THE EXTENSION OF THE DONOR-ACCEPTOR CONCEPT

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Abstract - The donor-acceptor approach - well established in
coordination chemistry - is extended for application to any kind of
molecular interaction. Well documented results from quantum-chemical
analysis are used to provide simple rules for bond length variations due
to variation of the molecular environment. The structural changes
caused by molecular interactions are not restricted to the immediate
surroundings. They extend throughout the phases and indeed cause
specific structural arrangements within the areas of phase boundaries,
through which highly specific information transfer can take place.
Emphasis is given to structural features and to interactions in solutions
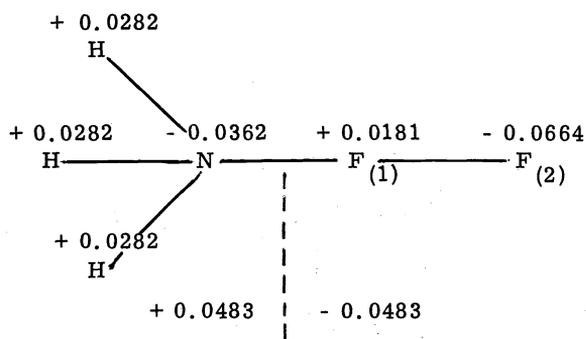of solvent mixtures.

STRUCTURAL CHANGES IN MOLECULES DUE TO DONOR-ACCEPTOR INTERACTIONS - STRUCTURAL VARIABILITY

First of all I wish to express my thanks to the Organizers of this Conference who
suggested a talk on Non-Aqueous Solution Coordination Chemistry. As a result of
these investigations I shall propose a broader point of view in that I shall attempt
to show the applicability of the donor-acceptor concept to any type of molecular
interaction ranging from solid state physics to biochemistry. Based on the ideas
and on the results of quantum chemistry, I shall not consider a molecule as such
(under ideal gas-like conditions), but rather stress the molecule's structural
changes due to changes in molecular environment and relate them to changes in
thermodynamic and kinetic parameters. In this way I shall not be concerned with
the question of the bonding forces involved. I shall talk not only on electron densities
but rather on charge density patterns, as any change in electron density is
connected with changes in the relative positions of the nuclei and hence with
changes in bond lengths and bond angles.
Let us start with the consideration of a typical donor-acceptor reaction
$D + A \rightleftharpoons D \rightarrow A$. In the course of this reaction the charge density rearrangement is due
to the contributions from charge transfer and polarization effects, which cannot be
separated unambiguously (1,2).
The extent of charge transfer from an ammonia molecule to a fluorine molecule has been
calculated to be 0.0483 electron (3). The $F_{(1)}$-acceptor atom, aquires a small positive
charge, as the original decrease of fractional positive charge is overcompensated by
passing over the negative charge gained from the donor atom including part of that
originally situated at the acceptor atom to other areas of the acceptor molecule, e.g. in
the case under consideration towards the $F_{(2)}$-atom. This has been described as the
spillover effect of negative charge from the acceptor atom. The original loss of negative
charge at the N-donor atom of the ammonia molecule is overcompensated by attracting
electron charge from the terminal hydrogen atoms. The increase in fractional negative
charge at the donor atom has been termed pileup effect (1,2). In that way the polarities
of the bonds adjacent to the donor-acceptor interactions e.g. both the N-H and the
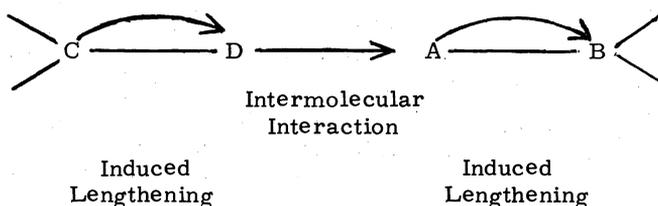F-F bonds are polarized and hence lengthened (2).

$$+ 0.0282$$
$$\text{H}$$

$$+ 0.0282 \qquad -0.0362 \qquad + 0.0181 \qquad - 0.0664$$
$$\text{H} \longrightarrow \text{N} \longrightarrow \text{F}_{(1)} \longrightarrow \text{F}_{(2)}$$

$$+ 0.0282$$
$$\text{H}$$

$$+ 0.0483 \quad \mid \quad - 0.0483$$

Thus, the charge distribution, usually assigned to donor and acceptor atoms after complexation in organic chemistry, e.g.

$$-\text{N}^+ \longrightarrow \text{C}^-$$
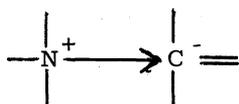
is therefore not in agreement with the facts (2).

