

Investigations of Formaldehyde Oxime, its Polymers and Coordination Compounds. II

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The Infrared Spectrum of Poly(formaldehyde oxime)

Det Kongelige Danske Videnskabernes Selskab
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Synopsis

The infrared spectra of solid poly(formaldehyde oxime) and three deuterated species: poly(formaldehyde-d₂ oxime), poly(formaldehyde oxime-d) and poly(formaldehyde-d₂ oxime-d) have been measured in the region 4000-300 cm⁻¹. Vibrational assignments have been made for all the fundamentals on the basis of the observed isotopic frequency shifts and by comparing the spectrum of poly(formaldehyde oxime) with the spectra of related polymers. The assumption that the backbone of poly(formaldehyde oxime) is a planar zig-zag chain is consistent with the results obtained.

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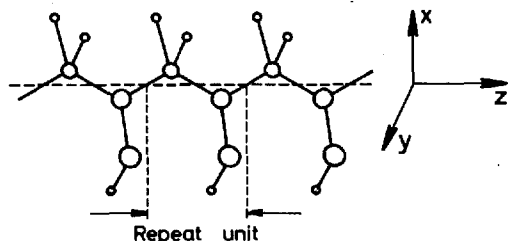
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I. Introduction

In the preceding paper¹ evidence was presented supporting the view that the so-called "triformoxime" is not a trimer of formaldehyde oxime but a chain polymer. The present investigation was undertaken to substantiate this conclusion.

The infrared spectra of poly(formaldehyde oxime), $(\text{CH}_2\text{NOH})_n$, as well as of its deuterated species, poly(formaldehyde- d_2 oxime), $(\text{CD}_2\text{NOH})_n$, poly(formaldehyde oxime- d), $(\text{CH}_2\text{NOD})_n$, and poly(formaldehyde- d_2 oxime- d), $(\text{CD}_2\text{NOD})_n$, have been measured. Both $(\text{CH}_2\text{NOH})_n$ and $(\text{CD}_2\text{NOH})_n$ were prepared in two different ways, *viz* by a polymerisation and by a polycondensation (see II.1). The products from the two types of reaction are referred to as A and B, respectively, in the present paper. The other two species, $(\text{CH}_2\text{NOD})_n$ and $(\text{CD}_2\text{NOD})_n$, were, however, prepared only by polycondensation.

The two compounds A and B have been shown not to be crystalline by the X-ray powder diffraction. The assignments of the infrared spectra have therefore been based on the assumption that poly(formaldehyde oxime) is an amorphous chain polymer, the backbone of which is a planar zig-zag chain, of repeating $-\text{CH}_2\text{NOH}-$ units as indicated in Fig. 1.



- OXYGEN
- NITROGEN
- CARBON
- HYDROGEN

Fig. 1. Poly(formaldehyde oxime) chain. The carbon and nitrogen atoms lie in the xz -plane (cp. Fig. 2), the CH, NO, and OH bonds in the xy -plane.

II. Experimental

1. Preparations

As discussed in the preceding paper¹ a polymer of formaldehyde oxime can be obtained either by spontaneous polymerisation of the (gaseous or liquid) monomer (products A) or by polycondensation of formaldehyde with hydroxylamine in aqueous solution (products B).

It was not possible to achieve a satisfactory degree of exchange of OD groups for OH groups simply by treatment of the polymeric products with D₂O, possibly because of the existence of strong hydrogen bonds in these compounds. The deuterated species were therefore prepared by condensation of CH₂O or CD₂O with deuterated hydroxylamine in D₂O. Even then complete deuteration could not be achieved (cf. IV.1).

The CD₂-compounds were prepared from paraformaldehyde-d₂, which was either depolymerised to CD₂O or transformed into (CD₂NOH)₃HCl, the latter two of which furnished the polycondensate (B) or the polymer (A), respectively (see Ref. 1, p. 17).

2. Spectroscopic Procedure

The infrared spectra of the compounds in KCl, KBr, CsCl and CsBr discs (1-3 mg sample in 300 mg matrix) were measured in the region 4000-300 cm⁻¹ using a Perkin-Elmer Model 225 spectrometer. The resolution was 1-2.5 cm⁻¹ throughout the entire frequency region. The absolute accuracy of wavenumber readings on the spectrometer itself is better than ±0.02 % and on the recorded spectra it is about ± 0.5-1 cm⁻¹. However, the accuracy of the frequencies given is believed to be no better than ± 1-2 cm⁻¹ for narrow bands and ± 3-5 cm⁻¹ for broad bands and shoulders. This is mainly due to the fact that the positions of most of the bands are somewhat dependent on the matrix material used. This is especially true for the (CH₂NOH)_n bands at 430 cm⁻¹ and 3300 cm⁻¹ for which variations in band frequency of about 5 and 10 cm⁻¹, respectively, have been observed. The accuracy of ± 0.5-1 cm⁻¹ in measurement of the band frequencies was obtained by expanding the spectra adequately. The following abscissa expansions were used:

spectral region	cm ⁻¹ per cm on the chart paper
3500-2000 cm ⁻¹	50 cm ⁻¹ /cm and 10 cm ⁻¹ /cm
2500-1000 cm ⁻¹	25 cm ⁻¹ /cm and 5 cm ⁻¹ /cm
1000- 400 cm ⁻¹	10 cm ⁻¹ /cm
460- 300 cm ⁻¹	5 cm ⁻¹ /cm

III. Theory

Symmetry and Normal Vibrations

The general theory of the internal vibrations of chain molecules has been thoroughly treated by several authors.² However, for the convenience of the reader a brief survey of the general features of the theory will be given.

For a non-linear molecule containing N atoms the number of nonzero normal vibrational modes is $3N-6$. The infrared spectrum of a polymer might therefore be expected to be very complicated, showing a large number of absorption bands. However, it may be shown that for an infinite polymer chain which is regularly arranged in a series of repeating units of identical conformation only those vibrational modes can be infrared (or Raman) active for which all such units are vibrating in phase. These are the so-called factor group vibrations. If there are r atoms in the repeating units the number of modes of non-zero frequency will be $3r-4$, since there are 4 modes of zero frequency (three translations of the whole chain and one rotation around the chain axis).

For real polymer chains containing a finite number N of repeating units a splitting of each vibrational mode into N vibrations is to be expected due to the interaction between the N adjacent repeating units. However, it turns out that of the N vibration frequencies the factor group vibration frequency is by far the most intense. All the others are either of zero intensity or quite weak.

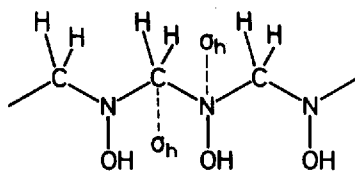


Fig. 2. Symmetry elements in an extended, infinite poly(formaldehyde oxime) chain.

From considerations of the symmetry elements of the repeating unit the symmetry species can be predicted. Fig. 2 shows the symmetry elements for the repeating unit of an infinite extended poly(formaldehyde oxime) chain. Here σ_h is a mirror plane in the xy -plane. The symmetry elements of the infinite extended poly(formaldehyde oxime) chain is the unit translation (which is equivalent to the identity E for the repeating unit) in addition to an infinite number of mirror planes σ_h . These elements form a line group and the elements of the repeating unit together with the unit translation form a sub-group of the line group, a so-called factor group. This group is not, however, a point group, but it can be shown that there is a point group which is isomorphous with the factor group. For the poly-

(formaldehyde oxime) chain with the symmetry elements E and σ_h this point group is C_s . In Table 1 are given the symmetry species and the number of vibration modes including zero modes.

