

## Infrared Spectra of High Polymers. VIII. Polyvinyl Nitrate\*

S. KRIMM AND C. Y. LIANG†

Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan

The infrared spectrum of polyvinyl nitrate has been obtained in the extended region of 70 to 3600  $\text{cm}^{-1}$ . Polarized infrared measurements were made on oriented specimens in the range of 350 to 3600  $\text{cm}^{-1}$ . Since x-ray diffraction patterns indicate no crystallinity, the analysis has been based on an assumed atactic configuration. With the help of previous studies of high-polymer spectra and results obtained on small molecules, it has been possible to make a complete assignment of all of the expected fundamentals. Dichroic measurements have not only permitted a decision on the assignment of the controversial  $\text{NO}_2$  rocking and bending modes, but suggest certain details concerning the local configuration of the nitrate group. There seems to be evidence that, although the specimen is not crystalline, a significant proportion of the chains have configurations not far from a planar zigzag chain.

## INTRODUCTION

THE infrared spectrum of polyvinyl nitrate,  $(-\text{CH}_2-\text{CHONO}_2-)_n$ , does not seem to have been reported in the literature. In the present paper we wish to discuss the spectrum of this polymer and propose a complete assignment of its fundamental frequencies. This is based on infrared spectral data in the range of 70  $\text{cm}^{-1}$  to 3600  $\text{cm}^{-1}$ , almost the entire range having been investigated with polarized radiation; a discussion of the fundamental frequencies of analogous small molecules; and comparison with results obtained by a detailed study of other vinyl polymers.

## EXPERIMENTAL RESULTS

The specimens used in this investigation had a nitrogen content of about 15.1%. A comparison with the theoretical value of about 15.7% indicates that the impurity content of the polymer was low. Films were prepared by casting from acetone solution. Orientation was introduced by stretching heated films. X-ray diffraction photographs gave no indication of crystalline reflections, so it must be presumed that an oriented amorphous structure prevailed.

The infrared spectrum of polyvinyl nitrate is shown in Fig. 1. The numbers adjacent to the curves represent the specimen thickness in inches. In the polarized portion of the spectrum, *viz.*, that part above 350  $\text{cm}^{-1}$ , the solid curve represents absorption with the electric vector perpendicular to the stretching direction, while the broken curve represents absorption with the electric vector parallel to this direction. When absorption predominates for one or other of these orientations, the band is designated as a perpendicular,  $\sigma$ , or parallel,  $\pi$ , band, respectively. The frequency, relative intensity, and polarization of each infrared band is listed in Table I. The assignments listed in the last column of the Table are discussed in the following section.

## INTERPRETATION AND DISCUSSION

## 1. Structure of Polyvinyl Nitrate

The structure of this polymer has not been determined, so that inferences will have to be based on pertinent results obtained from smaller molecules. We will assume that the structure is based on the head-to-tail arrangement of monomer units common to vinyl polymers. Of particular interest is the question of the planarity of the  $\text{ONO}_2$  group. The evidence from crystallographic studies on smaller molecules is sparse, but structural investigations of the nitrate ion<sup>1,2</sup> favor

