be formulated thus:

$$\Delta E_b = Kq_i + V_i + l, \qquad (11)$$

where

$$V_i = \sum_{j \neq i} q_j / R_{ij}$$

is the molecular potential in the vicinity of the nucleus i, q_i the charge on the atom i, R_{ij} the distance between the nuclei i and j, and l a constant determined by selecting the starting point of the readings. The constant K is approximately equal to the integral of the electrostatic interaction between the internal orbital under consideration and the valence orbital in the same atom. Eqn. (11) can be simplified to

$$\Delta E_b = K' q_i.$$

According to the free ion model[82], $K' \simeq 1/r$, where r is the radius of the valence shell. The radius of the radial distribution density of valence electrons in carbon, oxygen, and nitrogen atoms is approximately 1 Å (1 Å ≃ 2 atomic units) and, when a single electron is removed, the shift in the binding energy of the internal electrons per unit charge is 14 eV.

The free ion model can be improved by taking into account the fact that the valence electrons are not transferred to an infinite distance on formation of a chemical bond. If the distance between the nuclei is R_{ij}, the shift of the internal electron energy can be formulated as follows:

$$\Delta E_b = \left(\frac{1}{r} - \frac{\alpha}{R_{ij}}\right) q_i, \qquad (12)$$

where α is the Madelung constant[83]. For ionic crystals, the shift of the internal electron energy calculated by Eqn. (12) is approximately 5 eV per unit charge. However, it is clear that the use of even an improved free ion model for the calculation of the shift of the internal electron energy when one electron is removed in complexes with appreciably covalent bonds cannot in principle lead to a satisfactory quantitative estimate of the degree of charge transfer. This is why the degree of charge transfer which we estimated with the aid of the improved free ion model does not agree very well with data obtained by other methods.

Charge transfer in the complex $ICl.C_5H_5N$ has been investigated[84] using $K' = 14$ eV per unit charge. A change in the energy of the ^1S state of the nitrogen atom by 0.9 eV leads to the appearance of a $+0.06\ e$ charge on the nitrogen atom of the pyridine molecule. When we used $K' = 5$ eV per unit charge, the charge on the nitrogen atom was found to be $+0.18\ e$, i.e. closer to the transferred charge obtained from dipole moment and NQR data.

The photoelectronic spectra of certain complexes of tin halides have been studied[85] and the shift of the internal electrons of the donor atom directly involved in complex formation has been determined[85]. We estimated the degree of charge transfer Δ in these complexes also using $K' = 5$ eV per unit charge (Table 14).

Table 14. The degrees of charge transfer in the complexes $SnCl_4.L_2$ obtained from photoelectronic spectra[92].

Complex	ΔE_b, eV	Δ, e
$SnBr_4 \cdot 2(C_6H_5)_3PO$	0.2	0.04
$SnCl_4 \cdot 2(C_6H_5)_3PO$	0.2	0.04
$SnCl_4 \cdot 2(CH_3)_2NCS$	0.9	0.18
$SnBr_4 \cdot \alpha, \alpha'\text{-}C_{10}H_8N_2$	1.7	0.34
$SnCl_4 \cdot 2C_5H_5N$	2.0	0.40

A recently published report[86] describes a study of photoelectronic spectra of $SbCl_5$ solutions for certain n-donor solvents. The energies of the binding of $3d_{5/2}$ internal electrons of the antimony atom were compared with the enthalpies of formation of the complexes or with Gutman's donor numbers (DN).[87] The observed correlation between ΔE and DN (Fig. 3) is described by a straight line. However, it is known that the change in electron density at halogen atoms in the complexes obtained from NQR spectra (Δ_{Cl}) depends directly on DN.[67] Comparison of these two correlations, the dependence of ΔE on DN and of Δ_{Cl} on DN, makes it possible to obtain the relation between ΔE and Δ_{Cl}, which can be represented in the following form:

$$\Delta E = 321.5 + 3.16\,\Delta_{Cl} \pm 0.2 \text{ (eV)}. \qquad (13)$$

The fairly large error precludes quantitative estimates of the shift of the binding energy of the internal electrons of the antimony atom, but Eqn. (13) permits a qualitative estimate of the change in this energy.

