Weak Chemical Interactions

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PREFACE

There are currently two types of weak interactions in chemistry, often referred to as non-valent interactions. These are hydrogen bonding and halogen bonding. Meanwhile, weak interactions play a significant role in the chemistry of molecular crystals and other systems, determining their structure and physical properties. The present book deals with the nature of both types of weak interactions. The greatest attention is paid to all types of hydrogen bonds, from weak to ultrashort, and to their characteristics in vibrational spectra, i.e., frequencies, half-widths and intensities, as parameters necessary for their diagnosis. The results of the study of vibrational spectra of halogen-halogen bonds are also presented, which allow us to draw a certain conclusion about its nature.

The text contains a large number of Raman spectra of compounds – organic and inorganic. All of them were obtained in the course of the author's work.

The book is addressed, first of all, to students and scientists whose interests lie in the field of research of chemical, biological, pharmaceutic systems.

The author will be grateful for the comments and feedback sent to the address: kolesov@niic.nsc.ru

INTRODUCTION

Weak interaction between molecules generates the occurrence of molecular crystals. And although crystals of some simple substances (hydrogen, halogens, nitrogen, and oxygen), organometallic compounds, crystals of polymers and proteins are also referred to as molecular crystals, we will discuss here the most common molecular crystals formed by small organic molecules.

Weak interactions include hydrogen, halogen and van der Waals bonding. Van der Waals bonding, i.e. the interaction of random and permanent dipole moments of neighboring molecules is purely electrostatic, well known and will not be discussed here. Therefore, the purpose of this work is to describe the role of hydrogen and halogen bonds in the formation of molecular crystals.

The interaction of atoms with each other is determined by several components that are predominantly electrostatic in nature [1]. Chemical bonds formed with the electrostatic participants are called non-valent and are classified as weak. However, the bond becomes strong if molecular orbitals are occurred and electron density shared on them. In this case, the bond is usually called valent.

Hydrogen and halogen bonds have been increasingly and persistently attributed in the literature to non-valent interactions. Hydrogen bonds, however, vary quite widely, from weak to ultrashort, and it is not clear whether the entire range can be classified as non-valent. The nature of the halogen bond is also still under discussion. The aim of the present book is precisely to find out to which of the interactions, valent or non-valent, the last two types of bonds belong. The book pays special attention to hydrogen bonding because of its great importance and prevalence in chemistry.

The hydrogen bond energy is about an order of magnitude higher than the van der Waals energy, but is the weakest among all types of valent bonds.

Hydrogen bonding has been discussed very intensively in the literature during the entire 20th century, but in recent years the level of discussion has been decreasing. The reason for this is the recently available modern quantum chemical calculation programs. The result of the calculation is usually a description of the molecular orbitals and the vibrational spectrum of the compound. This is very important information. However, researchers are often interested in issues related to trends, functional dependencies, and the main factors influencing certain characteristics of compounds to make it possible to predict their properties from their composition and structure. This fully applies to the assessment of the characteristics of hydrogen bonds. In the first chapter of this book, an attempt is made to discuss issues related to the general principles of hydrogen bond formation. Knowledge of these principles makes our work conscious and allows for meaningful experimentation.

The hydrogen bond is significantly inferior to the traditional chemical (valent) bonding in strength (energy), but even more significantly surpasses it in a variety of properties. The length of a hydrogen bond of the same type can vary over a broad area, and its spectroscopic parameters in vibrational spectra vary so much that the reliable assignment of the bands in the spectrum to hydrogen bond vibrations is still a difficult problem.

Over the past 50-70 years, numerous attempts have been made to describe hydrogen bonds, mainly in terms of their structural parameters and manifestations in vibrational (IR and Raman) spectra. A large number of monographs and reviews on hydrogen bonds in various systems have appeared [1-10]. However, the authors' desire to give an exhaustive description of the structural parameters and spectra of all compounds that form the full range of hydrogen bond properties led to excessive detail in the description of experimental data, complicating a clear presentation of the subject of the research. The complexity of the definition (or classification) of the hydrogen bond lies in the fact that it can involve various groups of atoms of the periodic table (oxygen, nitrogen, carbon, halogens, and metals), and in some cases, individual molecular orbitals. And in each case, the properties of the bond become deeply individual. In addition, the simplest (and most common) hydrogen bond consists of three atoms: donor, acceptor, and hydrogen. And if the structural position of the donor and acceptor is determined with acceptable accuracy, then the position of the hydrogen atom on the bond is often not established at all, but is set by the experimenter. However, it is the latter parameter that determines the spectral properties of the hydrogen bond. It is therefore clear that for many years, right up to recent years, hydrogen bonding constituted a difficult (almost incomprehensible) problem.

This book does not provide a detailed description of each of the huge number of hydrogen bond manifestations, but an exposition, close to phenomenological, of the conditions and features of the occurrence of hydrogen bonds in a wide range of their energies.

It is assumed that the reader has a basic understanding of the hydrogen bond. Therefore, many of its non-fundamental details are not considered here: single- and multicenter bonds, bond angle, etc. Moreover, in order to focus the reader's attention on the main physical and chemical aspects of the hydrogen bonding, and not on all possible manifestations of it, further in the text we will consider mainly the O–H···O bond as the most widespread and studied and only rarely resort to other types of hydrogen bonding.

The study of halogen interaction is only at the beginning of its way. The interpretation of experimental data given in the literature is mostly declarative and lacks sufficient substantiation. For this reason, the aim of the present work is to find out to what extent the electron density in the halogen-halogen contact is isolated on the contacting atoms, and the halogen-halogen bond itself is non-valent.

