

**Nature of the Hydrogen Bond. III. The Measurement of the Infrared Absorption Intensities of Free and HydrogenBonded OH Bands. Theory of the Increase of the Intensity Due to the Hydrogen Bond**

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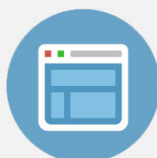
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## Nature of the Hydrogen Bond. III. The Measurement of the Infrared Absorption Intensities of Free and Hydrogen-Bonded OH Bands. Theory of the Increase of the Intensity Due to the Hydrogen Bond

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The integrated intensities of the infrared OH bands of various compounds have been measured for the free and the hydrogen-bonded states. It is found that the integrated intensity of either the free or the hydrogen-bonded OH band increases as the frequency decreases. It is concluded that the main factor increasing the integrated intensity of the intermolecularly hydrogen-bonded OH bands is the charge transfer through the hydrogen bond. The sign of the change of the dipole moment of the free phenol with the OH distance is discussed. An explanation is given for the weakness of the OH bands of the chelate compounds.

IN the preceding paper of this series,<sup>1</sup> the results of measurements on the intensities of the OH bands of a few phenol-proton acceptor complexes have been reported. The intensities of the OH bands of phenol and some other compounds in free and hydrogen-bonded states have been studied further and, based on these results, a theoretical explanation of the enhancement of the intensities due to the hydrogen bonding has been attempted.

### EXPERIMENTAL

The apparatus and method to measure the absorbances are the same as those employed in the preceding work.<sup>1</sup> Throughout this work, the concentration of the donor was made so small that the mutual association of the donor molecules was negligible, and the thickness of the cell was chosen so as to give absorbances which were most suitable for the precise intensity measurements. For the intensity measurements of the free OH bands, which are sharp, the error due to the finite resolving power cannot be avoided completely. It was estimated that the peak intensity of the free OH band of phenol in *n*-heptane solution obtained in the present measurements is about 20% smaller than the quantity corrected for the infinitesimal slit width. The intensity measurements of the free OH bands of other compounds studied in this work can be made more accurately, as they are broader than that of phenol. The integrated intensity (denoted in this paper by  $A$ ) is calculated approximately

by the formula,

$$A = (\pi/2) \cdot (\text{half-width}) \cdot a_{\text{max}},$$

where  $a_{\text{max}}$  is the absorption coefficient,  $(\log_e(I_0/I) \cdot (1/cl))$ , liter/mole·cm) at the band maximum and  $\pi/2$  is a correction factor introduced by assuming that the shapes of the bands are represented by Lorentz curves.<sup>2</sup> The exact calculation of the band area is tedious and, for some cases, impossible owing to the overlap of the free and bonded bands. The method mentioned above is suitable for the present purpose.

### RESULTS AND DISCUSSIONS

The intensities and other spectral data for the free OH bands are listed in Table I, and those for the OH bands of the intramolecularly or intermolecularly hydrogen-bonded compounds in Table II. Some of the compounds listed in these tables are studied in carbon tetrachloride and others in *n*-heptane. As the free OH bands of phenol in the two solutions are nearly identical in frequency and in intensity, it is conceivable that the frequency and the intensity of any OH band in carbon tetrachloride is very similar to those in *n*-heptane.

As is known, the integrated intensity  $A$  of a fundamental infrared absorption band is given, if the mechanical and electrical anharmonicities are neglected,\*

<sup>2</sup> D. A. Ramsay, *J. Am. Chem. Soc.* **74**, 72 (1952).

\* N. D. Coggeshall, in *J. Chem. Phys.* **18**, 978 (1950), showed by the use of the point charge model that the ratio of the squares of the transition moments for the bonded and free OH bands is calculated as 1.16 if the mechanical anharmonicity is taken into account. As Francis has pointed out (*S. A. Francis, J. Chem. Phys.* **19**, 505 (1951)), the ratio, multiplied by that of the peak frequen-

<sup>1</sup> H. Tsubomura, *J. Chem. Phys.* **23**, 2130 (1955).

TABLE I. Observed data of the free OH bands.

