

Figure 6. "Quartet" and "triplet effects" observed in carbon-13 spectra with coherent proton decoupling ($\Delta = 4$ kHz, $F_{\max} = 6.7$ kHz). (a) Methyl iodide in the usual cylindrical sample tube, 3 cm high, showing a 1:6:6:1 peak height ratio. (b) Methyl iodide in a 35- μ L bulb under the same conditions, showing the expected 1:3:3:1 ratio. (c) Methylene chloride in a cylindrical tube, showing a central peak 3.6 times taller than the outer peaks.

depth of a liquid in a cylindrical tube should reduce the differential broadening to some extent.

The simulations shown in Figures 4 and 5 suggest that, although the magnitude of the "quartet effect" diminishes very close to resonance and very far from resonance, it is nevertheless significant over essentially the entire experimental

range and cannot be completely avoided by a suitable choice of offset. In practice Δ and F must be chosen so as to keep the splittings reasonably small to avoid overlap problems in crowded spectra, and with these settings the broadening by decoupler field inhomogeneity will tend to be large.

This problem provided the impetus for the development of an alternative method for observing the proton-carbon multiplet splittings in carbon-13 spectra, a technique known as "J-scaling".⁹ Since this method is insensitive to the inhomogeneity of the decoupler field it should be particularly useful where off-resonance proton decoupling gives ambiguous results.

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Heat Capacity and Structure in Liquids. Application to the Structure of Water

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Abstract: Hydrogen-bonded molecules and long-chain molecules have recently been shown to have abnormally high liquid heat capacities. It is now further shown that these abnormal values can only be accounted for by postulating an isomerization reaction. An analysis is made of the heat capacity contribution $\Delta C_{p(\text{isom})}$ of a simple isomerization reaction $A \rightleftharpoons B$ and it is shown that $C_{p(\text{isom})}$ can amount to as much as 8-10 cal/mol·K depending on the thermochemistry of the isomerization. Application is made to H_2O and it is shown that $\Delta H = 2.2 \pm 0.2$, $\Delta S = 8.0 \pm 1$ will account for the excess ΔC_p over the range 0-100 °C. These yield mole fractions for X_B of 0.5 at 0 °C and 0.75 at 100 °C. If form A is assumed ice-like then $\Delta V = 3.2$ cm³/mol and setting the coefficient of expansion $\alpha_{\text{H}_2\text{O}} = 0$ at 4 °C leads to a simple expression for the molar volume of water which reproduces the coefficient of thermal expansion very well in the range 0-100 °C with no additional assumptions. With additional assumptions about the compressibilities of the two forms, the minimum at 45 °C in the compressibility of water can also be reproduced.

Introduction

The molar heat capacity at constant pressure, C_p , increases when a gas is condensed to a liquid at constant temperature. This increase in C_p , $\Delta C_{p(\text{vap})}$, turns out to be nearly a constant¹ for what are termed normal liquids,² namely, those that have Trouton constants ($\Delta H_{\text{vap}}/T_B$) equal to 20 cal/mol·K (eu). For the others, "abnormal" liquids, the departure of $-\Delta C_{p(\text{vap})}$

from an average value of about 12 eu³ at 25 °C can be used to provide quantitative information about their structure and hence also information about their other "abnormal" properties.

Heat Capacity of Liquids

A general quantitative approach to $\Delta C_{p(\text{vap})}$ has been difficult because of the paucity of data on C_p for both liquids and

gases. Part of these difficulties have been removed by the development of simple, empirical additivity rules for the accurate estimation of C_p for gases⁴ and recently in restricted regimes of temperature for liquids.^{5,6}

From the viewpoint of statistical mechanics, the condensation of a dilute gas (density ≤ 10 atm equivalent at 0 °C) converts three translational and three rotational degrees of freedom and a pressure-volume term (PV) into six modes of motion in the liquid plus a corresponding PV term. If we consider the liquid as a disordered lattice these modes can be identified as follows.

Three modes are associated with the translational oscillations or librations of the centers of gravity of the molecules in a potential cage of near neighbors; three modes are associated with the torsional oscillations of the molecules about their centers of gravity, and finally the pressure-volume term becomes the potential energy of expansion of the entire liquid lattice.