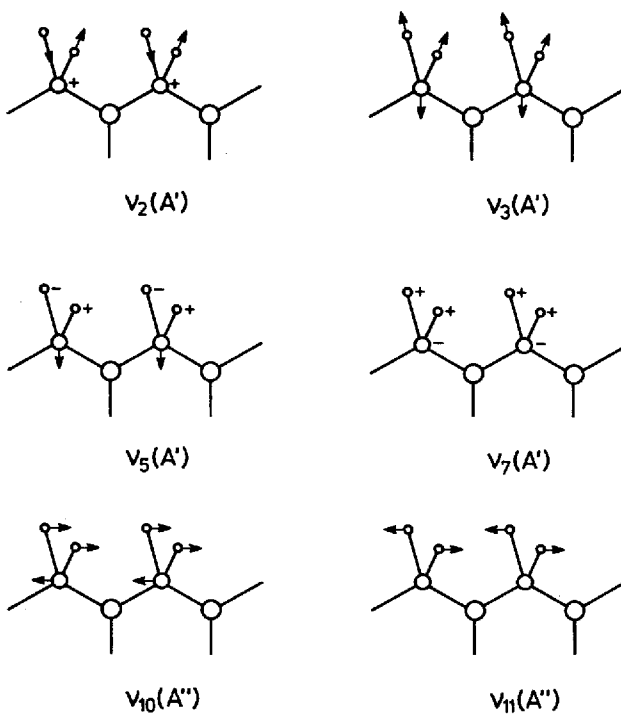
Table 1. Symmetry species for the point group C_s and for the isomorphous line group of the poly-(formaldehyde oxime) chain. Number of vibration modes.

Point group C_s	E	σ_h		
Line group	E	σ_h	Zero modes	Number of vibration modes*
A'	+1	+1	T_x, T_y, R_z	12
A''	+1	-1	T_z	6

* Number of vibration modes for an isolated, extended, infinite poly(formaldehyde oxime) chain (including zero modes).

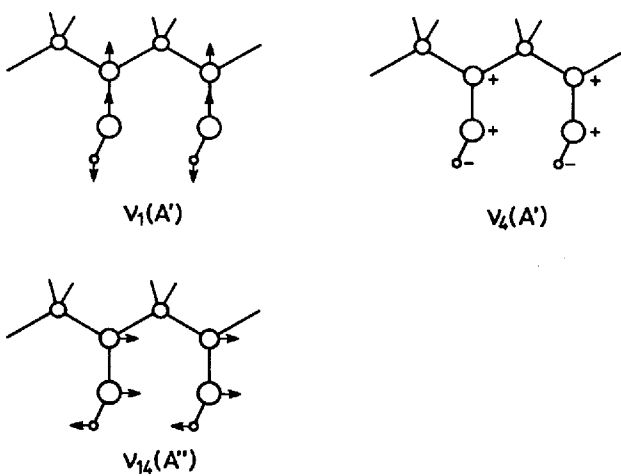
The characterization of chain molecules by line groups is, however, only correct if interaction between neighbouring chains can be neglected. Although there is a vibrational interaction between adjacent chains it is usually small compared with the interaction between adjacent repeating units within the same chain. For crystalline polymers this inter-chain interaction is regular and well-defined and is expected to cause a splitting of the absorption bands into a number of peaks, depending on the number of chains passing through a unit cell and on the selection rules. For amorphous polymers the interaction is of a random nature and for most compounds will give rise to a broadening of absorption bands. The line group analysis can therefore be considered to be a reasonable satisfactory approximation for amorphous polymers.

It follows from Table 1 that vibrations of species A' must be symmetrical with respect to both types of symmetry operation and that vibrations of species A'' are antisymmetric with respect to the mirror plane. The normal vibrations of a single poly(formaldehyde oxime) chain are shown in Figures 3, 4 and 5. The symmetry coordinates have been chosen in such a way that each of them – besides having the correct symmetry – also represents a rough approximation to the real mode of vibration for the chain.



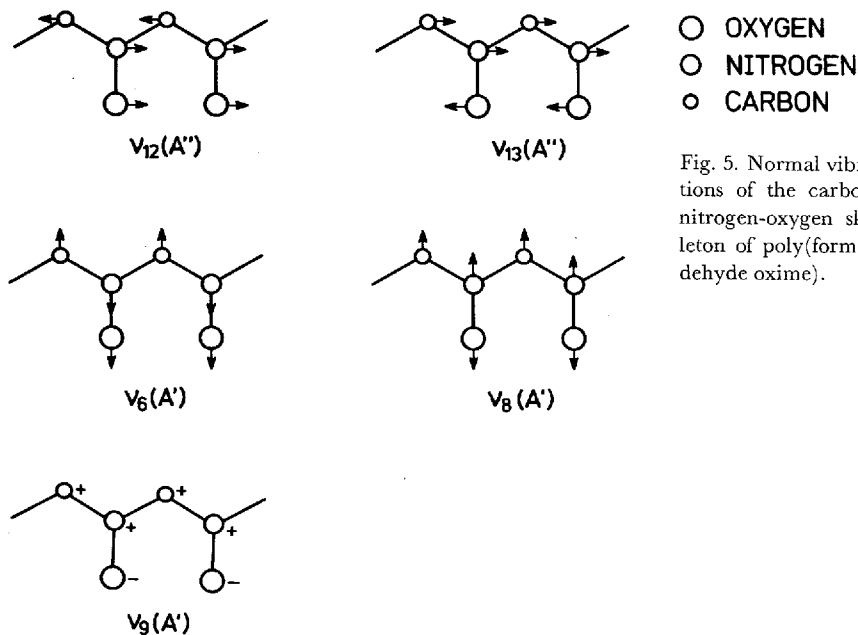
○ NITROGEN
○ CARBON
● HYDROGEN

Fig. 3. Normal vibrations of the CH₂ groups of poly(formaldehyde oxime). The CH₂ groups are shown slightly twisted with respect to the *xy*-plane.



○ OXYGEN
○ NITROGEN
○ CARBON
● HYDROGEN

Fig. 4. Normal vibrations of the OH groups of poly(formaldehyde oxime). The OH groups lie in the *xy*-plane but are shown slightly twisted.



In the high frequency range (above 2000 cm^{-1}) the true normal coordinates are in general well approximated by group symmetry coordinates, *i.e.* the $\text{CH}_2(\text{CD}_2)$ and $\text{OH}(\text{OD})$ stretching vibrations may be considered to be “pure” vibrations. However, at lower frequencies coupling between vibrations may occur if the groups are vibrating with nearly the same frequency, if they are situated near to each other and if the vibrations have the same symmetry. In such cases the fundamental vibrations will be rather “impure” because the valence coordinates mix in forming the normal coordinates, *i.e.* the group symmetry coordinates will be poor approximations to the true normal coordinates.

IV. Discussion of the Spectra

1. Results

The infrared spectra of poly(formaldehyde oxime), $(\text{CH}_2\text{NOH})_n$, and its deuterated species $(\text{CD}_2\text{NOH})_n$, $(\text{CH}_2\text{NOD})_n$ and $(\text{CD}_2\text{NOD})_n$ were measured in the solid state as described above. The spectra are shown in Figures 6, 7, 8, 9, 10, 11 and

12. It can be seen that apart from being rather simple the spectra of $(\text{CH}_2\text{NOH})_n$ formed by polymerisation (A) and by polycondensation (B) look very much the same; this is also true for $(\text{CD}_2\text{NOH})_n$. The indication is thus that the structures of A and B are very similar.

