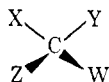


take advantage of the greater charge remaining in the  $C(2p_z)$ ; (2) this decrease in bond angle in  $AB_2$  systems as  $B$  becomes more electronegative is expected to be a general result, not dependent on the presence of "lone pairs" on the external atoms. This dependence of geometry on electronegativity has been previously discussed in terms of "rehybridization," but we have shown that it is equally explicable using MO concepts. The MO description is probably a superior one because one can often relate the bond angle trends to differences in  $b_2$  and  $a_1$  orbital energies, which can be measured in photoelectron spectroscopy.

Interesting future issues include the following. (1) An attempt to understand the geometry of the alkali oxides, which appear to be an exception to the general electronegativity rule. (2) Geometry changes in rigid ring systems<sup>31</sup> on electronegative substitution may well be made explicable by considering the geometry variations in the model system



as  $X$ ,  $Y$ ,  $Z$ , and  $W$  undergo electronegativity changes. (3) Attempts to quantify the orbital energy differences and their changes with angle might involve the IC-SCF procedure<sup>32</sup> for determining the orbital energies and Bartell's second-order Jahn-Teller formalism<sup>33</sup> for examining their angle dependence. (4) Finally, we have not given a definitive answer to the question posed in our title. As Pople pointed out,<sup>12</sup> the experimental evidence is clear in terms of increased C-F bond strength in fluoromethanes with increased fluorine sub-

(31) C. M. Weeks, W. L. Duax, and M. E. Wolff, *J. Amer. Chem. Soc.*, **95**, 2865 (1973); and P. A. Kollman, D. D. Giannini, W. L. Duax, S. Rothenberg, and M. E. Wolff, *ibid.*, **95**, 2869 (1973).

(32) S. T. Elbert, S. R. Langhoff, and E. R. Davidson, *J. Chem. Phys.*, **57**, 2005 (1972).

(33) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).

stitution and this can be explained simply by noting that successive fluorine substitution makes the C-F bonds more ionic and, thus, stronger. Therefore, one does not have to invoke "nonbonded attraction" to explain the exothermicity of reactions like  $2CH_3F \rightarrow CH_4 + CH_2F_2$  and  $2CH_2CHF \rightarrow C_2H_4 + CH_2CF_2$ .<sup>34</sup> In comparing the Mulliken populations on the carbon for ethylene, monofluoroethylene, and 1,1-difluoroethylene, one finds a near linear decrease in charge, indicating that in monofluoroethylene the C-F carbon finds it energetically favorable to donate as much charge as the carbon in ethylene to a fluorine substituent. Thus, the evidence appears strong that in  $AB_2$  molecules (or fragments) "nonbonded attractions" are more likely to be due to changes in the nature of the A-B bonds than to specific  $A \cdots A$  "attractive forces."

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(34) Compilations of thermochemical data ((1) D. R. Stull and H. Prophet, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 37 (1971), and (2) "Thermochemistry of Organic and Organometallic Compounds," J. D. Cox and G. Pilcher, Ed., Academic Press, New York, N. Y., 1970) indicate that the reactions  $2CH_3F \rightarrow CH_4 + CH_2F_2$  and  $2C_2H_3Cl \rightarrow C_2H_4 + CH_2CCl_2$  are exothermic by 13.7 and 4.2 kcal/mol, respectively. There are no data on vinyl fluoride ( $C_2H_3F$ ), but from the above it is very likely that  $2C_2H_3F \rightarrow C_2H_4 + CH_2CF_2$  is exothermic, indicating an energetic driving force for geminal C-F bonds. This effect does not continue through  $CF_3$ , since the heats for the reactions,  $2CH_2F_2 \rightarrow CHF_3 + CH_3F$  and  $2CHF_3 \rightarrow CH_2F_2 + CF_4$  are  $-2.8$  and  $+2.3$  kcal/mol. It should also be noted that further support for the fact that there is no attraction in *cis*-1,2-difluoroethylene (compared to 1,1-difluoroethylene) comes from the fact that the enthalpy for the reaction  $2CH_2CF_2 \rightarrow C_2H_4 + C_2F_4$  is  $+15.5$  kcal/mol.