The _first bond length variation rule_ expresses the inverse relationship between inter-molecular and intramolecular bond lengths adjacent to the sites of interaction (2, 3).

$$\text{C} \longrightarrow \text{D} \longrightarrow \text{A} \longrightarrow \text{B}$$

Intermolecular
Interaction

Induced   Induced
Lengthening   Lengthening

The increase in bond length may be represented by a full bent arrow connecting the bonded nuclei and pointing into the direction of the electron shift.
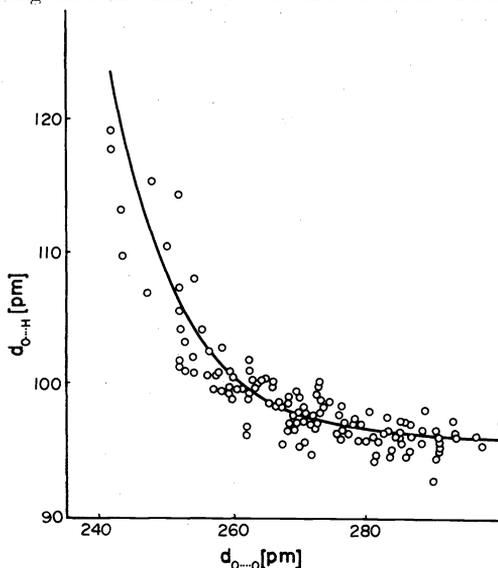

Fig. 1.   Relationship between "intramolecular" O——H and "intermolecular" O---O bond distances in crystalline hydrates (J.O. Lundgren and I. Olavsson, "The Hydrogen Bond - Recent Developments in Theory and Experiment", P. Schuster et al. Eds., North Holland Publ. Co. Amsterdam, 1976).

For example, there is a relationship between the intermolecular O••••O and the intra-
molecular O—H bond distances in crystalline hydrates (4): the formation of the inter-
molecular O→H coordinate link (usually denoted O--—H) induces an increase in adjacent
H——O bond length: the shorter the intermolecular bond distance the greater the intra-
molecular bond distance (fig. 1).
Another example is provided by considering the bond length variations in the course of
nucleophilic addition to acetone. The shorter the N→C bond distance resulting from the
nucleophilic addition, the greater becomes the intramolecular C=O bond distance (5);
the carbonyl carbon is increasingly displaced from the plane of its three original ligands
and pulled toward the donor atom resulting in increasing pyramidalization (Fig. 2). The
structure of the tetrahedral subunit with two oxygen atoms attached to the same carbon
atom represents an extreme case of O→C =O interaction where the addition reaction
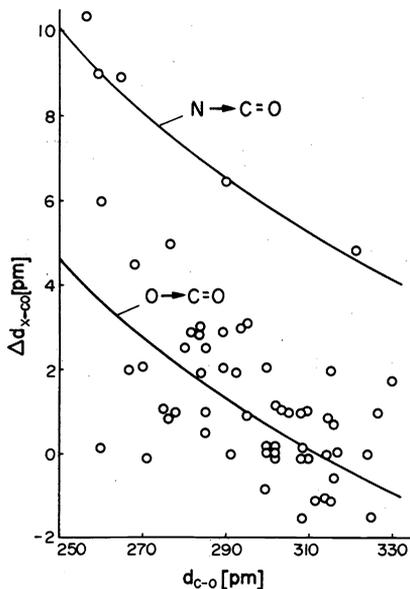has proceeded to completion (5).

Fig. 2.   Relationship between "intermolecular" X→CO and "intramolecular"
          C—O distances in acetone in the presence of various donor molecules
          (H.B. Bürgi, J.D. Dunitz, E. Shefter, Acta Cryst. B 30, 1517 (1974)).

There is a remarkable distortability of coordination polyhedra of copper(II)-complexes (6).
Correlations have been found to exist between axial and equatorial bond lengths in CuO_6,
CuN_6 and CuN_4O_2 chromophores in that decreasing axial bond lengths are reflected in
increasing equatorial bond lengths and vice versa. The transition between the various
types of coordination is practically continuous within a considerable bond length range (6)
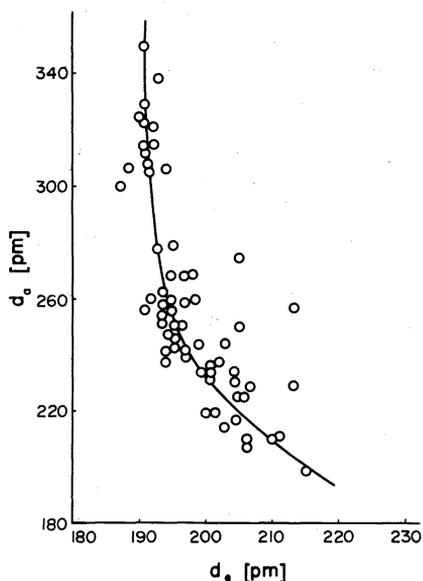(Fig. 3).

Fig. 3. Relationship between axial distances d_a and equatorial distances
d_e in CuO_6, CuN_6 and CuN_4O_2 chromophores (J. Gažo, I. B. Bersuker,
J. Garaj, M. Kabešová, J. Kohout, H. Langfelderova, M. Melnik,
M. Serator, F. Valach, Coord. Chem. Revs. 19, 253 (1976)).

