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Low-frequency vibrational spectroscopy of amides and urethanes

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Abstract. The application of the methods of low-frequency vibrational spectroscopy to studies of amides and urethanes including polyamides, polypeptides, and proteins is critically analysed. Special attention is concentrated on the spectroscopic studies of intermolecular interactions and in particular on spectral features of the intrinsic vibrations of hydrogen bonds. The methods are considered that allow one to identify experimentally the bands in the region of 90 – 130 cm^{-1} associated with the vibrations of the **hydrogen bridge. The potential and limitations of the methods of low-frequency spectroscopy for the investigation of these classes of compounds are discussed. The bibliography includes 131 references.**

I. Introduction

Compounds containing amide and urethane groups constitute an important class of substances that are widely used in the processing and production of polymeric materials (polyamides and polyurethanes), and are of special importance in molecular biology (polypeptides and proteins). Among the structural methods used for the investigation of the structure of these compounds, vibrational spectroscopy occupies a prominent position contributing to the solution of many problems in the physical chemistry and chemistry of polymers.[1]

The so-called middle spectral region of vibrational frequencies, which is normally used, falls in the range of wavenumbers from 400 to 4000 cm^{-1}. The low-frequency spectral region, which lies below 400 cm^{-1}, is much less studied. Nevertheless, this interval, usually called the low-frequency region, allows one to gain information that is inavailable by other methods. Low-frequency spectroscopy is used in both the physics of solids, in the study of radiation absorption by magnetic, ferromagnetic semiconducting, and other materials,[2] and in physical chemistry, in the study of barriers to internal rotation, charge transfer compounds, inorganic complexes, intermolecular interactions, vibrations of crystal lattices, *etc*.[3]

The low-frequency spectral region is of interest for the studies of amides and urethanes because first of all bending and torsional vibrations of the molecular skeleton manifest themselves in this region. These vibrations are especially sensitive to the spatial structure of molecules and to intermolecular interactions. It is in this region that the intrinsic vibrations of the hydrogen bond and intermolecular vibrations of crystal lattices are observed.

Three major experimental methods are used for the investigation of the low-frequency region of vibrational spectra, namely, far infrared spectroscopy (FIR),[3] low-frequency Raman spectroscopy (Raman),[4] and inelastic neutron scattering (INS).[5] It is well known that IR and Raman spectroscopy are complementary to each other because the selection rules for symmetric molecular systems for the IR and Raman usually differ. However, even in the absence of symmetry, the combined use of these methods is very helpful, for there is no direct relationship between intensities in these two types of spectra. If, for example, in the IR spectrum a band of some vibration is weak and overlaps another band, it can manifest itself distinctly in the Raman spectrum, and *vice versa*. The INS method is less accessible to researchers, but it is attractive since there are no selection rules for these spectra, and in many cases the INS spectrum contains therefore more bands than the IR or Raman spectra. Recently FIR spectroscopy has gained wide usage for a number of experimental reasons. This is determined by the fact that since the 60s serial diffractional spectrometers for this region are being manufactured and, especially, in the context of the development of Fourier spectroscopy, which covers the low-frequency region of the spectrum, too.

There is no difference in principle in the approaches to the interpretation of the spectra in the middle and far regions: normal coordinate analysis, the method of group frequencies (though in the low-frequency region this method has a limited application because organic compounds seldom have group bands in this region), the method of examination of isotopically-substituted compounds, and some other methods are used in both cases. However, there are specific features in the low-frequency region consisting, first of all, in the fact that intermolecular vibrations manifest themselves in this region (as has already been mentioned), which is primarily typical of crystalline compounds and some associated liquids. Therefore, for normal coordinate analysis of crystals in both middle and far frequency regions, strictly speaking, the structure and symmetry of the crystal lattice should

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be considered. A numerical calculation of frequencies is substantially complicated due to the large number of atoms that are to be taken into account. These calculations are possible and are being conducted [6] for crystals of low-molecular-weight compounds, whereas in the case of polymeric molecules, they can be performed only for the polymers with simple structure such as polyethylene [7] and polypropylene.[8]

The following approach is used as a rule for the interpretation of the spectra of crystalline polymers. A normal coordinate analysis is run for an isolated chain; sometimes, for polypeptides and proteins with the helical structures, the hydrogen bonds stabilising these structures are taken into consideration. Then, the symmetry of the crystal lattice is analysed, and the number and activity of the expected intermolecular vibrations is determined from the group theory. The assignment of these vibrations in the spectrum is usually made empirically on the basis of selection rules, polarisation, *etc*., though the methods of approximate calculations of the frequencies have been developed for intermolecular vibrations.[6]

A fairly complete bibliography (up to 1969) covering all the problems of FIR spectroscopy has been compiled by Bloor.[9] Unfortunately, more recent publications,[10–13] in which FIR spectroscopy of organic and in particular polymeric compounds have been considered, are incompatible with the above-mentioned review [9] in the scope of problems and coverage of references. To our knowledge, there are no reviews devoted especially to low-frequency Raman spectroscopy.

The purpose of the present review is the consideration and systematisation of the principal results accumulated to date of investigations concerning the application of low-frequency spectroscopy to the studies of amides and urethanes. The range of problems associated with the band assignment in this region is defined.

In most cases, the interpretation of low-frequency spectra is a rather complicated task. Vibrations of the bonds between heavy atoms, skeletal, bending, and torsional vibrations sensitive to the spatial structure and intermolecular association, vibrations of crystal lattices and polymeric chains, and the intrinsic vibration of the hydrogen bond are located in this frequency region. In each specific case, the band assignment most often requires special investigations. As intermolecular interactions are of special interest for the studies of amides and urethanes, let us dwell on the methods of identification of the bands originating from the vibrations of hydrogen bonds.

II. Methods for the assignment of bands in the low-frequency region of vibrational spectra to the hydrogen bond modes

The absorption bands sensitive to the presence of hydrogen bonds can be identified if the hydrogen bond is fully or partially broken or somehow changed. Dilution is one of the methods used to this end. Thus the analysis of the vibrational spectra of solutions, in which the hydrogen bond in the compound under study is broken upon dilution in the middle IR region of vibrational frequencies allows one to make a definite conclusion on the presence or the absence of H-bonds. However, the application of the dilution method in the low-frequency region is markedly complicated for it is impossible to measure FIR spectra at low concentrations. If thick layers are used, weak bands corresponding to H-bonds are obscured by the bands associated with strong absorption by the solvent.

Hydrogen bonds are more often studied by the method of dissolution in polyethylene matrices.[14] This method has been developed specially for the FIR region as polyethylene is practically transparent in the low-frequency region. The spectra of compounds measured in the polyethylene matrix at room temperature and at the temperature of liquid nitrogen correspond to the 'normal' spectra of these compounds in solutions of different concentrations. This phenomenon has been used by Jakobsen and Brasch [15] in the investigation of hydrogen bonds in phenol derivatives. It was found that when phenol adsorbed as a polymer with hydrogen bonds was slowly heated, it was transformed into a monomeric form as a result of H-bond cleavage and, on the contrary, cooling restores the system of hydrogen bonds. Thus, 'dilution' can be achieved by changing the temperature.

The method of matrix isolation [16] is rather efficient. The principle of this method is to hold the molecule in a solid inert medium at temperatures that are sufficiently low to prevent translational motions of the molecules. Knozinger and Schrems [17] have reviewed the data on the studies of hydrogen bonding obtained by FIR spectroscopy.

The phenomenon of a change in the H-bond strength with temperature and pressure is also used for studies of hydrogen bonding. High sensitivity of the hydrogen bonds to temperature results from an equilibrium shift of the process of H-bond formation, which leads to a change in the proportion of the groups taking part in the intermolecular interaction. This causes substantial changes in the spectra in the frequency region corresponding to vibrations of the groups involved in the hydrogen bond formation, which is normally used as the key criterion for the presence of the hydrogen bond.[18] The application of the technique of high pressures in spectral studies also provides a possibility to reveal changes in the bands sensitive to the hydrogen bond, since high pressure (up to 160 000 atm) affects intermolecular interactions and hence their vibrational characteristics.[3]

The deuteration method is widely used for the assignment of bands in the middle IR region to the modes involving the hydrogen atom. In the spectra of deuterated analogues, the frequencies associated with the vibrations of the hydrogen atom are always shifted. However, in the low-frequency region of the spectrum, deuteration is not so efficient and does not always lead to the desired result, since the frequency shift for the bands of the hydrogen bond is $1-5\ cm^{-1}$ (see Ref. 19) and sometimes is not observed at all. This originates from the fact that this is not the vibration of the hydrogen atom relative to the proton acceptor but that of the proton donor relative to the proton acceptor. However, if this small frequency shift does take place, the FIR method registers it quite reliably.