To a very good order of approximation, the condensation of gas to liquid has very little effect on the internal modes of motion of a molecule.² The small perturbations in frequencies associated with these internal modes is seldom larger than a few percent and has a negligible effect on their heat capacity contributions. This is a physically quite reasonable result since the average energy of interaction of a liquid molecule with each of its Z nearest neighbors is a small quantity of the order of $2\Delta E_{\text{vap}}/Z \approx 18RT_B/Z$ for normal liquids (T_B = boiling temperature). Since $Z \approx 12$ for normal liquids this interaction is of the order of $1.5RT_B$ or about 1 kcal when $T_B \approx 350$ K. This is very small compared to the energies of bonds.

This latter circumstance makes it possible to use the additivity laws very extensively developed for gases⁴ to compute the contributions of the lattice modes for liquids where heat capacities are known even when the gas heat capacity is not known.⁵ For a polyatomic, nonlinear, dilute gas the contributions of these modes to $C_{p(g)}$ is 8 eu. Hence the contributions of the internal modes to $C_{p(g)}$ is $(C_{p(g)} - 8)$ eu. If $C_{p(\text{liq})}$ is the measured heat capacity of the liquid then the contributions of these lattice modes, which we shall call $C_{p(\text{lat})}$, is given by

$$\begin{aligned} C_{p(\text{lat})} &= C_{p(\text{liq})} - [C_{p(g)} - 8] \\ &= -\Delta C_{p(\text{vap})} + 8 \end{aligned} \quad (1)$$

For normal liquids where $-\Delta C_{p(\text{vap})}$ at 25 °C has been found to be about 12 eu³ we see that the lattice modes will have a value of $C_{p(\text{lat})} \approx 20$ eu. It is possible to further break these down as follows.

The librational motions of the center of gravity of a liquid molecule in the cage of its nearest neighbors is expected to approximate a low-frequency harmonic oscillator. If these frequencies are below 200 cm^{-1} they can be taken as classical oscillators with $C_p = R$.⁴ Thus the three center of gravity modes are expected to have a C_p contribution of $3R = 6$ eu.

The three torsional modes of the molecule in its liquid cell will similarly behave as low-frequency oscillators if there is a barrier to free rotation. This will give them an upper limit of $3R = 6 \text{ eu}^7$ or if very anharmonic $3.3R = 6.6 \text{ eu}$. For nearly spherical molecules such as CH_4 or very symmetrical molecules such as C_2H_6 or CH_3Cl , the effective barrier to rotation about one or more of the inertial axes may be $\leq RT$ so that the torsion approaches a free rotation. In that case the contributions of these modes will approach a lower limit each of $R/2 = 1 \text{ eu}$. Thus the three torsional contributions will be between 3 and 6.6 eu.

The lattice expansion is then represented by a contribution $C_{p(\text{exp})} \approx 8 \text{ eu}$ given by the difference between 20 eu, the average value for normal liquids of $C_{p(\text{lat})}$, and 12 eu, the anticipated contributions from the center of gravity motions. This is in excellent agreement with various theoretical and empirical estimates of this contribution for normal liquids. As an example

we note that from thermodynamics we have

$$C_{p(\text{exp})} = C_p - C_v \equiv VT \frac{\alpha^2}{\beta} \quad (2)$$

Using typical values of $V \approx 100 \text{ cm}^3/\text{mol}$, $T \approx 300 \text{ K}$, $\alpha \approx 1.1 \times 10^{-3}/\text{K}$, and $\beta = 1 \times 10^{-4} \text{ atm}^{-1}$ we estimate a value for $C_{p(\text{exp})} \sim 8.5 \text{ eu}$.

Abnormal Liquids

If we restrict our attention to liquids below their boiling points we will find that $C_{p(\text{exp})}$ is usually less than 8.5 eu and since the six center of gravity modes will not exceed $6R = 12 \text{ eu}$ we do not expect to find $-\Delta C_{p(\text{vap})}$ in excess of about 12 eu. However, a number of liquids show significant deviations from this behavior.^{3,5} Quite generally we find that H_2O and alcohols show marked departures in excess of this value. In addition we find that flexible, long-chain molecules with more than eight consecutive single bonds will show progressively larger values for $-\Delta C_{p(\text{vap})}$. We shall classify these as abnormal liquids.