The situation is analogous within a homologous series of carbonyl compounds. The
metal-carbon distances may be considered as intermolecular, by which the adjacent
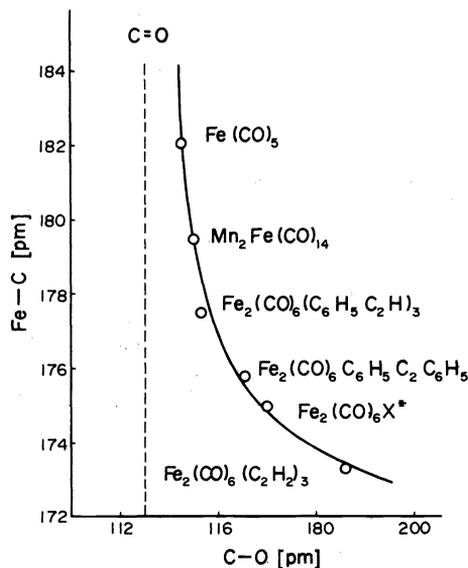C — O bonds are effected: the shorter the M — C bond, the longer the C — O bond (7)
(Fig. 4).

Fig. 4. Relationship between Fe — C distances and C — O distances
in iron carbonyls (V. Gutmann, Coord. Chem. Revs. 15, 207
(1975)).

Bond length variations are not confined to the bonds adjacent to the sites of an inter-
molecular interaction. Subsequent characteristic changes in bond lengths are induced
throughout the molecules as the charge density rearrangement is taking place. According
to the second bond length variation rule a bond is lengthened when the electron shift takes

place from the more electropositive to the more electronegative atom in the uncomplexed species and it is shortened when it occurs from the more electronegative to the less electronegative atom (2,8). In molecules where atoms of alternating electronegativities are subsequently arranged, alternating bond lengthening and bond shortening will be induced.

The following changes in charge densities have been calculated for the dimerization of water molecules (9).
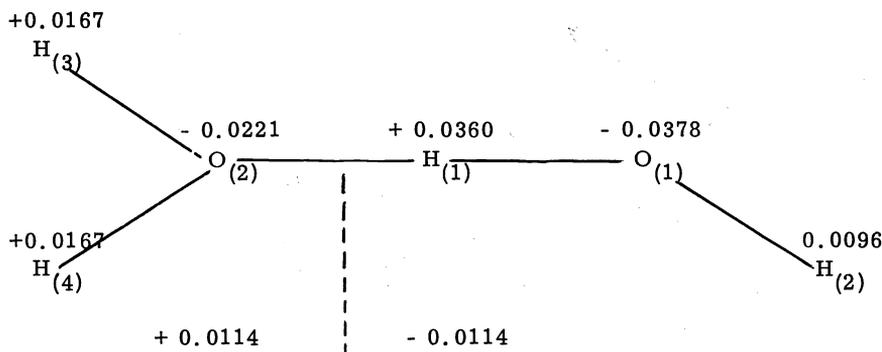
In the dimeric unit the hydrogen atoms are no longer equivalent. The $H_{(3)}$ and $H_{(4)}$ atoms in the donor component are more acidic, than in the monomer, the $H_{(1)}$-acceptor atom incorporated in a hydrogen bond carries an even greater partial positive charge (spill-over effect), and the terminal $H_{(2)}$ atom of the acceptor component has become less acidic. Neither the O——H bonds, nor the oxygen atoms remain equivalent. The $O_{(1)}$-atom is more strongly basic than the $O_{(2)}$-donor atom. While the H_3——$O_{(2)}$, $H_{(4)}$——$O_{(2)}$ and $H_{(1)}$——$O_{(1)}$ bonds have been lengthened (electron shift from the less electronegative H-atom to the more electronegative O-atom), the $O_{(1)}$——$H_{(2)}$ bond is shortened (electron shift from the more electronegative O-atom to the less electronegative H-atom). A slightly bent solid arrow denotes increase and a dashed arrow a decrease in bond distance.
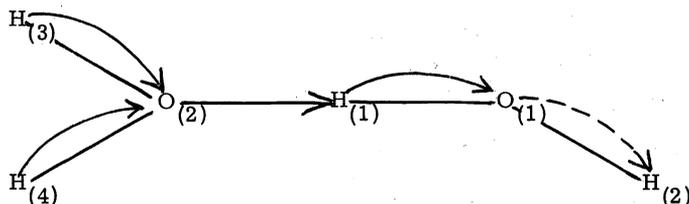

Such cooperative effects are not confined to adduct formation and indeed, they result from changes in any molecular arrangement: they lead to a new structure pattern for the whole system under consideration (2). The structural variability of a given molecule in different molecular environments, for example in different solvents, is reflected in its chemical variability (2).
Alterations in fractional charges for sequences of carbon atoms are related to alternating nucleophilic and electrophilic properties (10). Individual differences in C——H bonds in organic acid halides RCOX with R = C_4H_9, C_5H_{11} and C_6H_{13} in different media are reflected in different chlorination behaviour. Attack by an acceptor solvent at the acyl group results in C——H bond lengthening which increases with distance from the acyl group. However, the terminal C——H bonds are lengthened to a much smaller extent (11).