Comparative analysis of the spectra of a series of related compounds is often applied to interpret the spectra. For example, comparison of the FIR spectra of a series of carboxylic acids allowed one to distinguish the bands belonging to the hydrogen bond from those associated with intramolecular modes.[20] The application of this method along with other methods to polymeric systems also gives positive results.[21]

Reliable data on the assignment of a band to the vibration of the hydrogen bridge can be obtained by replacing the hydrogen atom by a group that does not form a hydrogen bond. This method was used in studies of the inherent modes of the hydrogen bond in the simplest amides.[22]

In the case of anisotropic systems such as oriented polymers, monocrystals, definite information can be gained from the polarised spectra. In the majority of cases, the direction of the hydrogen bond is close to that of the A–H valency bond. The knowledge of the structure of the anisotropic system and the dichroic ratio of the bands allows the proposed assignment to be proved or demolished. This method is widely used in studies of oriented polymeric systems in the middle IR region [23] and sometimes in the low-frequency region.[12]

As for low-frequency Raman spectra of liquid systems, the difficulties in their measurement is associated with the large half-width of the band due to Rayleigh scattering. Nielsen [24] has developed the technique of the $R(v)$ representation for the low-frequency Raman spectrum, which permits subtraction of the background of the Rayleigh scattering so that a rather distinct low-frequency spectrum can be obtained, which can be successfully compared with the FIR spectrum. According to this technique, the spectrometer is connected with a computer and

processing of the spectra is carried out automatically. Nielsen and co-workers have performed a series of investigations by means of the $R(\nu)$ representation; in particular, low-frequency Raman spectra for compounds containing the amide group have been studied. This method is especially valuable because it allows the investigation of biological systems in aqueous solution.

Naturally, it is desirable to use a complex of the methods described to obtain reliable results.

Definite progress can be achieved in the studies of intra- and intermolecular vibrations if experimental results are supplemented with theoretical calculations. The number, type, character, and optical activity of the intermolecular modes can be predicted from theoretical calculations for crystalline systems.[6, 25] At present, methods for calculation of these frequencies have been developed. Service programmes are available for these calculations on big and personal computers.[26, 27]

III. Low-molecular-weight amides

The simplest secondary amide, *N*-methylacetamide (*N*-MAA), is often considered as a model of an amide unit in polyamides, polypeptides and proteins. This is the reason for an interest in the investigation of its structure. Numerous papers are devoted to the study of the vibrational spectra of *N*-MAA. These investigations were started in the 50s and are still in progress.

It is well known that *N*-MAA is liquid at temperatures above 28 °C; in the solid state it can exist in two crystalline forms:[28] as a disordered crystal in the temperature interval from 28 to 10 °C, and as an ordered crystal at temperatures below 10 °C. The skeleton of the molecule has a planar structure with a *trans*-arrangement of the carbon atoms of the two methyl groups.[28] However, the presence of the *cis*-form is also suggested, which allows the fine structure of vibrational bands to be explained.[29]

The vibrational spectra of *N*-MAA have been well studied both experimentally and theoretically. The characteristic bands of the modes of the amide group have special names from 'Amide I' to 'Amide VII'.[1]

Since *N*-MAA is convenient as a model compound, recently a normal coordinate analysis has been performed in detail for this compound [30–32] in order to obtain the force field that can be applied to calculations of the spectra of polypeptides and proteins.

The FIR spectra of *N*-MAA and related compounds were first studied by Itoh and Shimanouchi.[33] Two bands at 201 and 102 cm^{-1} are observed in the FIR spectrum of liquid *N*-MAA (Fig. 1). The authors assign the band at 201 cm^{-1}, which is shifted to 185 cm^{-1} upon deuteration of the methyl groups, to the torsional mode about the C–N bond. The absorption at 102 cm^{-1} is associated with the intrinsic mode of the hydrogen bond. This assignment is based on the fact that this band, which is typical also of other simple amides,[22] is shifted by *ca.* 3–4 cm^{-1} upon deuteration of the NH-group and disappears upon replacement of the hydrogen atom at the nitrogen by another group (Fig. 1). The deuteration of the methyl groups does not affect the frequency of this mode.

The data obtained from the FIR spectra are confirmed by investigations of the low-frequency Raman spectra of *N*-MAA,[34, 35] which, in particular, show that the band in the region of 100 cm^{-1} is shifted to the low-frequency region as the temperature increases (Fig. 2). The authors[22,34] believe that the *N*-MAA molecules in the liquid state form linear chains *via* hydrogen bonds and have a structure close to that of the disordered crystal phase.

The problems of association of the *N*-MAA molecules in the liquid state and in CCl_4 solution have been discussed in more detail.[36–38] A detailed analysis of frequencies and intensities of the amide associates formed *via* the hydrogen bonds has been performed on the basis of normal coordinate analysis and an experimental study of the IR spectra of *N*-MAA in solution.[36] A force field and a set of electrooptical parameters were proposed for H-bonded associates of *N*-MAA molecules. The complex contour of some bands 'Amide I', 'Amide II' in solution might be rationalised by the existence of associates of various length.

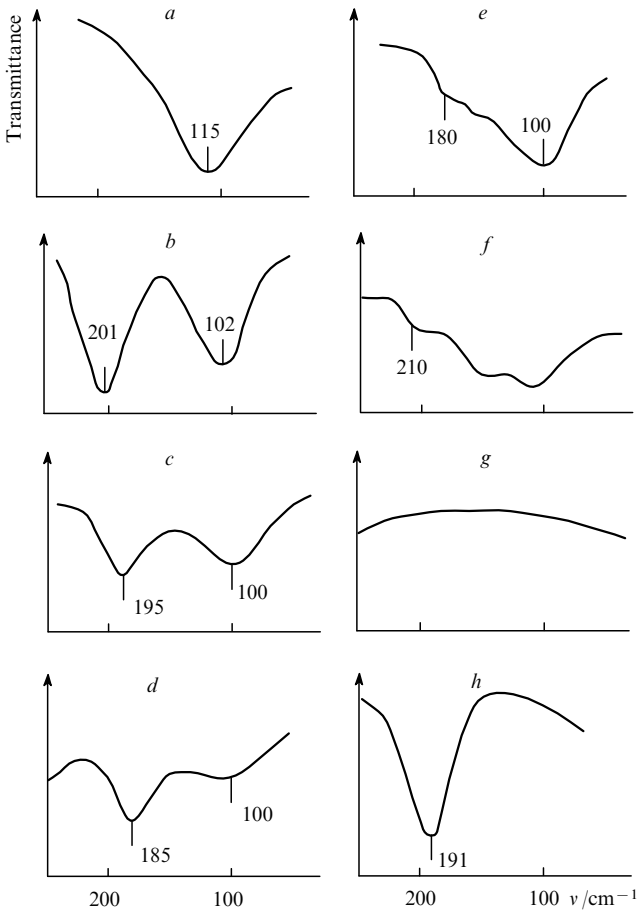


Figure 1. The FIR spectra of model amides and related compounds.[33] (*a*) $HCONHCH_3$, (*b*) $CH_3CONHCH_3$, (*c*) $CD_3CONHCH_3$, (*d*) $CD_3CONHCD_3$, (*e*) $EtCONHCH_3$, (*f*) $CH_3CONHEt$, (*g*) $HCON(CH_3)_2$, (*h*) CH_3COOCH_3.

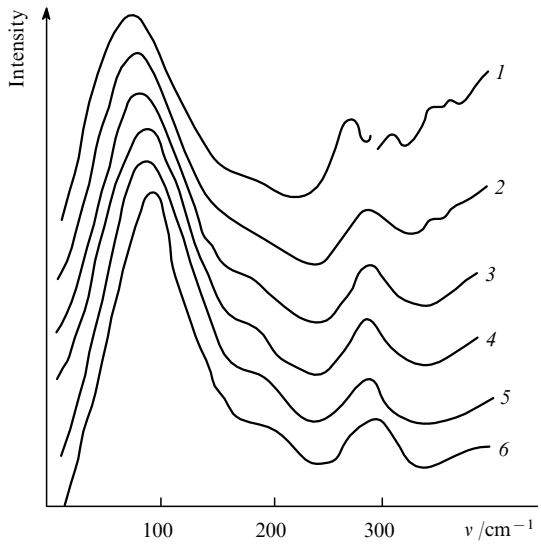
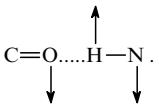


Figure 2. The smoothed $R(\nu)$ spectrum of liquid *N*-MAA at different temperatures (°C): (*1*) 165, (*2*) 150, (*3*) 120, (*4*) 90, (*5*) 60, (*6*) 30.

The comparison of absorption bands in the middle IR region in the spectra of tetramer, pentamer, and hexamer shows that a specific saturation of the frequency shifts takes place as the degree of association increases, then only the band contour changes.[37] On the contrary, in the FIR region where the bands of the hydrogen bond modes are located, a systematic shift to the low-frequency region occurs with an increase in the number of molecules in the complex. According to calculations of the frequencies for the final chains, the dependence of the frequency on the number of the *N*-MAA molecules in the associate manifests itself well in the range of the NH stretch (3348, 3338, 3334, and 3330 cm^{-1} for $n = 2, 3, 4$, and 6, respectively) and in the FIR region, where the intrinsic vibration of the H-bond manifests itself (121, 105, 101, and 98 cm^{-1} for $n = 2, 3, 4$, and 6, respectively). The comparison of the calculated frequency for the hydrogen bond vibration with that in the experimental spectra makes it possible to estimate the size of associates in liquid *N*-MAA ($n = 2-6$).