Compound	Solvent	$\nu_{\max}$ , $\text{cm}^{-1}$	Half-width $\text{cm}^{-1}$	$a_{\max}$	$A \times 10^{-4}$	$\partial\mu/\partial r \times 10^{10}$
Phenol	<i>n</i> -Heptane	3617	18	412	1.16	1.62
Phenol	$\text{CCl}_4$	3612	17	475	1.27	1.69
Methanol	$\text{CCl}_4$	3647	28	76	0.334	0.86
<i>p</i> -Nitrophenol	$\text{CCl}_4$	3594	24	535	2.02	2.12

by the following formula:

$$A = 10^{-3}(N_0\pi/3mc^2)(\partial\mu/\partial r)^2. \quad (1)$$

Here  $A$  is in units of  $\text{liter} \cdot \text{mole}^{-1} \cdot \text{cm}^{-2}$ ,  $N_0$  the Avogadro number,  $m$  the reduced mass in grams, and  $(\partial\mu/\partial r)$  the first derivative of the dipole moment with respect to the displacement at the equilibrium point in units of  $10^{-10}$  esu.<sup>†</sup> For the present case,  $r$  may be approximately set equal to the change of the OH internuclear distance from its equilibrium value. The last columns of Table I and II give the  $(\partial\mu/\partial r)$  values calculated by use of Eq. (1).

The data given in Table II concerning acetonitrile, ethyl acetate, ethyl ether, and hexamethylene tetramine are those already reported, but are cited there in order to facilitate comparison of the results.

The OH band of phenol-chlorobenzene complex has a large shoulder at the shorter wavelength, indicating that a considerable amount of phenol is free (Fig. 1). As is shown by the broken lines in this figure, the spectrum can be divided into two bands, the smaller one having the peak frequency identical to that of the free phenol. From the height of this band and the molar

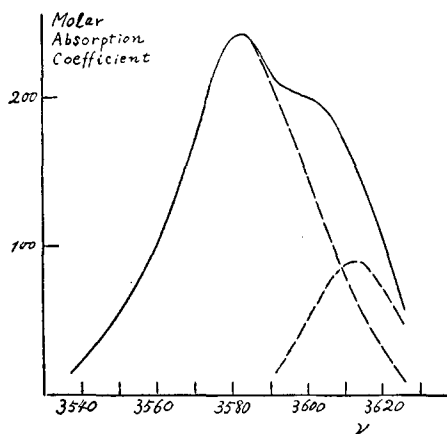


FIG. 1. The OH absorption curve of the phenol-chlorobenzene complex in carbon tetrachloride.

cies, should represent the ratio of the integrated intensities. As the experimentally obtained ratio of the integrated intensities is very much larger than 1.16, we must consider that  $\partial\mu/\partial r$  (see the later part of this paper) is largely changed by the hydrogen bond. We assume in this paper that the change in  $\partial\mu/\partial r$  is the main factor increasing the integrated intensity and that the neglect of the anharmonicity does not affect the matter seriously.

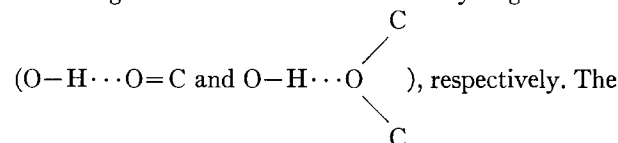
<sup>†</sup> For the derivation of Eq. (1), see, for instance, R. Ladenburg, *Z. Physik* 4, 451 (1921); B. L. Crawford and H. L. Dinsmore, *J. Chem. Phys.* 18, 983 (1950); G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1949), Chapter III.

absorption coefficient of the OH band of free phenol in carbon tetrachloride, the concentration of free phenol is estimated. It leads to the conclusion that about 78% of phenol is bonded. The intensity listed in Table II is the value of the area under the left side broken curve, divided by  $0.78 \times$  (the total concentration of phenol).

The OH band of the phenol-tetrachloroethane system has a nearly symmetrical figure, the peak frequency being only  $18 \text{ cm}^{-1}$  smaller than that of free phenol, and the half-width being about twice larger than that of free phenol. In this case we cannot divide the spectrum into the free and the bonded band. Rather it is very likely that the spectrum is in its nature not a superposition of two distinct bands, but is a group of bands that have continuously varying frequencies. For this system, therefore, the total integrated intensity was calculated and listed in Table II.

The OH bands of salicyl aldehyde and methyl salicylate are so broad that they overlap with the aromatic CH bands. The values for the half-width and the intensities listed in Table II are those obtained from the curve drawn by subtracting the CH absorption of benzaldehyde from the OH absorptions of these compounds, and, hence, may be inaccurate.