The longer a given bond, the greater the polarity and the greater the electrophilic and oxidizing property at its terminal atom of positive partial charge and the greater the nucleophilic and reducing property at its terminal atom of negative fractional charge. The longer the bond, the greater its ease to heterolytic bond fission (2).
Solvent effects on conformational changes have been established for acetamide, donor attack occuring at the N——H hydrogen atoms and acceptor attack at the oxygen atom of the C=O group (12). The N——H bonds are increasingly lengthened with increase in solvent donor number, while the lengthening of the C=O groups is related to the solvent acceptor

number. Each of these interactions contributes to shortening of the C——N bond.   Up to a
donor number of 20 only one proton NMR signal is found, showing equivalence of free
rotationability of the C——N-bond. For solvent donor numbers greater than 23 two
H-NMR signals are found which indicates strengthening of the C——N bond to that extent
that it can no longer rotate (12).
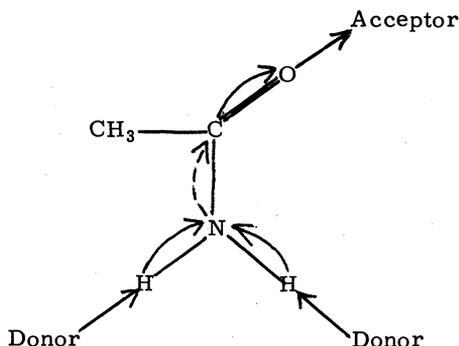
The _structural variability_ of a given molecule as a result of its molecular environment is
reflected in the individual characteristic of its reactivity. The molecular environment is
also subject to structural variability and hence a molecular system should be considered on
a whole.

STRUCTURAL FEATURES IN THE SOLID PHASE

The above considerations are not confined to interactions which result in the formation of
coordinate covalent bonds. Indeed, any molecular interaction provokes a rearrangement of
the charge-density pattern and this can be regarded as a result of a donor-acceptor inter-
action. This leads to changes in bond distances not only in the immediate neighbourhood of
interaction. The occurrance of _cooperative effects_ within a solid phase are evidenced, for
example, by the drastic increase of the conductivity of a germanium crystal by inserting
one antimony atom for every 100 million germanium atoms. The additional interactions
cause weakening of the adjacent Ge-Ge-bonds and strengthening within the next
coordination sphere. Each strengthening causes lengthening in the immediate neighbourhood
and vice versa. Thus within a certain microscopic area the changes in bond distances due
to an additional interaction follow the second bond length variation rule, and in principle
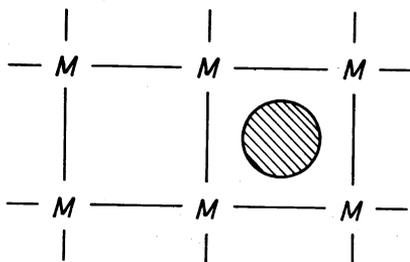they are continued throughout the crystalline phase (2).
Evidence about the measurable size of the _distorted transition zone_ is provided by the
work of Weiss (13), who has shown that the information contained at the surface of an
aluminosilicate structure, as determined by appropriate LEED experiments is transmitted
to further layers of SiO_2 when they are allowed to grow on the surface. The remarkable
result of this study is that the original information was not completely lost before the
formation of 20 molecular layers of SiO_2 corresponding to a distance of approximately
6 400 pm (2).
A vacancy defect, the so called Schottky-defect causes bond shortening, e.g. local lattice
contraction in its immediate surrounding (2). This has been confirmed for the NaCl-type
structure of $TiC_{0.83}$, where one out of six octahedral holes is unoccupied: the mean
Ti-C-bond distances are shorter than in the more regular crystal of stoichiometric
composition TiC (14). The vacancy is stabilized by local lattice contraction, which
corresponds to an inner surface tension.

```
      |        |        |
  — C — Ti — C —
      |                 |
  — Ti    (  )    Ti —
      |                 |
  — C — Ti — C —
      |        |        |
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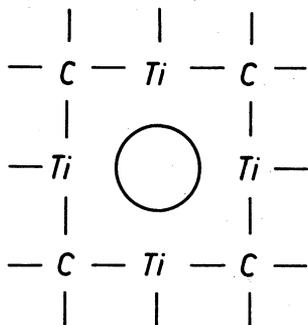
Ti— C — bonds around the hole are shorter

By analogy, an interstitial position will lengthen the adjacent bonds

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      |                |                |
  — M ———— M ———— M —
      |                |                |
      |                | ⊘            |
      |                |                |
  — M ———— M ———— M —
      |                |                |
```