TABLE I. Infrared spectrum and assignments for polyvinyl nitrate.\*

Frequency $\text{cm}^{-1}$	R.I.	Polarization	Assignment
$\sim 50(?)$			$\gamma_t(\text{NO}_2)(?)$
210	vw		$\gamma_r(\text{C}-\text{ONO}_2)$
270	w		$\gamma_r(\text{O}-\text{NO}_2)$
367	w	$\pi$	$\gamma_w(\text{O}-\text{NO}_2)$
464	w	$\pi$	$\gamma_w(\text{C}-\text{ONO}_2)$
555	m	$\sigma$	$\gamma_r(\text{NO}_2)$
695	s	$\sigma$	$\delta(\text{NO}_2)$
753	s	$\pi$	$\gamma_w(\text{NO}_2)$
838	sh	$\sigma(?)$	$\gamma_w(\text{O}-\text{NO}_2) + \gamma_w(\text{C}-\text{ONO}_2) = 831$
870	vs	$\sigma$	$\nu(\text{ON})$
930	vw	$\sigma$	$2 \times \gamma_w(\text{C}-\text{ONO}_2) = 928; \gamma_w(\text{O}-\text{NO}_2) + \gamma_r(\text{NO}_2) = 922$
1015	vw	$\sigma$	$\nu(\text{CO})$
1075	m	$\sigma$	$\nu_s(0)$ and $\nu(\text{CC})$ (amorphous)
1115	w	$\pi$	$\nu_+(\pi)$
1277	vs	$\sigma$	$\nu_s(\text{NO}_2)$
1340	w	$\sigma$	$\delta(\text{CH})$
1389	w	$\pi$	$\gamma_w(\text{CH}_2)$
1435	s	$\sigma$	$\delta(\text{CH}_2)$
1634	vs	$\sigma$	$\nu_s(\text{NO}_2)$
1735	m	—	$2 \times \nu(\text{ON}) = 1740; \nu(\text{C}=\text{O})$ (impurity)
1835	vw	—	$\gamma_r(\text{NO}_2) + \nu_s(\text{NO}_2) = 1832$
1960	vw	$\sigma$	$\delta(\text{NO}_2) + \nu_s(\text{NO}_2) = 1972$
2141	vw	$\sigma$	$\nu(\text{ON}) + \nu_s(\text{NO}_2) = 2147$
2545	w	$\sigma$	$2 \times \nu_s(\text{NO}_2) = 2554$
2900	m	$\sigma$	$\nu_s(\text{CH}_2)$
2933	m	$\sigma$	$\nu_s(\text{CH}_2)$
2967	w	$\sigma$	$\nu(\text{CH})$
3269	w	$\sigma$	$2 \times \nu_s(\text{NO}_2) = 3268$
3460	w	—	$2 \times \nu(\text{C}=\text{O}) = 3470$ (impurity)

\*  $\nu$  = stretching,  $\delta$  = bending,  $\gamma_t$  = twisting,  $\gamma_w$  = wagging (out-of-plane, or  $\parallel$  chain axis),  $\gamma_r$  = rocking (in-plane, or  $\perp$  chain axis).

<sup>1</sup> V. Luzzati, *Acta Cryst.* 6, 152, 157 (1953).

<sup>2</sup> R. M. Curtis and R. A. Pasternak, *Acta Cryst.* 8, 675 (1955).

\* Presented in part at the American Physical Society, Chicago, Illinois, March, 1958.

† Present Address: Research and Development Division, American Viscose Corporation, Marcus Hook, Pennsylvania.

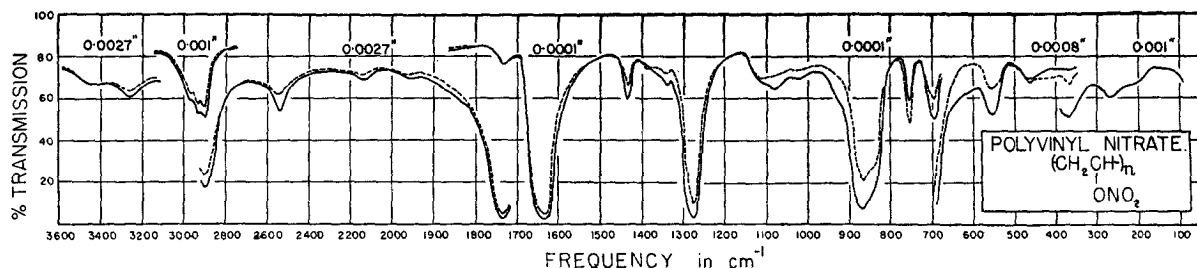


FIG. 1. Infrared spectrum of oriented polyvinyl nitrate. For polarized spectra above  $350\text{ cm}^{-1}$ : — indicates absorption with electric vector perpendicular to orientation direction, - - - indicates absorption with electric vector parallel to orientation direction.

a planar configuration, and the  $\text{ONO}_2$  group in pentaerythritol tetranitrate<sup>3</sup> is found to be planar. We will therefore assume that this is the case in polyvinyl nitrate. There is some indication<sup>3</sup> that the carbon atom adjacent to the  $\text{ONO}_2$  group lies slightly off the plane of the latter.