The spectrum of the dilute carbon tetrachloride solution of ethyl lactate shows two small peaks near the main OH band, namely, at  $3450$  and  $3613 \text{ cm}^{-1}$ . The  $3450 \text{ cm}^{-1}$  band does not correspond to the intermolecularly hydrogen-bonded molecules because it does not disappear by dilution even to  $0.00452$  mole/liter. This band may be the first overtone of the  $\text{C}=\text{O}$  vibration. The main peak and the  $3613 \text{ cm}^{-1}$  peak will be due to the two molecular species characterized by the stronger and weaker intramolecular hydrogen bonds



intensity and half-width listed in Table II are those for the main band. The two small peaks are so small that they do not obstruct the intensity measurements of the main band.

#### Relation between the Intensity and the Wave Number

The integrated intensities of the free and the hydrogen-bonded OH bands are plotted against the wave

TABLE II. Observed data of the bonded OH bands.

Donor	Acceptor	Concentration of acceptor	Solvent	$\nu_{\max}$ cm <sup>-1</sup>	Half-width cm <sup>-1</sup>	$a_{\max}$	$A \times 10^{-4}$	$\partial\mu/\partial r \times 10^{10}$
Phenol	C <sub>2</sub> H <sub>5</sub> Cl <sub>4</sub>	67 vol. %	CCl <sub>4</sub>	3600	38	334	1.99	2.1
Phenol	Chlorobenzene	67 vol. %	CCl <sub>4</sub>	3583	40	358	2.25	2.2
Phenol	Acetonitrile	0.1 mole/l	<i>n</i> -Heptane	3478	77	415	5.02	3.36
Phenol	Ethyl acetate	0.08 mole/l	<i>n</i> -Heptane	3461	160	334	8.40	4.34
Phenol	Ethyl ether	0.08 mole/l	<i>n</i> -Heptane	3362	115	444	8.03	4.24
Phenol	Hexamethylene tetramine	0.02 mole/l	CCl <sub>4</sub>	3070	280	281	12.4	5.27
Salicyl aldehyde	...	...	CCl <sub>4</sub>	3180	150	76	1.79	2.0
Methyl salicylate	...	...	CCl <sub>4</sub>	3210	125	165	3.24	2.7
Ethyl lactate	...	...	CCl <sub>4</sub>	3547	43	131	0.89	1.41

numbers at the band maxima in Fig. 2. It can be seen that, except for a few bands, the points thus obtained lie on a smooth curve. The relatively low intensities of the OH bands of ethyl lactate, salicyl aldehyde, and methyl salicylate will be discussed in a later part of this paper. Similarly, the point for the phenol-ethyl acetate complex does not lie on this curve. The large half-width and the irregular shape of the OH band of this complex suggest that it consists of two bands. Hence, it is natural that the apparent peak frequency of the band has no significance. Also, the assumption of the Lorentz curve seems to cause large error for this band.

It is interesting to note that the intensities of the free OH bands of various compounds increase with their acidities. In regard to the OH bands of the intermolecularly hydrogen-bonded phenol, it is seen that the intensity increases with the shift of the frequency due to the hydrogen bonding. As the shift of the frequency is a good measure of the energy of the hydrogen bond, we may conclude that the intensity increases with the energy of the hydrogen bond.

### The Effect of Nonpolar Solvents on the Intensity

It is expected from both the classical theory given by N. Q. Chako<sup>3</sup> and the quantum-mechanical theory given by E. Hirota<sup>4</sup> that the intensity of either the visible or the infrared band in nonpolar solvents is larger than that in gaseous state because of the polarization of the solvent. It is desirable to know the magnitude of this effect before discussing the effect of hydrogen bond. The theories themselves can, in principle, give the ratio of intensities in gaseous state and in solution. As for the quantity, however, we cannot rely upon the theories because of their approximate nature. Therefore, we had better draw our conclusion from experimental facts. According to G. M. Barrow,<sup>5</sup> the intensity of the C=O band of acetone in carbon tetrachloride is 1.3 times as large as that in vapor phase. On the other hand, the intensities of the degenerate C—Cl stretching vibration band of chloroform in nonpolar solvents are substantially equal to those in vapor

phase.<sup>6</sup> From these results, it may be concluded that the effect of the nonpolar solvents on the intensity is very much smaller than that of the hydrogen bonding. Based on this conclusion, we hereafter discuss, for simplicity, the effect of the hydrogen bond as if the hydrogen-bond complex was placed in a vacuum.