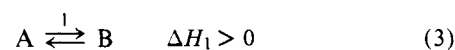
The fact that H_2O and the alcohols fall in this category is no surprise. They are long recognized to be exceptional in their liquid properties. Nor is the inclusion of long-chain molecules in this category surprising. Pitzer defined an "acentric" factor to permit characterization of liquids composed of very asymmetrical molecules in terms of deviations of properties from those of liquids composed of symmetrical or roughly spherical molecules.⁸ The perhaps surprising feature here is that the abnormality in C_p shows up only for liquids whose molecules exceed chains of C_8 .

The case of water is of particular interest. $C_{p(L)}(\text{H}_2\text{O}) = 18.0 \text{ eu}$ at 25 °C. However, the abnormally small coefficient of thermal expansion of H_2O over the range 0–60 °C is such that $C_{p(\text{exp})}(\text{H}_2\text{O}) \approx 0$. Thus in this range we would be forced to attribute the entire 18 eu to the internal modes together with the six center of gravity modes. The internal modes have very high frequencies and contribute 0 to C_p . But we have seen that the center of gravity modes cannot exceed about 12 eu. There is then an unaccounted contribution of about 6 eu to $C_{p(l)}(\text{H}_2\text{O})$. Similar arguments can be made for the excess heat capacity of the alcohols and long-chain compounds. In the absence of any other mechanical motion to which to assign the excess heat capacity we shall invoke a phenomenological explanation—*isomerization*.

Let us assume that the excess heat capacities of what we have called abnormal liquids are to be assigned to the phenomenon of isomerization. For the moment we are not concerned with the nature of this isomerization, whether it is a chemical change or a physical change such as a change in conformation, packing, or coordination.

Isomerization Heat Capacity

A chemical isomerization, if it is accompanied by energy changes, for example, if it is endothermic, can contribute a significant amount to the apparent heat capacity of a system even when the molar heat capacities of the two or more isomeric forms may be the same. Let us consider a single equilibrium between two isomeric forms of a molecule A and B:



Let us further assume that A and B mix like regular liquids,² are miscible in all proportions, and have a negligible heat of mixing. We can then treat the mixture as an ideal liquid and write for the enthalpy of the mixture:

$$H_{\text{mix}} = x_A H^\circ_A + x_B H^\circ_B \quad (4)$$

where x_A and x_B are the mole fractions of A and B and $x_A = 1 - x_B$. Then the heat capacity of the mixture is given by

Table I. Values of Isomerization Heat Capacity, $C_{p(\text{isom})}/R$, as a Function of $\Delta H_1/RT$ and $\Delta S_1/R^a$

	$\Delta H_1/RT$					
	0	1	2	3	4	5
0	0 (1)	0.2 (0.4)	0.42 (0.14)	0.43 (0.05)	0.3 (0.018)	0.2 (0.007)
1	0 (2.7)	0.25 (1)	0.79 (0.37)	0.95 (0.14)	0.7 (0.05)	0.4 (0.018)
$\Delta S_1/R$ 2	0 (7.4)	0.2 (2.7)	1.0 (1.0)	1.8 (0.37)	1.7 (0.14)	1.1 (0.05)
3	0 (20)	0.1 (7.4)	0.79 (2.7)	2.25 (1.0)	3.2 (0.37)	2.7 (0.14)
4	0 (55)	0.05 (20)	0.42 (7.4)	1.78 (2.7)	4.0 (1.0)	4.9 (0.37)

^a Values of K_1 are shown in parentheses.

$$C_{p(\text{mix})} = \left(\frac{\partial H_{\text{mix}}}{\partial T} \right)_p = x_A C_{pA}^\circ + x_B C_{pB}^\circ + H_A^\circ \frac{\partial x_A}{\partial T} + H_B^\circ \frac{\partial x_B}{\partial T} \quad (5)$$

$$= C_{pA}^\circ + x_B (C_{pB}^\circ - C_{pA}^\circ) + (H_B^\circ - H_A^\circ) \left(\frac{\partial x_B}{\partial T} \right) \quad (6)$$

$$= C_{pA}^\circ + x_B \Delta C_{p1}^\circ + (\Delta H^\circ_1) \left(\frac{\partial x_B}{\partial T} \right) \quad (7)$$

We note that even when $\Delta C_{p1}^\circ = 0$ there is a contribution to $C_{p(\text{mix})}$ arising just from the enthalpy change in the isomerization ΔH°_1 .