The main method for studying weak bonds adopted in this work is Raman spectroscopy of molecular crystals. In order for the reader to clearly understand how the results presented here were obtained, the first chapter provides a description of the methodological features of obtaining and processing the spectra of molecular crystals. Examples of measuring polarized spectra of crystals as a source of additional and valuable information are presented. The second chapter offers a general description of the hydrogen bond, developed by the author in recent years. Chapters 3-7 are devoted to the study of various types and aspects of hydrogen bonding, from weak to extremely strong, inter- and intra-molecular. The last chapter presents the results of a study of the interaction between halogen atoms in molecular crystals and their adaptation to the existing concept of the halogen bonding.

CHAPTER 1

METHODOLOGICAL ASPECTS OF RAMAN SPECTROSCOPY OF MOLECULAR CRYSTALS

1.1. General remarks

As already mentioned, intermolecular interaction in molecular crystals is determined by the weak van der Waals interaction and about an order of magnitude stronger hydrogen bonding (but still weak in relation to other, traditional types of chemical bonds). The relationship between the one and the other can be very different. For example, amino acids have developed hydrogen bonds and are capable of forming bulky networks of hydrogen bonds, and the van der Waals interaction can be neglected. Compounds with an acetamide group, for example, paracetamol, form hydrogen bonds in only one plane, and interplanar interactions are van der Waals interactions. In crystals of benzoic acid, two neighboring molecules are linked by a strong (relatively) hydrogen bond, forming dimers, and the interaction between the dimers is van der Waals.

The most interesting feature of molecular crystals is the strong dependence of their structure on temperature and pressure. The organic molecules that make up the crystal, as a rule, are low-symmetry, the network of their bonds with neighboring molecules reflects the structure of the molecule, and the bonds themselves are weak and easily subject to stretching or compression under external influence. This causes the fact that with a change in temperature or external pressure, various intermolecular bonds in the crystal change to different degrees, as a result of which the molecules in the unit cell are forced to correct the relative orientation, tracking the change in all interactions with the environment. In other words, molecules in a cell are orientationally mobile. This mobility includes both small rotations of molecules in the cell as a whole, and rotations of individual fragments of a molecule relative to each other, a change in the conformation of molecules, a change in the direction of hydrogen bonds (i.e., switching a bond from one acceptor to another), the emergence of multicenter hydrogen bonds, and others. Consequently, by changing the lattice parameters of a crystal, one can trace how the intermolecular interactions are organized in it. It is the orientational and conformational mobility of molecules, as well as the switching of hydrogen bonds and the formation of new ones, and finally, structural phase transitions, are the subject of study of molecular crystals.

Another compelling reason for the need to study the dynamics of molecular crystals is as follows. Recently, approaches to the study of biological objects have been persistently developed. These compounds are so complex that the use of traditional physical methods in their usual form often encounters serious difficulties. And if NMR-, EPR-, and Mössbauer spectroscopy deal with individual nuclei (atoms) in molecules and their use can be quite effective, then all $3n$-6 normal vibrations will inevitably appear in the vibrational spectrum (excluding the case of resonance on vibrations of one selected fragment in molecule), which, of course, causes the overlap of vibrational modes and the registration of broad structureless bands in the spectrum.

At the first stage, however, one can start by investigating small components, the “building blocks” from which complex biological objects are built. Some of these components are amino acids and compounds with an acetamide group, many of which are drugs. Studies of molecular crystals formed by these compounds are extremely useful both in themselves and in terms of their properties as a component of biological molecules.

The vibrational spectrum of a crystal obtained under standard conditions (ambient temperature, zeroth external pressure) does not involve information about the degree and hierarchy of various weak intermolecular interactions in the crystal. To obtain this information, it is necessary to vary the crystallographic parameters using external impacts.

The effects observed in the vibrational spectra of molecular crystals, depending on the external influence, are so diverse that it is currently impossible to make a general description of them. Therefore, this chapter will discuss, on the one hand, the methodology and set of experimental techniques used in the study of molecular crystals, and on the other hand, we will try to show, using several specific examples, what a researcher may encounter when working with molecular crystals.

The lattice parameters can be varied using temperature or pressure. Undoubtedly, the application of external pressure is the most direct and immediate way of changing the lattice parameters. However, since the experiment is carried out at room temperature, many lines in the spectrum are already significantly broadened, and in the low-frequency region of crystal vibrations they are broadened so much that they overlap with each other and form wide bands that do not allow the correct decomposition procedure into components. This deprives the experimenter of the opportunity to trace the frequency of the most interesting vibrations, namely, translational intermolecular modes, which directly reflect changes in the hydrogen bond network. A change in temperature in the range of 4 K – 300 K (at higher temperatures, many molecular crystals begin to break down) also makes it possible to vary the lattice parameters, but in a smaller range than in the experiment with pressure (the lattice parameters change in the temperature range of 4 K – 300 K to approximately the same degree as when the external pressure changes from 0 to 1▯ 2 GPa).

However, with decreasing temperature, the lines narrow significantly, which, firstly, often reveals new spectral features that are inaccessible at room temperature, and, secondly, it allows one to describe the behavior of the spectral parameters of vibrational modes (frequency, half-width, and integral intensity) by well-known analytical expressions that facilitate detection and interpretation of ongoing structural changes. This makes it necessary to measure spectra of molecular crystals at different temperatures. In what follows, we will use temperature as a tool for influencing the crystal lattice parameters.

1.2. Methodological features

Temperature measurements

Modern optical helium cryostats for Raman measurements are installed in place of the object stage of the entrance microscope of the spectrometer. Temperature controls are completely computerized, and in reality, there is only one problem - the problem of achieving adequate thermal contact of the sample with the cryostat cold finger. The use of various special adhesives for this purpose is not an optimal solution, since there is always the possibility of strong luminescence from the adhesive. In addition, it is often necessary to install the sample on the cold finger in such a way that the contact area between the cold finger and the crystal is minimal, for example, when installing on a thin crystal face or the end plane of a needle-shaped specimen.