## A Model Calculation of the Intramolecular Vibration Spectrum of Liquid Water

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**Abstract:** The eigenfrequency spectrum corresponding to intramolecular vibrations in the Weres-Rice model of water is calculated. Additional assumptions, beyond those fundamental to the water model, must be employed to convert the calculated spectrum to a form which can be compared with experimental data. It is shown that the spectrum predicted by the Weres-Rice model is not in disagreement with the observed infrared and Raman spectroscopic data.

The analysis of the vibration-rotation spectrum of an isolated molecule has been used successfully, for many years, to obtain information about its structure. Indeed, much of our knowledge of chemical bonding is derived from studies of this kind. In contrast, the available studies of infrared and Raman spectra of liquids, wherein molecules interact strongly, have not

yielded much direct information about their structure. In part this failure merely reflects the inadequacy of current theories of the liquid state. However, in part it also stems from the nature of the recorded spectra, which generally only show broad features which are difficult to correlate with properties of the liquid structure. Spectroscopic studies of the liquid state are,

despite the above remarks, of considerable value, since they provide data against which theoretical models can be tested. Thus, such studies play the role of narrowing the field of speculation, rather than being definitive probes of structural detail. With this in mind we remark that Weres and Rice have proposed, in a recent publication,<sup>1</sup> a locally correlated cell model of liquid water. The predicted thermodynamic properties and the predicted low-frequency *intermolecular* vibration spectrum are in fairly good agreement with the experimental data. The purpose of this paper is to test further the Weres–Rice model by comparing the predicted and observed *intramolecular* vibrational spectra.

As will be shown in the following text, the Weres–Rice (WR) model of water has a vibrational spectrum which, at the very least, is not in disagreement with the observed spectrum. The cautionary note in this statement is designed to warn the reader that while the vibrational spectrum for the WR model is readily calculated, conversion of that spectrum into a form which can be directly compared with the observed infrared and Raman spectra requires assumptions concerning the energy dependence of transition probabilities, influence of disorder on selection rules, the nature of band broadening, etc. We show that simple assumptions suffice to transform the WR model spectrum to an absorption spectrum in rather good agreement with experiment. However, it must be recognized that these needed extra assumptions are not part of the WR model and, because they may not be equally valid everywhere (*e.g.*, across the spectrum), the cited agreement is not definitive support for the model. On the other hand, the calculations lead to the strong inference that the WR model is not in serious disagreement with experimental data.

### Model and Method of Calculation

As implied in the statement of purpose made in the introductory section, we adopt the WR model of liquid water. For our present purpose this means accepting, as a model of the local molecular structure, the cell configurations and corresponding weights reported by them. However, the WR model treats only the properties of an assembly of rigid water molecules interacting *via* a (modified) Ben-Naim–Stillinger (BNS) potential;<sup>2</sup> no allowance is made for intramolecular nuclear motion or its coupling to intermolecular motion. Yet, to describe the high-frequency vibration spectrum of the liquid it is necessary to have a description of the potential energy in terms of both intramolecular and intermolecular coordinates; hence the BNS potential of the WR model must be replaced.

Consider first the internal motions of an isolated water molecule. We have chosen to describe these by employing a valence force field model with four force constants.<sup>3</sup> These constants describe the potential energy of the molecule, in the harmonic approximation, in terms of OH bond stretching ( $k$ ), bond–bond stretching interaction ( $k_{12}$ ), OHO bending ( $k_\theta$ ), and a bond stretching–angle bending interaction ( $k_{r\theta}$ ).

(1) O. Weres and S. A. Rice, *J. Amer. Chem. Soc.*, **94**, 8983 (1972).

(2) A. Ben-Naim and F. H. Stillinger in "Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes," R. A. Horne, Ed., Wiley, New York, N. Y., 1972.

(3) See, for example, G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1945.