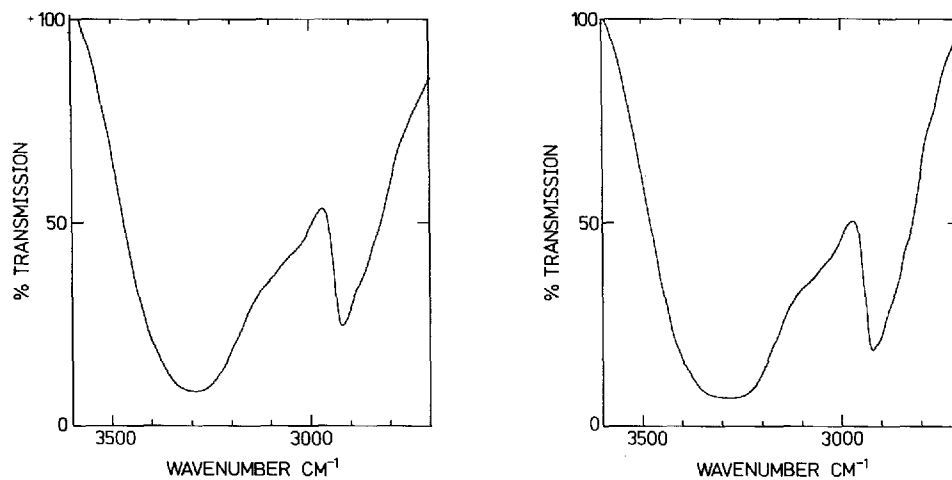


Fig. 6. Infrared absorption bands of $(\text{CH}_2\text{NOH})_n$ in the region $3600\text{-}2700\text{ cm}^{-1}$. Left: compound A. Right: compound B.

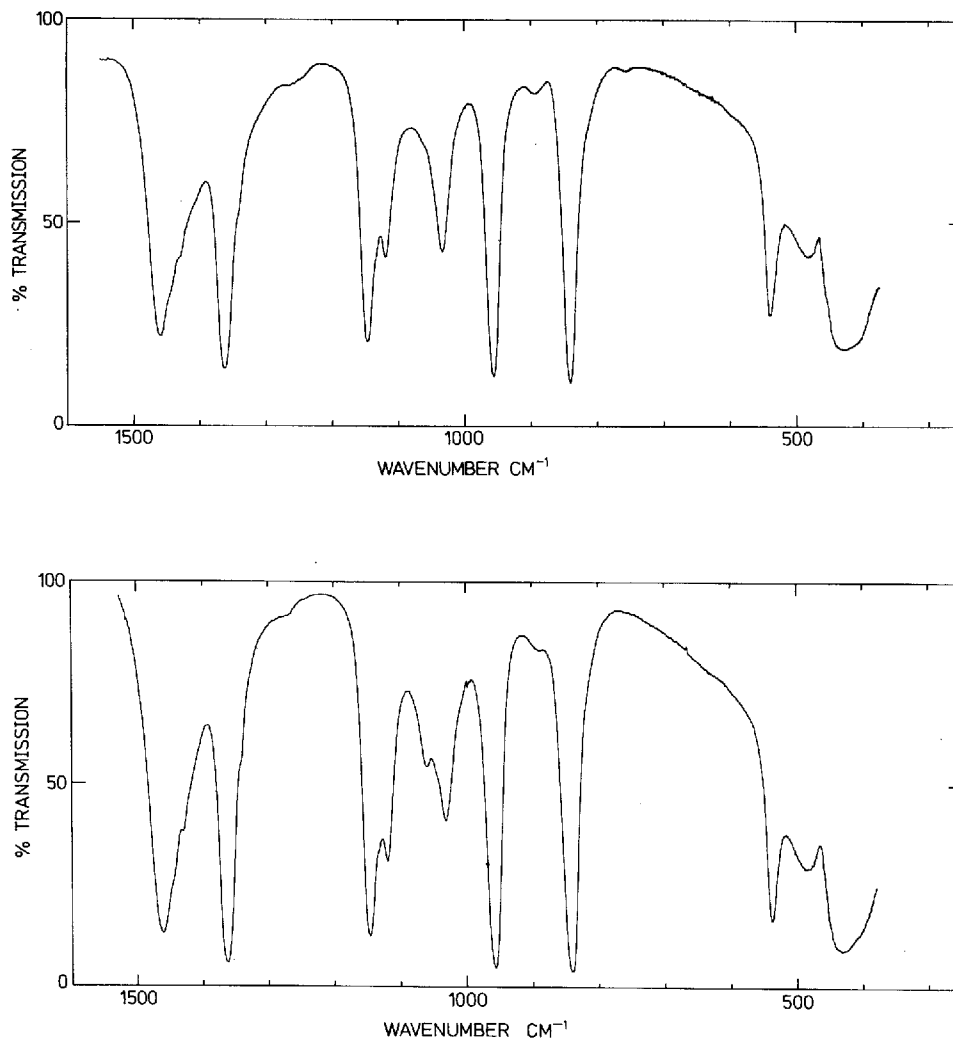


Fig. 7. Infrared spectrum of $(\text{CH}_2\text{NOH})_n$ in the region $1550\text{-}400\text{ cm}^{-1}$. Upper spectrum: compound A. Lower spectrum: compound B.

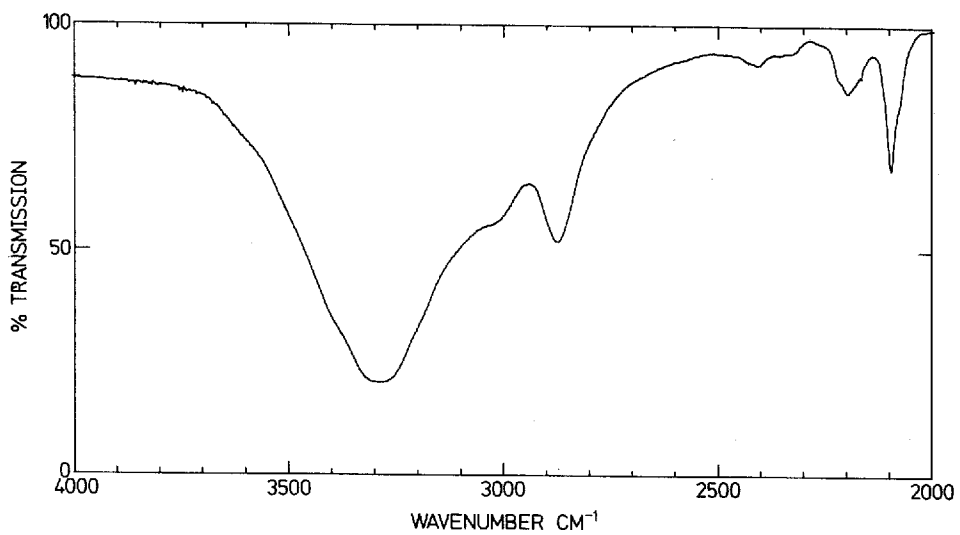
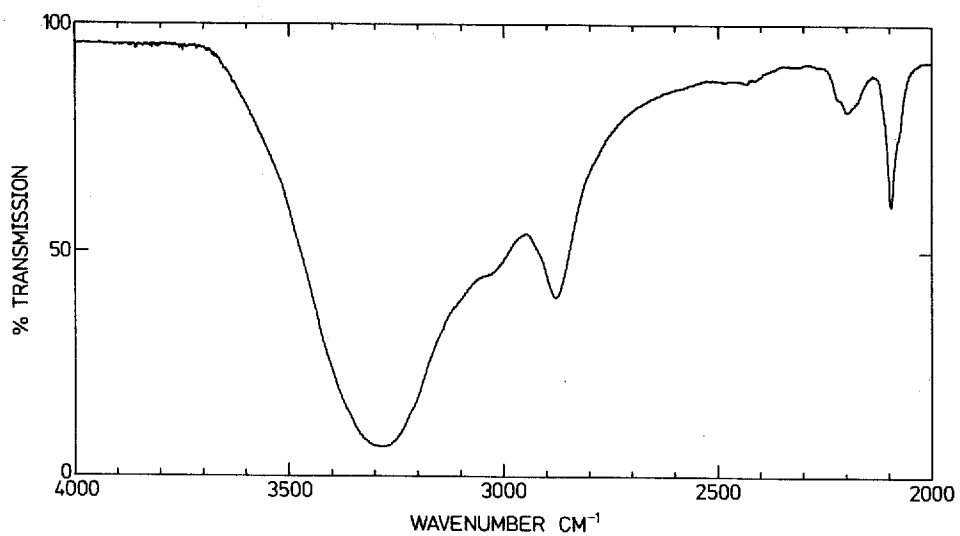


