Approaches to the Study of van der Waals Interactions in Solids

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Z. Naturforsch. **48a**, 471–477 (1993); received January 4, 1993

Van der Waals forces are of short range. In molecular crystals the interacting atoms or groups of atoms of a molecule are fixed in their position with respect to the atoms of the neighboring molecules. From measurements of the intermolecular interactions via properties which can be assigned to the individual atoms (groups), such as hyperfine interactions or vibrational frequencies, as a function of the intermolecular distances, the van der Waals (vdW) potentials may be evaluated.

We propose the use of discrete changes of intermolecular distances for studying vdW-interactions, the method of "Several Solid States",

a) by combining a molecule A with different moleculs B_i in stoichiometric proportions and in a crystallographically ordered way to molecular solid complexes;

b) by investigating the changes of atomic (group) properties in systems with two ore more solid phases appearing in the phase diagram as a function of temperature (pressure). This way of using several solid states is offered only by chance;

c) by using the fact that in many molecular solids there is more than one molecule in the asymmetric unit of the elementary cell in the crystal structure, and therefore several vdW-potentials for chemically identical intermolecular neighbors;

d) by the synthesis of compounds containing the atoms (groups), the vdW-interactions of which one wants to study, with one or more centers of chirality. With one center of asymmetry in the molecule one finds the molecule considered in two different situations of vdW-contacts at least, and, in first approximation, one can assume identical intramolecular interactions (besides the optical activity). Two chirality centers within the molecule lead to three (at least) different crystal fields: a) $(\pm)$; b) $(--)$ respectively $(++)$; c) $(--, ++)$.

Examples of hyperfine interaction studies, based on this "Several Solid States" concept are discussed.

Introduction

There is a wealth of information on van der Waals (vdW) interactions of atoms and molecules from experiments and theory for the gaseous and the liquid state of matter. Describing the interparticle potential energy by a Lennard-Jones ansatz, the force fields are well understood [1], and by molecular dynamics calculations the intermolecular potentials are found as well as physical properties of the particles. The state of the art is quite satisfactory because the dynamics of the particles in the mentioned states of matter average the potentials in space and time and allows an application of the mean field Lennard-Jones potential

$$U = f(\alpha/r^n + \beta/r^m). \tag{1}$$

However, therefrom one can conclude about the vdW-pair potential U_{ij} (i,j two next nearest molecules, in the time average) only by introducing a geometrical model and further assumptions.

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Considering the simple case of molecules AB, in the solid state the positions are fixed and we are able to measure the distances $d(A_i - A_j)$, $d(B_i - B_j)$, and $d(A_i - B_j)$. There is the problem of dynamics in the solid state, and the distances d are mean distances at the temperature the experiment is performed. The influence of molecular dynamics in the solid state on the vdW-potential shows up in the lattice energy of systems having as well ordered as orientationally disordered solid states. We consider, as an example, the compounds CBr_4 (**1**) and Cl_3C-CCl_3 (**2**). Both compounds are in their high temperature solid phase (I) in a completely orientational disordered state (plastic state). In this state there is no translational motion of the center of gravity of the molecules, besides some translational diffusion. The centers of gravity form a simple crystal lattice, body centered cubic, Im3m, $Z = 2$. In the completely ordered state, phase II (**1**) and phase III (**2**), the vectors $\boldsymbol{r}$(C–Br) and $\boldsymbol{r}$(C–Cl), respectively, are fixed with respect to the basis vectors of the crystallographic unit cell. In case of compound (**2**) there exists an intermediate phase II, located on the temperature axis between I and III, in which hindered rotations of the molecule around the axis C–C occur.