Consider, now, a water molecule hydrogen bonded as in one of the WR cell configurations. Clearly, the force field is different from the valence force field of a free molecule. We have accounted for this change by representing the potential energy of stretching a hydrogen-bonded OH in the Lippincott–Schroeder form<sup>4</sup>

$$V_{\text{OHO}} = D_0[1 - \exp(-\alpha)] - D_0^* \exp(-\beta) + A[\exp(-bR) - \frac{R_0}{2R} \exp(-bR_0)] \quad (1a)$$

$$\alpha = n(r - r_0)^2/2r \quad (1b)$$

$$\beta = n^*(r^* - r_0^*)^2/2r^* \quad (1c)$$

$$n = k_0 r_0 / D_0 \quad (1d)$$

In eq 1,  $R$  is the instantaneous O–O separation and  $R_0$  the equilibrium O–O separation,  $r$  and  $r_0$  refer to the instantaneous and equilibrium OH nuclear separations on the "covalently bonded" side of O–H···O, while  $r^*$  and  $r_0^*$  refer to the corresponding quantities on the "hydrogen-bonded" side. Finally,  $k_0$  and  $D_0$  are the stretching force constant and dissociation energy of the covalent OH bond, with  $k_0^*$  and  $D_0^*$  the corresponding quantities for the hydrogen bond. Schroeder and Lippincott showed that the parameter  $b$  has the same value ( $4.80 \times 10^8 \text{ cm}^{-1}$ ) for many hydrogen-bonded systems, which we adopt, while the parameter  $A$  is determined by the condition of mechanical equilibrium  $(\partial V_{\text{OHO}}/\partial R)_{R=R_0} = 0$ . Clearly, by evaluating appropriate derivatives of  $V_{\text{OHO}}$  the force constants for OH stretching, H···O stretching, O–H···O bending, and intermolecular coupling are obtained.

In the WR model the molecules are partially or fully tetrahedrally coordinated. Therefore, the appropriate reference free molecule valence force field is for a water molecule with HOH angle  $109^\circ 28'$ , instead of the true free molecule value  $105^\circ 31'$ . Given the observed free molecule spectrum,<sup>3</sup> any three of the four force constants  $k$ ,  $k_{12}$ ,  $k_\theta$ ,  $k_{r\theta}$  can be calculated under the assumption that the HOH angle is  $109^\circ 28'$ . Of course,  $k_{r\theta}$  is the smallest of these. We adopted for it the value shown in Table I and calculated  $k$ ,  $k_{12}$ , and  $k_\theta$ . The potential  $V_{\text{OHO}}$  was then adjusted, *via* the values of  $D$  and  $D_0^*$ , so that the curvature in  $r$  approached the value  $k$  in the limit  $R \rightarrow \infty$ . The results of these calculations are also shown in Table I.

As written  $V_{\text{OHO}}$  cannot describe intermolecular torsion. The effects of this motion were included in the potential energy of a given cell configuration by adding the appropriate part of the BNS potential to the terms already described. In order to simplify the calculations, the torsional force constants for relative rigid body motion of molecules were evaluated only for pair displacements (*i.e.*, twisting only a pair of molecules holding all others fixed in orientation). A detailed calculation for the case of a water trimer showed that the torsional force constant is accurately approximated by this procedure.

Any particular WR cell configuration may be thought of as a supermolecule, some of the parts of which interact *via* the full BNS potential and some *via* only the central component of the BNS potential. The force

(4) E. R. Lippincott and R. Schroeder, *J. Chem. Phys.*, **23**, 1099 (1955); R. Schroeder and E. R. Lippincott, *J. Phys. Chem.*, **61**, 921 (1957).