The complex structure of the amide bands can alternatively be explained by assuming that *cis*- and *trans*-isomers coexist in solutions of *N*-MAA,[38] which is based on examination of the spectra of solutions at various temperatures and concentrations. The 'Amide I' band was separated into four Gaussian components, which the authors relate to the *cis*- and *trans*-isomers of *N*-MAA. However, from our viewpoint these results do not contradict the explanation of the complex contours of the bands by the existence of associates of different length.[36,37] Moreover, the dependence of the enthalpy of the hydrogen bond formation on the chain length of associates is proposed,[38] which cannot but influence the frequencies of the 'Amide I' and 'Amide II' bands.

ab initio Calculations performed by Nielsen[22] as well as normal coordinate analysis for the *N*-MAA molecules[33] indicate that the band at 100 cm^{-1} is the bending vibration of the hydrogen bond of the type



The crystalline *N*-MAA was studied by FIR,[33] Raman,[39] and INS[40] spectroscopy in the low-frequency region. On going from liquid to disordered crystal, the frequency of the hydrogen bond mode in the IR spectrum[33] shifts from 102 to 125 cm^{-1} (Table 1). The passage to the ordered crystal results in its further shift to 130 cm^{-1} and a new band appears at 90 cm^{-1}, the intensity of the latter increasing with a decrease in temperature. Simultaneously, the band at 201 cm^{-1} shifts to higher frequencies and splits into two components at 221 and 243 cm^{-1}. The crystal existing at temperatures below 10 °C exhibits two torsional vibrations (A_2 and B_2) about the C—N bond. For structures of C_{2v} symmetry, the A_2 mode is inactive in the IR, and the appearance of two torsional modes about the C—N bond means that the structure of the crystal unit of *N*-MAA deviates from this group symmetry.

Normal coordinate analysis[33] for the crystal lattice of *N*-MAA with consideration of the hydrogen bond confirms the presence of two torsional modes in the crystal: 205 (A_2) and 227 (B_2) cm^{-1}. In addition, it is shown that the band in the region of 130 cm^{-1} is associated with librational lattice modes and that in the range of 90 cm^{-1} belongs to translational lattice vibrations. Hence, according to the data from Ref. 33, temperature changes in the crystal affect the frequency shift for the torsional vibration much more significantly than the frequency of the hydrogen bond vibrations (see Table 1).

Table 1. The frequencies (ν/cm^{-1}) of H-bond bands in the spectra of *N*-MAA in the region of 30–300 cm^{-1}.

Phase state of *N*-MAA	Method	Temperature / °C	ν in the region		Ref.
			100 cm^{-1}	200 cm^{-1}	
Liquid	Raman	30	102	201	35
Disordered crystal	IR	15	125	201	33
Ordered crystal	IR	10	130 90	210	33
	IR	−80	132 90	221 243	

The Raman[39] and INS[40] spectra of crystalline *N*-MAA and its isotopomers supplement information from the IR spectra. The frequencies observed in the IR, Raman, and INS spectra of crystalline *N*-MAA[39] are presented in Table 2. About 10 lines are recorded in the region below 200 cm^{-1} in the Raman spectrum. The authors[39] believe that the lattice modes (external vibrations) are in the region below 110 cm^{-1} because isotopic substitution has little influence on the frequencies of these bands; the torsional vibrations about the C—N bonds manifest themselves in the region of 120–170 cm^{-1}. Calculation of the potential function for this torsional vibration revealed two symmetric energy minima separated by a small potential barrier, which suggests that the skeleton of the molecule is non-planar. Provided this result is applied to the peptide group, this can be important for understanding the physicochemical properties of polypeptides and proteins.

Formamide and its derivatives have been studied in the liquid by the method of the $R(\nu)$ representation (Raman) in the low-frequency region.[34,41,42] The conclusions on the structure of H-bonded chains of formamide are analogous to the results obtained for *N*-MAA. The bands in the region of 150–200 and 110 cm^{-1} observed for formamide are interpreted as librational modes of the molecules associated *via* the hydrogen bonds, which is in accordance with the data on degrees of the line depolarisation, temperature measurements, and the spectra of solutions.

IV. Polyamides

A large body of publications is devoted to investigations of polyamides by IR spectroscopy in the middle frequency region (see, for example, Refs 1, 43, and references cited therein) in which the problems of the structure and orientation of molecules, the hydrogen bond formation, *etc*. have been discussed. However, there are relatively few publications on the FIR spectra of polyamides. The emphasis is on revealing the correlation between the FIR spectra of polyamides and the conformations of the molecular backbone, because a number of skeletal and torsional bands sensitive to conformations are located below 700 cm^{-1}.

Nylons are known to exist in three crystalline modifications. In the α- and β-forms, planar extended chains have the *trans*-

Table 2. The comparison of frequencies and intensities of the bands in the IR, Raman, and INS spectra for *N*-MAA.

Method	T/K	ν /cm^{-1} [a]								Ref.
IR	93		130 s				90 s			33
Raman	35	164 s		127 s	105 vs	98 sh	91 m	73 w	65 w	39
INS	5	164 s	153 s	126 w	104 w		87 w		62 vw	40

[a] Accepted notations for band intensities: vs is very strong, s is strong, m is medium, w is weak, vw is very weak, sh is shoulder.

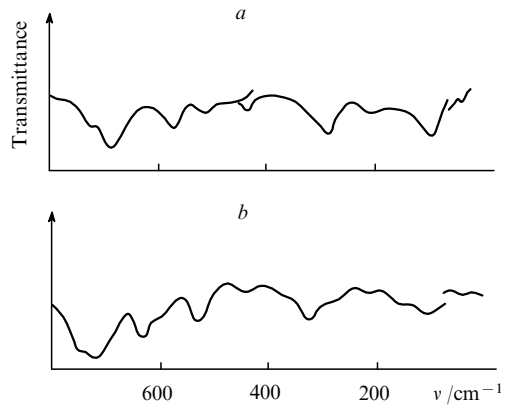


Figure 3. The IR spectra of the α- (*a*) and γ-forms (*b*) of nylon-6.[45] Hereinafter gaps in the spectra are connected with the special features of the equipment used: with changing of diffraction gratings, filters, changes in the thickness of the samples, *etc*.

conformation, in the γ-modification chains are turned about ordinary bonds neighbouring the amide groups.

A series of various kinds of nylons has been studied by the FIR [44, 45] and INS [46] methods. The IR spectra of nylon-6 in the α- and γ-modifications [45] are presented in Fig. 3. It is seen that the spectra in the low-frequency region differ substantially. Analysis of the spectra of 18 polyamides (nylons-*n*,*m* and nylons-*n*) made it possible to reveal the common bands typical of the planar and non-planar conformations and to give an empirical assignment for a number of bands (Table 3).[44] The difference in chain conformations is responsible for the different frequencies of such bands as 'Amide V', 'Amide VI', and 'Amide VII', which manifest themselves in the regions 700, 600, and 230–300 cm^{-1}, respectively. The bands associated with bending and torsional modes of the amide and methylene fragments of the chains appeared to be sensitive to chain rotation.[21] The examination of the 'Amide VII' bands sensitive to conformation and bending vibrations in the range of 300 cm^{-1} allowed one to investigate chain conformations in polyamide fibres and fabrics, in particular, for nylon-6 depending on the method of sample preparation.[47] The 'Amide VII' mode for the pseudo-hexagonal crystal structure has a frequency of 205 cm^{-1}. It is noted that the X-ray diffraction method cannot distinguish satisfactorily the crystalline forms of nylon-6, in this case FIR spectroscopy appears to be very useful.

Table 3. The low-frequency absorption bands (cm^{-1}) of the amide groups for polyamides in various crystalline forms.

α-Form	γ-Form	Assignment [a]
690	715	'Amide V' (γ, NH)
580	630	'Amide VI' (γ, C=O)
360	–	Deformation of the skeleton $-CH_2-CONH-CH_2-$
230	300	'Amide VII' (τ, CONH)

[a] γ is out-of-plane modes, τ is torsional modes.

Jakes and Krimm [48] have performed normal coordinate analysis for a series of amides and polyamides. They calculated the valence-force field for this class of compounds. The calculations performed for a series of molecules containing the amide groups fit well the experimental spectra in the middle region of frequencies. No detailed analysis of the low-frequency region has been carried out, the authors only mentioned that skeletal and torsional vibrations of the chain manifest themselves in the region below 500 cm^{-1}.

Tadokoro *et al*.[21] calculated the frequencies in the far region for nylon-6 having the planar conformation of the chain (α-form). Besides nylon-6, these authors studied a series of polyesters $[-(CH_2)_m-CO-O-]_n$ (m = 1, 2, 4, 5) having the planar zigzag structure in the crystalline state. The absorption bands in the spectra of the polyesters studied and nylon-6 appeared to be related to similar modes. Comparative interpretation of the spectra of these compounds was made on the basis of band calculations [21] (Table 4). It was shown that bending and torsional modes of the chain backbone and the amide group are located in the region below 700 cm^{-1}.

Table 4. The assignment of group bands in the spectra of aliphatic polyesters and nylon-6.[21]

Frequency /cm^{-1}	Band assignment [a]	
	aliphatic polyesters	nylon-6 (α-form)
730–630	δ(C=O), ν(CH), δ(skeletal)	–
690	–	'Amide V'
590–580	γ(C=O)	'Amide VI'
523 [b]	δ(CH_2-CO-O), δ(skeletal)	δ(CH_2-CO-N), δ(skeletal)
450–430	δ(OCH_2-CH_2), δ(CH_2-chain)	δ(NCH_2CH_2), δ(CH_2-chain)
370–295	δ(CHCOOCH), δ(CH_2-chain)	δ(CHCONHCH), δ(CH_2-chain)
233–195	τ(−CO−O−), τ(CH_2-chain)	τ(CH_2-chain)
150–90	τ(CH_2-chain), τ(−CO−O−)	τ(CH_2-chain)

[a] Accepted notation (here and in Tables 5 and 6): ν is stretching, γ is out-of-plane, δ is bending, τ is torsional vibrations. [b] This band appears when the number of the CH_2 groups exceeds 5.