We can reduce this equation further by expressing the mole fraction x_B in terms of the equilibrium constant for reaction 1, K_1 . For an ideal mixture:

$$\frac{x_B}{x_A} = K_1 = \frac{x_B}{1 - x_B} \quad (8)$$

and

$$x_B = \frac{K_1}{1 + K_1} \quad (9)$$

Taking the logarithmic derivative of this last equation with respect to temperature we have:

$$\begin{aligned} \left(\frac{\partial \ln x_B}{\partial T} \right)_p &= \left(\frac{\partial \ln K_1}{\partial T} \right) - \frac{1}{(1 + K_1)} \left(\frac{\partial K_1}{\partial T} \right) \\ &= \left(\frac{\partial \ln K_1}{\partial T} \right) \left[1 - \frac{K_1}{1 + K_1} \right] = \frac{1}{(1 + K_1)} \left(\frac{\partial \ln K_1}{\partial T} \right) \end{aligned} \quad (10)$$

Hence from eq 9 and 10:

$$\left(\frac{\partial x_B}{\partial T} \right)_p = \frac{K_1}{(1 + K_1)^2} \left(\frac{\partial \ln K_1}{\partial T} \right) \quad (11)$$

$$= \frac{K_1}{(1 + K_1)^2} \left(\frac{\Delta H_1}{RT^2} \right) \quad (12)$$

Since from thermodynamics:

$$-RT \ln K_1 = \Delta H_1 - T \Delta S_1 \quad (13)$$

and

$$\left(\frac{\partial \ln K_1}{\partial T} \right) = \frac{\Delta H_1}{RT^2} \quad (14)$$

Thus we can rewrite eq 7:

$$\begin{aligned} C_{p(\text{mix})} &= C_{pA}^\circ + \left(\frac{K_1}{1 + K_1} \right) \Delta C_{p1}^\circ \\ &\quad + R \left(\frac{\Delta H_1}{RT} \right)^2 \frac{K_1}{(1 + K_1)^2} \end{aligned} \quad (15)$$

When ΔC_{p1}° is small, only the last term in eq 15 can contribute to an abnormally large entropy for the mixture.

Let us consider this further. For values of K_1 which are very small or very large, i.e., 0.1 or 10, the equilibrium will be at one limit or the other, mostly A or mostly B, and the $C_{p(\text{mix})}$ will

be either C_{pA}° or C_{pB}° with a small contribution from the reaction. The term $K_1/(1 + K_1)^2$ is symmetrical with respect to values of K_1 and $1/K_1$ and has a maximum value of $1/4$ at $K_1 = 1$. It is a flat maximum about $K_1 = 1$ since for $K_1 = 1/4$ or $K_1 = 4$ it has the value 0.16, only a 33% reduction in value. Hence the reaction can only have a large contribution to $C_{p(\text{mix})}$ where $(\Delta H_1/RT)$ is large. It cannot be too large or K_1 will become too small (eq 13) unless we invoke very large values of ΔS_1 .

Table I shows some examples of this isomerization heat capacity contribution for different values of $\Delta H_1/RT$ and $\Delta S_1/R$. Values are also given for K_1 , shown in parentheses. We note that $C_{p(\text{isom})}$ does not exceed R until $(\Delta H/RT)$ exceeds 2. The values of $\Delta S/R$ and $\Delta H/RT$ selected for Table I have been chosen to span the range anticipated for liquids deviating markedly from normal in their Trouton constants.