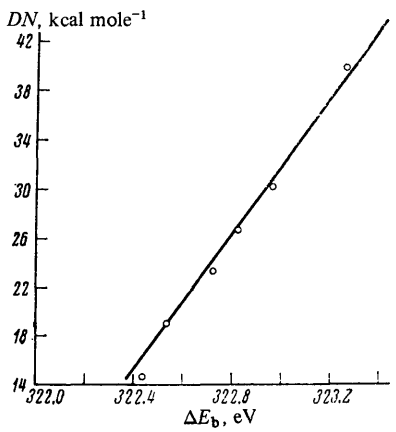


Figure 3. Relation between ΔE_b and DN.

It is now clear that X-ray electronic spectroscopy together with NQR and quantum-chemical calculations can yield unique information about the charge distribution in complexes among all the atoms of the interacting molecules. However, there have been so far no studies dealing with the X-ray electronic spectra of all the atoms in the complex. It is therefore of interest to carry out such investigations with the aid of the X-ray electronic spectra of the complexes which have been studied by other methods.

VII. QUANTUM-CHEMICAL CALCULATIONS

Quantum-chemical calculations constitute nowadays one of the principal methods whereby one can estimate the changes in the charge on each atom of the complex. However, the charge depends markedly on the chosen method of calculation. The most rigorous calculations of the *ab initio* type can be carried out only for small molecules with a small number of orbitals. On the other hand, semi-empirical calculations yield an electron density distribution which depends significantly on the choice of the parameters of the calculation. Furthermore, the use of semi-empirical methods for calculations on complexes is limited by the lack of sufficiently reliable parameters for elements with a large number of orbitals. As a result, comparatively few calculations have so far been made on complexes of the $\pi\sigma$, $n\sigma$, and $n\nu$ types.

We shall begin the discussion of the available data with non-empirical methods, which lead to more accurate results.

A calculation has been made[88] on BF_3 complexes with various ligands by the *ab initio* method. Table 15 presents the distributions of the transferred charge in the acceptor molecule which were calculated from the orbital populations. It can be readily seen that there is a significant shift of electron density in these complexes to the fluorine atoms ($\Sigma\Delta_F$) of the acceptor molecule. Furthermore, part of the charge is transferred to the boron atom (Δ_B). The distribution of the transferred charge in the acceptor molecule is different for different complexes. Table 15 presents the ratios of the charge transferred to the boron atom and of the degree of charge transfer (Δ_B/Δ).

Table 15. The degrees of charge transfer in the complexes $BF_3.L$.[88]

L	Δ, *e*	Δ_B, *e*	Δ_F, *e*	$\Sigma\Delta_F$, *e*	Δ_B/Δ, *e*
NH_3 (eclipsed)	0.269	0.092	0.059	0.177	0.34
	0.269	0.080	0.063	0.189	0.30
NH_3 (staggered)	0.285	0.105	0.060	0.180	0.37
	0.285	0.093	0.064	0.192	0.33
H_2O	0.217	0.052	0.055	0.165	0.24
	0.217	0.040	0.059	0.177	0.18
H_2S	0.297	0.204	0.031	0.093	0.69
	0.297	0.192	0.035	0.105	0.65
Ne	0.122	0.047	0.025	0.075	0.39
	0.122	0.035	0.029	0.087	0.29
Ar	0.215	0.146	0.023	0.069	0.68
	0.215	0.134	0.027	0.081	0.62
CO	0.074	−0.010	0.028	0.084	−0.14
	0.074	−0.022	0.032	0.096	−0.30
F^-	0.411	0.090	0.107	0.321	0.22
	0.411	0.078	0.111	0.333	0.19
Cl^-	0.472	0.250	0.074	0.222	0.53
	0.472	0.238	0.078	0.234	0.50