A normal coordinate analysis has been performed for isolated chains.[21] The spectra measured at the temperature of liquid nitrogen appeared to be similar to those taken at room temperature, and the intermolecular modes did not manifest themselves in the experimental IR spectrum.

The band observed in the region of 100 cm^{-1} is believed to be associated with the coupled torsional vibrations of the methylene chains and the amide group. This band has a complex contour, its frequency shifts somewhat upon deuteration of the NH group and becomes more intense when the samples underwent annealing and thermal treatment. From these facts, the data from the studies of low-molecular-weight amides, and the fact that the paper cited reports the spectra of films,[21] which doubtless contain the bands of the hydrogen bond, it was reasonable to assign the band in the region of 100 cm^{-1} (or, probably, one of its components) to a mode of the hydrogen bond.

It was this interpretation that was given by Frank and Fiedler [49] who considered the IR spectra of nylons in the region of 20–400 cm^{-1}. They assigned the absorption band in the region of *ca*. 100 cm^{-1} in all the spectra examined to the translational motion of the bonded amide groups of neighbouring chains, which they represented by the model of coupled oscillators. The frequency of this band is practically the same in the spectra of α- and γ-nylons despite the difference in conformations of the macromolecules. It can only be noticed that the half-width of the band is somewhat smaller for α-nylons.

An attempt to study moments of inertia for a repeating unit of the polymeric chain has been made on the basis of the data on the frequencies of the absorption bands assigned to the torsional modes about the C–N bond.[49] The bands at 630 cm^{-1} (nylon-2),

374 cm^{-1} (nylon-4) and 291 cm^{-1} (nylon-6) were assigned to the torsional modes about the C–N bond, the decrease in the frequency with the chain length increase was explained by the dependence of the absorption frequency on the moment of inertia of a repeating unit of the polymer. However, on going to nylons with a longer repeating unit, further decrease in the frequency was not observed. In this case, the determination of the moments of inertia for repeating units can hardly be considered correct because the band assignment is not justified, and the frequencies 630 cm^{-1} and 374 cm^{-1} are too high to be assigned to the torsional modes about the C–N bond.

Fibres of poly-*p*-phenyleneterephthalamide (Kevlar-49), the representative of aromatic polyamides, have been studied by FIR spectroscopy.[47,50] The FIR spectra of oriented samples in polarised light are reported without any band assignment,[47] and an attempt to interpret the spectra is made.[50] The bands were assigned (Table 5) taking into consideration data on the band dichroism and comparing the spectra obtained with those for the model low-molecular-weight substance, benzanilide, in the condensed state and in solution. The assignment of the bands associated with the intramolecular modes of the amide group in the low-frequency region is, in general, in accordance with the data on nylons. However, the assignment of the bands associated with the intermolecular vibrations raises some difficulties. For example, the bands at 253, 287, and 305 cm^{-1} assigned to external vibrations have too high frequencies for a repeating unit of such a large mass.

Table 5. The absorption bands in the IR spectra of benzanilide and poly-*p*-phenyleneterephthalamide (fibre 'Kevlar-49')[50] in the region of 30–400 cm^{-1}.

Benzanilide		Kevlar-49	Dichroism	Assignment [a]
solution	condensed state	fibre		
Intramolecular modes				
109	108	112	$\pi+\sigma$	$\tau(C_p-NH)+\delta(CONH)$
180	184	198	$\pi>\sigma$	$T'(A')+\delta(C_p-CONH-C_p)$
209	202	216	$\sigma>\pi$	$\tau(C-N)$
295	307	331	$\pi+\sigma$	$\delta(CONH)$
356	370	348	$\pi>\sigma$	$\delta(C_p-CONH-C_p)$
Intermolecular modes				
–	61	67	$\pi+\sigma$	$T'(A'')$
–	90	83	$\pi+\sigma$	
–		138	$\sigma>\pi$	$R'(A')$
–		160	$\sigma>\pi$	$R'(A'')$
–	240	253	$\pi>\sigma$	$R'(A'+A'')$
–	263	287	$\pi+\sigma$	with the participation of H-bond
–		305	$\pi+\sigma$	

[a] Mode: *T* — translational, *R* — librational.

Hence, the investigation of the FIR spectra and normal coordinate analysis for polyamides allowed the interpretation of these spectra. The features of the hydrogen bond in the low-frequency region are considered, and the bands sensitive to chain conformations are revealed. This provided a possibility to apply the low-frequency region of the spectra for analytical purposes.

V. Polypeptides and amino acids

The interest in the structure of amino acids and polypeptides stems from the rapid development of molecular biology. The knowledge of the structure of amino acids gives the key to understanding the structure of proteins. The application of molecular spectroscopy to the studies of biological systems started in the 60s. Since that time, a number of monographs[51–53] and reviews[54,55] has appeared reflecting the situation in this field. The problems of molecular spectroscopy of amino acids in the middle frequency region are discussed in the monograph by Parker.[56]

The examination of the low-frequency region of the spectrum is of interest, first of all, from the viewpoint of investigation of intermolecular modes including the intrinsic modes of the hydrogen bond. Series of amino acids such as glycine, D,L-alanine, D,L-leucine, and others have been studied.[57] The authors have clearly demonstrated the advantages of low-temperature spectral investigations by showing distinct shifts of the bands belonging to intermolecular modes with a decrease in temperature (Fig. 4). Assuming that the frequencies of torsional vibrations depend on temperature, the bands in the region of 500 and 200 cm^{-1}, which are 10–20 cm^{-1} shifted upon cooling to 113 K, were assigned to the torsional modes of the NH and C–C groups, respectively. The bands in the region of 100–130 cm^{-1}, which are less shifted (by 5–7 cm^{-1}), were assigned to the stretch of the NH...O hydrogen bridge.

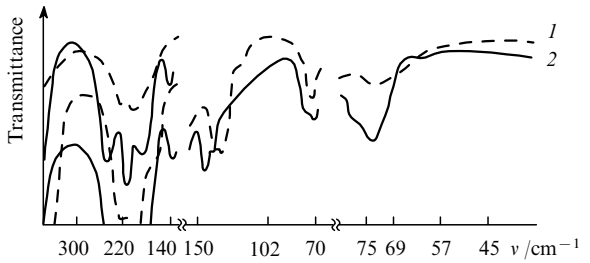


Figure 4. The FIR spectrum of α-glycine at 298 K (*1*) and 113 K (*2*).[57]

The FIR spectra of crystalline L-alanine have been comprehensively studied.[58,59] Using the method of deuteration, temperature measurements, and normal coordinate analysis for crystalline L-alanine, Bandekar *et al.*[59] reported a detailed assignment of the bands observed in the IR and Raman spectra of crystalline L-alanine in the region of 40–500 cm^{-1}. The calculations showed that the vibration of the hydrogen bond manifests itself at a frequency of 146 cm^{-1}, it contributes, however, to other vibrational modes with frequencies of 110–150 cm^{-1}. The correctness of the assignment of the bands associated with the vibrational modes of the hydrogen bonds is proved by their small shift (3 cm^{-1}) upon deuteration of L-alanine, which, as was mentioned above, is typical of amides. The plot of the dependence of the position of the peak at 146 cm^{-1} on temperature is depicted in Fig. 5. On the basis of these data, the authors

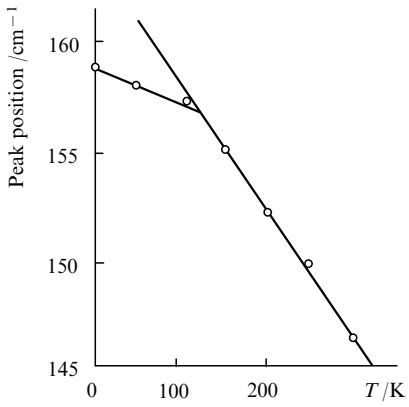


Figure 5. Temperature change in the position of the peak at 146 cm^{-1} in the IR spectrum of crystalline L-alanine at 300 K.[59]

have performed the calculation of vibrational frequencies in the spectrum of L-alanine at 6 K. In this way the authors could follow the change in the potential energy of the crystal as the temperature decreases.

The comprehensive investigation of the spectra of low-molecular-weight amides and polyamides permitted a relatively simple progression to the interpretation of the spectra of polypeptides with the aim of establishing their structure. The bands of the amide modes such as 'Amide I' and 'Amide II' in the IR spectra and 'Amide I' and 'Amide III' in the Raman spectra (the 'Amide II' line is weak in the Raman spectra) are the main tool in this case. Although these bands reflect the structure of polypeptides, the molecules of which can exist in the helical and planar extended forms, the spectral features of different conformations can be substantially supplemented by the data on the low-frequency spectra as the low-frequency modes are especially sensitive to chain conformations. In addition, in a number of cases, low-frequency modes make it possible to quantify the content of different conformers because the bands in the low-frequency region associated with different chain conformations do not overlap neighbouring bands whereas the amide bands in the middle region , as a rule, overlap one another.

Polyglycine $(-NH-CH_2-CO-)_n$ is a polypeptide of the simplest structure, which can also be considered as a polyamide. Polyglycine exists in two crystalline modifications differing in the chain structure: polyglycine-1 (PG-1) with the planar chain conformation and polyglycine-2 (PG-2) with the helical structure. This polypeptide has been well studied by the methods of vibrational spectroscopy.[1] Thus the existence of two rotameric structures was first predicted from the data of IR spectroscopy.[60]

The FIR spectrum of polyglycine was first studied by Miyazawa,[61] who found that the spectra of PG-1 and PG-2 differ substantially. The INS spectra of polyglycine in the low-frequency region are reported.[62,63] The availability of the IR, Raman, and INS spectral data has stimulated calculations of frequencies that have been carried out for both isolated chains [63] and crystals.[64,65] Fanconi [66,67] has performed an experimental and theoretical investigation of the low-frequency spectra of polyglycine in various forms and presented the most complete interpretation of the bands observed in the spectra.