M—M—bonds around an interstitial position are longer

Since such lattice deformations are not confined to a certain restricted area, structural gradients within microscopic regions exist in any material (2). Indeed, ideal crystals cannot be found in nature and their existence at temperatures above zero is principally impossible on thermodynamic grounds(15). Its existence would require that the equilibrium constants for equilibria involving changes between vacant, interstitial positions and the ideal positions being zero, which is only possible at T = 0. The thermal equilibrium is coupled with certain "defects" from the ideal arrangement, which appear essential in stabilizing the real crystal.
Thus it might be more realistic to speak of "structure regulating centers" (16) rather than of defect structures or perturbations. In fact, the nature and number of structure-regulating centers is also important for the properties of the real crystal (2).
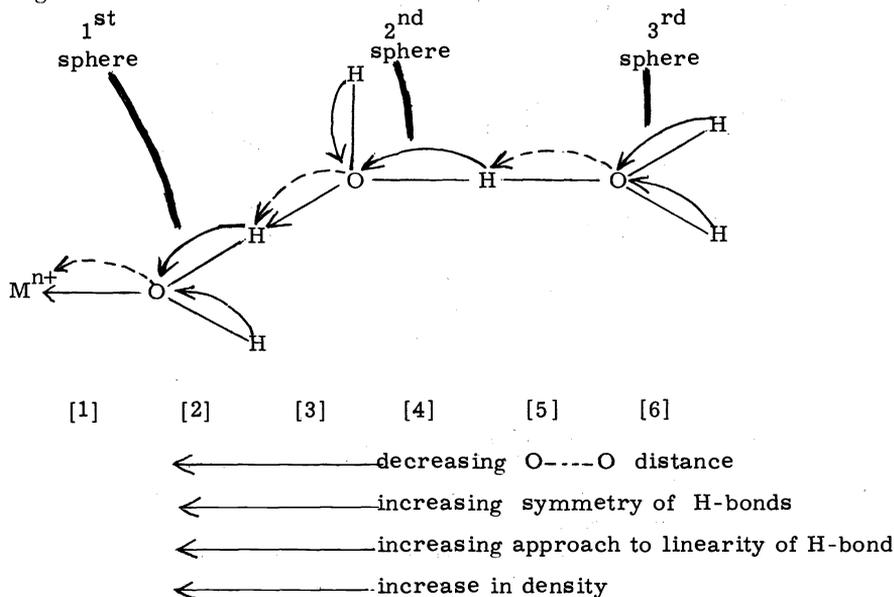
STRUCTURAL FEATURES IN THE LIQUID PHASE

The analogous consideration of solute-solvent-interactions by the donor-acceptor approach, allows an understanding of the so-called "specific" effects which are outside the electrostatic interpretation. It is characteristic for this approach to consider the changes both in solute and in solvent structure.
The greater the solute concentration the smaller is the number of water molecules

available for each solute particle and hence the smaller the structural changes of the solute. Structure and property of a solute in a given solvent is therefore also a function of its concentration. This fact is taken into account by thermodynamics in that activities are used rather than concentrations. Indeed the activity coefficient may be structurally interpreted as representing the concentration-dependent structural variation of the solute, as compared to its structure in the same solvent at infinite dilution.

The influence of solute particles on the structure of the solvent up to considerably large distances is supported by the results of quantum chemical model calculations using a STO-3 G basis set for linear water polymers under the influence of cations and ion pairs (17). They indicate that even a water molecule at a distance of more than 30 000 pm could experience still the influence of a beryllium ion.

The structure of the solvent is influenced both by the nature and by the concentration of the solute. The structural changes are in principle not confined to limited areas as they extend throughout the liquid phase, although it is true that their extent is decreasing with increasing distance from the solute. Both the geometry and the energy of the inner-core-solvate complex is changed by outer sphere coordination (18). The coordination of the first hydration sphere around a metal ion leads to lengthening of the intramolecular $O\!-\!\!-\!H$ bonds [2] and hence to increase in acidities at the hydrogen atoms. Between the first and second coordination sphere hydrogen bonding [3] is stronger than between uncoordinated water molecules (2,16). The electron drift from the oxygen atoms of the second-sphere water molecules is continued through the oxygen atoms toward the cation leading to the following changes: Decrease in metal ion-inner-sphere bond [1], decrease in fractional positive charge at the coordination center, increase in $H\!-\!\!-\!O$-bond distance [2] and to a smaller extent in [4] (outer-sphere effect for donor ligands (19,20)). The formation of further hydration layers leads to cooperative effects in the same direction. Hence the O---O distances increase as a function from their distance from the metal ion. Decrease in intermolecular O---O bond is paralleled by higher symmetry and smaller extent of bending of the hydrogen bonds.