Fig. 8. Infrared absorption bands of $(\text{CD}_2\text{NOH})_n$ in the region 4000-2000 cm^{-1} . Upper spectrum: compound A. Lower spectrum: compound B.

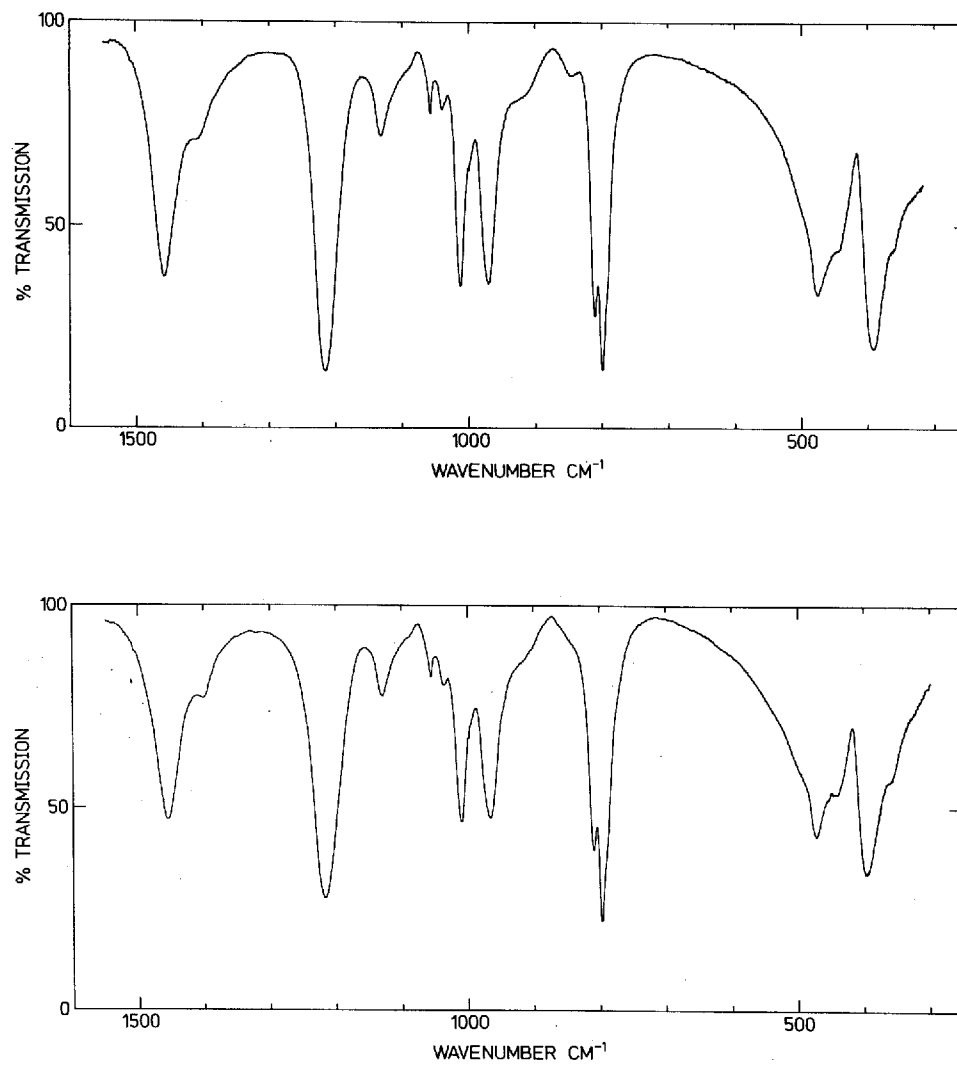


Fig. 9. Infrared spectrum of $(\text{CD}_2\text{NOH})_n$ in the region $1550\text{-}300\text{ cm}^{-1}$. Upper spectrum: compound A. Lower spectrum: compound B.

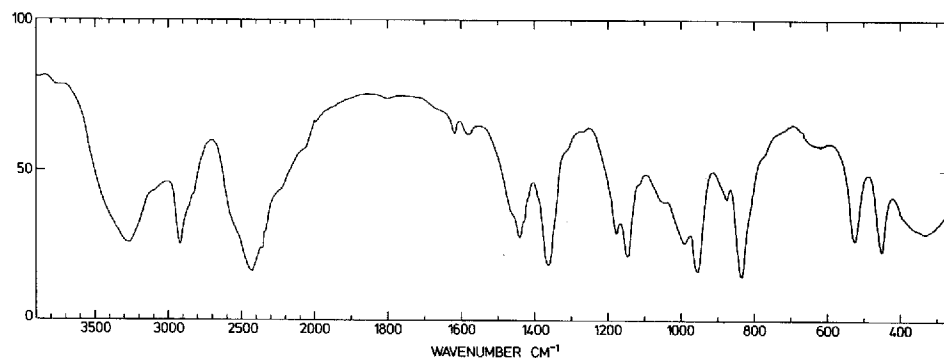


Fig. 10. Infrared spectrum of $(\text{CH}_2\text{NOD})_n$ in the region $4000\text{-}350\text{ cm}^{-1}$.

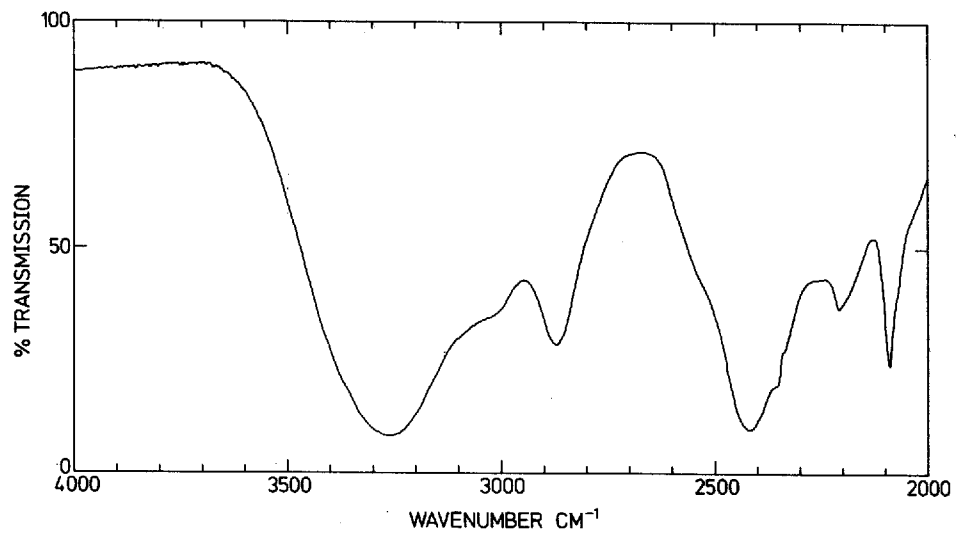


Fig. 11. Infrared spectrum of $(\text{CD}_2\text{NOD})_n$ in the region $4000\text{-}2000\text{ cm}^{-1}$.