Much attention has been devoted to calculations on borazane BH_3NH_3.[89-95] The results of these studies agree well with one another. As an example, Table 16 lists the populations of the atomic orbitals in the BH_3, NH_3, and $BH_3.NH_3$ molecules[89] and our calculated degrees of charge transfer Δ. The greatest changes were observed in the populations of the $2p_z$ orbitals of the boron and nitrogen atoms. When the complexes are formed, 0.1 *e* is transferred to the orbitals of the boron atom and 0.16 *e* to the 1*s* orbitals of the three hydrogen atoms. Evidently, in this complex there is also a significant displacement of electron density to the hydrogen atoms of the acceptor molecule. The complexes $BH_3.CO$,[89] $BF_3.C_6H_5CHO$,[96] BF_3 complexes with ethers[97], and $BH_3.PH_3$ [98] have also been investigated by the *ab initio* method. All the calculations lead to the same charge distributions as for the complex $BH_3.NH_3$. One need only note that, in the boron halide complexes, the shift of electron density to the halogen atoms is greater than the shift to the hydrogen atoms in the BH_3 complexes. This is probably associated with the greater electronegativity of the halogen atoms.

We can now proceed to the discussion of the semi-empirical methods for calculations on complexes. Calculations have been made[99,100] on complexes of iodine with benzene, pyrrole, furan, and thiophen on the basis of the perturbation theory. The change in charge distribution in the $I_2.C_6H_6$ complex[99] is illustrated in Fig. 4, which shows that the charge is distributed uniformly between the two iodine atoms. In the remaining complexes, the charge distribution is similar. However, the use of more accurate methods of calculation leads to a different charge distribution in the acceptor molecule. Thus the electronic structures of the complexes $I_2.C_6H_6$ and $I_2.NH_3$ have

been investigated[101] by a modified PNDO method. An excess positive charge of 0.06 *e* appears in the $I_2.C_6H_6$ complex on the iodine atom directly coordinated to the ring, while on the other iodine atom there is a negative charge of −0.09 *e*. Such charge distribution is consistent with the marked influence of polarisation in the complexes. The charge distribution in the complex $I_2.NH_3$ (Fig. 5*a*) is the same as in the benzene complex, but the low degree of charge transfer is inconsistent with experimental data for iodine complexes with *n* donors. The charge distribution in the complexes $F_2.NH_3$ and $Cl_2.NH_3$, obtained by the PNDO method[102], is illustrated in Figs. 5*b* and 5*c*. The electron density at the halogen atoms linked directly to the nitrogen atom is also reduced in these complexes.

Table 16. The orbital populations in $BF_3.NH_3$.[89]

Atom	Orbital	BH_3	NH_3	$BH_3.NH_3$	Δ, *e*
B	*s*	3.137		2.994	−0.143
	$2p_x$, $2p_y$	0.902		0.876	−0.026
	$2p_z$	0		0.275	0.275
H_B	*s*	1.020		1.075	0.055
N	*s*		3.516	3.518	0.002
	$2p_x$, $2p_y$		1.210	1.347	0.137
	$2p_z$		1.861	1.677	−0.184
H_N	*s*		0.734	0.621	−0.113

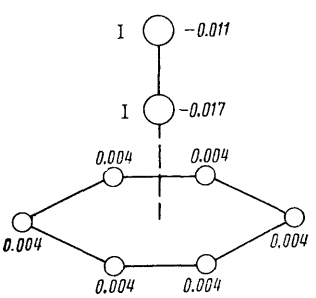


Figure 4. The changes in the atomic charges in the complex $I_2.C_6H_6$.[97] The charges are positive on the I atoms and negative on the C atoms.

Among complexes of *v* acceptors, the calculation on the octahedral complex $TiCl_4.2HCN$ by the CNDO method[103] is of interest. The calculation is one of the first designed to investigate the electronic structure of complexes of the donor–acceptor type in which the central atom contains *d* electrons. The calculated degree of charge transfer proved to be 0.2 *e*. It is interesting to trace the changes in the populations of the valence atomic orbitals on complex formation. Table 17 shows that the population of the *s* orbitals of the titanium atom diminishes, the overall population of the *p* orbitals increases, and the population of the *d* orbitals remains unchanged. There is a significant increase in the pupulations of the p_z and d_{z^2} orbitals of the titanium atom on complex formation, but, owing to the decrease of the populations of the other orbitals, the overall charge on the titanium atom remains unchanged. There is a significant increase in electron density at the chlorine atoms, the increase being greater at the equatorial atoms than at the axial atoms. Although the titanium atom has a partially filled *d* shell, in contrast to tin or antimony atoms, the similarity of the complex formation processes permits a comparison of the charge distribution in the acceptor molecule in the $TiCl_4.L_2$ complexes with that in the complexes $SbCl_5.L$ and $SnCl_4.L_2$. Table 17 shows that the nature of the changes in the charge on the acceptor atoms in the $TiCl_4.L_2$ complexes is the same as in the complexes $SbCl_5.L$ and $SnCl_4.L_2$, which has been demonstrated by the NQR method.