[1]   [2]   [3]   [4]   [5]   [6]

←————————————decreasing O----O distance

←————————————increasing symmetry of H-bonds

←————————————increasing approach to linearity of H-bond

←————————————increase in density

The solvent molecules are more tightly arranged the smaller their distance from a structure-regulating solute. Thus, we have <u>structural gradients and density gradients</u> within the microscopic areas of a liquid phase (2). Such effects are also indicated by the results of spectroscopic studies at low temperatures (21). The liquid system is not at rest. In fact it can be considered as an oscillating system. Analysis of Raman data on aqueous solutions lead to the conclusion that solute-solute interactions must be <u>mediated by the water molecules</u> themselves and that the structural changes have collective character, i.e. they must be considered with the correlated behaviour of a reasonably large number of solute particles (22).

In a solvent mixture the effect of preferential solvation of the more strongly solvating solvent component must be considered, which results also in a <u>gradient in analytical composition</u> within any microscopic region of the solution (2). The variation of donor

properties as a function of the mole fraction of the binary solvent mixture can be accounted for by preferential solvation. This results in a positive deviation from the ideal straight line in the donor number-mole fraction plot of the binary mixture (Fig. 5).
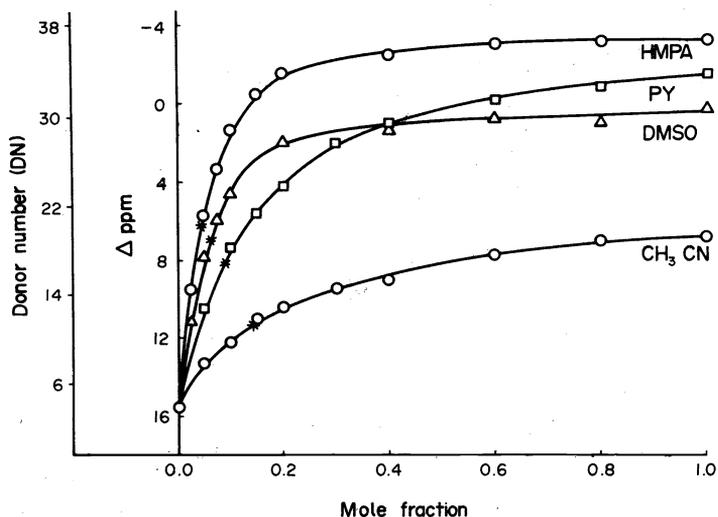

Fig. 5   Chemical shift of the ^{23}Na NMR resonance in $NaClO_4$ solutions as a function of solvent composition in mixtures of nitromethane and HMPA, pyridine, DMSO and CH_3CN respectively (M.S. Greenberg, A.I. Popov, Spectrochim.Acta 31 A, 697 (1975).

In order to account for negative deviations as observed for the acceptor properties in the system H_2O-HMPA (Fig. 6) the solvent-solvent interactions in each particular mixture must be considered. They may lead to structural features entirely different from those characteristic for each of the components.
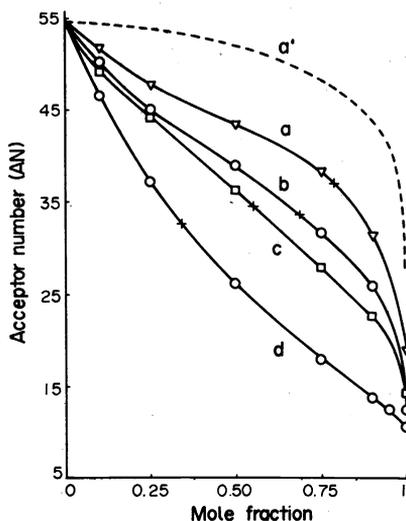

Fig. 6   Acceptor Numbers in binary mixtures of water and (a) = acetonitrile, (b) = acetone, (c) = pyridine and (d) = hexamethylphosphoric amide. x represent isosolvation points. a' allows for the polymeric nature of liquid water assuming a cluster size of 10 (U. Mayer, W. Gerger, V. Gutmann, Mh. Chem. 108, 489 (1977)).

The acceptor properties of mixtures of water with an aprotic solvent is a function of the donor properties of the aprotic co-solvent (23): in such mixtures the plot of the donor