The difficulty in recording the spectra of both powders and crystals at different temperatures is establishing reliable thermal contact with the cryostat coolant line so that the recorded temperature of the coolant line corresponds to the sample temperature. An almost ideal solution is to place the sample in a heat-conducting medium, for example, metallic indium, which, on the one hand, is (subject to its high chemical purity) soft and ductile enough so that a fragile and small sample can be embedded in it, and on the other hand, provides a reliable thermal contact of the sample with the cold finger. For this purpose, cavities are made in the copper substrate, which is usually mechanically contacted to the cryostat cold finger, and filled with metallic indium. Then, in indium, pits are squeezed out in such a shape that the sample placed in them takes the desired orientation. The installed sample is pressed with indium on all sides by careful movements (the crystal is very fragile!) so that only its upper edge remains open for recording the spectrum. The powdered sample can be pressed into metallic indium with little pressure.

Polarization measurements

Polarization measurements make it possible to compare the direction of atoms displacement in the vibrational mode with the crystallographic direction. This greatly enriches the information obtained and makes polarization measurements necessary in many cases. However, measuring polarized spectra as a function of temperature is extremely labor-intensive and requires at least three times more effort than the same measurements of unpolarized spectra. A good alternative is to measure polarized spectra at alone (room) temperature and unpolarized spectra at different temperatures. Examples of studies of molecular crystals of amino acids using polarization measurements, as well as the significance of the information extracted and its exceptional importance for understanding the processes occurring in crystals will be given in paragraphs 1.3 and 1.4.

When measuring the polarized spectra of molecular crystals, the following aspects should be taken into account. 1. Crystals with low symmetry are birefringent, i.e. capable to rotate the plane of polarization of the incident and scattered light. For this reason, it is always best to choose the direction of the polarization vector of the incident light parallel to the crystallographic axis. In this case, the rotation of the plane of polarization is minimized. 2. Many crystals (for example, all crystals of amino acids except glycine) are chiral (this does not apply to racemates, i.e. crystals containing both enantiomers equally). Both effects, i.e. birefringence and chirality, can either enhance or neutralize each other. 3. In Raman microscopes in the backscattering geometry, the effective depth of the sample, from which the scattered radiation is collected, is small and is regulated by the confocal aperture. Limiting the effective scattering depth dramatically reduces the effect of rotating the plane of polarization. Otherwise, it would be difficult to explain why the lines in the spectra presented below are often strictly polarized, i.e. demonstrate high intensity in one crystallographic direction and zero in the other two.

Crystal orientation

Of course, a reliable determination of the direction of the crystallographic axes is carried out on a single crystal X-ray diffractometer. However, this procedure is time consuming and not always justified. The point is that to record the temperature dependences of polarized spectra, it is necessary to have several samples (this is dictated by the measurement conditions, see below). Samples of crystals, as a rule, are small in size (up to tenths of a millimeter), and their mechanical strength is extremely low. In other words, the prepared sample may break, be lost, or become unusable for measurements for some reason. Therefore, a reasonable alternative is to select several samples for measurement and orientate them using their Raman spectra.

Monoclinic crystals usually have the form of either elongated polyhedrons (needles) or plates, i.e. have a selected direction coinciding with one of the crystallographic axes. Let's conditionally call this selected direction the z-axis. The other two axes, conventionally x and y, are located in the cross section perpendicular to z, and to find them, it is necessary to compare the spectra polarized along the directions perpendicular to the sample faces as shown in Fig. 1.1.

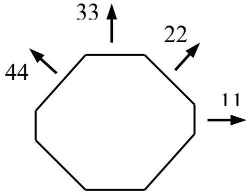


Fig. 1.1. Registration of polarized spectra in the crystal plane perpendicular to the selected z-axis to determine the orientation of the sample

For this, it is not necessary to obtain high-quality spectra in the entire range; it is sufficient to have, for example, the spectra of the low-frequency region of crystal vibrations. If a pair of spectra polarized along mutually perpendicular directions (in the figure, for example, directions 11 and 33) differ from each other in the position and intensities of the main lines, then these directions coincide with the crystallographic axes. The tabular values of the Raman tensor for a given symmetry group are determined for fixed directions of the crystallographic axes of this group.

Therefore, the Raman tensor for any of the vibrational modes of the spectra under consideration takes the same value when rotated by +45° and –45° around z (the components of the rotated tensors may have different signs, but the line intensity in the polarized spectrum is proportional to the square of the Raman tensor component). Consequently, the spectra of the other pair, polarized along the directions rotated by ~ 45 relative to the first, (i.e., spectra 22 and 44), should be essentially the same. Thus, we get three selected directions coinciding with the crystal axes, and we can carry out polarization measurements. The binding of the selected directions to specific crystallographic axes of a previously known crystal structure can be done later, after obtaining complete spectra in different directions, in accordance with the intensities of characteristic vibrations in the polarized spectra. The modes of stretching vibrations N–H···O and O–H···O of hydrogen bonds are especially useful for this purpose, since they are polarized and their being in the spectrum usually does not cause difficulties. The proposed method for determining the direction of the crystal axes is not rigorous, but it is accurate enough for carrying out polarization measurements.

Registration and processing of spectra

When recording spectra for a long time, it is difficult to maintain constant conditions that provide the required spectral measurement accuracy. A slight change, for example, in room temperature, will shift the frequency calibration of the spectrometer by a few inverse centimeters. In addition, the intensity of the recorded spectra depends on the parameters of the input and output radiation paths, which the experimenter cannot completely control, as a result of which the measured spectra are different in band intensities for reasons not related to the state of the sample. Therefore, before starting to process the arrays of sample spectra obtained during temperature and polarization measurements, it is necessary to correct the spectra in wavenumber and intensity.

Wavenumber correction is achieved by recording a stable line, laser line (when spectrometer is supplied with “notch” or “edge” filters) or some other reference line (for example, lines of Ne-lamp), in each spectrum.