**Table I.** Force Constants and Other Parameters Used in the Model Spectrum Calculation

A. Potential Parameters	
$D_0$	$= 8.198 \times 10^{-12}$ erg
$D_0^*$	$= 5.653 \times 10^{-12}$ erg
$b$	$= 4.80 \times 10^8$ cm $^{-1}$
$r_0 = r_0^*$	$= 0.97 \times 10^{-8}$ cm (free molecule)
$n$	$= 9.05 \times 10^8$ cm $^{-1}$
$n^*$	$= 13.13 \times 10^8$ cm $^{-1}$
B. Liquid Parameters	
$R_0$	$= 2.82 \times 10^{-8}$ cm (0°); $2.88 \times 10^{-8}$ cm (100°)
$r_0$	$= 0.995 \times 10^{-8}$ cm (0°); $0.988 \times 10^{-8}$ cm (100°)
C. Force Constants	
$k$ (free molecule)	$= 7.6478 \times 10^5$ dyn/cm
$k$ (H-bonded molecule)	$= 7.2036 \times 10^5$ dyn/cm (0°) $= 7.6784 \times 10^5$ dyn/cm (100°)
$k_{12}$	$= -0.0798 \times 10^5$ dyn/cm (temp indep)
$k_{r\theta}$	$= -0.01979 \times 10^{-3}$ dyn (temp indep)
$k_\theta$	$= 6.679 \times 10^{-11}$ erg (temp indep)
$k_R$	$= 0.1302 \times 10^5$ dyn/cm (0°) $= 0.02335 \times 10^5$ dyn/cm (100°)
$k_{rR}$	$= 0.8216 \times 10^5$ dyn/cm (0°) $= 0.4254 \times 10^5$ dyn/cm (100°)
$k_\sigma$	$= 0.08581 \times 10^{-11}$ erg (0°) $^a$ $= 0.04054 \times 10^{-11}$ erg (100°)
$k_{\text{torsion, sym eel}}$	$= 0.00522 \times 10^{-11}$ erg (0°) $= 0.00647 \times 10^{-11}$ erg (100°)
$k_{\text{torsion nonsym eel}}$	$= 0.00173 \times 10^{-11}$ erg (0°) $= 0.00181 \times 10^{-11}$ erg (100°)

$^a k_\sigma$  measures the bending of O-H...O about a hydrogen-bonded H.

constant corresponding to motion in only the central component of the BNS potential is small relative to those already considered ( $0.0287 \times 10^5$  dyn/cm). It is, then, a good approximation to regard any particular WR cell configuration as a superposition of six disjoint internally hydrogen-bonded subconfigurations, namely a monomer, trimer, pyramidal tetramer, tetrahedral pentamer, linear pentamer, and cyclic hexamer. In this approximation the nonhydrogen-bond interaction between nearest neighbors is neglected. It is of some interest to note that some of the subconfigurations mentioned have several "coordination isomers," and the linear pentamer and cyclic hexamer (which has a chair form cyclohexane-like geometry) also have "equatorial" and "axial" type conformers.

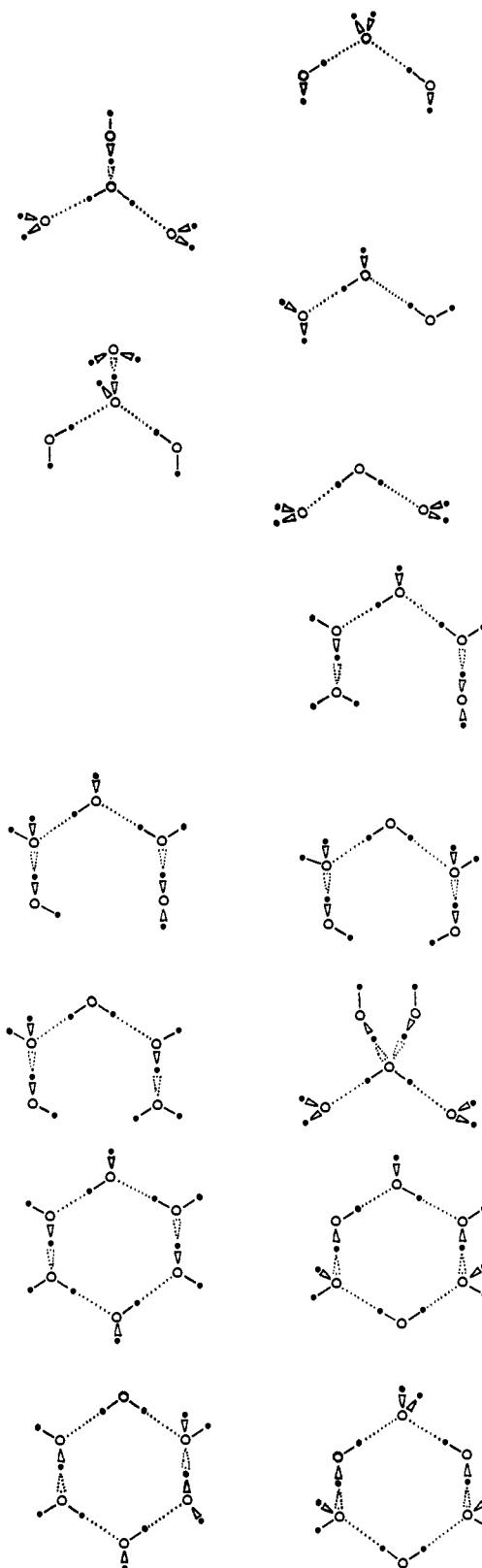
One further simplification in the analysis must be mentioned. For any given WR cell configuration, approximated as described by a superposition of disjoint subconfigurations, the normal mode analysis was carried out including all "isomeric" forms of the subconfigurations up to the tetramer, for five "isomers" of the linear pentamer and four "isomers" of the cyclic hexamer, for a total of sixteen "isomeric" species. All of these "isomeric" forms are schematically represented in Figure 1.