number of the aprotic solvent vs. the position of the isosolvation point shows a straight line (23) (Fig. 7). This reveals a decrease in acceptor properties with increasing donor number, due to the establishment of new structural features in the solvent mixture (23), such as
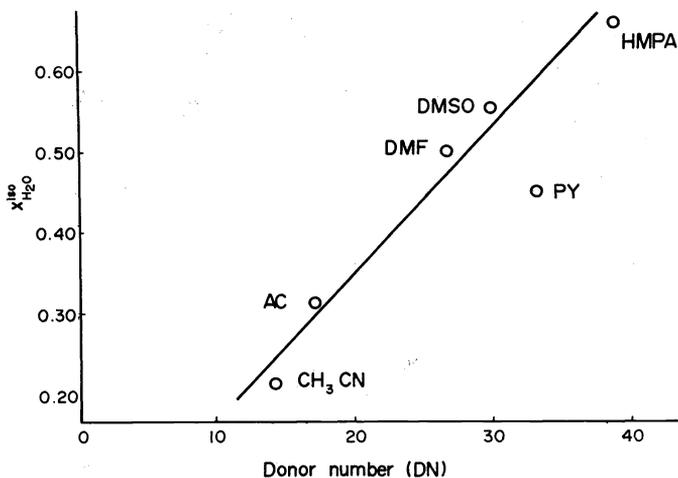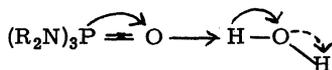
$$(R_2N)_3P = O \longrightarrow H-O\underset{H}{\overset{}{\cdots}}$$

Fig. 7.   Isosolvation points for binary mixtures of water
and various aprotic solvents as a function of the donor number
of the aprotic component (U. Mayer, W. Gerger, V. Gutmann,
Mh. Chem. 108, 489 (1977)).

The coordinating properties of a solvent mixture may further be influenced by its dielectric properties, as soon as ionization phenomena are involved (24). For example, in mixtures of trifluoro-acetic acid and nitrobenzene a maximum in acceptor number is found at a certain molar ratio (Fig. 8). This is due to partial protonation of the Et_3PO probe as such protonation equilibria are decisively influenced by the dielectric properties of the medium.
The consideration of all three contributions namely preferential solvation, solvent-solvent interactions and dielectric contributions allows the interpretation of various features observed in solvent mixtures.
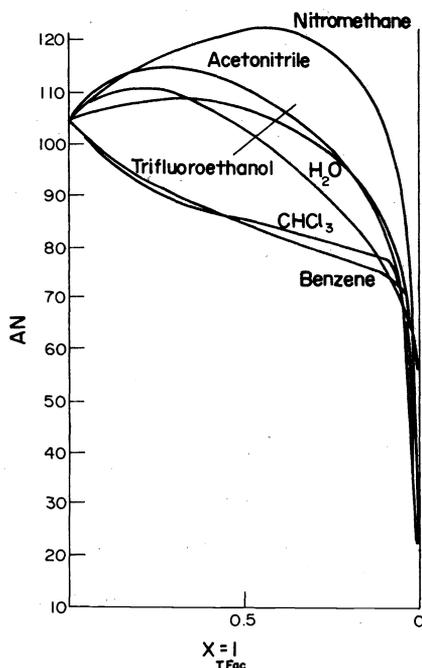
Fig. 8. Acceptor Numbers of mixtures of trifluoroacetic acid and
nitromethane, acetonitrile, trifluoroethanol, water, chloroform
and benzene as a function of the molar fraction (U. Mayer,
V. Gutmann, E. Spitzenberger, Unpublished).

STRUCTURAL FEATURES AT INTERFACES

The application of the extended donor-acceptor concept may be of considerable value for
structural considerations at interfaces. A crystal surface may be considered as an area
of lattice distortion (25). The coordination number of a surface atom is smaller than that
of an atom within the lattice. This implies a lattice contraction within the surface area (2).
This effect has been studied by the LEED technique within the last few years. For
example, for the upper layer of the silver (110) plane a real contraction of 7 % has been
found (26, 27). Such effects can be compensated by the occurrance of adsorption. Indeed,
the stronger the adsorption, e.g. the stronger the molecular interaction with the surface
atoms, the greater will be the lengthening of the adjacent bonds (first bond length
variation rule). For example the O——H bond lengthening on an aerosile surface is
greater, the higher the donor number of the adsorbate attacking at the H-atoms (28)
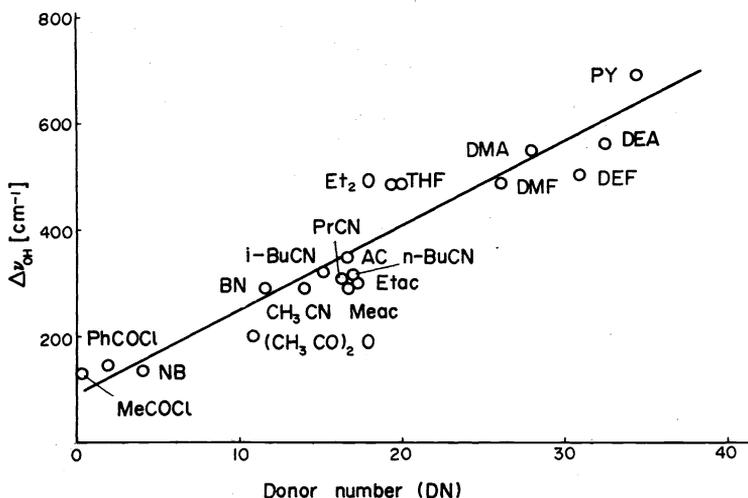(Fig. 9).
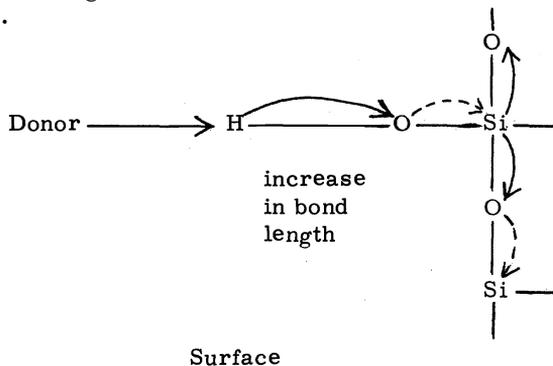
Surface