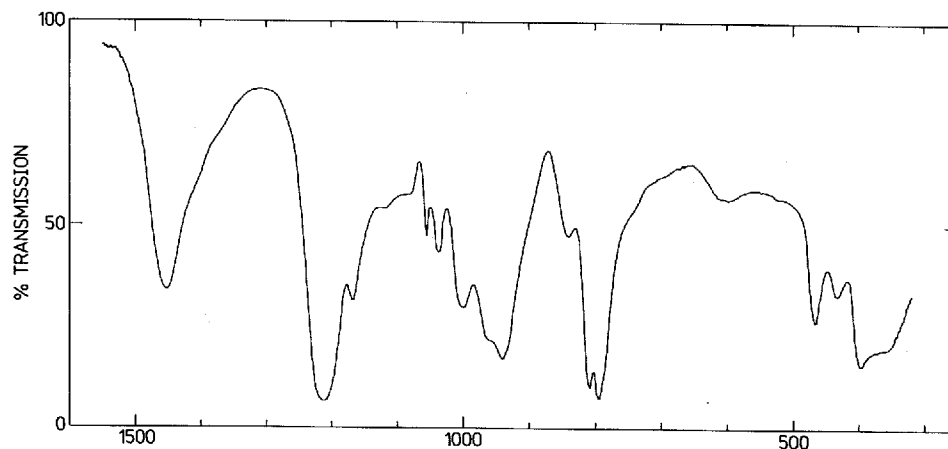


Fig. 12. Infrared spectrum of $(\text{CD}_2\text{NOD})_n$ in the region $1550\text{-}300\text{ cm}^{-1}$.

In the spectra of $(\text{CH}_2\text{NOD})_n$ and $(\text{CD}_2\text{NOD})_n$ two strong absorption bands are found at 2400 cm^{-1} and 3300 cm^{-1} . The former originates from the OD stretching vibration while the band at 3300 cm^{-1} is the OH stretching band also observed in the spectra of (CH_2NOH) and $(\text{CD}_2\text{NOH})_n$. This shows that both of the two OD deuterated samples still contain OH groups. Now, the change in dipole moment with respect to the vibrational coordinate $\left(\frac{\partial\mu}{\partial Q}\right)$, which determines the integrated absorption intensity of a fundamental band, is expected to be considerably smaller for the OD vibration than for the OH vibration, thereby giving rise to a lower intensity of the OD band as compared with the OH band. This makes it difficult to estimate the relative content of OD groups in the samples of $(\text{CH}_2\text{NOD})_n$ and $(\text{CD}_2\text{NOD})_n$ merely by comparing the observed intensities of the OD and OH stretching bands in the two spectra. However, since the observed intensity of the OD band in the spectra of $(\text{CH}_2\text{NOD})_n$ and $(\text{CD}_2\text{NOD})_n$ is greater than, and about equal to the intensity of the OH band, respectively, one may conclude that the degree of deuteration for both samples is considerably higher than 50%. By comparing the intensity ratios for other bands in the spectra of the two samples the content of OD groups has been estimated to about 80-90% for the $(\text{CH}_2\text{NOD})_n$ sample and 70-80% for the $(\text{CD}_2\text{NOD})_n$ sample. Although deuteration is thus far from complete it has proved possible to unambiguously assign the fundamental bands of $(\text{CH}_2\text{NOD})_n$ and $(\text{CD}_2\text{NOD})_n$ and to obtain reliable values of the band frequencies.

As discussed above the interaction between adjacent chains in amorphous polymers is expected to produce a broadening of the infrared absorption bands. This is in good agreement with the experimental results of the present investigation. No sharp bands are observed in the spectra, the half-band widths of most of the bands being 20-40 cm^{-1} . However, a few bands show greater half-band widths. The band at 3300 cm^{-1} (O-H stretching) seen in the spectra of $(\text{CH}_2\text{NOH})_n$ and $(\text{CD}_2\text{NOH})_n$, and the band at 2415 cm^{-1} (O-D stretching) observed in the spectra of $(\text{CH}_2\text{NOD})_n$ and $(\text{CD}_2\text{NOD})_n$ display half-band widths of ca. 400 cm^{-1} . The exceptional broadening of these two bands almost certainly arises from inter-chain and perhaps intra-chain hydrogen bonding. Likewise, the bands at 430 cm^{-1} and 335 cm^{-1} in the spectra of $(\text{CH}_2\text{NOH})_n$ and $(\text{CH}_2\text{NOD})_n$, respectively, which originate from the OH and OD out-of-plane deformation modes, are rather broad with half-band widths of 100-150 cm^{-1} . For the 1460 cm^{-1} band (OH bending), however, the broadening is less pronounced, the half-band width being only 50-60 cm^{-1} .

2. Procedure of Assignment

It follows from the above discussion, that the number of fundamental bands which one will expect to find in the infrared spectrum of poly(formaldehyde oxime) is $3r - 4 = 14$, since there are six atoms in the repeating unit (cp. Fig. 1) and all the normal vibrations are infrared active according to the selection rules.

For the assignment of the observed bands to fundamental frequencies the following procedure was adopted:

- (1) Bands which shifted appreciably on deuteration of OH groups were assigned as OH vibrations.
- (2) Bands which showed appreciable shifts on deuteration of CH_2 groups were assigned as vibrations involving CH_2 motions.
- (3) Bands which were only slightly affected on deuteration of OH groups and CH_2 groups must correspond to skeletal vibrations.
- (4) The assignments of the fundamental frequencies of poly(formaldehyde oxime) should compare reasonable well with the results obtained by other workers for related polymers such as polymethylene, polyoxymethylene and polyvinyl alcohol (see Table 3).

As far as points (1), (2) and (3) are concerned it must be kept in mind, however, that coupling between OH(OD) or $\text{CH}_2(\text{CD}_2)$ deformation vibrations and skeletal vibrations may decrease the isotopic frequency shifts for the OH and CH_2 deformation bands considerably, while on the other hand appreciable shifts of the skeletal bands will be observed as a result of the coupling.

In general one may conclude that whenever the ratio $\nu^{\text{H}}/\nu^{\text{D}}$ of an OH or a CH_2 group vibration frequency to the new frequency arising on deuterium substitution

has a value in the range 1.3-1.4, the OH (and OD) or CH₂ (and CD₂) vibration in question may be considered a "pure" group vibration. For "pure" skeletal vibrations ν^H/ν^D will be close to 1.0, while ratios of 1.1-1.2 for hydrogen vibrations as well as skeletal vibrations are indicative of strong coupling and therefore of "impure" or "mixed" vibrations.