To correct spectra by intensity, the easiest way is to carry out the following procedure. First, the integral intensity of the entire spectrum obtained is determined. After this, as a result of computer decomposition of the spectrum into components, the integral intensity of the desired vibrational mode is found. Dividing the latter by the total integral intensity of the spectrum will make it possible to determine its relative intensity in the spectrum, which does not depend on the changing conditions for recording the spectrum.

Vibrational spectra of molecular crystals are very complex and usually consist of several tens of lines in the range from ~20 to 3600 cm^{-1}.

In this case, only the modes of stretching vibrations of the hydrogen atom in the C–H, N–H, and O–H bonds can be assigned with sufficient certainty. All other vibrations are mixed, and it is rather difficult to determine the degree of participation of various bonds or fragments of the molecule in them on the basis of experimental data; one can only give a tentative description. Quantum-chemical calculation of vibrational spectra of molecules using modern programs gives very good results, but it should be borne in mind that the reliability of the calculation extends mainly to intramolecular vibrations. And if there is a need to have information about the spectrum of intramolecular vibrations, then such a calculation is uncontested. However, low-frequency crystal vibrations, as well as various deformations of molecules, and torsion modes, which are directly dependent on intermolecular interactions, are no longer so reliably determined by calculation. In this case, the calculation is carried out, as a rule, for one specific structural form of both the molecule and the crystal and does not cover possible transformations with changes in temperature.

For this reason, as a first step, one can try to find those features in the behavior of the spectral characteristics of vibrations that, on the one hand, will make it possible to reliably assign a given line, and on the other hand, to establish the structural changes occurring in the crystal. These features are manifested primarily in the temperature dependence of the spectral parameters of the mode. The wavenumber of each mode, especially low-frequency mode should, as a rule, decrease with increasing crystal temperature, which is a consequence of the anharmonicity of the interaction potential and the associated increase in the interatomic distance (see Appendix 3). If this does not happen, then, most likely, we are dealing with such a change in the orientation of the molecule in the cell, which causes an increase in the intermolecular hydrogen bond and subsequent inductive effects in the molecule. The intensity of low-frequency modes (<600 cm^{-1}) increases with increasing of temperature due to an increase in the population of the exited states of given vibration, and the intensity of high-frequency modes should not change normally with temperature. However, it is precisely in the behavior of the intensity of vibrational modes that various anomalies are most often observed, the cause of which is not always possible to find out.

Of course, the discussion of the spectra is based on concepts common to all molecular crystals, according to which the frequency range 20–200

cm^{-1} includes crystalline (intermolecular), 150–600 cm^{-1} torsion, 600–1700 cm^{-1} – intramolecular, and 2500–3600 cm^{-1} stretching C–H, N–H, and O–H vibrations. The latter are usually hydrogen bonded.

In order to show the effectiveness of Raman spectroscopy using polarization and temperature measurements, we will give several examples of studies of molecular crystals, covering various classes of compounds.

1.3. Spectra of amino acid crystals

Amino acids include organic compounds, the molecule of which simultaneously contains carboxyl and amine groups (Figure 2.1).

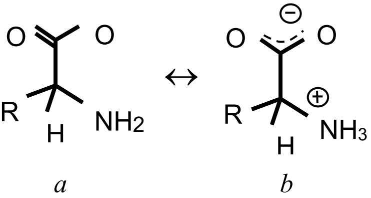


Fig. 1.2. Amino acid in normal form (*a*) and in the form of zwitterion in crystal (*b*).

Figure 1.2, *a* shows the amino acid molecule as it exists in the gas phase. When a crystal is formed, the hydrogen atom of the carboxyl group is transferred to the amino group of the neighboring molecule due to the greater affinity of the nitrogen atom for hydrogen. In this case, a zwitter ion (double ion) is created, positively charged from the side of the formed NH_3^+ group and negatively from the side of the COO residue. (The question of the magnitude of the charge can be solved using a quantum chemical calculation).

The simplest amino acid is glycine, NH_2 CH_2 COOH, where one hydrogen atom plays the role of the radical fragment R (Fig. 1.2).

Glycine crystallizes in three polymorphs, α, β, and γ. The structure of α-glycine is shown in Fig. 1.3.

We will not discuss the entire spectrum of glycine in this section. Let us consider only a small part of it, concerning the features of the behavior of the bifurcation hydrogen N–H···O bond in the α-glycine crystal.

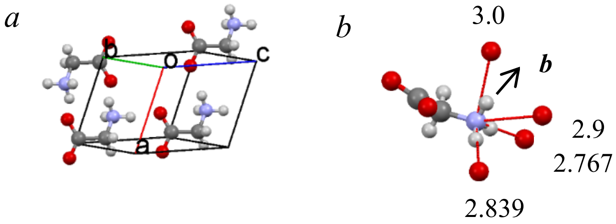


Fig. 1.3. *a* – Fragment of the α-glycine structure. *b* – A diagram of three hydrogen bonds of the NH_3 group with the acceptor oxygen atoms of neighboring molecules (the bond in the ***b*** crystallographic direction is bifurcational). The N···O distance (Å) is placed next to the corresponding acceptor.

The polarized spectra of low-frequency crystalline vibrations of α-glycine at 5 K are shown in Fig. 1.4. Figure 1.5 shows the dependences of the peak position, the half-width, and the intensity of the 118 cm^{-1} mode, which is intense in the ***bb*** spectrum. All three spectral characteristics of the mode demonstrate an example of normal behavior with temperature, i.e. behavior characteristic of anharmonic vibrations (see Appendix 3).