The normal modes of the WR cell subconfigurations were calculated using a modification of the method introduced by Gwinn.<sup>5</sup> This method is particularly convenient in our case because of the (general) lack of simplifying symmetry properties of the WR subconfigurations.

## Results

Figures 2a and 2b display, in histogram form, the results of our calculations. They are constructed by superposing the eigenfrequencies for the four dominant

(5) W. D. Gwinn, *J. Chem. Phys.*, **55**, 477 (1971).



**Figure 1.** Subconfigurations used in the model calculation.

WR cell configurations with the weights found by Weres and Rice.

It is difficult to make a comparison of the calculations displayed in Figures 2a and 2b with experimental data, since the former refer to eigenfrequencies only, while the latter include transition probabilities and inevitable broadening from sources not included in the

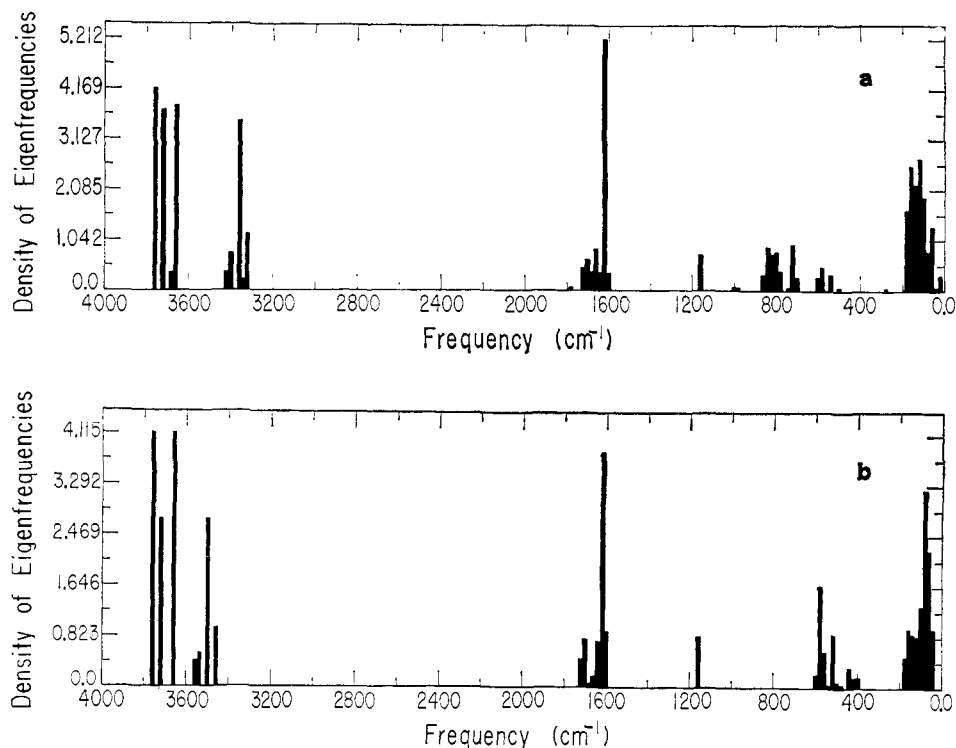


Figure 2. Eigenfrequencies of the WR model at 0° (a) and at 100° (b).