Heat Capacity of Water

Eisenberg and Kauzmann⁹ have discussed the properties and structure of water and commented on the configurational heat capacity (here $C_{p(\text{isom})}$) in terms of structural changes. $C_{p(\text{H}_2\text{O})}(\text{l}) = 18.1$ eu and changes by less than 1% from 0 to 100 °C. They have calculated $C_{v(\text{H}_2\text{O})}(\text{l})$ over this range. It decreases nearly linearly from 18.1 eu at 0 °C to 16.3 eu at 100 °C. They also estimate the center of gravity contributions to C_v using frequencies derived from ice. This gives a value of 9 eu for these six modes at 0 °C increasing linearly to 10 eu at 100 °C. On this basis the maximum value of $C_{p(\text{isom})}$ would vary from 9.1 eu at 0 °C to 6.2 eu at 100 °C.

If we take the extreme position that the center of gravity modes in liquid water have their classical limit of $6R$ then we would estimate $C_{p(\text{isom})}$ as <6.2 eu at 0 °C and <4.4 eu at 100 °C. A conservative choice might be the mean values of 7.7 ± 1.6 eu at 0 °C and 5.5 ± 1.5 eu at 100 °C. Such a choice would allow for contributions to C_v from the mole fraction term in eq 7 (second term on the right-hand side) and eq 15. If we assume that the low-energy A form of water is ice-like in its properties while the high-energy B form is more classical in its properties, then ΔC_{p1}° could be 2.6 eu and the contribution of this term might vary from about 1 to 2 eu over the 0–100 °C range. However, it can have small negative as well as positive values and this raises somewhat the upper limits for $C_{p(\text{isom})}$.

For $C_{p(\text{isom})}^\circ = 7.7$ eu at 0 °C we can interpolate from the values shown in Table I that $H_1/RT \approx 4.1$ with $\Delta S_1/R = 3.5$. At 0 °C this leads to $\Delta H_1 = 2.2$ kcal/mol. At 100 °C, $C_{p(\text{isom})}^\circ = 5.5$ yields for the same choice of $\Delta S_1/R = 3.5$, the value $\Delta H_1/RT = 3.4$ for $\Delta H_1 = 2.5$ kcal/mol, in reasonable agreement. The uncertainties in $C_{p(\text{isom})}$ permit a 15% uncertainty in the choices of $\Delta H/RT$ and $\Delta S/R$.

Within this range the values $\Delta H_1/RT = 4.6$ at 0 °C (3.4 at 100 °C) together with $\Delta S_1/R = 3.4$ form a self-consistent set. They give $K_1 = 0.30$ at 0 °C and $C_{p(\text{isom})}^\circ = 7.6$ eu at 0 °C and $K_1 = 1.0$ at 100 °C with $C_{p(\text{isom})}^\circ = 5.6$ eu. The mole fractions are $x_A = 0.77$, $x_B = 0.23$ at 0 °C, and $x_A = x_B = 0.50$ at 100 °C. These also yield $\Delta H_1 = 2.5$ kcal/mol and $\Delta S_1 = 6.7$ eu.

For comparison the earlier values listed, $\Delta H_1/RT = 4.1$ at 0 °C and $\Delta S_1/R = 3.5$ give $K_1 = 0.54$ and $x_B = 0.36$ at 0 °C.

At 100 °C these yield $K_1 = 1.66$ and $x_B = 0.62$, $x_A = 0.25$ with $C_p^{\circ}(\text{isom}) = 4.2$ eu.

A final set which will turn out to be more compatible with the volume behavior of water is $\Delta H_1/RT = 4.0$, $\Delta S_1/R = 4.0$, and $K_1 = 1$ at 0 °C. This gives $\Delta C_p(\text{isom}) = 8.0$ eu and $x_B = 0.5$ at 0 °C. At 100 °C, $K_1 = 2.9$, $x_B = 0.75$, and $\Delta C_p(\text{isom}) = 3.2$ eu. This gives $\Delta H_1 = 2.2$ kcal and $\Delta S_1 = 8.0$ eu.

We note from the foregoing that as anticipated, $C_p^{\circ}(\text{isom})$ is very sensitive to $\Delta H_1/RT$ but much less to $\Delta S_1/R$. In consequence values of K and x have relatively large limits of uncertainty relative to $C_p^{\circ}(\text{isom})$.