Fig. 9.   Relationship between shift in wave number of O——H valence
          band on aerosile and the donor number of the adsorbate
          (W. Horill, H. Noller, Z. phys. Chem. (Frankf.) 100, 155
          (1976)).

Since adsorption leads to increasing bond distances within the surface area of the
adsorbent and hence to decreasing electron density, a corresponding decrease must be
involved in desorption. When a gas is adsorbed on a solid surface, a change in pressure
leads to changes in adsorption and hence in bond distances! This means that a crystal
surface is not rigid, but rather distortable (2).

The adsorbate is also structurally effected. For example, Yates and King (29) have
shown that the so-called ∝-CO state of carbon monoxide adsorbed on a clean
tungsten surface is similar to the "carbonyl-type" CO ligands in $W(CO)_6$ (I). As the CO
coverage of the surface is increased, a slight strengthening of the CO bonds is found (II)
since the availability of tungsten d-electrons for back donation towards the adsorbed
CO molecules is decreased by increasing CO coverage (29). This shows that not only the
surface W-atoms attacked by carbon monoxide are involved, but rather at least the whole
surface area of the metal.
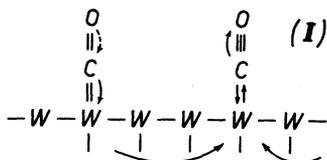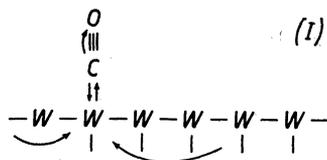
The extent of structural changes within the adsorbed molecules is greater (a), the smaller their number, and thus the "thinner" the layer and (b) the stronger the interaction between adsorbens and adsorbate. Such considerations are of interest for the understanding of the "supporter effect" in heterogeneous catalysis, of corrosion phenomena, epitaxy, mechano-chemistry and membrane phenomena (2).

It has been pointed out that each structure-regulating center within a lattice causes a contraction of the adjacent layers, and these in turn have structural effects on the following layers. Thus the effects are not confined to a certain area (28) and hence there will be regions in which the effects of two or more structure regulating centers will be matching each other (2). A structural-regulating center near the phase boundary will cause additional structural effects in a certain interface area. Thus any surface is characterized by inhomogeneities, e.g. a highly differentiated structural order reflecting the structural features within the bulk material. Thus the surface area may be considered as containing the structural information of the bulk material. It is the order of these highly differentiated inhomogeneities of the surface structure, which are responsible for the very specific interactions at phase boundaries.

In a liquid the structure-regulating centers are not at rest. Thus the inhomogeneities at the surface area are continuously changing, as they reflect the dynamic pattern of the order in the bulk liquid. The liquid surface is therefore a charge density pattern which is fluctuating in time and in space even when no interactions at the phase boundaries took place. Such effects have been concluded from specific calculations based on the many body theory for a liquid-vapor interface of a simple fluid (30). They indicate the existence of long-range ordering within the interfacial zone. The physical manifestations of this order are surface waves, characteristic interfacial modes in which the motions of widely separated portions are strongly correlated.

The additional shortening of the bonds between the molecules within the surface area will be greater the greater the number of structure regulating centers, e.g. the greater the solute concentration. Thus we obtain a structural interpretation for the phenomenon of vapor pressure lowering (31): at any given temperature the mean bond strength between solvent molecules near the phase boundary is greater the greater the number of solute particles.

CONCLUSIONS

The most remarkable aspect is the applicability of the bond length variation rules both in the liquid and solid phase (and in principle also in the gaseous phase) virtually independent from the interpretation of the bonding forces. Changes in structural parameters as provoked by change in molecular environment are correlated to differences in thermo-dynamic and kinetic parameters and in most cases to those of the empirical parameters of the donor-acceptor approach, namely the donor number and the acceptor number (2), which have been presented in great detail elsewhere (2, 32, 33). In this way hitherto unrelated facts and phenomena can be correlated. The consideration of far-reaching effects provide an understanding of the behaviour of solutions, of real crystals and of interactions at interfaces. The transfer of molecular information is not restricted to a limited number of atoms or molecules. Ordering principles at a level which is higher than that of specific interactions between isolated individual particles must be recognized.

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