simple WR model. We have made a crude transformation of the data represented in Figures 2a and 2b so as to simulate an absorption spectrum. The transformation consists of replacing each computed eigenfrequency with a Gaussian peak. The widths of the Gaussians were computed by comparing our eigenfrequency spectrum for the tetrahedral pentamer and that calculated by Curnutte and Bandekar in the 3400- $\text{cm}^{-1}$  region.<sup>6</sup> These investigators simulated the spectrum of water by computing the eigenfrequencies of only the tetrahedral pentamer but allowing for a distribution of symmetric pentamers with O-O distances and weights taken from the water radial distribution function. The effective half-width of our spectrum (a measure of eigenfrequency distribution) was subtracted from the half-width of the Curnutte-Bandekar spectrum, and the difference was used to define the half-width of the broadening Gaussian. In our crude transformation we assume that the spectral broadening has the characteristic that the ratio of half-width to peak position is a constant. The eigenfrequency spectrum of Figures 2a and 2b, transformed as described, is displayed in Figures 3a and 3b. Finally, by assuming that the transition probability is constant over the entire spectrum, the smoothed spectra of Figures 3a and 3b can be converted into plots of transmittance *vs.* frequency; these are shown in Figures 3c and 3d. The prominent features of the plots in Figures 3c and 3d are summarized in Table II.

Given the crudeness of the transformation from the calculated eigenfrequency spectrum to the absorption spectrum and, of course, the approximations inherent in the WR model, we regard the agreement between experiment<sup>7</sup> and calculation to be rather good.

(6) B. Curnutte and J. Bandekar, *J. Mol. Spectrosc.*, **41**, 500 (1972).

(7) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford University Press, Oxford, 1969.

Table II. Features in the Crude Synthetic Absorption Spectrum

Assignment	Calculated band <sup>a</sup> parameters, $\text{cm}^{-1}$	Observed band <sup>b,7</sup> parameters, $\text{cm}^{-1}$
OH stretch	$\omega = 3720, 3360$ Fwhm = 540	$\omega = 3920, 3490, 3280$ Fwhm $\approx 400$
Association	Not present	$\omega = 2125$ Fwhm = 580
HOH bend	$\omega = 1610$ Fwhm = 140	$\omega = 1645$ Fwhm = 75
Libration	$\omega \approx 720$ Fwhm $\approx 300$	$\omega \approx 685$ Fwhm $\approx 600$
Hindered translation	$\omega \approx 140, 60^c$	$\omega \approx 160, 60^d$

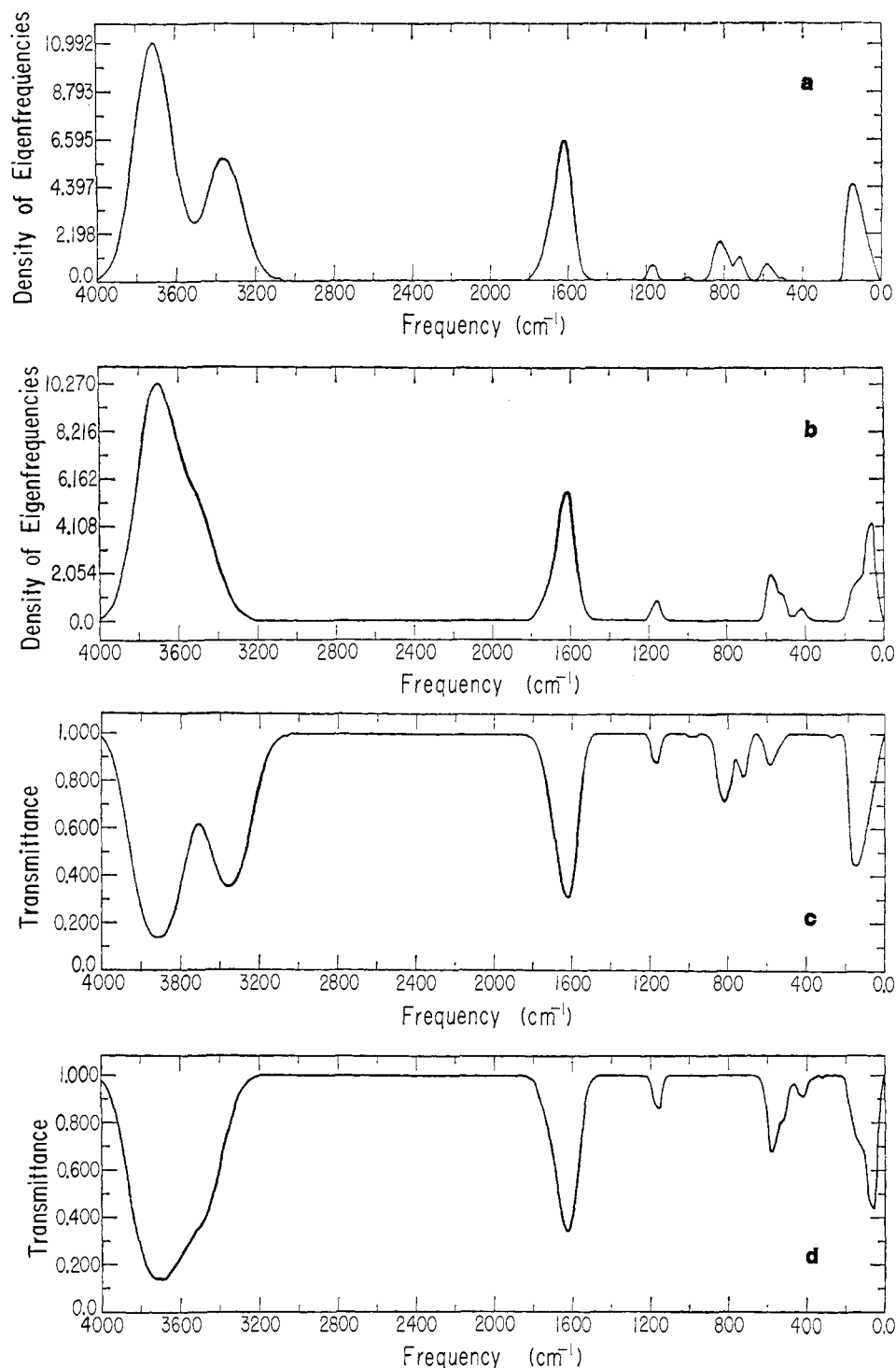
<sup>a</sup> 0°. <sup>b</sup> 25°. <sup>c</sup> Apparent only in the unbroadened histogram.  
<sup>d</sup> From Raman spectrum.