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The dynamic disorder in the plastic phase I of the two compounds considered leads to an averaging of the angles between neighboring molecules and, as a consequence, to a mean expansion of $d(Br_i{-}Br_j)$ and $d(Cl_i{-}Cl_j)$, respectively. The consideration of halogen-halogen interaction only is justified from the molecular geometry of both compounds in question. The mean vdW potential is weakened compared to the ordered phases II. Thermodynamics shows this. For CBr_4 the enthalpy of sublimation has been determined to be 49.4 kJ/mol (plastic phase I) and 54.4 kJ/mol (phase II) [2]. For hexachloroethane the values are 51.27 kJ/mol (plastic phase I) and 58.92 kJ/mol (phase II) [3].

Growing interest is found in chemistry to know about the vdW pair interaction potentials. One field of interest is "Molecular Modeling", of high capacity in synthetic chemistry, chemical kinetics, biochemistry, etc. There are two guiding effects in this field, the geometrical aspect, that is the space available for a molecule A and molecule B to make contact at certain points, and the force field between the atoms (groups) A_i and B_j. An other topic is the intramolecular structure of macromolecules, polymers, biopolymers, which is for most polymers solely determined by the vdW intergroup (atom) interaction, in biopolymers with considerable admixture of hydrogen bond energy.

It therefore seems to be justified to think about possibilities to study vdW fields in the ordered solid state to gain individual potentials

$$U_{ij} = f\left[(\alpha_i\alpha_j)^{1/2}/(r_{ij})^n + (\beta_i\beta_j)^{1/2}/(r_{ij})^m\right]. \qquad (2)$$

The geometrical mean in (2) for the coefficients α, β is one possible ansatz.

Besides the solid state approach to the problem there are other ways for studying pair vdW-potentials such as molecular beam scattering experiments, spectroscopy (IR, UV) of vdW-clusters [4], or beam microwave spectroscopy, to mention a few of them. We shall not discuss these approaches further as we shall not touch the use of matrix spectroscopy in the study of vdW-potentials.

The Solid State van der Waals Interactions

Experimental Methods

The experimental ways to study vdW pair interactions in molecular solids have to be a combination of several methods. There are, however, some necessary basic investigations in any case.

First, the intra- and intermolecular geometry of the chemical particles has to be known from diffraction experiments as accurately as possible, and most promising is here the combination of X-ray- and neutron diffraction, the X–N-method [5], at temperatures as low as possible to slow the dynamics of molecules and lattice down to the insurmountable zero point modes. From the X–N-experiments, by Fourier synthesis, the location of the nuclei, the intra- and intermolecular distances, and the electron density distribution $\varrho\,(x\,y\,z)$ are available [5, 6]. If one could reach this goal, the problem would be solved because from an accurate knowledge of $\varrho\,(x\,y\,z)$ a potential distribution $U\,(x\,y\,z)$ can be derived and therefrom all the multipole contributions to the vdW potential could be calculated; only the Heitler-London dynamical electron polarization would be an open question, in any case a necessary contribution from theory to the problem. Numerous approaches have shown that today the experimental accuracy available is not sufficient for answering this question.

The Thermodynamical Approach

The first step, X–N-experiments plus the measurement of the compressibility tensor, is a true solution to the problem in simple cases, as shown long time ago by Born et al. [7]. A change of pressure leads to a change of the distances $d(A_i - A_j)$ and measuring these changes U_{ij} may be determined. In praxi the solution of the problem is not simple and practically restricted to one single interaction, $A_i \leftrightarrow A_j$ or $A_i \leftrightarrow B_j$. Borns approach was successfull for highly symmetric ionic crystals, e.g. solids of the NaCl-type or the CsCl-type. For molecular crystals composed of several different atoms (groups) the separation of the total effect, the experimentally found compressibility tensor, into individual components is not possible by experiment, and besides measurements of the compressibility on single crystals a structure determination as a function of P would be necessary (see the discussion in [8, 9].

In any case, an important information on the sum of the U_{ij} in the solid state one would consider, is the lattice enthalpy one finds from the measurement of the heat capacity $C_P = f\,(T)$ plus the enthalpy of sublimation ΔH_{sub}. Any determination of individual vdW pair potentials must give, in sum, the lattice energy.