Although the possibility of free rotation about the C—O and O— $\text{NO}_2$  bonds exists, examination of space filling molecular models indicates that such rotation is restricted as a result of steric interference between neighboring atoms. For example, the atoms of the  $\text{CH}(\text{ONO}_2)$  group are less likely to be all in one plane than not, because of the steric interference between an oxygen atom of the  $\text{NO}_2$  group and the hydrogen atom. If neighboring nitrate groups are all on the same side of the chain, i.e., the structure is isotactic, then the molecular models indicate that the equilibrium configuration in a planar zigzag chain, on the assumption that the O— $\text{NO}_2$  bond is perpendicular to the chain axis, will be one in which the O—O axis of the  $\text{NO}_2$  group makes an angle of roughly  $60^\circ$  with the carbon chain axis. If rotations occur about the CO bond, such as to move the O— $\text{NO}_2$  bond away from the above perpendicular position, then the O—O axis of the  $\text{NO}_2$  group tends to be more nearly perpendicular to the chain axis. Although both configurations undoubtedly occur, it will be seen later that they each give rise to different predictions concerning the dichroism of certain absorption bands, and that it is possible to determine which extreme case is the best approximation to the actual configuration.

The poor x-ray diffraction patterns indicate that the structure of our specimens is most probably not an isotactic one (which might be expected to yield a highly crystalline polymer). It is likely that the substituent  $\text{ONO}_2$  groups are to be found at random on either side of the carbon chain, i.e., the structure is atactic. Molecular models indicate the feasibility of a syndiotactic structure, i.e., one in which the  $\text{ONO}_2$  groups are alternately on either side of the carbon chain, but we have not considered this as a major configurational component. The primary reason is that syndiotactic structures, such as polyvinyl chloride,<sup>4</sup> give rise to

splittings in the fundamental frequencies. Although there is some indication in the spectrum of polyvinyl nitrate of broadening of some of the bands, the splitting which would be involved is smaller than that observed in the spectra of syndiotactic polymers.<sup>4</sup>

## 2. Predicted Spectrum

The conclusions of the previous section indicate that the spectroscopic unit in polyvinyl nitrate is most likely to be a single monomer unit, and that this unit has no symmetry. The latter follows from the observation that the configuration in which the  $\text{ONO}_2$  plane is perpendicular to the chain axis is an unfavored one. Although this precludes an exact prediction of the polarization of the normal modes, it has been seen that the orientation of the  $\text{ONO}_2$  group is in fact somewhat restricted and an estimate can therefore be made of the dichroism of certain modes. This, of course, will depend upon knowledge of the form of the vibration.

On the basis of a factor group analysis<sup>5</sup> of the normal modes, we predict  $(3 \times 9) - 4 = 23$  fundamental frequencies for polyvinyl nitrate. (A factor group analysis for such a single chain will give results which are not far wrong, except for chain skeletal modes, when applied to a completely amorphous structure. In addition, we will see later that there is evidence that much of the chain structure approximates fairly closely to a planar zigzag configuration.) The forms of the normal modes of methyl nitrate have been estimated<sup>6,7</sup> but not calculated exactly; nor is it feasible to determine at present the forms of the normal vibrations in polyvinyl nitrate. It will therefore be necessary to classify the fundamentals in terms of the normal modes of component groups in the spectroscopic unit. From the relative constancy of such group frequencies in many different molecules we know that this is a fairly good approximation. Any particular case must, however, be approached with caution and the realization of the possible inadequacy of the group mode description.

The 23 normal modes are taken to be distributed as follows among the groups:  $\text{CH}_2 - \nu_a, \nu_s, \delta, \gamma_w, \gamma_t, \gamma_r$  (6);

<sup>5</sup> C. Y. Liang, S. Krimm, and G. B. B. M. Sutherland, *J. Chem. Phys.* **25**, 543 (1956).

<sup>6</sup> J. Lecomte and J. P. Mathieu, *J. chim. phys.* **39**, 57 (1942).

<sup>7</sup> H. Wittek, *Z. physik. Chem. (Leipzig)* **B52**, 153 (1942).

<sup>3</sup> A. D. Booth and F. J. Llewellyn, *J. Chem. Soc.* 837 (1947).

<sup>4</sup> S. Krimm and C. Y. Liang, *J. Polymer Sci.* **22**, 95 (1956).