The calculations described in this paper will be least accurate in the low-energy region (say, below 300  $\text{cm}^{-1}$ ) for which Weres and Rice have reported the spectrum obtained from the same model by a different method. Nevertheless, as shown in Table II, the principal features of the spectrum below 300  $\text{cm}^{-1}$  are tolerably well accounted for by the present calculations.

We find that the OH stretching region of the synthetic spectrum has two distinct bands, the higher frequency component (3720  $\text{cm}^{-1}$ ) corresponding to non-hydrogen-bonded OH with assigned fwhm  $\sim 240$   $\text{cm}^{-1}$ , and the lower frequency component (3360  $\text{cm}^{-1}$ ) corresponding to hydrogen-bonded OH with assigned fwhm  $\sim 200$   $\text{cm}^{-1}$ .

Note that the synthetic spectrum under discussion has no absorption in the "association band" region, consistent with the assignment of that band in the observed spectrum to excitation of vibrational overtones or combinations, or both.<sup>7</sup>

The present calculation is designed to be most accurate for the description of intramolecular vibrational



**Figure 3.** Smoothed eigenfrequency distribution for the WR model at  $0^\circ$  (a) and at  $100^\circ$  (b). Simulated absorption spectrum for the WR model at  $0^\circ$  (c) and at  $100^\circ$  (d).

motion. It is, therefore, not surprising that in the librational region the synthetic spectrum has more structure than does the observed spectrum. This is likely due to inadequacies in the BNS representation of the force field between molecules, as well as to model approximations such as the use of a common nearest neighbor separation and the discrete lattice approximation of the WR model.

Comparison of the synthetic spectra for 0 and  $100^\circ$  and the corresponding observed spectra provides a further test of the WR model. We observe, first, that on raising the temperature from 0 to  $100^\circ$  the WR

model predicts that the lower frequency component of the OH stretch shifts to higher frequency (see Figures 2a and 2b). In the smoothed synthetic spectrum the net effect is to cause the two to merge, the resultant at  $100^\circ$  being one peak with a shoulder (see Figures 3c and 3d). Of course, there also is a shift of the mean of the spectral distribution toward higher frequency accompanying this change in temperature. The predicted change is in the same direction and is of roughly the same magnitude as the shift observed for HDO in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ .<sup>7</sup> On the other hand, in the libration region the WR model predicts that the mean of the

spectral distribution shifts to lower frequency as temperature increases, as expected because of changes in intermolecular interaction accompanying thermal expansion. The predicted change is in the correct direction, but the rate of change is much larger than that observed. This discrepancy is, again, not surprising in view of the above mentioned sensitivity of libration motion to the intermolecular potential.