Molar Volume of Water

The heat capacity anomaly in liquids requires a phenomenological two-component system in order to be resolved and this must affect all other properties as well. Thus the simplest, ideal model for the volume of such an isomerizing liquid can be written in terms of the A and B components as

$$V_L = x_A V_A + x_B V_B \quad (16)$$

$$= x_A [V_A^{\circ} + (T - T_0)\alpha_A V_A^{\circ}] + x_B [V_B^{\circ} + (T - T_0)\alpha_B V_B^{\circ}] \quad (17)$$

where V_A , V_B , V_A° , and V_B° are the molar volumes of A and B and the superscripts refer to some reference temperature T_0 . α_A and α_B are the coefficients of expansion of the two components and are assumed to be constant. In addition we assume that A and B mix with no significant volume changes. In terms of $x_B = (1 - x_A)$:

$$V_L = V_A^{\circ} + x_B \Delta V^{\circ} + (T - T_0) \{ \alpha_A V_A^{\circ} + x_B (\alpha_B V_B^{\circ} - \alpha_A V_A^{\circ}) \} \quad (18)$$

The coefficient of expansion of $\alpha_L^{\circ} \equiv V_L^{\circ-1}(\partial V_L/\partial T)_p$ is given by

$$\alpha_L^{\circ} = \frac{\Delta V^{\circ}}{V_L^{\circ}} \left(\frac{\partial x_B}{\partial T} \right) + \left\{ 1 + x_B \left(\frac{\alpha_B V_B^{\circ}}{\alpha_A V_A^{\circ}} - 1 \right) \right\} \frac{\alpha_A V_A^{\circ}}{V_L^{\circ}} + (T - T_0) \left(\frac{\alpha_B V_B^{\circ} - \alpha_A V_A^{\circ}}{V_L^{\circ}} \right) \left(\frac{\partial x_B}{\partial T} \right) \quad (19)$$

In order for α_L° to be zero at the reference temperature which we shall choose at 4 °C (T_0) we require

$$\left(\frac{\partial x_B}{\partial T} \right)_0 = - \left\{ 1 + x_B \left(\frac{\alpha_B V_B^{\circ}}{\alpha_A V_A^{\circ}} - 1 \right) \right\} \frac{\alpha_A V_A^{\circ}}{\Delta V^{\circ}} \quad (20)$$

$(\partial x_B/\partial T)_0$ is given by eq 12 and using the thermodynamic parameters described earlier is in the range 2.9×10^{-3} to 3.7×10^{-3} .

Taking ΔV° negative we see that any of a large set of values for the remaining parameters will fit eq 20. These can be arbitrarily reduced by using some known values for ice for the A species.

From eq 18, neglecting the small term containing α , we can obtain a relation between ΔV° and V_A° using the known value of $V_L = 18.0$ cm³/mol at 0 °C and our estimated value of x_B .

$$\Delta V^{\circ} \approx (V_L - V_A^{\circ})/x_B \quad (21)$$

This equation places more severe restraints on the possible values of x_B than the C_p considerations. If, for example, we choose $V_A^{\circ} = 19.6$ cm³/mol, the value for ice we find $\Delta V^{\circ} = (1.6/x_B)$ cm³/mol. For the several choices of values of K_1 considered earlier the self-consistent set will yield values of $\Delta V^{\circ} = -7.0$ cm³/mol which would require a molar volume for liquid-like H₂O of 12.6 cm³/mol, which seems unreasonably low. A value of $K_1 = 1$ at 0 °C ($x_B = 0.50$) gives the most reasonable value of $\Delta V^{\circ} = -3.2$ cm³/mol. This gives $V_B^{\circ} = 16.4$ cm³/mol and on substituting in eq 20 allows us to calcu-

Table II. Some Calculated and Observed Values for the Coefficient of Expansion of Liquid Water

temp, °C	K_1	x_1	$10^4 \alpha_L$, °C ⁻¹ , calcd (eq 19)	$10^4 \alpha_L$, °C ⁻¹ , obsd (ref 10)
100	2.92	0.75	7.4	7.5
50	1.86	0.65	4.7	4.6
4	1.06	0.53	0	0
0	1.00	0.50	-0.2	-0.68
-10	0.86	0.46	-1.4	-2.9
-20	0.73	0.42	-2.7	-6.8

late $\alpha_B = 1.23 \times 10^{-3}$, a very reasonable value for a normal liquid.