### The Charge Transfer Moment

As is shown in Tables I and II, the  $\partial\mu/\partial r$  for the OH band of phenol is greatly increased by hydrogen bonding. For example, the  $\partial\mu/\partial r$  for the phenol-ethyl ether complex, whose binding energy is probably less than 5 kcal/mole,<sup>7</sup> is about 2.6 times as large as that of free phenol. It can hardly be supposed that the properties of the OH bond (charge distribution, equilibrium bond distance, etc.) change to a large extent on hydrogen bonding, because the energy of the hydrogen bond is very small compared to the OH bond energy. It seems therefore, to be very improbable to attribute such a large change in  $\partial\mu/\partial r$  to the change of the electronic distribution in the OH group. It is also hardly possible

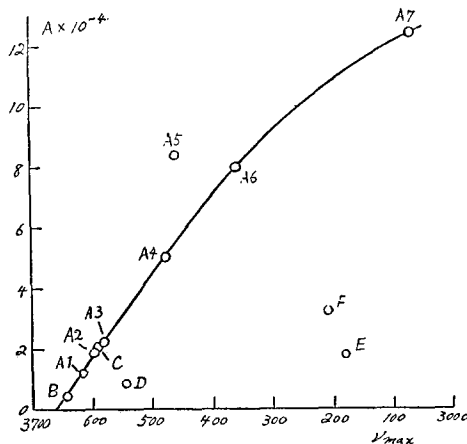


FIG. 2. The curve of integrated intensity vs  $\nu_{\max}$ . (A1) phenol, free, (A2) phenol bonded with tetrachloroethane, (A3) phenol bonded with chlorobenzene, (A4) phenol bonded with acetonitrile, (A5) phenol bonded with ethyl acetate, (A6) phenol bonded with ethyl ether, (A7) phenol bonded with hexamethylene tetramine, (B) methanol, free, (C) *p*-nitrophenol, (D) ethyl lactate, (E) salicyl aldehyde, (F) methyl salicylate.

<sup>3</sup> N. Q. Chako, J. Chem. Phys. 2, 644 (1934).

<sup>4</sup> E. Hirota, Bull. Chem. Soc. Japan 26, 397 (1953); 27, 295 (1954).

<sup>5</sup> G. M. Barrow, J. Chem. Phys. 21, 2008 (1953).

<sup>6</sup> D. H. Whiffen, Trans. Faraday Soc. 49, 878 (1953).

<sup>7</sup> S. Nagakura, J. Chem. Soc. Japan 74, 153 (1953).

that the electrostatic polarization of the proton-acceptor increases  $\partial\mu/\partial r$  greatly.<sup>8</sup>

In the previous paper,<sup>9</sup> it has been emphasized that the polar resonance structure which has the intermolecular coordinate bond makes some contributions to the energy of the hydrogen bond. According to the conclusion, we may express the wave function of the ground state of the hydrogen-bond complex by the formula,

$$\Psi = c_N \Psi_N + c_P \Psi_P, \quad (2)$$

where  $c_N$  and  $c_P$  are the coefficients under the constraint that  $c_N^2 + c_P^2 = 1$ , and  $\Psi_N$  and  $\Psi_P$  are the wave functions attached to the following resonance structures,<sup>10</sup>



where X is the atom which accepts the proton. In the *P*-structure, there is the electron transfer from the lone pair AO (atomic orbital) of the proton acceptor to the valence AO of the oxygen atom of the proton donor accompanied by the establishment of the covalent bond between H and X. Then, the dipole moment due to the contribution of the *P*-structure may be given by the formula,<sup>11</sup>

$$\mu_T = \mu_P c_P^2, \quad (3)$$

where  $\mu_P$  is the dipole moment associated with the *P*-structure, being approximately expressed by the product of the charge of an electron and the  $\text{O} \cdots \text{X}$  distance. In the case where the latter is 2.8 Å, it is ca 13 D. It can be therefore understood that  $\mu_T$  is appreciably large, though  $c_P^2$  at the normal OH distance is quite small.