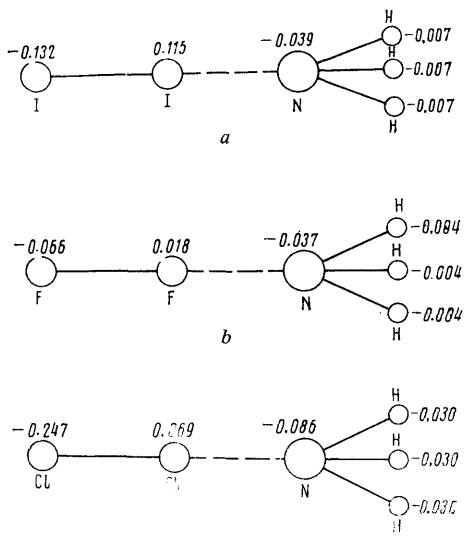


Figure 5. The changes in the atomic charges in the complexes $NH_3.Hal_2$.[99,100] The charges are positive on the halogen atoms remote from the nitrogen atoms and negative on the halogen atoms linked to the nitrogen atoms.

Table 17. The orbital populations in the complex $TiCl_4.2HCN$.[103]

Atom	Orbital	$TiCl_4$	HCN	$TiCl_4.2HCN$	Atom	Orbital	$TiCl_4$	HCN	$TiCl_4.2HCN$
Ti	*s*	0.31	—	0.21	N	*s*		1.80	1.75
	p_x	0.15		0.16		p_x		1.16	1.20
	p_y	0.15		0.14		p_y		1.16	1.19
	p_z	0.15		0.26		p_z		1.06	1.08
	$d_{x^2-y^2}$	0.17		0.12		*q*		−0.18	−0.22
	d_{xy}	0.44		0.53	C	*s*		1.19	1.16
	d_{z^2}	0.17		0.69		p_x		0.87	0.85
	d_{yz}	0.44		0.14		p_y		0.88	0.85
	d_{xz}	0.44		0.19		p_z		0.95	0.93
	q	1.56		1.56		*q*		0.11	0.21
$Cl^{ax}_{1,2}$	*s*	1.97		1.99					
	p	5.42		5.44	H	*s*		0.93	0.89
	q	−0.39		−0.43		*q*		0.07	0.11
$Cl^{eq}_{3,4}$	*s*	1.97		1.99					
	p	5.42		5.46					
	q	−0.39		−0.45					

Calculations have been made[104] on complexes of organometallic compounds and boron and aluminium halides by the CNDO method. Table 18 presents the changes in the

charges of the component atoms which we calculated from the authors' data. As in the preceding calculations, the formation of boron and aluminium halide complexes entails a significant increase of electron density at the halogen atoms.

Calculations have been made by the Hückel method for a number of BF_3 complexes[105-107], where the charge distribution in the acceptor molecule proved to be similar to the charge distribution obtained in calculations by more accurate methods.

One must note that, although different methods of calculation yield different orbital populations, the transferred charge and the nature of its distribution in the same complexes depend little on the specific method of calculation. The charge distribution obtained by quantum-chemical calculations on complexes of both σ and v acceptors agree well with the charge distribution obtained with the aid of experimental methods for the investigation of complex compounds.

Table 18. The degrees of charge transfer in boron and aluminium complexes.