Table 6 contains the assignment of the low-frequency modes for PG-1, which demonstrates the participation of the hydrogen bonds in vibrational modes in this region. As can be seen from Table 6, the band at 133 cm^{-1} observed in the FIR spectra of polyglycine is assigned to the nearly pure stretching vibration of the hydrogen bond as it accumulates 92% of the potential energy. An intense band at 82 cm^{-1} in the Raman spectrum results from the non-planar bending vibrations of this bond. Comparison of the band frequencies for polyglycine and *N*-MAA in the low-frequency region shows that the vibrations of the hydrogen bond give the bands of the same frequencies. These are the bands at 130 and 90 cm^{-1} for crystalline *N*-MAA [33] and 133 and 82 cm^{-1} for solid polyglycine. This gives reason to suppose that the hydrogen bond in the amide structures is characterised by the same vibrational frequencies regardless of the size of the molecule.

There is a discrepancy in the interpretation of the bands observed in this spectral region proposed by different authors. Itoh [33] and Nielsen[22] assign the bands at 130 and 90 cm^{-1} observed for *N*-MAA to the bending and stretching modes of the hydrogen bridge, respectively, whereas Fanconi [67] interprets the band at 133 cm^{-1} for polyglycine as a stretching and that at 82 cm^{-1} as a bending vibration. These conclusions were made on the basis of theoretical calculations and seem to call for further consideration.

A number of publications [68–74] are devoted to the studies of low-frequency spectra of the simplest chiral polypeptide, poly-L-alanine, the molecules of which also exist in two forms, *viz*. as the α-helix and the planar form. Normal coordinate analysis has been performed for both forms over all the spectral intervals (including the low-frequency region).[75–77] On the whole, the theoretical and experimental data were in satisfactory agreement.

Table 6. Experimental and calculated frequencies for polyglycine-1 $(-NH-C^1H_2-C^2O-)_n$.[67]

Frequencies /cm^{-1}			Assignment, potential energy distribution (%)
experiment		calculation	
296 K	120 K		
599 (Raman)	599 (Raman)	623 ($\dot{E}_3$)	$\gamma(C^2O)$ (43), $\delta(C^1C^2)$ (25)
587 (Raman)		572 ($\dot{A}$,$\dot{E}_1$)	$\nu(C^1C^2)$ (12), $\delta(C^2O)$ (26), $\gamma(C^2O)$ (49)
327 (Raman)	328 (Raman)	319 ($\dot{A}$)	$\delta(C^1C^2N)$(48), $\delta(NC^1C^2)$ (15), $\nu(NC^1)$ (12)
320 (IR)		329 ($\dot{E}_1$)	$\delta(C^1C^2N)$ (48), $\delta(NC^1C^2)$ (15), $\nu(NC^1)$ (12)
285 (IR)		264 ($\dot{E}_3$), 267 ($\dot{E}_2$)	$\delta(C^2NC^1)$ (41), $\delta(C^2O)$ (31)
260 (Raman)	260 (Raman)	257 ($\dot{E}_1$)	$\delta(C^2NC^1)$ (54), ν(O...H) (21)
215 (IR)		207 ($\dot{E}_1$)	$\delta(C^2NC^1)$ (43)
211 (Raman)	214 (Raman)	201 ($\dot{A}$)	$\delta(C^2NC^1)$ (21), $\delta(C^1C^2N)$ (11), γ(NH) (30)
170 (Raman)	175 (Raman)		
133 (IR)		149 ($\dot{E}_3$)	ν(H...O) (92)
		137 ($\dot{E}_1$)	$\delta(NC^1C^2)$ (27), $\tau(C^1C^2)$ (10), $\tau(C^2N)$ (13)
		131 (A)	$\delta(NC^1C^2)$ (33), $\tau(C^1C^2)$ (11), ν(O...H) (11)
111 (Raman)	114 (Raman)	106 (B_3)	γ(NH) (22), $\tau(C^2N)$ (21), $\tau(C^1C^2)$ (20)
82 (Raman)	87 (Raman)	75 (B_1)	γ(NH...O) (36), $\gamma(C^2=O...H)$ (18), δ(NH...O) (17)
		69 (B_2)	$\tau(C^1C^2)$ (30), $\tau(C^1N)$ (29), γ(NH...O) (18), $\tau(C^2N)$ (11), γ(NH) (13)

Itoh *et al*.[78–80] studied the FIR spectra for a series of poly-(α-amino acids) having helical and planar conformations of the chain and showed that each conformation has its own set of frequencies in the low-frequency region. In particular, in was shown [69,70] for a series of polypeptides that the 'Amide V' band has a frequency about 610 cm^{-1} for compounds in the α-form, that for compounds in the β-form is in the region of 700 cm^{-1}, and a diffused band at 650 cm^{-1} corresponds to the disordered form. Itoh *et al*.[78–80] examined the low-frequency spectra of a series of poly-(α-amino acids) and showed that the FIR region allows one to analyse the chemical and conformational composition of these homopolymers and copolymers of different amino acids.

It should be noted that Krimm and coworkers made a significant contribution to theoretical analysis of vibrational spectra of polypeptides. They have published a great number of papers including a series of papers having the common title 'Vibrational analysis of peptides, polypeptides and proteins' (*ca*. 40 publications). Thus the first publication of this series dates back to 1976,[81] and one of the recent papers dates back to 1988.[82] Krimm *et al*. have shown that normal coordinate analysis provides a rather full understanding of vibrational spectra of polypeptides and of a series of proteins having secondary structures such as α-helix, and β-layers. Normal coordinate analysis has been performed over the whole frequency interval up to lowest frequencies and in various approximations: for isolated molecules, with and without regard to hydrogen bonds, and for crystals. The value of this work is also in the fact that the force field established allowed one to perform calculations of the spectra of various conformations for both polypeptides and simplest proteins.

Recently low-frequency modes of polypeptides and proteins have attracted attention of researchers. The authors of

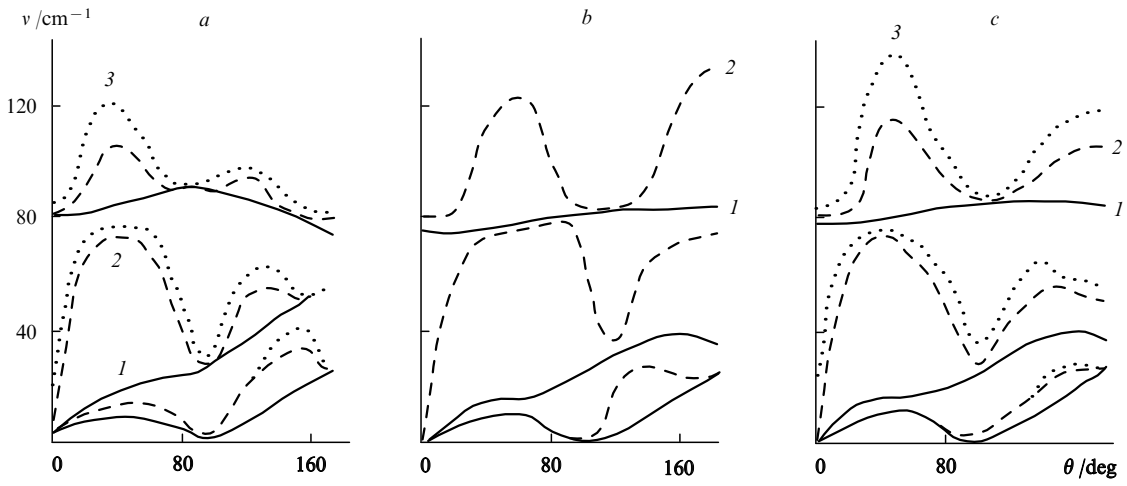


Figure 6. The low-frequency phonon-dispersion curves for the seven-masses model (*a*), one-mass model (*b*), and two-masses model (*c*) of poly-L-alanine in the form of the α-helix calculated for three values of the force constants: $F(\mathrm{NH...O}) = 0$ (*1*), $F(\mathrm{NH...O}) = 0.15 \times 10^{-3}$ (*2*), and $F(\mathrm{NH...O}) = 0.3 \times 10^{-3}$ dyne Å^{-1} (*3*).[90]

Refs 83–85 believe that these modes play a definite role in biological processes. In particular, vibrations of the α-helix belong to these modes. 'Breathing' and acoustic longitudinal (of the type of 'stretching accordion') and transverse vibrations are the most interesting among them.

Itoh *et al.*[72] and Fanconi *et al.*[86] were the first to calculate the frequencies of vibration of the α-helix for poly-L-alanine. The former authors considered a simplified model of the helix, in which the CH_3 group was considered as a single mass and the presence of the stabilising hydrogen bonds was taken into account. Normal coordinate analysis showed that the frequencies of 690, 370, and 260 cm^{-1} and in the region of 40–140 cm^{-1} correspond to helix deformations. The band in the range of 260 cm^{-1} was assigned to the 'breathing' mode, which was later confirmed by the Raman spectra.[87] The force was developed that allowed one to interpret the optically active modes of the α-helix, to calculate the frequencies of the modes with various phase difference and to obtain dispersion curves. Using these curves, which reflect the density of vibrational states, the INS spectra of poly-L-alanine were interpreted.[86] The vibrational frequencies appear to depend on the phase difference in the region below 1000 cm^{-1}, this dependence being especially pronounced in the region below 200 cm^{-1} where two acoustic modes are observed. These modes are strongly affected by hydrogen bonds.