$c_P$  depends on the overlap and exchange integral over the lone-pair AO of the proton acceptor and the hydrogen 1s AO, and also on the energy difference between the two resonance structures. As these values change very sensitively with the  $\text{H} \cdots \text{X}$  distance,  $\mu_T$  will oscillate with the OH vibration. Coulson and Danielsson<sup>12</sup> calculated the quantity which corresponds to  $c_P^2$  for the water-water hydrogen bond. Taking the  $\text{O} \cdots \text{O}$  distance as 2.8 Å, they obtained the  $c_P^2$  values of 0.014, 0.029, and 0.042 for the OH distance of 0.8 Å, 1.0 Å, and 1.2 Å, respectively. By use of the result, we obtain

$$\partial\mu_T/\partial r = \mu_P \partial c_P^2/\partial r \approx 13 \times 0.07 \approx 0.9 (10^{-10} \text{ esu}).$$

The value thus obtained suggests that the charge transfer is the most important factor which determines the increase of  $\partial\mu/\partial r$ . The  $\partial\mu/\partial r$  for the hydrogen-bond

complex may be, therefore, expressed as a first approximation by the formula

$$\partial\mu/\partial r \approx \partial\mu_0/\partial r + \partial\mu_T/\partial r, \quad (4)$$

in which  $\mu_0$  is the dipole moment for the free molecule.

### The Sign of $\partial\mu_0/\partial r$

For the intermolecular  $\text{O}-\text{H} \cdots \text{O}'$  hydrogen bond, at least in dilute solutions, the proton may in general be assumed as situated on the straight line which connects two oxygen nuclei.  $\mu_T$  is a vector which lies approximately along this line and directs out from  $\text{O}'$  to O. In the case where we define, as a convention, this direction to be positive,  $\partial\mu_T/\partial r$  is also positive, since  $|\mu_T|$  increases with  $r$ . The direction of  $\mu_0$ , in general, does not coincide with that of the OH bond. For the present purpose, however, it seems to be sufficient to consider only the component of  $\mu_0$  along the OH direction, since the other components will not change appreciably with  $r$ . Hence, there are only two cases where  $\partial\mu_0/\partial r$  is either parallel or antiparallel to  $\partial\mu_T/\partial r$ .

For molecules such as water, alcohols, and phenols, it may be assumed that the dipole moment associated with the OH group will be the only one which is affected seriously by the OH distance. This can be divided into two terms: the atomic dipole of the oxygen atom which arises mainly from the *s,p*-hybridization, and the dipole due to the polarity of the OH bond, both of which are conceivable to be positive.<sup>13</sup> When the OH distance increases, the latter is expected to increase, if the contribution of the polar resonance structures such as ( $\text{O}-\text{H}^+$ ) is not seriously changed by the change in the OH distance. The atomic dipole is, on the other hand, expected to decrease, because the *s*-character in the valence AO decreases as the OH distance increases.<sup>14</sup> Therefore, the sign of  $\partial\mu_0/\partial r$  cannot be determined by a simple qualitative argument. Also it is very difficult to determine it by the nonempirical calculations.<sup>15</sup>

We may calculate the  $\partial\mu_T/\partial r$  for the phenol-ethyl ether complex using observed values and Eq. (4) as follows:

$$\begin{aligned} \partial\mu_T/\partial r &= |\partial\mu/\partial r| \mp |\partial\mu_0/\partial r| \\ &= 4.3 \mp 1.7 = 2.6 \quad \text{or} \quad 6.0 (10^{-10} \text{ esu}), \end{aligned}$$

where the minus and the plus sign correspond to the

<sup>13</sup> J. A. Pople, Proc. Roy. Soc. (London) **A202**, 323 (1950); **A205**, 163 (1951).

<sup>14</sup> W. Moffitt, Proc. Roy. Soc. (London) **A202**, 548 (1950).

<sup>15</sup> R. Mecke, in the Discussions Faraday Soc. **9**, 161 (1950), concluded from the observed infrared intensities of the overtones that for phenol and hydrogen halides,  $\partial\mu_0/\partial r$  is negative. But his argument seems to afford no decisive conclusion on this point. There are two independent papers which conclude that  $\partial\mu/\partial r$ 's for hydrogen halides are negative: E. Bartholomé, Z. physik. Chem. **B23**, 131 (1933); R. P. Bell and I. E. Coop, Trans. Faraday Soc. **34**, 1209 (1938). The reasoning of the former paper is very indirect and seems not to be conclusive. The reasoning of the latter is convincing, but it seems to be doubtful whether the experimental accuracy is sufficient for their arguments. Moreover it is not evident whether the  $\partial\mu_0/\partial r$ 's for phenol and hydrogen halides have the same sign.

<sup>8</sup> We can make a rough estimate of the moment electrostatically induced at the acceptor by the use of the atomic polarization of the constituent atoms. For ethyl ether it is about one-tenth the original OH moment.

<sup>9</sup> H. Tsubomura, Bull. Chem. Soc. Japan **27**, 445 (1954).