### Discussion

The calculations described in this paper have much in common with those reported by More O'Ferrall, Koepl, and Kresge<sup>8</sup> and by Curnutte and Bandekar.<sup>6</sup> Both of these investigations are concerned with vibrational analysis of a model of liquid water in which a central molecule is in a tetrahedral environment. The former group considered a water molecule tetrahedrally bonded to two O atoms (regarded as fragments of water molecules) and to two OH groups (similarly regarded) and also the vibrational spectra of derivative models characterized by removal of one or more of the peripheral O and/or OH groups. In contrast, Curnutte and Bandekar studied only one kind of symmetric molecular environment, namely a water molecule tetrahedrally bonded to four others to form a 15 atom pentamer. The existence of disorder in the liquid was simulated by considering the set of all tetrahedral pentamers with O-O separations distributed as in the radial distribution function of the liquid. The WR model has some of the characteristics of each of those mentioned. Like the More O'Ferrall, *et al.*, work it includes bonded and unbonded configurations but much larger and more complex than they considered. Like the Curnutte and Bandekar work it treats the variability of coupling by making the OH stretching force constant a function of O-O separation. As a result the WR model accounts for broadening of the spectrum of the liquid as a combination effect arising from the spread of frequencies associated with subconfigurations of the full cell configuration on which is superimposed the spread generated by the distribution of O-O separations. As emphasized in the introductory section, we regard the comparison between the predictions of any liquid model and experiment as a test of internal consistency and not as definitive support for the model. Consistent with this point of view we note that Curnutte and

Bandekar show that an isosbestic point in a spectrum (which they find for their model) need not be interpreted as evidence for equilibrium between different molecular species. Similarly, the WR model accounts, at least qualitatively, for the temperature dependence of the observed vibrational spectrum even though the populations of the dominant WR cell configurations are essentially the same at 0 and 100°. Just as in the Curnutte and Bandekar calculations, it is the effects of thermal expansion that dominate the changes in the calculated spectrum as the temperature changes.

Aside from the approximations inherent in the WR model, the calculations we have described also suffer from inadequate knowledge of the dependence of the potential energy on the nuclear positions. The potential employed, based on the described superposition of part of the BNS potential, the Lippincott-Schroeder potential for OH stretching in the hydrogen-bonded environment, and a harmonic potential for other intramolecular motion, classifies water molecules into three categories based on the local structure. These are the donor H-bonded molecule, the acceptor H-bonded molecule, and the double donor H-bonded molecule. We denote these  $d$ ,  $a$ , and  $d_2$ , respectively. Now, in terms of the subconfigurations of the WR cell configurations, we identify nine H-bonded species, namely "free,"  $d$ ,  $d_2$ ,  $a$ ,  $a_2$ ,  $ad$ ,  $ad_2$ ,  $a_2d$ , and  $a_2d_2$ . It is reasonable to expect these to have somewhat different bond-bond interactions (reflected in  $k_{12}$ ,  $k_{\theta}$ , and  $k_{r\theta}$ ), but our calculations have allowed only the stretching force constant ( $k$ ) to change from species to species. This approximation, based on lack of information, is potentially very serious with respect to  $k_{\theta}$ . However, at present there does not appear to be any reason to doubt the general findings already described. This conclusion is supported by some preliminary calculations, based on use of the data of Van Thiel, Becker, and Pimentel,<sup>9</sup> to provide a different set of force constants from those displayed in Table I.

**Acknowledgment.** This research has been supported by a grant from the National Science Foundation. We have also benefited from the use of facilities at the University of Chicago provided by the Materials Research Laboratory program of the National Science Foundation.

(8) R. A. More O'Ferrall, G. W. Koepl, and A. J. Kresge, *J. Amer. Chem. Soc.*, **93**, 1 (1971).

(9) M. Van Thiel, E. D. Becker, and G. C. Pimentel, *J. Chem. Phys.* **27**, 486 (1957).