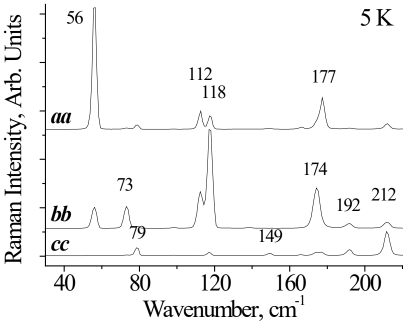


Fig. 1.4. Polarized spectra of crystalline vibrations of α-glycine at 5 K. The definitions ***aa***, ***bb*** and ***cc*** imply the directions of the polarization vector of the incident (first symbol) and the scattered (last symbol) light with respect to the crystal axes.

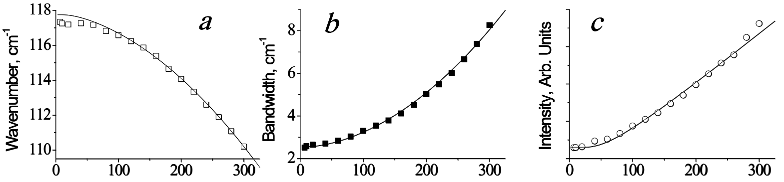


Fig. 1.5. Dependence of the peak position (a), half-width (b) and the relative intensity (c) of the 118 cm^{-1} mode on temperature of α-glycine.

Fig. 1.6 shows the dependence of the peak position of the 73 cm^{-1}mode in α-glycine as an example of the anomalous behavior of the vibrational mode on temperature.

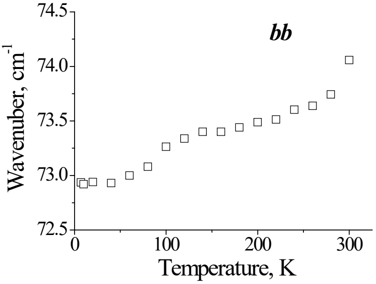


Fig. 1.6. Peak position of the translational mode 73 cm^{-1} as function of temperature in α-glycine.

The unusual increase in the vibration frequency with increasing temperature is most likely related to a change in the intermolecular hydrogen bond, since the frequency range ~100 cm^{-1} refers to crystalline (external) vibrations. The hydrogen bond in α-glycine in the direction along the ***b***-axis of the crystal (i.e., in the direction of polarization of the incident and scattered light) is bifurcational (Fig.1.3, *b*), and an increase in the frequency of the mode vibration with increasing temperature can be caused either by an increase in the entire hydrogen bond (which is unlikely), or an increase in the mode of that component of the bifurcation coupling, which is characterized by a larger force constant. To find out the reason for the anomalous behavior of the mode, it is necessary to turn to what happens in the high-frequency region of the stretching N–H vibrations of a given N–H···O hydrogen bond.

The frequency range 2500-3600 cm^{-1}, the most stable and reliable from the point of view of assigning the observed lines, includes stretching vibrations of CH, CH_2 and CH_3 groups (2900-3100 cm^{-1}), hydrogen-bonded N–H ($\leq$ 3500 cm^{-1}) and O–H ($\leq$ 3600 cm^{-1}). And if the vibrational frequencies of C–H usually very weakly depend on temperature, then the dependence of the vibrational frequencies of N–H and O–H is much stronger due to the change in the lengths of hydrogen bonds with a change in the temperature of the crystal. The polarization of these modes is rigidly related to the direction of the corresponding hydrogen bonds in the crystal lattice.

Fig. 1.7 shows the polarized spectra of α-glycine in the range of C–H and N–H stretching vibrations. Modes at 2975 and 3009 cm^{-1} refer to symmetric (in phase) and asymmetric (in out-of-phase) stretching vibrations of the CH_2 group, respectively. Band 3127 cm^{-1} – to the vibration of one of the hydrogen-bonded N–H, 2899 cm^{-1} – to the other.

The third intense and wide band, 2607 cm^{-1}, also relates to N-H hydrogen bonded vibrations, but its position in the spectrum and some features are so atypical for a vibrational mode of this type that there are still no comments on this topic in the literature.

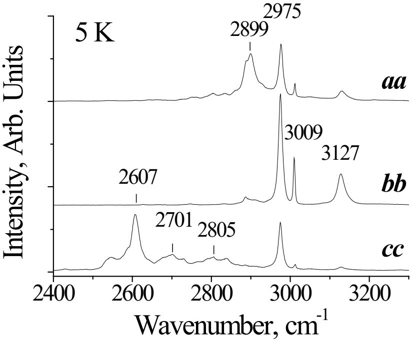


Fig. 1.7. Polarized spectra of α-glycine in the range of C–H and N–H stretching vibrations.

Let us consider in more detail the behavior of the 3127 cm^{-1} mode, since it is related to the bifurcation hydrogen bond along the crystallographic direction ***b*** of the crystal (Fig. 1.3, *b*). This mode is complex and consists of two components, 3127 and 3135 cm^{-1} (Fig. 1.8).

The dependences of the position of the maximum and the integrated intensity on the temperature of each component are shown in Fig. 1.9.

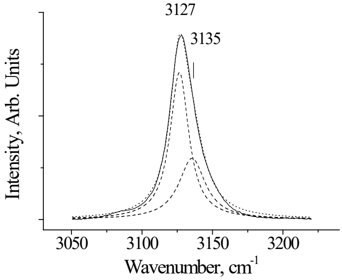
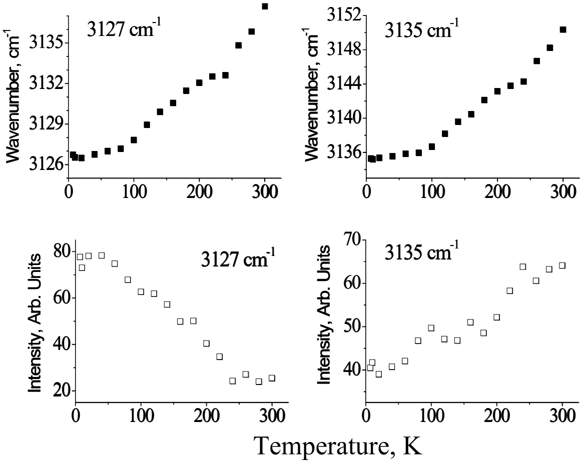


Fig. 1.8. Deconvolution of the N–H stretching vibration mode in the N–H···O hydrogen bond along the ***b***-axis of the α-glycine crystal at 5 K.



a *b*

Fig. 1.9. Dependence of the peak position and the integrated intensity of the components 3127 (*a*) and 3135 cm^{-1} (*b*) of the N–H stretching mode in the N–H···O hydrogen bond along the crystallographic ***b*** axis of the α-glycine crystal.