The calculations show that in the case of the α-helix with a finite number of elementary units, the bands reflecting the helix length appear in the spectrum. Thus the frequency of the mode of the type 'stretching of the accordion' is inversely proportional to the helix length (*n* is the number of repeating units).

n	10	15	20	25	30	40	50	75	100
ν /cm^{-1}	67	50	40	32	28	24	20	15	11

Hence, the helix length can be estimated from longitudinal acoustic modes that manifest themselves in the Raman spectra. This method has found wide application in the studies of simple synthetic polymers such as polyethylene, polyoxymethylene, *etc.*[88,89] In particular, the method permits the determination of the thickness of lamellas formed in polymers under various conditions. Using experimental data on longitudinal acoustic modes observed, the Young's modulus of the helix can be easily calculated, which, for instance, is $E = 2.31 \times 10^{11}$ dyne cm^{-2} for poly-L-alanine.[72]

The calculation of low-frequency modes for helices of more complex polypeptides becomes cumbersome due to the great number of atoms. In this case, simplified models can be used. Fanconi and Peticolas[90,91] considered three simplified models of α-helix with poly-L-alanine as an example in order to calculate the lowest-frequency modes. The first model is a seven-masses model including all the atoms of the elementary unit in which only the CH_3 group is considered as a single mass. This model is the closest to the structure of the real molecule. The second model is a one-mass model in which a repeating unit is considered as a single point mass. The third model is a two-masses model in which a chemical repeating unit devoid of the mass of the amide oxygen, is taken for one mass (this mass is located at the place of the oxygen atom in the α-helix), and the mass of the hydrogen atom located in its real position is taken for the other mass. In all the three models, the hydrogen bond is considered as a bond between the amide hydrogen and the third nearest oxygen atom thus allowing the helix structure to be reproduced.

Dispersion curves were calculated for three values of force constants of the hydrogen bond, namely, 0.3×10^{-3} dyne Å^{-1} (this force constant was taken from the force field for formic acid), 0.15×10^{-3} dyne Å^{-1} (the force constant was taken from the force field for *N*-MAA), and 0 dyne Å^{-1}. The comparison of two dispersion curves obtained on the basis of these models and corresponding to the lowest-frequency modes shows (Fig. 6) that they are in good agreement with one another, the seven-masses model fits the two-masses model the best. Therefore, the lowest-frequency modes for helical structures can be calculated on the basis of a simple model that takes into account only intramolecular hydrogen bond. There is reason to suppose that this approach can be useful for the analysis of low-frequency modes of proteins.

VI. Proteins

Investigation of proteins by means of IR spectroscopy is a difficult task, for proteins have much more complex structures than synthetic polymers and polypeptides. Investigation of proteins is usually based on the analysis of the amide bands that provide information on the conformation of the backbone and side chains, on hydrogen bonding, *etc.*[92,93] As a rule, the low-frequency region remains beyond the authors' attention.

Buontempo *et al.*[94,95] were among the first to study the FIR spectra of proteins. They have analysed the possibility of gaining structural information from the low-frequency modes. The authors found the presence of a wide intense absorption band centred near 150 cm^{-1} in all the FIR spectra for a series of globular proteins. Changes in the protein conformations and denaturation influence insignificantly the spectral pattern. No fine structure of the spectra in this region could be detected neither by increasing the resolution of the instrument nor by lowering the temperature of the sample. The authors supposed that the band broadening observed in the spectra of proteins originated from a

superposition of many bands corresponding to individual oscillators that have different force constants and effective masses. Since the proteins that differ significantly in the structure have practically the same spectra, the authors [94,95] believe that the nature of this broad absorption can be rationalised by the anharmonic interaction between weak vibrations *via*, in the first turn, the H-bonded groups.

Chirgadze and Ovsepjan [96,97] have performed more detailed investigations and have found that FIR spectroscopy can be useful for studies of conformational changes in, and denaturation of, proteins. The spectra of myoglobin reported in these papers and in Ref. 95 exhibit a broad absorption but with a rather pronounced fine structure (Fig. 7). It is seen from Fig. 7 that the bands at 376, 417, 422, and 470 cm^{-1} for natural myoglobin disappear upon denaturation of the protein in the alkaline medium, and the spectral pattern in the region below 300 cm^{-1} changes. Using the data on polypeptides with the structure of the α-helix and bearing in mind that 77% of the amino acidic residues are included in such a helix in the myoglobin under study, the authors associate the bands disappearing upon denaturation with the helical fragments of the protein molecule and propose the assignment for these bands. The changes in the bands at 324, 422, and 470 cm^{-1} reflect the changes in conformations of both the backbone and side chains. The authors obtained sufficiently good differential spectra by subtracting the spectrum of the natural protein from that of the denatured myoglobin. These spectra, however, should be regarded with due caution because false bands may result from subtraction, which have no physical meaning. These investigations [96] have led to the conclusion that FIR spectroscopy provides definite information even for such complex molecules as globular proteins.

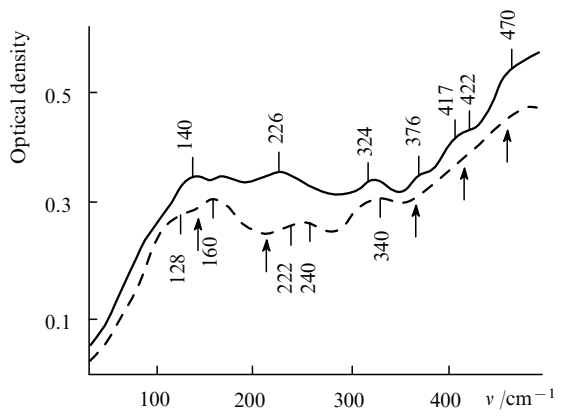


Figure 7. The IR spectrum of myoglobin in the natural (continuous line) and denatured states (dotted line). Arrows point to the changes in the spectra after denaturation.[97]

Other authors make the same conclusion (see, for example,[98,99]). Ataka *et al.*[99] showed that the quality of the FIR spectrum depends significantly on the method of sample preparation. He proposed to study proteins in the form of monocrystals, which made possible a decrease in the surface scattering and to obtain the material with a dense packing. In this case, the spectrum consisted of a number of pronounced absorption bands that were absent in the spectrum of the sample prepared as a powder.

The interpretation of some bands in the low-frequency region in the IR and Raman spectra for crystalline lysozyme has been carried out empirically [72] by comparing the spectra with the data on homopolypeptides and the above-considered myoglobin. The band assignment for lysozyme is, on the whole, close to that for myoglobin.[97] The authors supposed on the basis of the data of Ref. 72 that the bands at 56 and 25 cm^{-1} are associated with longitudinal acoustic modes of the finite chains in the α-helix having five and fifteen amino acid residues, respectively.

There is a quite definite regularity observed in the FIR region when passing from low-molecular-weight biological compounds to complex high-molecular structures. If the spectra of the former (for example, of amino acids) have a distinct structure, the spectra of the latter (for example, of proteins) contain a broad diffuse band having some fine structure (note that this picture is not observed on going from amino acids to polypeptides). The same trend is noticed for nucleic acid compounds.[100] The spectra of nucleosides in the low-frequency region are clear-cut, they contain well-resolved, rather intense bands, whereas the spectra of nucleotides, polynucleotides, and nucleic acids are composed of broad bands with indistinct peaks, as in the case of proteins.

The nature of broad background absorption observed in the FIR spectra of various proteins has been discussed in the papers mentioned above. Buontempo [95] believes that this absorption can be related to anharmonic interactions between low-frequency modes. According to Chirgadze,[97] at least a part of this absorption results from a wing of the broad 'Amide V' band. However, Ataka *et al.*[99] believe that the broad background in the low-frequency region originates from the absorption of water molecules present in proteins, which seems to be the closest to the truth. This follows from the comparison of the shape of absorption bands in the spectra of ice and normal water with that of crystalline lysozyme at liquid nitrogen temperature and at room temperature, respectively. In general, it should be noticed that the existence of the broad background absorption in the spectra of proteins makes it difficult to investigate their FIR spectra.

Direct normal coordinate analysis becomes difficult, if at all possible. It is connected with the fact that the secular equation for molecules containing a large number of atoms and devoid therefore of symmetry, has a very high order and its solution becomes problematic even for modern computers. However, in some cases calculations can be successfully used. Thus frequencies have been calculated [101] for β-coils that are difficult to identify in models, but occur in globular proteins together with the α-helices and planar β-structures.

The above-mentioned simplified methods for normal coordinate analysis of the α-helix developed for polypeptides [90] have been applied to the interpretation of low-frequency modes for one of the fragments of the α-helix in the pig insulin molecule.[102] The authors regarded various peptide residues as single masses. In this case, they dealt with a secular equation of the 60th order.

Raman spectroscopy is an efficient experimental tool for the studies of proteins in the region below 100 cm^{-1}. The examination of Raman spectra provides information on vibrations at very low frequencies, up to 20 cm^{-1}, *i.e.* in the region that is difficult to study by FIR spectroscopy. As was already mentioned, the water molecules present in proteins give undesirable anisotropic scattering in the frequency region of 50 cm^{-1} and below. Nevertheless, the necessary signal can be detected by both experimental expedients [103] and computer processing of the spectra.[104] In this way it became possible to approach the excitation line. Thus bands were observed [103–108] in the region of 20–40 cm^{-1} in the Raman spectra of a series of crystalline proteins, bands that disappear on dissolution of the protein in water. This behaviour of the bands can be explained either by their intermolecular nature or by the fact that these bands belong to the internal vibrations, which are rapidly damped out in the presence of water molecules.