CH- $\nu$ ,  $\delta$ ,  $\gamma_w$  (3); NO<sub>2</sub>- $\nu_a$ ,  $\nu_s$ ,  $\delta$ ,  $\gamma_w$ ,  $\gamma_t$ ,  $\gamma_r$  (6); O-NO<sub>2</sub>- $\nu$ ,  $\gamma_r$ ,  $\gamma_w$  (3); C-ONO<sub>2</sub>- $\nu$ ,  $\gamma_r$ ,  $\gamma_w$  (3); chain skeletal - $\nu_+$ (0),  $\nu_+$ ( $\pi$ ) (2). The modes of the nitrate group are divided into the internal modes of the NO<sub>2</sub> group and those (*viz.*, O-NO<sub>2</sub>) in which the NO<sub>2</sub> group moves as a unit. This is based on the nonequivalence of the three N-O bonds (the two bonds in the NO<sub>2</sub> group are double bonds, the other is a single bond), and the general similarity of some of the frequencies to those in nitroparaffins, in which the C-NO<sub>2</sub> grouping is found. In the C-ONO<sub>2</sub> modes the ONO<sub>2</sub> group is considered to move as a unit, perpendicular to the chain axis in the rocking mode,  $\gamma_r$ , and parallel to this axis in the wagging mode,  $\gamma_w$ . The dichroism expected for each mode will be discussed more fully under the detailed assignments for each group.

### 3. Assignment of CH<sub>2</sub> and CH Modes

Of the six CH<sub>2</sub> modes, we expect to observe  $\nu_a$ ,  $\nu_s$ ,  $\delta$ , and  $\gamma_w$ ;  $\gamma_t$  is undetectable in polyethylene,<sup>8</sup> and  $\gamma_r$  is generally very weak or unobservable in vinyl polymers,<sup>4,9-11</sup> so it will not be surprising if they are not observed in polyvinyl nitrate. The first three modes should exhibit perpendicular polarization in an oriented chain, while  $\gamma_w$  should show parallel polarization.† The  $\gamma_w$  mode is identified<sup>8</sup> with the  $\pi$  band at 1389 cm<sup>-1</sup>. The  $\nu_a$  and  $\nu_s$  modes are to be assigned to two of the three  $\sigma$  bands in the 2900 cm<sup>-1</sup> region, the other most probably being  $\nu$ (CH). Although these modes may not be separable, we have chosen to assign  $\nu_a$ (CH<sub>2</sub>) to the 2933 cm<sup>-1</sup> band and  $\nu_s$ (CH<sub>2</sub>) to the 2900 cm<sup>-1</sup> band. This would be consistent with their intensity being usually greater than that of  $\nu$ (CH), and with the general range of values found in other polymers (e.g., at 2942 and 2910 cm<sup>-1</sup> respectively in polyvinyl alcohol<sup>10</sup>). This places  $\nu$ (CH) at a somewhat high frequency, but it is possible that this could result from the influence of the closely neighboring O atom of the NO<sub>2</sub> group. The  $\delta$ (CH) mode, which is assigned to the  $\sigma$  band at 1340 cm<sup>-1</sup>, is also at a slightly higher frequency than usual, possibly for the same reason. The  $\gamma_w$ (CH) mode is usually weakly absorbing,<sup>4,9</sup> and it is therefore not surprising that we have failed to observe it.

### 4. Assignment of NO<sub>2</sub> Modes

Of the six expected modes of the NO<sub>2</sub> group, the two stretching frequencies,  $\nu_a$ (NO<sub>2</sub>) and  $\nu_s$ (NO<sub>2</sub>), are readily assigned on the basis of Raman<sup>7</sup> and infrared<sup>12</sup> studies on smaller molecules such as methyl nitrate to

<sup>8</sup> Krimm, Liang, and Sutherland, *J. Chem. Phys.* **25**, 549 (1956).

<sup>9</sup> Krimm, Liang, and Sutherland, *J. Polymer Sci.* **22**, 227 (1956).

<sup>10</sup> C. Y. Liang and S. Krimm, *J. Polymer Sci.* **27**, 241 (1958).

<sup>11</sup> C. Y. Liang and S. Krimm, *J. Polymer Sci.* (to be published).