A severe test of these parameters and the model is to calculate α_L° for water over the known range. Some values are shown in Table II.

The agreement is surprisingly good from the minimum at 4 °C to 100 °C. It should be commented that the parameters of eq 19 have been totally fixed by the volumes of ice and water at 0 °C and the heat capacity data. Thus the agreement in the values of α_L at 50 and 100 °C is striking. The model fails to reproduce the values of α below 4 °C but the deviations are only large in the supercooled region and it is not clear that "equilibrium" values are observed. However, even here the small discrepancies could be reduced or eliminated by choosing a more realistic coefficient of thermal expansion for water which increases slightly with temperature rather than remaining constant.

Compressibility of Water

The compressibility of water changes slightly from about 51×10^{-6} bar⁻¹ at 0 °C to 48×10^{-6} bar⁻¹ at 100 °C with a very shallow minimum of about 45×10^{-6} at 45 °C. Kauzmann¹⁵ has interpreted this minimum as being incompatible with a simple two-fluid model for liquid water such as the one considered here. The equation for β_{mix} , the compressibility of water obtained by differentiating eq 16, is given by

$$\beta_L \equiv - \frac{1}{V_L} \left(\frac{\partial V_L}{\partial p} \right)_T = x_A \frac{V_A}{V_L} \beta_A + x_B \frac{V_B}{V_L} \beta_B - \frac{\Delta V_1}{V_L} \left(\frac{\partial \beta}{\partial p} \right)_T \quad (22)$$

But since

$$\left(\frac{\partial x_B}{\partial p} \right)_T = \frac{K}{(1+K)^2} \left(\frac{\partial \ln K}{\partial p} \right) = - \left(\frac{\Delta V_1}{RT} \right) \frac{K}{(1+K)^2} \quad (23)$$

So that

$$\beta_L = \frac{x_A V_A \beta_A}{V_L} + \frac{x_B V_B \beta_B}{V_L} + \frac{(\Delta V_1)^2 K}{V_L R T (1+K)^2} \quad (24)$$

Kauzmann's observation was to the effect that the last term in eq 24 was always positive so that it was difficult to account for a minimum in β_L with increasing temperature if the compressibility of liquid "water" (β_B) were assumed to be greater than β_A if the latter were assigned the small value associated with ice. This reasoning is quite correct. In such a case if β_B is set equal to 80×10^{-6} bar⁻¹ to fit β_L at 0 °C then it leads to a value of β_L about 30% too high at 100 °C. If, however, we choose to suppose that the "ice-like" liquid differs from bulk ice solid in having a higher compressibility and set $\beta_A = 44$ and $\beta_B = 50 \times 10^{-6}$ at 0 °C then we find that β_L decreases slightly from 51 at 0 °C to 47 at 100 °C with a weak minimum near 40 °C. By assigning a small positive temperature coefficient

similar to that for normal liquids the minimum can be enhanced. Because ΔV and the choices of α are also open to variation there seems to be no difficulty in choosing mutually reasonable values which will fit all of the data considered here. In particular a choice of $\Delta V^\circ = 4.0 \text{ cm}^3$, $V_A^\circ = 20.0 \text{ cm}^3$, and $V_B^\circ = 16.0 \text{ cm}^3$ with slightly larger values for α_A and smaller values for α_B will give much improved fits in the supercooled region.

Discussion

The structure of water and models of multicomponent systems to represent the properties of water have been proposed by many authors.^{9,11} In most of these models relatively little attention has been given to the heat capacities and consequently most of these models have not reproduced C_p very well, this despite the fact that they have generally used more complex structures than that suggested here. All of the ones that have fitted either the thermodynamic properties or the molar volumes have arrived at ΔH_1 and ΔV_1 values similar to those used here.¹² The present results are of interest in that they suggest that the heat capacity data alone are sufficient to require a minimum two-component system to represent this property of water. The detailed molecular structure that satisfies these requirements is of course outside the scope of the present approach.¹³ It is of interest to note, however, that the differences in energy between an ice-like, tetrahedral structure of specific hydrogen bonds and a structure of dipole-linked chains with coordination of about 6 is comparable to the ΔH_1 values we have considered here.¹⁴