Determination of Individual Atomic (Group) Properties

Individual properties, which under certain assumptions can be assigned to atoms (groups) within the

molecule in the vdW solid, have to be studied. Such properties are hyperfine interactions (NMR-, NQR-, Mößbauer-resonance) and vibrational and librational modes (IR- and Raman-spectroscopy). The properties observed in the solid state should be compared with those found in the molecule without vdW interactions, that is in the gaseous state. Such a comparison would be quite valuable for the intramolecular angles and distances, too, by including electron diffraction and microwave spectroscopy in the study of vdW potentials in a chemical system.

There is a severe approximation in our discussion. We must assume that the condensation of a molecule into the solid state is adiabatic and a change of intermolecular geometry, for instance during a phase transition, is adiabatic with respect to intramolecular geometry and energy states.

The "Several Solid States" Approach

The vdW pair interaction is strongly dependent on the intermolecular distance $d(A_i - B_j)$. For several reasons, principal ones and experimental ones, we have excluded the possibility of a continuous variation of the thermodynamic state function P, see above.

To have information on as many distances $A_i - B_j$ as possible for the determination of U_{ij}, we have to change these distances stepwise by changing the neighborhood of the molecule considered, either chemically or by creating for one solid compound different solid phases.

The Chemical Change of Intermolecular vdW Interactions

Studying two component phase diagrams $A_x B_{1-x}$ as a function of the mol fraction x and the temperature T on often encounters the formation of stoichiometric solid phases $A_m B_n$. From such studies there are many systems $A_m B_n$ known where A is tetra-halogenated methane, CCl_4, CBr_4, CCl_3F, a halogen molecule (Cl_2, Br_2) etc. and B is an aromatic molecule, such as benzene, methylated benzene, or an ether [10–13]. Discussion is still going on about the nature of the interaction in such compounds $A_m B_n$. For example, in compounds CCl_4 · aromate, a charge transfer interaction is assumed by many authors. Of course by comparing A, B with A · B, charge transfer has to be considered. NQR measurements have, however, shown

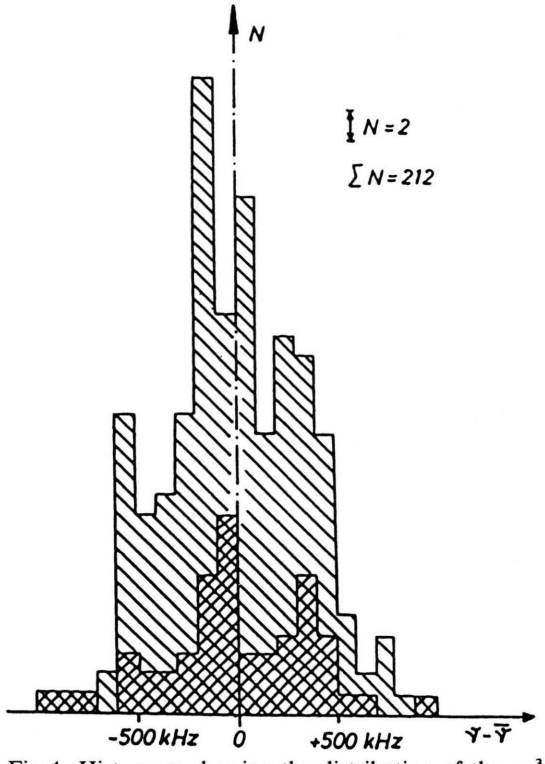

Fig. 1. Histogram showing the distribution of the ω-^{35}Cl-NQR frequencies, ν, around the average frequency, $\bar{\nu}$, of all chloroacetyl groups a) in chloroacetanilides, $Cl_xC_6H_{5-x}$ · $NHCOCH_{3-y}Cl_y$ (lower distribution: ⁂), b) in chloroacetanilides, $Cl_xC_6H_{5-x}NHCOCH_{3-y}$ · Cl_y, and in trichloroacetic acid (TCA) (overall distribution: \\\\\) [14]. $\Delta\nu$ is choosen as 100 kHz.

that one should not consider such molecular complexes as charge transfer but as vdW complexes, see the discussion in [14].