The vibrational frequencies of both components increase with increasing temperature, i.e. the hydrogen bond weakens. This unambiguously indicates that an increase in the frequency of the corresponding intermolecular translational mode 73 cm^{-1} (Fig. 1.6) is due to a change in the vibrational eigenvector. The intensity of the components changes in a mutually opposite direction. Consequently, the vibrations refer to two different states of the hydrogen bond: at a low temperature, the state with a stronger bond (mode 3127 cm^{-1}) is mainly populated, and at a high temperature, that with a weaker bond (mode 3135 cm^{-1}).

These simple observations allow us to draw conclusions about the nature of the hydrogen bifurcation bond. It is often believed that in a bifurcation bond, both acceptor atoms (i.e., oxygen atoms of neighboring molecules in this case) are simultaneously bonded to one proton of the N–H group using their lone electron pairs. The experiment presented here shows that in fact a proton forms a bond either with one acceptor or with another, being able to jump from one potential well formed along the N–H···O(1) bond to another related to the N–H···O(2) bond. The integral intensities of both components are determined with low accuracy due to the proximity of their vibration frequencies and overlap in the entire temperature range; therefore, at this stage, it is not possible to determine the potential barrier between two potential wells, as well as the mechanism for changing the localization of the proton at low temperatures – over- or under-barrier (tunnel). It should only be noted that the double-well potential of the bifurcation bond should not be confused with the double-well potential of each individual hydrogen bond, in which, according to theoretical concepts, one potential well (deep) is localized near the donor atom, while the other (shallower) is near the acceptor atom.

The hydrogen bond along the ***b***-axis of the crystal is one of the weakest in α-glycine, and fixing the mode of translational vibrations of this bond at 73 cm^{-1} sets the lower limit of the frequencies of translational intermolecular vibrations of hydrogen bonds in α-glycine. (It will be shown below in Chapter 4 that modes with frequencies of ~50 cm^{-1} are related to deformational intermolecular vibrations of hydrogen bonds, and this fixes the second reference point, which means that all modes with frequencies below 50 cm^{-1} are related to vibrations of van der Waals bonds).

1.4. "Anomalous" changes in the intensities of low-frequency modes in L-alanine

The vibrational modes with frequencies below 70 cm^{-1} in the spectrum of molecular crystal can refer either to bending vibrations of hydrogen bonds or to bond vibrations determined by the van der Waals interaction. Here we will try to explain what they are and how they are manifested in the spectrum of deformation crystal vibrations of hydrogen bonds. For this purpose, we present a description of the temperature dependence of the lattice vibrations of *L*-alanine crystals, demonstrating, on the one hand, the possibilities of polarization Raman spectroscopy, and, on the other hand, an attempt to explain the phenomenon that has not had a definite interpretation in the literature for a long time [1].

In 1988, Migliori et al. [2] noticed an anomaly in the temperature dependence of the intensity of two low-frequency Raman modes, 42 and 49 cm^{-1}, in *L*-alanine crystals. The intensity of the 49 cm^{-1} mode in bb polarization increased too strongly with temperature, and the 42 cm^{-1} mode too weakly compared to what was expected according to Maxwell-Boltzmann statistics. However, the change in temperature in the total intensity of both modes was normal. The authors of [2] assumed the existence of dynamic localization of vibrational energy, which could create an excessive intensity of the 42 cm^{-1} mode below 150 K. Both modes exhibit a similar behavior when the external pressure changes. This problem has been discussed for a long time in the literature by various authors, and various solutions have been proposed, but a definite point of view has not been worked out.

Fig. 1.10 shows a molecule of L-alanine in the zwitterionic form and a fragment of the structure of the crystal lattice of L-alanine.

Fig. 1.11 shows the polarized spectra of *L*-alanine in the region of lattice vibrations, and in Fig. 1.12 these spectra are shown at several different temperatures. The integrated intensities of modes 42 and 49 cm^{-1} (43 and 51 cm^{-1} at 5 K, Fig. 1.11) for different polarizations and depending on temperature are shown in Fig. 1.13. To calibrate the spectra by intensity, the 856 cm^{-1} mode was used, which, on the one hand, does not relate to intermolecular vibrations, and, on the other hand, has an energy that is high enough to make the temperature dependence of the intensity negligible.

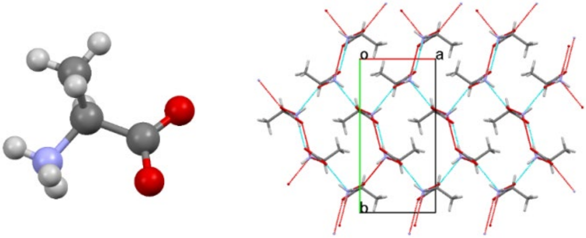


Fig. 1.10. *L*-alanine molecule in zwitterionic form and a fragment of the crystal lattice structure of L-alanine.