An active interest in vibrations at these frequencies is observed. These modes are believed to be potentially sensitive to the order and to play a key role in the biological functions of macromolecules. Thus the vibrations of subunits, or molecules as a whole, is supposed to determine the activity of immunoglobulin.

There are a number of approaches to the description of these vibrations. Several models have been developed in order to estimate their frequencies. A model has been proposed [109] in which two parts of the protein globule move relative to one

another, the presence of water damping these vibrations. The model proposed by Go [110] considers the protein molecule as a homogeneous elastic conglomerate, which is physically justified since in the case of low-frequency modes, the wavelength is large relative to the size of side pendants in the protein molecule. To estimate the frequencies of vibrational modes, the sample of protein was considered as a system of cubes arranged in space in a regular manner. This permitted the usage of boundary conditions and the consideration of an aggregate of elastic waves in this model system. Estimations have shown that the region of vibrational frequencies in this case is limited to an interval of $18-200\ cm^{-1}$.

Chou [111–114] has developed a theory of vibrations in a quasi-continuous model that allows one to calculate the so-called 'dominating low-frequency modes' for various biomacromolecules. These modes, usually termed 'breathing', correspond, in the author's opinion, to the line observed in the Raman spectra at the lowest frequency. They seem to have the maximum amplitudes and, from the biological point of view, can be considered as 'activating low-frequency modes', the existence of which will activate the biological function of the macromolecule. According to Chou's theory,[113] the frequency of these modes depends on the masses of the chains under consideration, the number of their coils, the number of hydrogen bonds, and the force constants of the latter. The low-frequency modes have been studied [114] for the immunoglobulin molecule, which is known to consist of 12 domains of light and heavy types. Considering the domains to be of three types, Chou assigned the bands at 28 and 36 cm^{-1} observed in the Raman spectrum [115] to the 'breathing' modes of different types of domain.

It should be noticed that in the studies of nucleic acids, the low-frequency modes of the types considered also attract interest, because these vibrations are associated with the destruction of helices and changes in hydrogen bonding in them. A series of investigations in this direction has been carried out.[116–122] Hence, the investigation of the low-frequency modes for complex biological systems may now be spoken of as a new field in molecular biophysics.

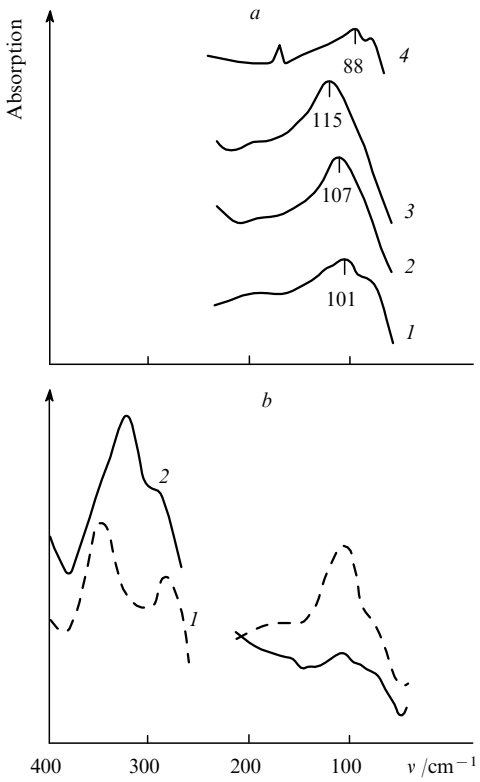


Figure 8. FIR (*a*) and polarised (*b*) spectra of partially crystalline polyurethane.[126]
(*a*) The IR spectra of amorphous (*1*) and oriented (*2*) samples measured at room temperature. Curves *3* and *4* represent the spectra of the oriented sample measured at −75 and 180 °C, respectively; (*b*) polarised spectra of polyurethane extended by 300%: (*1*) the axis of polarisation is orthogonal to the axis of extension, (*2*) the axis of polarisation is parallel to the axis of extension.

VII. Urethanes

Polyurethanes are very important for industry, that is why they are being widely investigated by a variety of methods including IR spectroscopy.[123] The appearance of a great number of publications devoted to compounds of this class has been stimulated by the creation of segmented polyurethanes exhibiting a number of valuable physicochemical properties. The application of spectral methods to the investigation of hydrogen bonding, orientational behaviour of rigid and flexible segments in the deformation appeared to be rather fruitful. However, a somewhat paradoxical situation exists in the spectroscopy of polyurethanes. There is a large body of publications devoted to the IR spectra of polyurethanes in the middle spectral region, whereas the data on Raman (excluding Refs 124 and 125) and FIR spectra for polyurethanes are practically lacking in literature. Only recently, the FIR spectra of polyurethanes have been reported.[126–128]

Partially crystalline polyurethane synthesised from diphenylmethyl diisocyanate and 2,4-toluylene diisocyanate has been studied.[126] The absorption bands at 101 cm^{-1} for the amorphous sample and at 107 cm^{-1} for the highly oriented sample were assigned to vibrations of the hydrogen bond. These bands are temperature-sensitive (Fig. 8), and the spectra of oriented samples exhibit perpendicular dichroism. As is seen in Fig. 8, in the spectrum of the highly oriented sample, the band at 107 cm^{-1} shifts to 115 cm^{-1} on cooling from room temperature to −75 °C. In the melt, this band has a frequency of 88 cm^{-1}. A large band width in the region of 100 cm^{-1} in the spectrum of polyurethane is related to the existence of different hydrogen bonds.

In the spectrum of a solution of the polyurethane in DMF, bands at 98 and 87 cm^{-1} are observed. The authors assign the former band to the inter-urethane hydrogen bonds and the latter to the bond between the urethane NH group and the carbonyl group in DMF. This choice of the solvent and concentration (30 mass %), is explained, probably, by the solubility of this polyurethane only in this solvent. However, DMF can form different types of hydrogen bonds with this compound and various self-associates. All this makes the band assignment rather ambiguous.

Analysis of the bands in the region of $270-400\ cm^{-1}$ was based on polarisation measurements for oriented samples. It is shown that the band at 320 cm^{-1} exhibits the parallel dichroism and is sensitive to the packing of the molecules, which is seen from the changes in its intensity and half-width. This band almost disappears in the amorphous sample. By analogy with the data on polyesters,[21] it is assigned to the coupled bending modes of the methyl and −O−CO−NH−C− groups, the main contribution to this mode being made by the bending vibrations of the methyl groups.

The bands exhibiting perpendicular dichroism are assigned to the torsional modes about the C−N bond (350 cm^{-1}) and to torsional vibrations of the CH_2 units (280 cm^{-1}) bound to the OCONH group. It might be expected that the frequency of the torsional vibration about the C−N bond should be affected by intermolecular interactions existing in the system, however, this band has the same frequency and intensity within a wide temperature interval for samples having different degrees of crystallinity, whereas the band at 100 cm^{-1} undergoes significant changes. Unfortunately, the region of $200-270\ cm^{-1}$ in which, according to the literature data,[21,45,46] these torsional modes are expected, is not covered by the interferometer used in Ref. 126.

Normal coordinate analyses for polyurethane molecules, which could be useful for a reliable assignment of the bands in the low-frequency region, are not yet available, which is why the interpretation of the bands presented in Ref. 126 has an empirical character.

Normal coordinate analysis has been performed for low-molecular-weight urethanes,[124, 125] in particular, for urethane of the simplest structure, methyl *N*-methylcarbamate.[129] Vibrational analysis for 2,6- and 4,6-polyurethanes based on 1,6-hexamethylene diisocyanate and for a model urethane, dimethyl-1,6-hexamethylenedicarbamate, allowed only planar modes to be assigned.[125] Hence, there is no full assignment of the bands in the low-frequency region for the polyurethanes.

The absence of reliable data on normal coordinate analysis for compounds containing the urethane group and on the low-frequency region of vibrational spectra has stimulated thorough experimental studies of urethanes by FIR spectroscopy.

A series of low-molecular-weight model urethanes has been experimentally studied [127] in the FIR region. The comparison of a series of spectra for various crystalline polyurethanes synthesised on the basis of 1,6-hexamethylene diisocyanate and 2,4- and 2,6-toluylene diisocyanates allowed one to reveal a number of absorption regions in the interval of 70–400 cm^{-1} typical of the vibrations of the urethane group, namely, 110–114, 140–170, 180–230, 270–290, 306–340, and 360–375 cm^{-1}. It was attempted to reveal the absorption bands associated with the intra- and intermolecular modes by means of temperature-dependent measurements. A decrease in temperature appeared to cause the most pronounced changes in the bands at 100–110 and 130–200 cm^{-1}, thus speaking for the assignment of these bands to the intermolecular modes (Fig. 9). A high-frequency shift of the former band, as in the case of crystalline amides, is insignificant (1–5 cm^{-1}). It is this band that is related to intrinsic vibrations of the hydrogen bond in amides [33] and in the above-considered polyurethane.[126] As for the region of 130–200 cm^{-1}, the most significant shift (15–25 cm^{-1}) as the temperature dropped to −140 °C was observed in the spectra of diurethanes synthesised from aliphatic diisocyanate. The 'Amide VII' band in which the torsional motion about the C—N bond makes the main contribution is known to lie in this region.[33, 57, 129] The torsional mode of the urethane group neighbouring the flexible polymethylene chain is supposed to depend on the conformation of the latter and on the hydrogen bond formed in the crystal, thus leading to a temperature dependence of this band. It is also possible that in the case of aliphatic urethanes, the intrinsic vibration of the hydrogen bond contributes significantly to the absorption at this frequency.