Molecular complexes AB, AB_2, etc., where B is an aromatic molecule, A a Lewis base, such as $AsCl_3$, $SbCl_3$, ..., (Mentschutkin-type complexes) have been investigated some time ago in the context of vdW interactions. In this group of compounds as well as in Lewis acid-Lewis base complexes the charge transfer is probably an intrinsic part of the interaction in the solid [15].

In the field of molecular complexes there is a large group of compounds $A_m B_n$ where A is an acid proton carrying molecule. B may be varied in a wide range. A rather large number of solid complexes with A = trichloroacetic acid, B varying from CH_3CN to $(CH_3)_3N$, has been studied by ^{35}Cl NQR and also by X-ray diffraction [16–21] The result in form of fre-

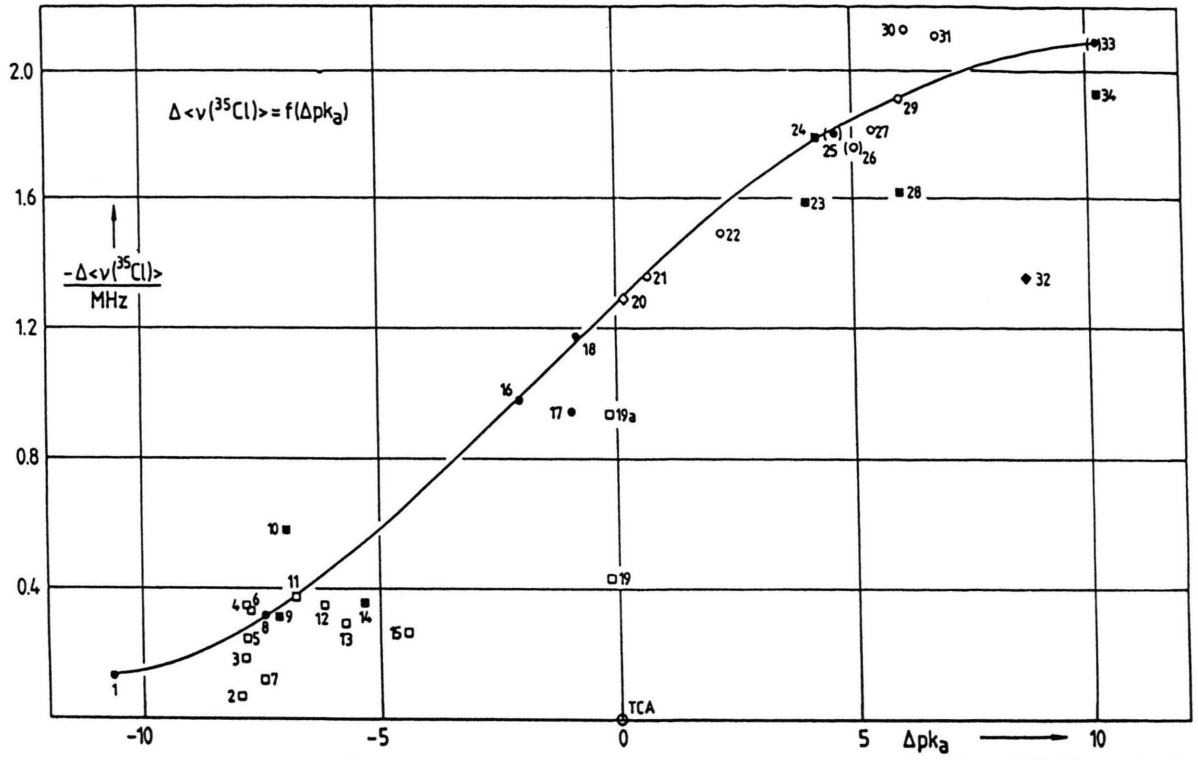

Fig. 2. Mean frequency shift $\Delta\langle\nu(^{35}Cl)\rangle$ in the compounds TCA · X as a function of Δpk_a (see (1) and (2)). The molecules correspond to different X. 1: Acetonitrile; 2: o-Toluic acid; 3: Benzoic acid: 4: Acetone; 5: m-Toluic acid; 6: Benzaldehyde; 7: Phenol; 8: Cyclohexanone; 9: o-Methylbenzaldehyde; 10: p-Methylbenzaldehyde; 11: Acetophenone; 12: Anisaldehyde; 13: Ethyl acetate; 14: 2,4,6-Trimethylbenzaldehyde; 15: tert-Butyl alcohol; 16: Acetamide; 17: α-Pyrrolidine; 18: Dimethylacetamide; 19: 2,6-Dimethyl-γ-pyrone; 19a: TCA · 2,6-Dimethyl-γ-pyrone; 20: Pyridine-N-oxide; 21: 4-Methylpyridine-N-oxide; 22: 3-Bromopyridine; 23: Aniline; 24: N-Methylaniline; 25: Pyridine; 26: 4-Methylquinoline; 27: 4-Methylpyridine; 28: N,N-Diethylaniline; 29: 2,4-Dimethylpyridine; 30: 2,6-Dimethylpyridine; 31: 2,4,6-Trimethylpyridine; 32: Ammonia; 33: Triethylamine [2]; 34: Triethylamine. References: □ [1]; ● [2]; ○ [7]; ◇ [10]; ◆ [11]; ■ this paper [19].