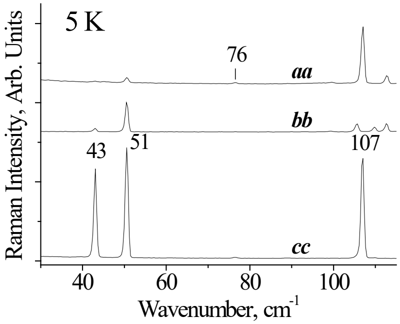


Fig.1.11. Polarized Raman spectra of *L*-alanine crystals at 5 K in the region of lattice vibrations. In the polarization spectrum designations, the first symbol indicates the direction of the polarization vector of the incident light, the second - of the scattered light with respect to the crystallographic axes of the crystal.

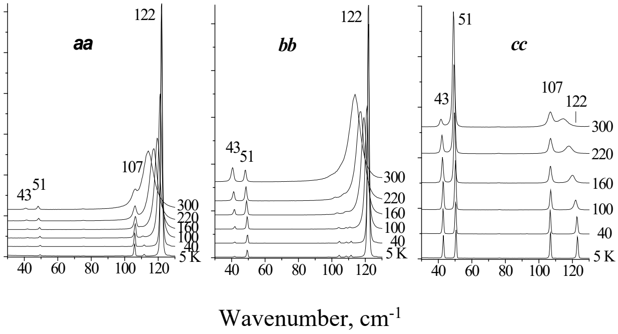


Fig. 1.12. Polarized spectra of lattice vibrations of *L*-alanine at different temperatures (polarization is indicated in the figures).

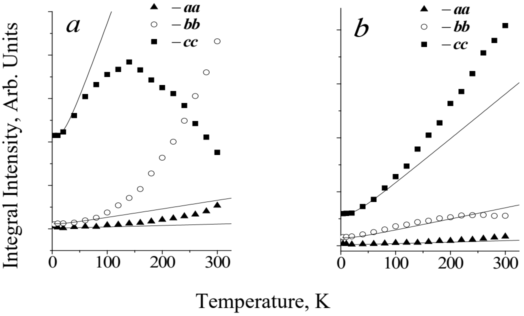


Fig. 1.13. Integral intensity of modes 42 and 49 cm^{-1} in polarized spectra depending on temperature: *a*) - 42 cm^{-1}; *b*) - 49 cm^{-1}. The solid curve for each dependence is the Maxwell-Boltzmann statistics with different initial values at low temperatures. The polarizations are indicated in the figures.

The intensity of both low-frequency modes changes with temperature in different ways, depending on the polarization of the light. The sum of intensities for each mode (i.e., the sum of intensities in ***aa***, ***bb***, and ***cc*** polarizations) is shown in Fig. 1.14 *a*, and the total intensity of both modes is shown in Fig. 1.14 *b*. It can be seen that only the latter obeys the Maxwell-Boltzmann statistics (solid curve in Fig. 1.14 *b*).

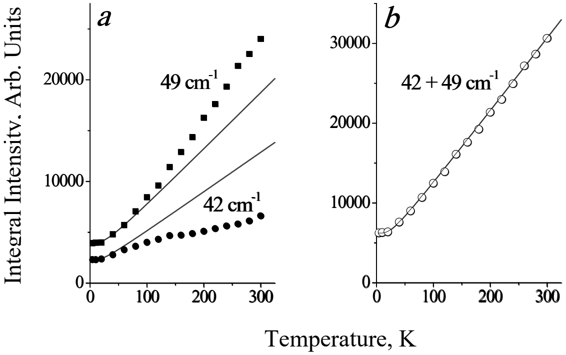


Fig. 1.14. Intensity of low-frequency modes as a function of crystal temperature: *a*) - total intensity (***aa*** + ***bb*** + ***cc***) of modes 42 cm^{-1} (solid circles) and 49 cm^{-1} (solid squares); *b*) is the sum of intensities of modes 42 and 49 cm^{-1}. Solid curves - Maxwell-Boltzmann statistics with different initial values.

Both modes show an anomalous temperature dependence of not only the intensity, but also the position of the maximum (Fig.1.15 *a*). At temperatures above 150 K, the 42 cm^{-1} mode deviates from the expected dependence to low wavenumbers, and the 49 cm^{-1} mode, on the contrary, to high wavenumbers.

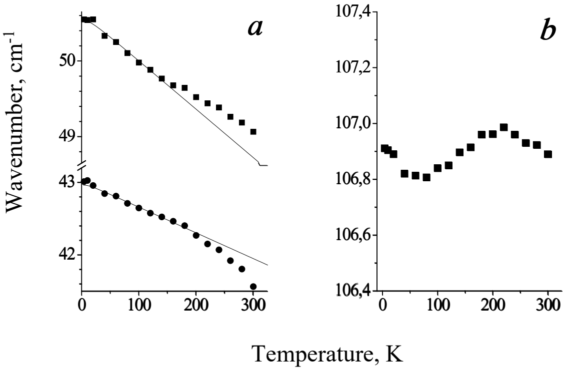


Fig. 1.15. Temperature dependence of the peak position of *a*) - modes 42 and 49 cm^{-1} and *b*) - mode 107 cm^{-1}.

To understand the anomalous behavior of low-frequency modes, it is necessary, first of all, to make their assignment. An exact description of the lattice vibrations of molecular crystals, obtained by quantum-chemical calculations, is still not available at present, but one can try to make a qualitative interpretation. The lowest vibration frequencies in molecular crystals are usually referred to as translational displacements of molecules as a whole. Taking into account the value of the force constant for a typical hydrogen N–H···O bond (~ 13 N/m) and the molecular weight of alanine (89 a.m.u), we can expect a value of ~ 100 cm^{-1} for the frequency of optical vibrations in L-alanine. The temperature dependence of the position of the maximum of the 107 cm^{-1} mode, which is intense in the ***cc*** spectrum, is shown in Fig. 1.15 *b*. The presented dependence does not reveal the steady decrease in the vibration frequency expected due to the manifestation of anharmonic effects (Appendix 3), but at the same time it agrees with the unusual behavior of the lattice parameter *c*, which demonstrates a slight decrease with increasing temperature, while the other two lattice parameters *L*- alanians, *a* and *b*, increase with temperature, which is normal. Thus, the assignment of the 107 cm^{-1} mode to the translational vibrations of *L*-alanine molecules in a chain oriented along the *c* axis of the crystal seems to be correct, which makes the assignment of the 42 and 49 cm^{-1} modes nontrivial, since the frequency of the latter is more than twice lower, and the force constant, therefore, must be four times less than the force constant of the translational modes.