† The  $\delta$ (CH<sub>2</sub>) mode is readily assigned (see reference 8) to the strong  $\sigma$  band at 1435 cm<sup>-1</sup>.

<sup>12</sup> J. C. D. Brand and T. M. Cawthon, *J. Am. Chem. Soc.* **77**, 319 (1955).

the strong  $\sigma$  bands at 1634 cm<sup>-1</sup> and 1277 cm<sup>-1</sup>, respectively. From the polarization properties of these bands in polyvinyl nitrate we can obtain information on the configuration of the nitrate group with respect to the polymer chain. We have seen from the earlier remarks on the structure of this polymer that the NO<sub>2</sub> group cannot be oriented with its plane perpendicular to the axis of a planar zigzag chain. One possible favorable orientation, it was noted, involves a rotation about the O-NO<sub>2</sub> axis. If the  $\nu_s$ (NO<sub>2</sub>) and  $\nu_a$ (NO<sub>2</sub>) modes are similar in form to those of a nonlinear triatomic molecule,<sup>13</sup> then, since the above orientation involves an angle of about 60° between the chain axis and the O-O axis, it can be seen that (in an oriented specimen) the  $\nu_s$ (NO<sub>2</sub>) mode will exhibit stronger  $\sigma$  polarization than will the  $\nu_a$ (NO<sub>2</sub>) mode. On the other hand, if the alternate configuration is assumed, *viz.*, the one which involves rotation about the CO axis and thereby results in an O-O axis which is perpendicular to the chain axis, then the predictions as to the relative  $\sigma$  polarization of  $\nu_s$ (NO<sub>2</sub>) and  $\nu_a$ (NO<sub>2</sub>) are reversed. Although the orientation introduced in our specimens is not very great, the observed dichroic ratios of the 1634 cm<sup>-1</sup> and 1277 cm<sup>-1</sup> bands are 0.79 and 0.65, respectively, a difference which is to be considered significant. (The dichroic ratio of a band is defined as the ratio of the optical density measured with radiation polarized parallel to the stretching direction to that measured with perpendicularly polarized radiation.) These figures denote a larger  $\sigma$  polarization for  $\nu_s$ (NO<sub>2</sub>), and therefore indicate that the first NO<sub>2</sub> group orientation above is favored. The polarization data, although not as complete as would be desirable, thus provide information on the local structure of the polymer chain.

We will consider next the assignment of the  $\gamma_w$ (NO<sub>2</sub>) mode. Its predicted polarization is  $\pi$ , and there is no difficulty in assigning it to the  $\pi$  band at 753 cm<sup>-1</sup>. It is found at 759 cm<sup>-1</sup> in methyl nitrate.<sup>12</sup>

The assignments of the  $\delta$ (NO<sub>2</sub>) and  $\gamma_r$ (NO<sub>2</sub>) modes have been somewhat controversial. Whereas some authors<sup>7,12</sup> assign to these modes bands near 580 and 660 cm<sup>-1</sup> in methyl nitrate, others,<sup>14</sup> primarily on the basis of the analysis of nitric acid<sup>15</sup> (HONO<sub>2</sub>), have suggested an inverted order for these assignments. The bands in question in polyvinyl nitrate are the two  $\sigma$  bands at 555 and 695 cm<sup>-1</sup>, which frequencies are close to the values observed in isopropyl nitrate.<sup>7</sup> There are several reasons why we favor the assignment of the  $\delta$ (NO<sub>2</sub>) mode to the 695 cm<sup>-1</sup> band and the  $\gamma_r$ (NO<sub>2</sub>) mode to the 555 cm<sup>-1</sup> band. First, in HONO<sub>2</sub>, whose symmetry is more certain than that of CH<sub>3</sub>ONO<sub>2</sub>, the only polarized band in the Raman spectrum assignable to  $\delta$ (NO<sub>2</sub>) is at 680 cm<sup>-1</sup>. Although the Raman spectrum

<sup>13</sup> G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), p. 66.

<sup>14</sup> J. F. Brown, Jr., *J. Am. Chem. Soc.* **77**, 6341 (1955).