quency statistics is shown in Figure 1. Therefrom a mean crystal field effect on the ^{35}Cl NQR of ± 500 kHz was figured out, which may be interpreted as a deviation of the acting electric field gradient, EFG, from the intramolecular EFG at the site of the nucleus ^{35}Cl within $\pm 1.5\%$. In case of compounds $Cl_3CCOOH \cdot B$, this is an incorrect interpretation. These compounds belong to the group of proton charge transfer complexes, and the shift in the EFG (^{35}Cl) is a mixture of the intramolecular proton transfer action and the influence of the vdW field [17, 18]. In Fig. 2 it is shown how the mean ^{35}Cl NQR frequency of the CCl_3 group in the molecular compounds $Cl_3CCOOH \cdot B$ depends on the pK_a of the molecule B. On the side of large negative pK_a, e.g. CH_3CN or $(CH_3)_2CO$, one may safely assume a vanishing proton transfer but vdW interactions $(H_3CCN)\cdots H-O-R$, $((CH_3)_2CO)\cdots H-O-R$.

The changes of the EFG (^{14}N) in complexes AB, where A is Cl_3CH and B is a nitrogen or oxygen containing molecule, are mainly due to the interaction in AB as a proton transfer complex [22]. Complexes formed by phenols and anilines belong to this class of compounds, too [23].

Several Solid States in one Compound Solids as a Function of the Thermodynamic State Functions T, P

An obvious method for creating several solid states with a homogeneous solid A is the search for phase transitions as a function of T and P. With respect to our goal the variables P and T would be appropriate, but for the reasons given above we shall not consider aspects of transitions as $f(P)$.