<sup>10</sup> Another polar resonance structure which has the covalent bond between O and X has been neglected for simplicity.

<sup>11</sup> Here the term,  $2c_N c_P \int \Psi_N \sum_i e_i z_i \Psi_P d\tau$ , is neglected. Equation (3) gives, therefore, the lower limit of  $\mu_T$ .

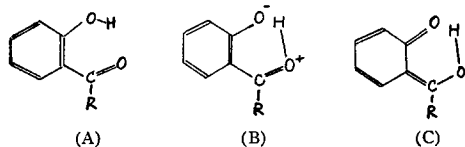
<sup>12</sup> C. A. Coulson and U. Danielsson, Arkiv Fysik **8**, 245 (1954).

cases of assuming the  $\partial\mu_0/\partial r$  as positive and negative, respectively. It is conceivable, from the shift of the OH bands, that the energy of the hydrogen bond between phenol and ether is of the same order of magnitude as that between two water molecules. As the energy of the hydrogen bond is the dominant factor among the factors which determine  $\mu_T$ , it can be expected that the values of  $\partial\mu_T/\partial r$  in these two types of hydrogen bonds do not differ very much from each other. Since the calculated value of  $\partial\mu_T/\partial r$  for the hydrogen-bonded water molecules is 0.9, we may regard 2.6 as the correct value of  $\partial\mu_T/\partial r$  for phenol-ethyl ether complex, and the  $\partial\mu_0/\partial r$  for phenol as positive.

There is another reason for believing the  $\partial\mu_0/\partial r$  to be positive. If it has negative sign, the  $\partial\mu/\partial r$  and hence the  $(\partial\mu/\partial r)^2$ , which is proportional to the intensity, will change with the energy of the hydrogen bond in such a way as shown in Fig. 3. This is in contradiction with the result shown in Fig. 2, which states that the intensity increases monotonously with the shift of the frequency due to the hydrogen bonding.

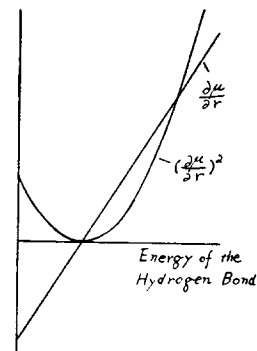
### The Intensities of the Chelate Compounds

The chelate compounds have the OH bands of abnormally low frequencies indicating that the hydrogen bonds in these compounds are particularly strong.<sup>16</sup> It is also recognized that the peak intensities of their OH bands are very weak. As for the band area, however, no quantitative measurement has been made before the present investigation. As is shown in Fig. 2, the intensities of salicyl aldehyde and methyl salicylate are considerably smaller than the values to be predicted by the intensity-frequency curve. This may be explained as follows. Of the resonance structures *A*, *B*, and *C* shown below, the structure of the charge-transfer type previously described is that of the *B*-type.



<sup>16</sup> Rasmussen, Tunnicliff, and Brattain, *J. Am. Chem. Soc.* **71**, 1068, 1073 (1949); M. Tsuboi, *Bull. Chem. Soc. Japan* **25**, 385 (1952).

FIG. 3. Qualitative curves which represent the dependence of  $\partial\mu/\partial r$  and  $(\partial\mu/\partial r)^2$  on the energy of the hydrogen bond under the assumption of  $\partial\mu_0/\partial r < 0$ .



The *B*-structure, being an ionic type, is less stable than the *C*-structure, which is characteristic of the chelate compounds. The existence of this structure increases the charge transfer through the hydrogen bond and is the main reason why the OH bands in these compounds have extraordinarily low frequencies. In these compounds, however, the charge transfer produces no large dipoles, because the nonpolar *C*-structure plays the dominant part; in other words, the moment due to the charge transfer with respect to the  $\sigma$  electrons is largely diminished by the counter-migration of the  $\pi$  electrons. This may account for the observed relatively weak intensities of the OH bands of these compounds.

Even for the case of the intramolecular hydrogen bond which does not lead to chelation, the moment due to the charge transfer through the hydrogen bond is conceivable to be diminished by the polarization due to the  $\sigma$  and inner-shell electrons of the cyclic part of the molecule. But the amount of the diminution will be considerably smaller than that for the case of the chelate compounds, since the polarization due to the  $\sigma$  and inner-shell electrons is smaller than that due to the  $\pi$  electrons. The observed intensity of the OH band of ethyl lactate seems to be in harmony with this conclusion.

### ACKNOWLEDGMENTS

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