Due to numerous hydrogen bonds with the environment, molecules in *L*-alanine crystals form both a three-dimensional network of hydrogen bonds and two-dimensional cycles located in mutually perpendicular crystallographic planes (i.e., ***ab***, ***bc*** and ***ac***). The crystal structure projected onto the ***ab*** plane is shown in Fig. 1.10. Some vibrational modes in such cycles can correspond to molecular displacements that characterize changes in angles rather than lengths of hydrogen bonds (i.e., a kind of bending vibration of hydrogen bonds). For example, these modes include the "breathing" vibration of molecules in a cycle. The frequency of the latter should be much lower than that corresponding to the translational displacements of molecules along the chain, which are related to purely stretching intermolecular vibrations of hydrogen bonds. Consequently, the 42 and 49 cm^{-1} modes can be attributed to such translational displacements of molecules, which result in "breathing" modes of molecular cycles. These latter correspond to bending vibrations of hydrogen bonds in the crystal lattice.

The key to understanding the anomalous behavior of the 42 and 49 cm^{-} modes on temperature and pressure is the fact that the degree of deviation of the spectral characteristics of both modes from the norm depends on the chosen crystallographic directions when recording polarized spectra (Figs. 1.12 and 1.13). This means that the orientation of the molecules in the crystal lattice relative to each other changes slightly with temperature/pressure. A change in the mutual orientation of molecules entails a change in the eigen vector of normal vibrations of the corresponding modes. The eigen vector of the vibration is directly related to its frequency. Above 150 K, the frequency of the 42 cm^{-1} mode decreases faster than expected for normal anharmonic behavior (see Appendix 3), while the frequency of the 49 cm^{-1} mode, on the contrary, is slower (Fig. 1.15 *a*). Consequently, with increasing temperature, the bending component of the complex vibration increases for the first mode (i.e., the force constant and frequency decrease), while the stretching component increases for the second mode (the force constant and frequency increase with respect to the theoretically expected). The behavior of the intensity of both modes can be understood if we take into account that the intensity of stretching vibrations (i.e., vibrations in which the length of hydrogen bonds is modulated) is much higher than the intensity of bending modes (i.e., without changing the lengths of hydrogen bonds). When the bending component of the 42 cm^{-1} mode increases with temperature, the intensity of this mode should decrease, which is observed in the experiment (Fig. 1.14 *a*). An increase in the stretching component of the 49 cm^{-1} mode should cause an increase in its intensity faster than that which follows from the Maxwell-Boltzmann statistics, which is also found in the experiment (Fig. 1.14 *a*).

Thus, the “anomalous” effects observed with a change in temperature and pressure for the intensity and position of the maximum of two low-frequency modes in the polarized Raman spectra of *L*-alanine crystals can be interpreted within the framework of simple and clear processes and without invoking any assumptions about “phase transitions” or “dynamic localization of vibrational energy”. Constant stress in the structure, accompanied by a change in the orientation of molecules in a three-dimensional network of hydrogen bonds, can explain the observed anomalies in Raman spectra corresponding to certain crystal orientations and light polarization, as a change in the relative contributions of "stretching" and "bending" components in two lattice modes. It is noteworthy that the total intensity of both modes, summed up for all polarizations, does not show any anomalies in the temperature dependence (Fig. 1.14 *b*). Since a three-dimensional network of hydrogen bonds is often formed in molecular crystals, similar anomalies in the region of low-frequency vibrations in polarized Raman spectra can be observed not only in L-alanine, but also in other compounds. For example, modes with frequencies of about 50 cm^{-1} in α-glycine show similar behavior.

Thus, the examples given in paragraphs 1.3 and 1.4 show that measurements of polarized spectra of oriented crystals at different temperatures make it possible to obtain information about the position of molecules in the crystal lattice and their response to weak external influences. The significance and content of this information significantly exceeds that which can be obtained from measurements of powders at a fixed temperature.

CHAPTER 2

GENERAL DESCRIPTION OF HYDROGEN BONDING

2.1. Definition, brief history, main stages of development

According to the IUPAC, 2011 recommendation "*The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation"* [1].

This strict definition is already fraught with the above-mentioned tendency to excessive detail and is perceived upon first reading with some difficulty. For this reason, readers are offered here another, possibly imperfect, but simpler and more compact definition: *The hydrogen bond is a weak chemical bond between the X–H group of one molecule and the electronegative Y atom of another* (*or the same*).

Usually a hydrogen bond is written as X–H···Y, where the dots represent the hydrogen bond itself. In this notation, X–H is a terminal fragment of one molecule, and Y is a terminal fragment of another molecule. X is a hydrogen bond donor, and Y is an acceptor. The electronegativity of an element that is part of a molecule is not constant and depends on the specific chemical conditions (for more details, see section 2.2).

The hydrogen bond was discovered at the beginning of the last century. It is not possible to establish the exact date of its discovery, since it is not clear from the publications of those years what exactly the authors had in mind when describing chemical reactions involving the polar group X–H. For the first time, the concept of hydrogen bonding appeared in the work of Huggins [2] and almost simultaneously in Latimer and Rodebusch [3]. The term "hydrogen bond" was first used by L. Pauling in 1930 [4]. But real interest in hydrogen bonding arose only a few more years later, when Bernal and Fowler [5] suggested that a high degree of short-range order in the structure of liquid water is provided by intermolecular bonds, which were then attributed to hydrogen bonds. This work, which assumes a