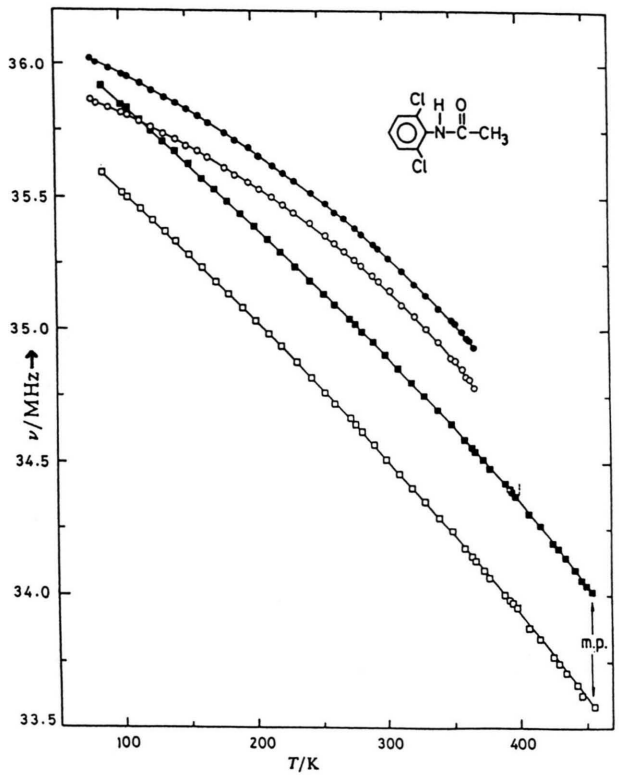

Fig. 3. Temperature dependence of the ^{35}Cl NQR spectrum of 2,6-$Cl_2C_6H_3NHCOCH_3$, phase I and phase II. ○, $\nu(^{35}Cl^{(6)})_{II}$; ●, $\nu(^{35}Cl^{(2)})_{II}$, □, $\nu(^{35}Cl^{(6)})_{I}$, ■, $\nu(^{35}Cl^{(2)})_{I}$ [25].

On varying the temperature, in molecular crystals often a phase transition (of first or higher order) occurs. Then we have the situation of two (or more) solid states, unfortunately at different temperatures. The structures of the phases have to be determined, and also the atom (group) properties, e.g. NQR, has to be studied and one finds the change of the vdW interactions of atom (group) A_i and A'_j for several distances $d(A_i, \ldots, A'_j)$ because from different phases different intermolecular distances follow. For an example of the use of two solid states of one compound and the study of crystal structures and ^{35}Cl single crystal NQR, see [24]. The main drawback of following this way to several solid states for one compound is the unpredictability whether a phase transition as a function of T occurs or not; the researcher can not work on the project he has in mind by plan.

The basic situation is similar for compounds crystallizing with different structures by variation of the crystallization conditions, e.g. the solvent. One may find metastable phases by crystallizing from different solvents and a stable phase from the melt if there are shallow minima in the Gibbs free energy. In Fig. 3 the results of an investigation of the stable and the metastable phase of 2,6-dichloroacetanilide is shown. The structure of the two phases has been determined and the ^{35}Cl NQR was measured on single crystals of both phases by Zeeman spectroscopy [25]. Each phase shows a ^{35}Cl NQR doublet assigned to $Cl^{(2)}$ and $Cl^{(6)}$ of the dichlorophenyl ring. The splitting is due to both, the intramolecular unequal electron distribution caused by the interaction of the dichlorophenyl ring system with the geometrically and electronically asymmetric acetamide substituent and the different vdW fields at $Cl^{(2)}$ and $Cl^{(6)}$. More obvious, the mean vdW fields at the chlorine sites differ considerable in the two phases of the compound.

Several Solid States of a Molecule in Solids with Several Molecules in the Asymmetric Unit of the Crystal Structure

A quite common type of several solid states of a molecule in the solid is the situation of multiple occupancy of the asymmetric unit in the unit cell of the crystal. Particularly in molecular solids, less often in ionic or metallic solids, it is found that the asymmetric unit contains more then one molecule. Classical examples are the carbon tetrahalides CCl_4 and CBr_4. In the ^{35}Cl NQR spectrum of CCl_4 16 lines are observed, and also 16 lines in the ^{79}Br NQR spectrum of CBr_4 at $T = 77$ K [26]. In both compounds the overall width of the spectrum is quite small. The 16 lines show that 4 molecules must be in the asymmetric unit and the four halogen atoms of each molecule are crystallographically independent. Symmetry and frequency differences are a consequence of the vdW potentials in the solid state. We can speak of 4 solid states of the molecules CCl_4 and CBr_4, respectively, in the 16 NQR line phases. It is worthwhile mentioning (see also above) that both compounds show, as a function of temperature, more than one phase characterized by the crystal symmetry and the space group. Why the multiplicity of molecules in the asymmetric unit appears, why one has this variety of vdW interactions halogen-halogen, is difficult to answer. A possible explanation is a Jahn-Teller effect, introduced by the vdW potentials, which increases the energy states, lowers the total energy of the solid, and stabilizes it. An example for this type of sever-