<sup>15</sup> Cohn, Ingold, and Poole, *J. Chem. Soc.* 4272 (1952).

of  $\text{CH}_3\text{ONO}_2$  has a strong polarized band at  $580\text{ cm}^{-1}$ , it is still possible that this could be associated with the in-plane  $\text{NO}_2$  rocking mode if the favored configuration is the one in which all the heavy nuclei are in the same plane. In addition, it should be noted that the band contour of the  $657\text{ cm}^{-1}$  infrared band of  $\text{CH}_3\text{ONO}_2$  is more in agreement with that expected for a  $\delta(\text{NO}_2)$  mode than for a  $\gamma_r(\text{NO}_2)$  mode.<sup>12</sup> Second, it is to be expected that the  $\delta(\text{NO}_2)$  mode will give rise to a transition moment parallel to that of the  $\nu_s(\text{NO}_2)$  mode, so that if our assignment is correct, the dichroic ratio of the  $695\text{ cm}^{-1}$  band should be the same as that of the  $1277\text{ cm}^{-1}$  band. The dichroic ratio of the  $695\text{ cm}^{-1}$  band, measured on the same specimen as that of the  $1277\text{ cm}^{-1}$  band, is found to be 0.65, exactly the same. It might be thought that the dichroic ratio of the  $\gamma_r(\text{NO}_2)$  mode should be, by analogy with that of  $\nu_a(\text{NO}_2)$ , larger than that of  $\delta(\text{NO}_2)$ . In fact the reverse is true: the dichroic ratios of the  $695\text{ cm}^{-1}$  and  $555\text{ cm}^{-1}$  bands, measured on the 0.0008-in. thick specimen, are 0.57 and 0.50, respectively. This reversal, however, does not seem to be too critical; it is entirely possible that, whereas the  $\nu_a(\text{NO}_2)$ ,  $\nu_s(\text{NO}_2)$ , and  $\delta(\text{NO}_2)$  modes are confined to the plane of the  $\text{ONO}_2$  group, the motions of the O atoms in the  $\gamma_r(\text{NO}_2)$  mode are not so strictly in this plane but more nearly perpendicular to the chain axis. Third, it seems reasonable to expect that, as is the case for  $\nu_a(\text{NO}_2)$  and  $\nu_s(\text{NO}_2)$ , the frequency and intensity ratios observed in the nitroparaffins<sup>16-18</sup> for  $\delta(\text{NO}_2)$  and  $\gamma_r(\text{NO}_2)$  will be approximately followed in the nitrates. In the nitroparaffins the  $\delta(\text{NO}_2)$  mode is the more intense, and is located, for example, at  $658\text{ cm}^{-1}$  in  $\text{CH}_3\text{NO}_2$ , at a frequency much higher than the  $\gamma_r(\text{NO}_2)$  mode. Thus, although the arguments are perhaps not indisputable, we believe that the evidence favors the assignment given.

Since the  $\text{NO}_2$  group is not free to rotate, a  $\gamma_t(\text{NO}_2)$  mode is expected. This cannot be identified with any certainty, but may be associated<sup>19</sup> with an absorption band which seems to be present at roughly  $50\text{ cm}^{-1}$ .

### 5. Assignment of Group and Chain Skeletal Modes

The assignment of the modes in which the  $\text{NO}_2$  group and the  $\text{ONO}_2$  group can be considered to move as rigid units will be discussed together. Consider first the two stretching modes,  $\nu(\text{CO})$  and  $\nu(\text{ON})$ . In  $\text{CH}_3\text{ONO}_2$  these have been satisfactorily assigned<sup>12</sup> to bands at  $1017\text{ cm}^{-1}$  ( $993\text{ cm}^{-1}$  in the liquid) and  $854\text{ cm}^{-1}$ , respectively. There is thus no ambiguity in their