V. Fundamental Frequencies

As already mentioned there are 14 fundamentals, *viz* nine of species A' and five of species A'' (cf. Table 1), whose assignments will be discussed in the present section. Using the approximation of group vibrations six of the fundamentals correspond to CH₂ vibrations and three to OH vibrations, the remaining five being skeletal vibrations (cf. Figures 3, 4 and 5). The resulting assignments are shown in Table 2. It can be seen that the fundamental frequencies of poly(formaldehyde oxime) formed by polymerisation (A) and by polycondensation (B), respectively, are almost identical, so that it is reasonable to conclude that the structures of the compounds A and B must also be very similar. For this reason and for the sake of simplicity the frequency values mentioned in the discussion below refer to the spectra of the compound B unless otherwise stated.

Table 2. Assignments and wavenumbers of fundamental bands for poly(formaldehyde oxime) and its deuterated species*.

Assignments	Species	(CH ₂ NOH) _n		(CD ₂ NOH) _n		(CH ₂ NOD) _n	(CD ₂ NOD) _n
		A	B	A	B	B	B
ν_1	A'	3300 ^a vs br	3290 ^a vs br	3290 ^a vs br	3300 ^a vs br	2435 ^a s br	2425 ^a s br
ν_2	A'	2923 s	2924 s	2195 w	2202 w	2924 s	2195 sh
ν_3	A'	2904 sh	2905 sh	2098 m	2101 m	2905 sh	2098 m
ν_4	A'	1460 s	1460 s	1455 s	1455 s	1177 m	1168 m
ν_5	A'	1444 sh	1444 sh	1130 w	1130 w	1442 m	1120 sh
ν_{10}	A''	1364 s	1364 s	1216 s	1217 s	1363 s	1214 s
ν_{11}	A''	1280 sh	1270 sh	915 [?] w	916 [?] w	1270 sh	—
ν_{12}	A''	1148 s	1148 s	1012 m	1011 m	1147 s	1001 m
ν_6	A'	1035 m	1031 m	968 m	968 m	994 m	940 m
ν_7	A'	957 s	958 s	811 m	810 m	957 s	809 m
ν_8	A'	841 s	841 s	799 s	799 s	837 s	795 s
ν_9	A'	540 m	539 m	474 m	474 m	527 m	468 m
ν_{13}	A''	457 sh	458 sh	442 sh	442 sh	452 m	435 m
ν_{14}	A''	430 ^a s br	437 ^a s br	395 s	397 ^a s	~335 ^a m br	359 m

* Abbreviations used: s, m, w, v, sh, br indicate strong, medium, weak, very, shoulder and broad, respectively. A and B denote two different ways of preparing the compounds (see text).

^a Band position dependent on the concentration of the sample in the disc and on the alkalimetal halide used as matrix (see text).

1. CH₂ Vibrations

In the C-H stretching region a strong absorption band is observed at about 2900 cm⁻¹ in the spectrum of (CH₂NOH)_n, the frequency at intensity maximum being 2924 cm⁻¹. Shoulders are seen on the low frequency side of the band at 2905, 2875 and 2855 cm⁻¹. The bands at 2924 and 2905 cm⁻¹ are assigned to asymmetric and symmetric CH₂ stretching vibrations, ν_2 and ν_3 , in good agreement with the values 2937 and 2908 cm⁻¹ obtained for polyvinyl alcohol (cf. Table 3). The remaining two bands are assigned as the first overtones of the OH bending vibration ν_4 and the CH₂ bending vibration ν_5 , the calculated values being $2\nu_4 = 2920$ cm⁻¹ and $2\nu_5 = 2888$ cm⁻¹. The observed anharmonicities, $\nu_{\text{obs.}} - \nu_{\text{calc.}}$, of -45 cm⁻¹ and -33 cm⁻¹, respectively, are, however, somewhat larger than expected for OH and CH₂ deformations, probably because of Fermi resonance with ν_3 and with the OH stretching vibration ν_1 at 3290 cm⁻¹. In the spectrum of (CD₂NOH)_n the only band observed around 2900 cm⁻¹ is a band of medium intensity at 2877 cm⁻¹ which must therefore be $2\nu_4$ (observed at 2875 cm⁻¹ in the spectrum of (CH₂NOH)_n). The ν_2 and ν_3 bands are found in the expected region at ca. 2200 and ca. 2100 cm⁻¹, the isotopic frequency shifts being of the magnitude expected for "pure" group vibrations.

Of the four CH₂ deformations the CH₂ bending vibration ν_5 is assigned to a shoulder of medium intensity at 1444 cm⁻¹ on the low frequency side of the strong band at 1460 cm⁻¹ which corresponds to the OH bending vibration ν_4 (see below). On C-deuteration the 1444 cm⁻¹ band shifts to 1130 cm⁻¹, the ratio $\nu^{\text{H}}/\nu^{\text{D}}$ being close to 1.3, while the 1460 cm⁻¹ band is barely affected. On deuteration of the OH groups ν_4 is weakened considerably so that ν_5 appears cleanly at 1442 cm⁻¹. The strong absorption at 1364 cm⁻¹ undoubtedly corresponds to the CH₂ wagging vibration ν_{10} which is found in the same region in the spectra of (CH₂)_n, (CH₂O)_n and (CH₂CHOH)_n (cf. Table 3). The isotopic frequency shift on C-deuteration is, however, only about 150 cm⁻¹, which yields a frequency ratio $\nu^{\text{H}}/\nu^{\text{D}}$ of only 1.12, indicating that the vibration is very "impure". As discussed at greater length below this is due to strong coupling between ν_{10} and the skeletal vibration ν_{12} in either (CH₂NOH)_n or (CD₂NOH)_n.

Table 3. Compilation of fundamental vibration frequencies for poly(formaldehyde oxime) (compound B) and some related polymers.

Approximate type of vibration	$(\text{CH}_2)_n$ ^{3,4} cm ⁻¹	$(\text{CH}_2\text{O})_n$ ⁵ cm ⁻¹	$(\text{CH}_2\text{CHOH})_n$ ^{6,7} cm ⁻¹	$(\text{CH}_2\text{NOH})_n$ cm ⁻¹
OH stretch.	—	—	~3340	~3290
CH ₂ asym.stretch.	2919	2979 2978	2937	2924
CH ₂ sym.stretch.	2851	2919	2908	2905
OH bend.	—	—	ca. 1430 ^c	1460
CH ₂ bend.	1473 1463	1471	1428 ^e	1444
CH ₂ wag.	1367 ^a 1352 ^a	1434 1381	1383 ^e	1364
CH ₂ twist.	1306 ^a	1286	?	1270
CC,CO or CN asym.stretch.	1131 ^b	1097 1091	1141	1148
CC,CO or CN sym.stretch.	1061 ^b	932	913	1031
CH ₂ rock.	731 720	1235 ^d 903	849 ^f	958
CO or NO stretch.	—	—	1093	841
CO or NO bend.	—	—	480	539
CO or NO wag.	—	—	410	458
OH wag.	—	—	610	437

^a Observed for amorphous polymer.³

^b From the Raman spectrum.

^c Coupling band: coupling of OH bending and CH₂ (or CH) wagging modes.

^d Coupling band: CH₂ rocking mode coupled with COC bending and CO sym. stretching modes.

^e From the infrared spectrum of $(\text{CH}_2\text{CHOD})_n$.

^f Observed for amorphous polymer.⁶

The CH₂ twisting vibration is found at 1306 and 1286 cm⁻¹ for $(\text{CH}_2)_n$ and $(\text{CH}_2\text{O})_n$, the bands being of very low intensity as a result of the small change in dipole moment during the vibration. For this reason the weak shoulder observed at about 1270 cm⁻¹ for $(\text{CH}_2\text{NOH})_n$ is assigned to the twisting vibration ν_{11} . On C-deuteration the band disappears and a weak band is then seen at 916 cm⁻¹. The latter is believed to correspond to the CD₂ twisting vibration (which is found at 909 cm⁻¹ for $(\text{CH}_2)_n$) possibly overlapped by the combination band $\nu_9 + \nu_{13} = 916$ cm⁻¹. Just as for polyoxymethylene the ratio $\nu^{\text{H}}/\nu^{\text{D}}$ is close to 1.4 indicating that the CH₂ twisting mode is a "pure" vibration.