References and Notes

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- (3) R. Shaw, *J. Chem. Eng. Data*, **14**, 461 (1969).
- (4) S. W. Benson, "Thermochemical Kinetics", 2nd ed, Wiley, New York, N.Y., 1976. D. W. Scott, *J. Chem. Phys.*, **60**, 3144 (1974), has made a very sophisticated correlation of the thermodynamic properties of hydrocarbons from which C_p for the gases can also be estimated to good accuracy (± 0.1 eu).
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- (7) If the asymmetry of the molecule is great and the barrier to rotation of the order of $(2-5)RT$ then the individual rotational motions may resemble hindered rotations in molecules with an extreme contribution to C_p of 2.3 eu each.
- (8) K. S. Pitzer et al., *Ind. Eng. Chem.*, **50**, 265 (1958), and earlier work.
- (9) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water", Oxford University Press, London, 1969, pp 171-175.
- (10) G. S. Kell, *J. Chem. Eng. Data*, **12**, 67 (1967).
- (11) A recent bibliography with 2000 references is given by D. T. Hawkins, *J. Solution Chem.*, **4**, 625 (1975).
- (12) See summary of models in ref 9, p 258.
- (13) A recent example of such efforts is given by J. C. Owlicki and H. A. Scheraga, *J. Am. Chem. Soc.*, **99**, 7403 (1977).
- (14) See discussion in ref 9, p 39. In a hypothetical chain-like structure, a near neighbor distance of about 2.8 Å between H_2O molecules in the chains and a mean interchain distance of about 3.1 Å would have the molar volume V_B° of water species B if the chains had an average of four nearest-neighbor chains. Six neighboring chains could relax the interchain distance to 3.3 Å.
- (15) W. Kauzmann, *Colloq. Int. CNRS*, **246**, 63 (1976). I am much indebted to Professor Kauzmann for bringing this paper to my attention in the course of reviewing my work. He has made an analysis of the physical properties of water very similar to the one presented here.

Vibrational Circular Dichroism in Amino Acids and Peptides. 2. Simple Alanyl Peptides

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Abstract: Vibrational circular dichroism (VCD) as well as Raman and infrared absorption spectra of alanine, alanylalanine, alanylalanylalanine, glycyllalanine, and alanylglycine are reported in the 2800-3100-cm⁻¹ region. Vibrational assignment of the carbon-hydrogen stretching modes of alanine is presented and an interpretation of the observed VCD spectrum is proposed. The arguments employed for the interpretation of alanine are subsequently utilized, along with considerations concerning subtle changes in chemical environment, to propose an interpretation of the VCD features of the alanyl peptides.

I. Introduction

The structure and conformation of amino acids, oligopeptides, polypeptides, and proteins have been studied extensively by spectroscopic methods owing to their direct relevance to the understanding of biochemical processes on a molecular level. Of these methods, X-ray diffraction of single crystals has provided the most accurate and detailed information. However, X-ray crystallographic methods are not applicable to solution phase samples where biological molecules may adopt altered conformations or undergo critical conformational changes while executing biological activity. Currently the most sensitive spectroscopic probes of solution phase conformation in proteins and related molecules are electronic optical activity, nuclear magnetic resonance, infrared absorption, and Raman scattering. Very often the results of several of these techniques must be combined to gain desired conformational inferences,

since no individual method is significantly superior to the others, or is so conclusive that supporting results are not helpful.

In view of this situation, we have undertaken the application of the newly developed technique of vibrational circular dichroism^{1a,b} (VCD) to the study of protein-related molecules. The overall aim of this work is to provide a new spectroscopic method of investigation which will combine the conformational and configurational sensitivity of electronic optical activity with the rich structural content of vibrational spectroscopy. In the present study of alanine and some of its simple oligopeptides we are investigating the VCD of a small group of closely related molecules in order to amplify some of the basic features of this new technique and to demonstrate the feasibility of further studies.

In a recent communication,² we reported the first observation of VCD of an amino acid, alanine, in the carbon-hydrogen