al solid states is presented in [27], where for one chemical compound, guanidinium (bis)-monochloroacetate, $C(NH_2)_3^+(ClH_2CCOO^- \cdots HOOCCH_2Cl)$, two phases with different structures have been found, one of them with two formula units in the asymmetric unit. In this compound, with the change of the phase not only the vdW potentials change but also the Coulomb field because we deal with an ionic compound.

As in the case of "several solid states" as a function of p, T, the situation is not satisfying. The experimentalist is in his goal to study vdW interactions in hand of nature. A third way, however, which we shall discuss now, seems to be the most flexible one in the "Several Solid States" concept.

Several Solid States by Chirality

Optically active molecules can crystallize in two solid states, on one hand as a (−) or (+) crystal and on the other hand in the optically inactive (±) state. The two states differ in the intermolecular interactions. The (±) crystal has a center of symmetry, which is absent for the (−) and (+) crystal.

With two optically active but chemically identical centers in the molecule, three different solid states can be produced. An example: In the ethane derivative 1,2-Cl_2-1,2-carboxylic acid, HOOC–CHCl–CHCl–COOH, there are two chirality centers, the two CHCl-groups. The mesoform of the molecule is defined by intramolecular combination of (+) and (−), having consequently a mirror plane as a molecular symmetry element. The (+, +) and (−, −) molecules crystallize with acentric symmetry elements and intermolecular fields which differ from those of the mesoform. A third solid phase, the combination of equal amounts of (+, +) and (−, −) molecules, is optically inactive as the mesoform but has different vdW potentials.

The synthesis of molecules with several optical active centers is in these days quite an advanced object of synthetic organic chemistry. Therefore, in principle, many combinations of atoms and groups could be studied in their vdW interaction by varying the distances via several solid states of chiral molecular solids. In [28] we present an example of this promising type for vdW potential studies by several solid states, the crystal structure and ^{35}Cl NQR of (−) β-(trichloromethyl)-β-propiolactone and a comparison with the (±) solid state [29]. We note here that we found in the (±) crystal a single carbonyl band in the infrared spectrum and a doublet in the (−) compound, the center of gravity of the latter one being shifted with respect to the position of the band in the (±) phase.

It seems that this way of "several solid states", using the chirality of molecules, is an interesting one in the study of vdW interactions.

With the different crystal structures and differing hyperfine (or other) interactions, one may evaluate the vdW fields. By calculating on a sound basis (Hartree-Fock self consistent field, HFSCF), the electron density distribution in the molecule in question may be calculated. Than, considering the next nearest neighbors by expanding the calculations to a cluster, one can evaluate the electron distribution of the molecule in the solid and therefrom the intermolecular potentials and the physical properties of atoms and groups in the molecule in the solid state.

Schmidt et al. [30] have performed such calculations, e.g. for 1,2,3-trichlorobenzene, the solid state of which belongs to the group of compounds with more then one molecule in the asymmetric unit, and for which compound the crystal structure is well known by X-ray diffraction combined with single crystal ^{35}Cl NQR spectroscopy [31], by neutron diffraction [32], also at different temperatures [33] and by single crystal ^2H NMR [34]. The influence of the crystal field shows up clearly in these calculations, and qualitative agreement between experiment and theory is found.

I am grateful to the "Deutsche Forschungsgemeinschaft" and to the "Fonds der Chemischen Industrie" for support.

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