assignment in polyvinyl nitrate to bands at  $1015$  and  $870\text{ cm}^{-1}$ , respectively. It is perhaps pertinent to inquire briefly as to whether these modes are as simple as indicated, or whether a coupled motion is more likely, leading, for example, to symmetric and antisymmetric stretching modes for the triatomic unit  $\text{CH}-\text{O}-\text{NO}_2$ . If the modes were completely separable as indicated, we would expect that the dichroism of the  $\nu(\text{ON})$  mode would be the same as that for  $\nu_s(\text{NO}_2)$  and  $\delta(\text{NO}_2)$ . In fact, the dichroic ratio of the  $870\text{ cm}^{-1}$  band, *viz.*, 0.57, indicates that the transition moment for this vibration is significantly more perpendicular to the stretching direction than that of  $\nu_s(\text{NO}_2)$ . It seems that this can only result if what we call  $\nu(\text{ON})$  is actually coupled somewhat to  $\nu(\text{CO})$ , so that the resulting transition moment is not exactly along the  $\text{O}-\text{N}$  bond direction. If we remember the observation<sup>3</sup> that the C atom is slightly off the  $\text{ONO}_2$  plane, then it is not difficult to visualize a configuration for this group such that the coupled  $\nu(\text{ON})$  mode will have a larger perpendicular dichroism than the  $\nu_s(\text{NO}_2)$  mode. It should be noted that the coupling is probably not too strong, *i.e.*, the identity of the major contributor is essentially preserved, since the intensities of these two bands [ $\nu(\text{ON})$  and  $\nu(\text{CO})$ ] are markedly different. This is the reason for our adhering to the simple designation for these modes.

In assigning the four remaining deformation modes, we are assisted by the fact that only four low-frequency bands are observed, of which two have  $\pi$  polarization. In  $\text{CH}_3\text{ONO}_2$ , the skeletal deformation mode is believed<sup>7,12</sup> to occur at about  $340\text{ cm}^{-1}$ . If we assume that this carries over to polyvinyl nitrate, then it is perhaps not unreasonable to tentatively assign the bands at  $367$  and  $270\text{ cm}^{-1}$  to  $\gamma_w(\text{O}-\text{NO}_2)$  and  $\gamma_r(\text{O}-\text{NO}_2)$ , respectively, *i.e.*, motions of the  $\text{NO}_2$  group as a unit. This leaves the  $464$  and  $210\text{ cm}^{-1}$  bands to be assigned to  $\gamma_w(\text{C}-\text{ONO}_2)$  and  $\gamma_r(\text{C}-\text{ONO}_2)$ , respectively. It might be noted that these fall close to values expected<sup>6</sup> for chain bending modes involving two monomer units, so that some mixing may occur.

The skeletal vibrations of a planar zigzag chain should give rise to two absorption bands,<sup>5,8</sup> a  $\pi$  band,  $\nu_+(\pi)$ , at about  $1137\text{ cm}^{-1}$ , and a  $\sigma$  band,  $\nu_+(0)$ , at about  $1070\text{ cm}^{-1}$ . It seems likely that the  $1115$  and  $1075\text{ cm}^{-1}$  bands in polyvinyl nitrate are to be associated with these modes. The band at  $1075\text{ cm}^{-1}$  probably contains a large contribution from the disordered chains,<sup>8</sup> but the presence of a  $\pi$  band at  $1115\text{ cm}^{-1}$  is indicative of the existence of a significant number of chains having an essentially planar zigzag configuration. If this is true, it emphasizes the fact that, although an oriented polymer does not give a good x-ray diffraction pattern, part of its chains may still have configurations which are essentially the same as those expected in a completely regular and crystalline structure.

<sup>16</sup> A. J. Wells and E. B. Wilson, Jr., *J. Chem. Phys.* **9**, 314 (1940).

<sup>17</sup> T. P. Wilson, *J. Chem. Phys.* **11**, 361 (1943).

<sup>18</sup> Smith, Pan, and Nielsen, *J. Chem. Phys.* **18**, 706 (1950).

<sup>19</sup> P. H. Lindenmeyer and P. M. Harris, *J. Chem. Phys.* **21**, 408 (1953).

## 6. Assignment of Combination and Other Bands

The remaining bands in the spectrum are all quite weak, except for that at  $1735\text{ cm}^{-1}$ , and seem to be satisfactorily assigned as combinations or overtones of the proposed fundamentals. While the  $1735\text{ cm}^{-1}$  band probably contains a large contribution from  $2\nu(\text{ON})$ ,

it is also likely that part of the band is due to  $\nu(\text{C}=\text{O})$ , perhaps resulting from some acetone which remained in the sample.

### ACKNOWLEDGMENT

The authors are grateful to E. I. du Pont de Nemours & Company, Inc., for supporting grants, during the tenure of which part of this work was done.