Complex	Δ, e	$\Delta_{B(Al)}$, e	$\Sigma\Delta_{CH_3(Cl)}$, e	Δ_N, e	$\Sigma\Delta_{CH_3}$, e	$\Delta_{B(Al)}/\Delta$, e
$B(CH_3)_3 \cdot N(CH_3)_3$	0.41	0.12	0.30	—0.16	—0.24	0.30
$BCl_3 \cdot N(CH_3)_3$	0.57	0.03	0.54	—0.19	—0.36	0.05
$Al(CH_3)_3 \cdot N(CH_3)_3$	0.38	0.22	0.16	—0.12	—0.24	0.60
$AlH_3 \cdot N(CH_3)_3$	0.42	0.41	0.02	—0.11	—0.30	0.98
$AlCl_3 \cdot N(CH_3)_3$	0.46	0.18	0.29	—0.14	—0.30	0.40

Table 19. Comparison of the degrees of charge transfer obtained by different methods.

Complex	i.r. Spectra	μ_{DA} (Δ H)	NQR	Quantum-chemical calculations
$Cl_2 \cdot C_6H_6$	0.06	—	0.03	—
$Br_2 \cdot 2CH_3CN$	0.06	—	0.03	—
$I_2 \cdot C_6H_6$	0.07	0.03 0.08	0.08	0.03
$I_2 \cdot NH_3$	—	0.13	—	0.04
$I_2 \cdot C_5C_5N$	0.21	0.23	0.21	—
$I_2 \cdot (CH_3)_3N$	0.43	0.34	—	—
$I_2 \cdot (CH_3)_2S$	0.30	0.22	—	—
$ICl \cdot C_5H_5N$	0.46	—	0.26	—
$ICl \cdot 4\text{-}CH_3C_5H_4N$	0.46	—	0.26	—
$IBr \cdot CH_3CN$	0.12	0.12	—	—
$BF_3 \cdot C_5H_5N$	—	0.71	—	0.48
$BCl_3 \cdot (CH_3)_3N$	—	0.86	—	0.57
$B(CH_3)_3 \cdot N(CH_3)_3$	—	0.50	—	0.41
$Al(CH_3)_3 \cdot N(CH_3)_3$	—	0.85	—	0.38
$SnCl_4 \cdot 2C_4H_8O$	—	0.68	0.23	—
$SnCl_4 \cdot 2CH_3CN$	—	0.34	0.34	—
$SnCl_4 \cdot 2C_5H_5CN$	—	0.29	0.40	—
$SbBr_5 \cdot AlBr_3$	—	0.23	0.20	—
$SbCl_5 \cdot CH_3OH$	—	0.54	0.29	—
$SbCl_5 \cdot CH_3CN$	—	0.40	0.23	—
$SbCl_5 \cdot POCl_3$	—	0.33	0.26	—

VIII. CONCLUSION

All the methods which have been used to determine the degree of charge transfer can be divided into two groups. One group includes the dipole moment and infrared spectroscopic methods. The degree of charge transfer is determined either from the dipole moment of the donor–acceptor bond or with the aid of force constants (or the stretching vibration frequencies) of the bonds. The nature of the changes in the charge on the atoms in the donor and acceptor molecules cannot then be determined. This is because the experimental quantities refer solely to the bonds and do not therefore permit inferences about the changes in the atomic charges. The second group of methods includes NQR, Mössbauer spectroscopy, X-ray electronic spectroscopy, and quantum-chemical calculations, which characterise directly the atoms in the molecule, and therefore permit estimates of the effective atomic charges.

Comparison of the degrees of charge transfer calculated for the same complexes by different methods permit certain conclusions. Although the methods in the second group, with the exception of quantum-chemical calculations, do not take into account the electron density in the region of the overlap of the wave functions of the donor and the acceptor, the numerical values of the degree of charge transfer are similar (Table 19). This shows that the electron density in the region of the donor–acceptor bond does not contribute significantly to the degree of charge transfer.

It is so far difficult to assess the accuracy of the charge transfer data obtained and it is therefore impossible to decide which method leads to more correct results. This is because each method is associated with certain assumptions, the role of which is not always susceptible to exact experimental estimation. Furthermore, one must bear in mind that neither the possibility of the formation of a π bond between the donor and acceptor molecules nor the possibility of their mutual polarisation is as a rule taken into account in calculations on the degree of charge transfer. In general, one should note that a procedure whereby account can be taken of polarisation in the estimation of the degree of charge transfer in stable complexes has been hardly developed so far, although it has been shown above that polarisation may play a significant role in complex formation processes.

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