The CH_2 rocking vibration in $(\text{CH}_2\text{O})_n$ has been assigned to a very strong band at 903 cm^{-1} , and for $(\text{CH}_2\text{CHOH})_n$ to a band of medium intensity at 849 cm^{-1} . In $(\text{CH}_2\text{NOH})_n$ two strong absorptions occur in this region, one at 958 cm^{-1} and the other at 841 cm^{-1} . For $(\text{CD}_2\text{NOH})_n$ these bands are shifted to 810 cm^{-1} and 799 cm^{-1} , respectively. Because of the larger isotopic shift of about 150 cm^{-1} the band at 958 cm^{-1} must be due to the CH_2 rocking mode ν_7 , whereas the 841 cm^{-1} band is due to a skeletal vibration, the N–O stretching vibration ν_8 (see below). The 810 cm^{-1} band of medium intensity is assigned to CD_2 rocking since the integrated absorption intensity of a CH_2 band in general decreases upon deuterium substitution; the strong band at 799 cm^{-1} must therefore arise from N–O stretching in $(\text{CD}_2\text{NOH})_n$. The low frequency ratio $\nu^{\text{H}}/\nu^{\text{D}}$ of 1.18 for the rocking vibration shows that it is considerably "mixed" like the CH_2 (or CD_2) wagging, the rocking vibration and the skeletal vibration ν_9 being strongly coupled (see below).

2. OH Vibrations

The O–H stretching vibration ν_1 of $(\text{CH}_2\text{NOH})_n$ occurs in the spectrum as a very strong and extremely broad band at about 3300 cm^{-1} which shifts to 2435 cm^{-1} on deuteration of the OH groups. Shoulders are observed in the spectrum of the $(\text{CH}_2\text{NOD})_n$ sample on the high frequency side of both bands, at approximately 3420 and 2560 cm^{-1} . These additional bands probably correspond to the asymmetric O–H and O–D stretching vibrations of HDO and D_2O , respectively, and arise from a small residue of D_2O and HDO in the sample.

The two OH deformations, *viz* the in-plane deformation (or bending) ν_4 and the out-of-plane deformation (or wagging) ν_{14} , are observed as strong, broad absorptions at 1460 and ca. 435 cm^{-1} . For $(\text{CH}_2\text{NOD})_n$ they are shifted to 1177 and ca. 335 cm^{-1} , respectively, the two bands being of medium intensity. The assignment of the OH bending vibration is in good agreement with the values of ca. 1430 and 1477 cm^{-1} which have been obtained for $(\text{CH}_2\text{CHOH})_n$ and solid acetone oxime $(\text{CH}_3)_2\text{C}=\text{NOH}$,⁸ respectively, while the OH wagging frequencies of 610 and 790 cm^{-1} for these compounds are considerably higher than that found for $(\text{CH}_2\text{NOH})_n$. However, the frequency ratio $\nu^{\text{H}}/\nu^{\text{D}} = 1.30$ shows that the 435 and 335 cm^{-1} bands are due to hydrogen and deuterium vibrations, respectively, and for this reason must be assigned to ν_{14} .

3. Skeletal Vibrations

The bands due to the five skeletal vibrations are found in the region $1200\text{--}400\text{ cm}^{-1}$. The asymmetric C–N stretching mode ν_{12} is assigned to the strong band at 1148 cm^{-1} in good agreement with the assignments for the corresponding skeletal vibrations of $(\text{CH}_2)_n$, $(\text{CH}_2\text{O})_n$ and $(\text{CH}_2\text{CHOH})_n$ (cf. Table 3). On C-deutera-

tion the band shifts to 1011 cm^{-1} . However, this vibration is not appreciably affected by deuteration of OH groups, the band being observed at 1147 cm^{-1} for $(\text{CH}_2\text{NOD})_n$. The large isotopic shift is an indication of strong coupling between the asymmetric C–N stretching vibration and a hydrogen (or deuterium) vibration, the observed frequency ratio $\nu^{\text{H}}/\nu^{\text{D}}$ being as high as 1.14. On the other hand, as mentioned above, the frequency ratio for the CH_2 wagging ν_{10} is unexpectedly low (1.12). Since coupling can occur only between vibrations of the same symmetry species it follows that it must be the asymmetric C–N stretching- and the CH_2 (or CD_2) wagging mode which couple strongly. It is therefore not really valid to ascribe the observed bands to “asymmetric C–N stretching” and “ CH_2 (or CD_2) wagging” since the actual mode of vibration in this case is a combination of both.

The symmetric C–N stretching (or CON bending) mode ν_6 gives rise to a band of medium intensity at 1031 cm^{-1} which shifts to 968 cm^{-1} on C-deuteration. The isotopic shifts indicates coupling, probably with the CH_2 (or CD_2) rocking vibration, both vibrations being of symmetry species A' . On deuteration of the OH groups the band appears at 994 cm^{-1} , the ratio $\nu^{\text{H}}/\nu^{\text{D}} = 1.04$ indicating weak coupling probably to the OH (or OD) bending vibration for which $\nu^{\text{H}}/\nu^{\text{D}} = 1.24$. As already mentioned, the strong band at 841 cm^{-1} is assigned to the N–O stretching mode ν_8 which like the ν_6 band is affected by C-deuteration, showing that the N–O stretching vibration is also a “mixed” vibration.

The remaining two skeletal bands, due to the NO bending mode ν_9 and the NO wagging mode ν_{13} , are expected to be found in the region below 800 cm^{-1} . In polyvinyl alcohol the CO bending frequency is situated at 480 cm^{-1} and the CO wagging at 410 cm^{-1} (cf. Table 3). The band of medium intensity at 539 cm^{-1} in the spectrum of $(\text{CH}_2\text{NOH})_n$ is therefore assigned to ν_9 whereas the shoulder which is just observable at ca. 458 cm^{-1} on the high frequency side of the strong band ν_{14} is presumed to correspond to ν_{13} .

The assignments are supported by the results obtained for the deuterated compounds. For $(\text{CH}_2\text{NOD})_n$ the bands are observed as separate bands of medium intensity at 527 and 452 cm^{-1} , respectively, while the 458 cm^{-1} band shifts on C-deuteration to 442 cm^{-1} . The 539 cm^{-1} band, however, shifts to 474 cm^{-1} for $(\text{CD}_2\text{NOH})_n$, the high frequency ratio $\nu^{\text{H}}/\nu^{\text{D}}$ of 1.14 revealing strong coupling between the NO bending- and probably the CH_2 (or CD_2) rocking vibrations.

4. Poly(formaldehyde- d_2 oxime- d)

The spectrum of $(\text{CD}_2\text{NOD})_n$ supports the assignments given above. All the fundamental CD_2 bands and bands due to skeletal vibrations coupled to CH_2 (or CD_2) vibrations are observed at frequencies close to but slightly lower than

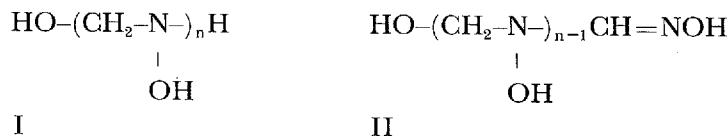
those observed for $(\text{CD}_2\text{NOH})_n$. Similarly, the OD bands are found at slightly lower frequencies than for $(\text{CH}_2\text{NOD})_n$, except for the OD wagging which appears at 359 cm^{-1} , *i.e.* at a higher frequency than in $(\text{CH}_2\text{NOD})_n$. The origin of this effect may be differences in hydrogen bonding in $(\text{CD}_2\text{NOD})_n$ and $(\text{CH}_2\text{NOD})_n$.

