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HYDROGEN BONDING AND TORSIONAL VIBRATIONS OF MOLECULES IN THE SERIES OF *n*-ALCOHOLS

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In paper (1), for *n*-paraffins, regularities were obtained indicating a definite connection between the lines of Raman spectra (r.s.) up to 500 cm^{-1} and the physical parameters of paraffins. Thus, for example, the dependences

$$T_{\text{pl}} = T_1^2/\nu_{\text{zh}}, \tag{1}$$

$$w = T_2^2/\nu_{\text{k}}, \tag{2}$$

were established, where T_{pl} and w are the melting temperatures and activation energies of viscous flow of representatives of the homologous series of *n*-paraffins, ν_{zh} and ν_{k} are the frequencies of the most intense lines of the Raman spectra in the liquid and crystalline states, and T_1 and T_2 are constants, respectively the same for all representatives of the *n*-paraffin series under consideration.

In paper (2), on the basis of (1), the dependence of the proton spin-lattice relaxation time in *n*-paraffins on the number of carbon atoms in the molecule was explained, and it was indicated that in the relaxation mechanism the main role is played by longitudinal deformation vibrations of the carbon skeleton of the molecules, which determine the value of w, i.e., in this case it is not intermolecular interactions of protons that are essential, but intramolecular ones.

The aim of the present work is to show that the regularity (1) also exists in *n*-alcohols, and, on the basis of the connection between T_{pl} and the most intense lines of the Raman spectra up to 500 cm^{-1} of liquid *n*-alcohols, to refine the assignment of the frequencies of these lines to a definite type of molecular vibrations. The second task is to make a judgment about the influence of hydrogen bonding on the established type of vibrations by comparing analogous regularities for *n*-alcohols and *n*-paraffins. *n*-Alcohols, as is known, having a

Fig. 1

Figure 1: Fig. 1

structure of carbon chains identical to the structure of the carbon chains of n-paraffins, differ substantially from the latter by the presence of a special type of intermolecular interaction called the hydrogen bond. As X-ray structural investigations have shown, they have a chain-like association of molecules by hydrogen bonds (^{3}).

Normal primary alcohols with the number of carbon atoms C_2–C_{12} were considered; their Raman spectra were taken for C_2–C_4 from (^{4}), for C_5–C_{12} from (^{5}), and the melting temperatures from (^{6}).

The quantities studied are plotted in Fig. 1 on a logarithmic scale in the same energy units (cm^{-1}) as a simple function of n, the number of carbon atoms in the molecule. In contrast to the previous work (^{1}), through the points T_{pl} not an averaged curve was drawn, but a broken line (line I), characteristic of dependences of T_{pl} on n in the case of homologous series of n-paraffins and their derivatives. The frequencies are denoted by filled circles; the sizes of these circles for the most intense lines in different spectra were taken to be the same, while within each spectrum, for other less intense lines, their sizes are approximately proportional to the visual intensity relative to the indicated most intense one.

It is easy to see from the figure that the frequencies $\nu_\varkappa$ are located symmetrically with respect to the points T_{m} with an axis of symmetry parallel to the n axis (line 2). To make this more evident, line 3, symmetric to line 1, has been drawn in the figure. The slight scatter of the frequency points may be attributed to the accuracy of the experimental determination both of T_{m} and of the frequencies of the spectral lines. For example, for alcohol C_5 in (7), instead of the value 366 cm^{-1}, 355 cm^{-1} is given, which places the point very well on the broken line 3, while the line 401 cm^{-1} is absent altogether; instead of the line 433 cm^{-1}, the line 440 cm^{-1} is given. It remains to be regretted that in (7) the intensities of the inter-

Fig. 1

secting lines are not indicated. Analogously, there is scatter in the literature values of the melting temperature for some alcohols. For example, for n-butyl alcohol (C_4), −89.6°C (6) and −79.9°C (11).

Thus, between T_{m} and the frequencies $\nu_\varkappa$ for n-alcohols in the liquid state, from the experimental point of view, there is an ideal correlation against the background of broken line 1, described by relation (1), as in the case of n-paraffins. The difference lies only in the values of the constant T_1, which deserves special discussion (for n-paraffins $T_1 \approx 205$ cm^{-1} or ≈ 295°K, for n-alcohols ≈ 215 cm^{-1} or ≈ 309°K).

The established correlation (1), which is regularly repeated for different homologous series, cannot be accidental and, apparently,

indicates the frequencies of those molecular vibrations which determine T_m. A review of the current literature on this question makes it possible to assign these frequencies ν_ℓ to torsional vibrations of molecules in the most stable trans-isomeric configuration, which has the minimum potential energy. This is based on the following information about the structure and the mechanism of the transition from the solid state to the liquid state in n-paraffins and their derivatives.

Paraffins and their derivatives in the solid state, and also in the liquid state (especially near the melting temperature), are molecular structures with a parallel orientation of the longitudinal axes of the molecules (^{8}). In this case, on the basis of the theory of closest packing (^{9}), depending on whether the number of carbon atoms in the molecule is even or odd, the packing density of the molecules in these structures is different.

Analysis of the low-frequency Raman spectra (^{10}) up to 500 cm^{-1} for solid and liquid n-paraffins makes it possible to judge the behavior of n-paraffins and their derivatives near T_m. In the solid state, molecular motion is very restricted (the spectra have only one single line). In this case, one of the essential types of molecular motion is evidently the deformation vibrations of the carbon skeleton of the molecules along their long axes. As was shown (^{10}) for n-paraffins up to C_{16} and in (^{2}) for higher representatives (on the basis of studies of proton spin-lattice relaxation), this type of molecular motion is retained in the liquid state as well.