## Measurement of the Isothermal Volume Dilution Accompanying the Unilateral Extension of Rubber

FRED G. HEWITT\* AND ROBERT L. ANTHONY

*Department of Physics, University of Notre Dame, Notre Dame, Indiana*

Using a torsion balance immersed in water and natural rubber ring specimens cured with di-tertiary-butyl-peroxide, measurements were made of the isothermal volume dilation of rubber for mean extensions  $\epsilon = 14, 33$ , and  $51\%$ , thus extending the results of Gee, Stern, and Treloar to lower strains. Chain molecular weights  $M_c = 3000, 4400, 5100$ , and  $5500$  were employed. The chain molecular weights were determined by swelling in benzene, the uncertainty in each determination being about  $10\%$ . Observed fractional volume increases ranged from  $3.2 \times 10^{-5}$  for  $\epsilon = 14\%$  and  $M_c = 5500$  to  $14 \times 10^{-5}$  for  $\epsilon = 51\%$  and  $M_c = 3000$ . Using Gee's expression for the volume dilation, but obtaining the slope of the stress-strain curve from the statistical theory, curves were fitted to the data. The fitting process constituted a determination of Young's modulus  $E$  for each rubber specimen. The resulting curves are in good agreement with those of Gee, Stern, and Treloar. Additional determinations of  $E$  were made from rough stress-strain curves and from the swelling data, the internal agreement between the three determinations being fair.

### INTRODUCTION

AS is well known, the differential Poisson's ratio for a soft gum rubber is very nearly  $0.5$ . Hence the change in volume accompanying the unilateral extension of such a rubber is very small. In spite of its small magnitude, this volume change is believed to be responsible for the major part of the internal energy component (strictly speaking, the enthalpy component) of the equilibrium rubber stress-strain curve in the low extension region.<sup>1,2</sup> Thus the determination of this volume change is important to a proper understanding of the thermoelastic behavior of rubbers.

Holt and McPherson<sup>3</sup> were among the first to attempt a measurement of this volume increase for a soft gum rubber. For extensions ranging from  $0$  to  $200\%$ , they were unable to detect any change in volume. Their work did serve, however, to place an upper limit on the possible magnitude of this volume increase, namely that it had to be less than  $0.2\%$ , which figure represented their experimental uncertainty. The first successful measurements reported in the literature appear to be those of Gee, Stern, and Treloar.<sup>2</sup> Using natural rubber

ring specimens cured with di-tertiary-butyl-peroxide (DTBP), these workers measured the increase in volume for samples having chain molecular weights of  $4900$  and  $9500$ . Measurements were confined to extensions lying in the approximate range of  $40$  to  $110\%$ . The volume increase observed ranged from about  $0.006\%$  to  $0.02\%$ , the largest value being observed for the sample of  $4900$  chain molecular weight at an extension of  $110\%$ . The work to be described was undertaken mainly for the purpose of extending the results of Gee, Stern, and Treloar to the region of lower strains.

### EXPERIMENTAL

The rubber specimens used in this work were molded rings of rectangular cross section, having an inside diameter of  $3.72\text{ cm}$ , an outside diameter of  $5.05\text{ cm}$ , and a height of  $1\text{ cm}$ . They were made from pale crepe natural rubber cured with di-tertiary-butyl-peroxide,  $3$  to  $4\text{ cc}$  of DTBP per  $100\text{ g}$  of raw rubber being added directly to the rubber on a mixing mill. The curing time for all samples was  $6\text{ hr}$  at  $280^\circ\text{F}$ . The cured samples were quite transparent, and the presence of bubbles or foreign matter in the samples was easily detected. Only specimens free of visible defects were employed in the volume dilation studies. Extension of the rubber rings was carried out under water by rolling the rings down an aluminum cone on to light aluminum rings. Considerable care was exercised to ensure thorough

\* Now at College of St. Thomas, St. Paul, Minnesota.

<sup>1</sup> K. H. Meyer and A. J. A. Van der Wyk, *Helv. Chim. Acta* **29**, 1842 (1946).

<sup>2</sup> Gee, Stern, and Treloar, *Trans. Faraday Soc.* **46**, 1101 (1950).

<sup>3</sup> W. L. Holt and A. T. McPherson, *J. Research Natl. Bur. Standards* **17**, 657 (1936).