In the spectra of urethanes containing the benzene ring, there is an absorption band at 350 cm^{-1}, which can be assigned to the vibrations of this group rather than to the torsional modes about the C—N bond.[126]

Interurethane hydrogen bonds play a substantial role in the formation of associates in amorphous oligourethanes based on oligodivinylisoprene. The features of structure formation in these associates have been studied by IR spectroscopy.[130]

The investigation of the FIR spectra for oligourethanes containing terminal and internal urethane groups has revealed an interesting feature.[131] It was found that the spectral picture in the region of 60–250 cm^{-1} is independent of the type of diisocyanate used in the synthesis, but is determined only by the arrangement of the urethane block. When the urethane fragments are terminal, association is facilitated for these compounds as compared to that for the compounds in which the urethane fragments are located inside the chain. In the latter case, the oligodivinylisoprene chains tend to block the urethane groups. Nevertheless, in this case, hydrogen bonds between the urethane groups are also formed. The data on the FIR spectra and on the bands of the NH— and C=O stretching vibrations indicate that not only the degree of association but also the system of hydrogen bonds are different for the oligomers with the terminal and internal positions of the urethane fragment, for the frequencies of the absorption bands of the bonded NH—, CO—, and NH...OC groups differ from one another.[131] It might be supposed that the bands at 105 and 85 cm^{-1} observed in the FIR spectra of oligourethanes with terminal and internal positions of the urethane groups, respectively, result from the vibrations of hydrogen bonds of various energies (Fig. 10).

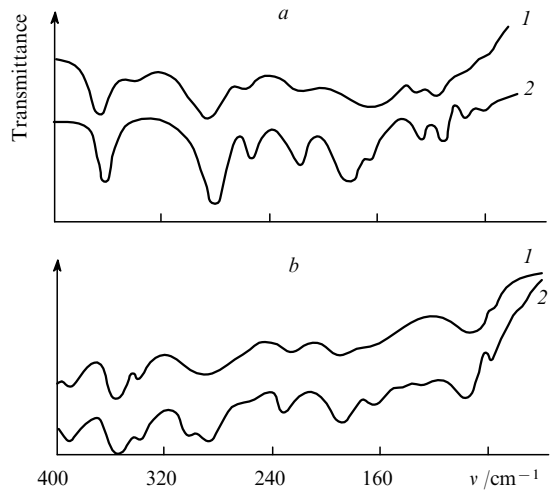


Figure 9. The IR spectra of diurethanes $CH_3CONH(CH_2)_6NHCOBu$ (*a*) and $CH_3CONHC_6H_4CH_2C_6H_4CONHCH_3$ (*b*) in the region of 40–400 cm^{-1} measured at 25 (*1*) and −140 °C (*2*).[127]

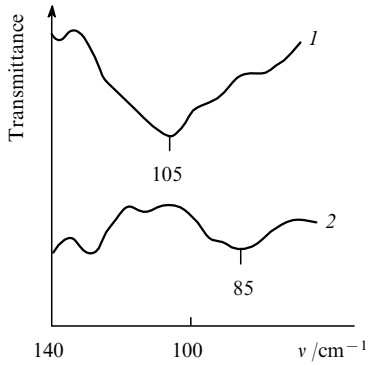


Figure 10. The IR spectra of urethane oligomers in the region of 60–140 cm^{-1} with the terminal (*1*) and internal (*2*) arrangements of the urethane fragment.[128]

Some polyurethanes have been studied by FIR spectroscopy.[127, 128] Temperature and polarisation measurements have revealed the absorption bands in the ranges of 130–200 and 80–100 cm^{-1} which are sensitive to the hydrogen bonds. As in the spectra of model diurethanes (see Fig. 9), two bands in the regions of 90 and 200 cm^{-1} appeared to be temperature sensitive (Fig. 11). Both bands exhibit preferentially a perpendicular dichroism (Fig. 12). The results obtained allowed the authors to suppose that the band at 200 cm^{-1} belongs to the torsional vibrations about the C—N bond and that at 90 cm^{-1} is assigned to vibrations of the hydrogen bond formed between the urethane groups.

The FIR spectra of more complex cross-linked polymers [127, 128] are very similar and independent of the nature of the diisocyanates used for the synthesis and of the concentration of cross-linkages in the polymer network. The authors of Ref. 131

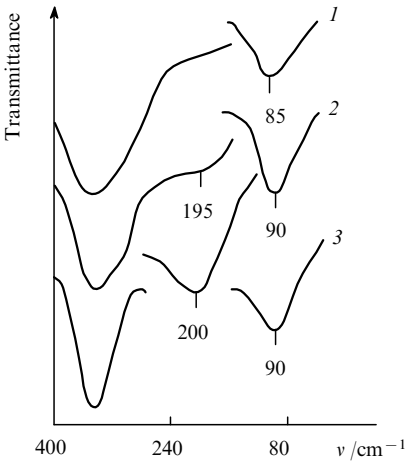


Figure 11. The IR spectra of polyurethane synthesised from polybutylene glycol adipate and diphenylmethane diisocyanate in the region of 60–400 cm^{-1} at 120 (*1*), 25 (*2*), and −140 °C (*3*).[128]

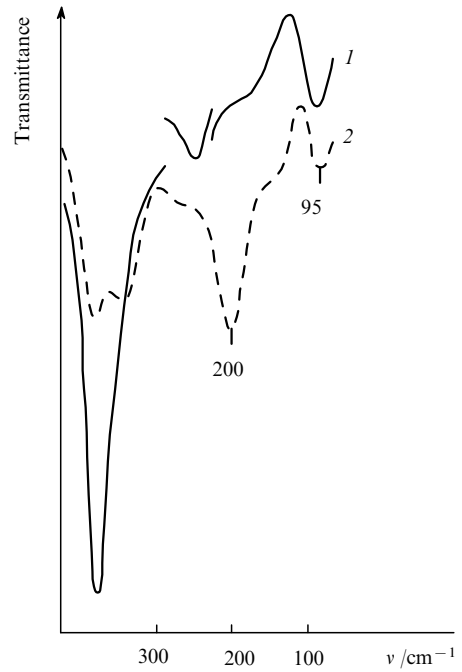


Figure 12. Polarised spectra of polyurethane synthesised from polybutylene glycol adipate and diphenylmethane diisocyanate extended by 350%.[128]
(*1*) The polarisation vector is parallel to the axis of extension, (*2*) the polarisation vector is orthogonal to the axis of extension.

connect the presence of the band at 85 cm^{-1} with the vibrations of the hydrogen bond.

Hence, from the FIR spectroscopic studies of urethanes that have recently been started, the absorption band was found that corresponds to the vibration of the hydrogen bond in these systems. This is a new step in research on the structure of polyurethane systems.

VIII. Conclusion

The presented material shows that the application of low-frequency vibrational spectroscopy to the investigation of amides and urethanes, and in particular, of biological objects, extends the capabilities of the analysis of molecular vibrations. Thus, many tasks connected with the studies of intramolecular and intermolecular vibrations can be successfully solved for low-molecular-weight and especially crystalline compounds. However, the application of low-frequency spectroscopy to the studies of such complex biological objects as proteins resulted in a modest success. In this case, the spectrum consists of broad diffused bands with weak separate peaks on the background of this band. The comparison of calculated and experimental spectra for simple proteins indicates that only a small part of the bands expected from calculations is observed in the experimental spectra. That is why the interpretation of the bands becomes problematic.

The use of low-frequency spectroscopy for the studies of relatively simple polymeric systems such as polyamides and polypeptides is undeniably successful. In many cases, it provides unique information. Certainly, only this method makes it possible to observe experimentally the bands of intermolecular vibrations including intrinsic vibrations of hydrogen bonds. The complex of techniques has been developed to assign experimentally the bands observed in the spectra to these modes. The technique of the $R(v)$ representation used in Raman spectroscopy provides a possibility to investigate hydrogen bonds in liquid amides.

The use of FIR spectroscopy in studies of conformational transformations in polyamides and polypeptides has shown its advantages over spectroscopy in the middle region, for the low-frequency region is especially sensitive to chain conformations. Low-frequency spectroscopy can be useful in studies of polymorphism in polymers and of the conformational composition of macromolecules both in the qualitative and quantitative aspects.

As a rule, IR spectroscopy is beneficial for investigations of polyamides and polypeptides in the low-frequency region, whereas the Raman spectra have been less studied. Therefore, investigations of Raman spectra in the region close to the excitation line are promising, because according to existing ideas the frequencies of longitudinal acoustic modes in helices of polypeptides, proteins, and nucleic acids as well as 'breathing' modes of globular systems are located in this region. The elucidation of the mechanism of these vibrations can provide a new tool for studies of vibrations of large molecular aggregates or macromolecules as a whole.

As far as the class of urethanes is concerned, it should be noticed that despite the obvious advantages of the low-frequency method, it has scarcely been used for studies of these objects. There is rather voluminous literature on the spectra of polyurethanes in the middle region. The role of the hydrogen bond and conformations of the molecules is very important for these compounds, that is why the examination of the low-frequency region of vibrational spectra is a very interesting and promising task for understanding the structure of the substance.

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