VI. Other Bands

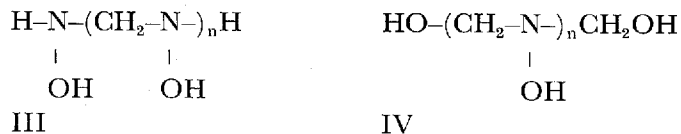
1. Terminal Groups

Since the poly(formaldehyde oxime) chains contain a finite number of repeating units, bands due to the terminal groups of the chains are expected to appear in the infrared spectra provided that the number of units is not too high, that the integrated intensities of the terminal group absorption bands are not too low, and that the bands are not obscured by other bands of the polymer.

When poly(formaldehyde oxime) is formed by polymerisation the composition of the polymer may be as in I or II below,



one of the terminal groups in formula II being an oxime group. When the polymer is formed in solution by polycondensation it may contain one $-\text{CH}_2\text{OH}$ terminal group (formula I) but it is also possible that it contains an $-\text{NHOH}$ terminal group (formula III) or that both of the terminal groups are $-\text{CH}_2\text{OH}$ groups (formula IV):



The $-\text{CH}_2\text{OH}$ group should give rise to a band near 1050 cm^{-1} due to the C-O stretching vibration. In the spectrum of $(\text{CH}_2\text{NOH})_n$ formed by polymerisation (A) a weak shoulder is observed at 1062 cm^{-1} . However, in $(\text{CH}_2\text{NOH})_n$ formed by polycondensation (B) a band of somewhat higher intensity appears at 1061

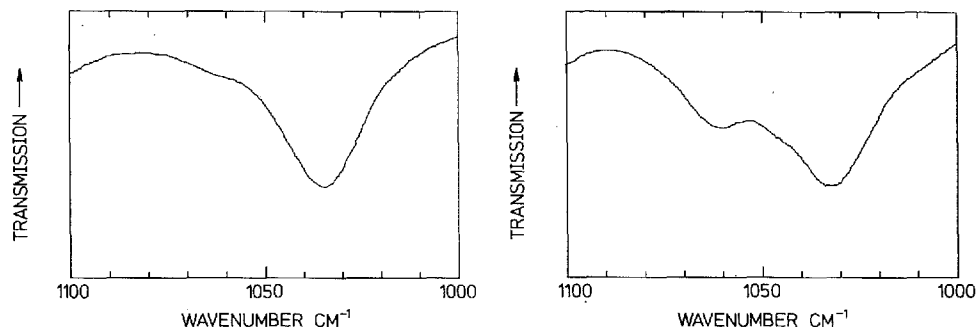


Fig. 13. Infrared absorptions of $(\text{CH}_2\text{NOH})_n$ in the region $1100\text{-}1000\text{ cm}^{-1}$. Left: compound A. Right: compound B.

cm^{-1} , separated from the 1031 cm^{-1} band (ν_6) (cf. Fig. 13). Both bands are believed to be due to the C–O stretching of the $-\text{CH}_2\text{OH}$ group, the difference in intensity indicating that the concentration of $-\text{CH}_2\text{OH}$ groups is higher in compound B than in compound A. This may be explained partly by assigning formula IV for B and formula I for A, and partly by assuming the occurrence of fewer repeating units in the chains of B. For the deuterated analogues of compound B the C–O stretching band is found at 1034 cm^{-1} for $(\text{CD}_2\text{NOH})_n$ and at 1050 cm^{-1} for $(\text{CH}_2\text{NOD})_n$, the isotopic shifts being of the expected magnitude; this band is not observed in the spectrum of $(\text{CD}_2\text{NOD})_n$ since it overlaps with other bands.

In the spectrum of $(\text{CH}_2\text{NOH})_n$ (both A and B) the weak band observed at 893 cm^{-1} is somewhat more intense for A than for B. This band is ascribed to the $-\text{NHOH}$ terminal group or the combination $\nu_{13} + \nu_{14}$ which in the spectrum of A is presumed to coincide with the N–O stretching mode of the $-\text{CH}=\text{NOH}$ terminal group. This is in good agreement with the infrared results for formaldehyde oxime $\text{CH}_2=\text{NOH}$, obtained by Califano and Lüttke,⁸ who found the N–O stretching mode at 888 cm^{-1} . For $(\text{CD}_2\text{NOH})_n$ this band appears as a weak shoulder at 896 cm^{-1} . The weak band at 878 cm^{-1} in the spectrum of $(\text{CH}_2\text{NOD})_n$ (compound B) is probably associated with the N–O stretching mode of the $-\text{NDOD}$ terminal group, the frequency for ND_2OD being 874 cm^{-1} . However, it may also be interpreted as being the combination band $(\nu_7 + \nu_{13}) - \nu_9 = 882\text{ cm}^{-1}$. The weak, broad absorption at 842 cm^{-1} in the spectrum of the fully deuterated compound B is probably a superimposition of several combination bands lying in the region $827\text{-}855\text{ cm}^{-1}$.

Finally a weak, broad band at ca. 485 cm^{-1} in the spectrum of $(\text{CH}_2\text{NOH})_n$, which is somewhat more intense for B than for A, is assigned to the OH wagging

vibration of the $-\text{CH}_2\text{OH}$ terminal group since it disappears on the deuteration of the OH groups. However, the OH(OD) wagging is not observed in the spectra of the deuterated species because of overlapping with strong fundamental bands.

2. Overtones and Combinations

In addition to the fundamental bands a considerable number of weak bands have been measured and interpreted as being overtone and combination bands, many of the bands appearing in the spectra as shoulders. A striking feature is that it has been necessary to explain most of the bands as difference bands. This is due to the considerable population of the low lying levels for the modes ν_9 , ν_{13} and ν_{14} .

The remaining bands have been interpreted as binary summation bands, except for a few bands which have been explained as ternary summation bands. The assignments of all the combination bands of $(\text{CH}_2\text{NOH})_n$ and its deuterated species will be given in a separate paper.⁹

Although the combination bands are generally much weaker than the fundamentals, two such bands of medium intensity have been observed in the spectrum of $(\text{CH}_2\text{NOH})_n$. As already mentioned above the band at 2875 cm^{-1} is assigned to the first overtone of the OH bending mode ν_4 , the exceptionally high intensity of the band being due to Fermi resonance, probably with the symmetric CH_2 stretching vibration ν_3 and the OH stretching vibration ν_1 . The band observed at 1121 cm^{-1} which is not seen for $(\text{CD}_2\text{NOH})_n$ and $(\text{CH}_2\text{NOD})_n$, is interpreted as $(\nu_{12} + \nu_{14}) - \nu_{13} = 1127\text{ cm}^{-1}$, in agreement with the deuteration experiments.

VII. Conclusion

The vibrational analysis of the infrared spectra of poly(formaldehyde oxime) and its deuterated analogues presented above lends strong support to the conclusion that poly(formaldehyde oxime) is a chain polymer, the carbon-nitrogen skeleton of which is a planar zig-zag chain. It has been established that the repeating unit of the extended polymer chain is $-\text{CH}_2\text{NOH}-$.

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