It is known that near T_m the volume of solid paraffins and their derivatives increases considerably (^{8}). The reason for this, apparently, is an increase in the amplitude of the longitudinal deformation vibrations of the molecular skeleton and the "stretching," "loosening" action of these vibrations. Under these conditions, created by deformation vibrations, at T_m a new type of molecular motion arises—the rotation of molecules (^{10}) about longitudinal axes passing through one of the rows of carbon atoms (in the spectra, in addition to the former single lines in the solid state, a new system of lines appears). It should be assumed that, as long as the externally supplied thermal energy is insufficient to transform the entire solid phase into a liquid one, the rotation of molecules in the liquid phase takes place in the energetically most favorable trans-isomeric configuration. With an increase in temperature above T_m, mobility of individual links of the molecules arises, which gives rise to rotational isomers. In this case, the higher the temperature, the greater the number of molecules in the state of rotational isomers and the greater their variety. However, at any not too high temperatures the dominant state of the molecules is evidently the principal, energetically most favorable trans-isomeric state.

The foregoing made it possible, as stated earlier, to assign the frequencies of the most intense lines of the spectra of n-alcohols in the liquid state, ν_ℓ, to the frequency of torsional vibrations of molecules in the trans-isomeric state, since the rotation is hindered. As an addition to this, attention should be paid to a noteworthy fact—the "broken" character of the change in the frequencies of these lines from one member of the series to another. This phenomenon can be correlated with the packing density of even-odd molecular structures on the basis of the theory of closest packing (^{9}) and explained by the determining influence of this packing on the frequency of torsional vibrations, since there is a correlation between the packing density and T_{m}.

Let us turn to the question of the influence of the hydrogen bond in n-alcohols on the torsional vibrations of molecules. For this purpose, in Fig. 1 the graphs for n-paraffins according to the data of (^{6}) and (^{10}) (cm^{-1}) are additionally given. The dotted line 4 is plotted from the values of the frequencies ν_k assigned to longitudinal deformation vibrations of the molecular skeleton (^{10}). The frequencies ν_k are indicated by triangles, the tips of which point to the frequency values. These val—

tions in (1) and (2) were correlated with the activation energies of viscous flow of the n-paraffins, and on this basis the reduced relation (2) was found. Line 5 is drawn according to the values of $T_{\mathrm{m.p.}}$. The broken line 6 is plotted symmetrically to line 5 with the axis of symmetry 7, so that one may judge the symmetry of the arrangement of the values ν with respect to the corresponding values of $T_{\mathrm{m.p.}}$. The frequency values of liquid n-paraffins in Fig. 1, as in the case of n-alcohols, correspond to the centers of the filled circles, the sizes of which have the same meaning as before. Among these frequencies there are also frequencies very close to ν_{k}, which are likewise assigned to longitudinal deformation vibrations.

Analysis of Fig. 1 makes it possible to note that, in the case of n-paraffins, correlation (1) is also satisfied rather well against the background of the broken line 6. On the basis of the previous arguments, we likewise assign the frequencies ν to torsional vibrations of n-paraffin molecules in the trans-isomeric configuration. It should be noted, however, that this correlation becomes clear beginning with $n = 8$, where a separation of deformation and torsional frequencies is clearly observed. For small n the clarity is somewhat impaired, evidently because of the influence of deformation vibrations on torsional vibrations. Such an influence in the case of n-alcohols is apparently small.

A conclusion about the influence of the hydrogen bond on the torsional vibrations of n-alcohol molecules may be drawn from a comparison of plots 1 and 3 for n-alcohols with plots 5 and 6 for n-paraffins. From this, first of all, it is easy to see a great similarity in the manner in which these dependences approach their lines of symmetry. However, there is also a difference. If one disregards the small difference in the positions of lines 2 and 7 (215 and 205 cm^{-1}), the main difference is that the dependences for n-paraffins are shifted, relative to the dependences for n-alcohols, by a number of carbon atoms equal to two. To verify this, plots $5'$ and $6'$ have been superposed in dashed form on plots 1 and 3 of the alcohols; these reproduce the outline of the dependences 5 and 6 of the n-paraffins, obtained by bringing lines z into coincidence with 2 and shifting plots 5 and 6 upward by two units of n. It is easy to see that plots 5′ and 6′ fit well onto plots 1 and 3, with the exception of the points corresponding to n-alcohol C_2 and n-paraffin C_4. The exception is evidently due to the too small size of the methylene "chain" in alcohol C_2. If this exception is disregarded, then, concerning the influence of the hydrogen bond on the torsional vibrations of n-alcohol molecules, the following conclusion may be drawn. The presence of a hydroxyl group in the alcohol molecule and of a hydrogen bond between molecules, from the standpoint of torsional vibrations, identifies the n-alcohol molecule quite well with an n-paraffin molecule in which the number of carbon atoms is greater by two than the number of these atoms in the alcohol molecule under consideration. Taking into account the optical equivalence[4] of oxygen and carbon atoms for Raman spectra, one may conclude that, from the standpoint of torsional vibrations, the existence of a hydrogen bond in n-alcohols is equivalent to the addition of one carbon atom to the methylene chain and to the non-associated existence of these molecules. Thus, the hydrogen bond leads to a quite definite decrease in the frequency of torsional vibrations of the molecules.

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Note: Figure translations are in progress. See original paper for figures.