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Combination from Liquid Water

by

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Submitted to Chemical Physics

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ISOSBESTIC POINT AND TEMPERATURE DEPENDENCE
OF THE $\nu_2+\nu_L$ RAMAN COMBINATION FROM LIQUID WATER

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ABSTRACT

A new component has been found near ≈ 2050 cm^{-1} in the Raman spectrum of liquid water. This component refers to the two-phonon combination $\nu_2 + \nu_L$ (where 2 refers to intramolecular bending, and L to libration), but the ν_2 and ν_L fundamentals involved in this two-phonon component arise from H$_2$O molecules hydrogen-bonded to 3, rather than to 4, nearest neighbors. The ν_2 bending fundamental from 3-bonded H$_2$O molecules was also uncovered. The new Raman data are in excellent agreement with published infrared data and theoretical calculations.

A-1

INTRODUCTION

A weak, broad vibrational band from liquid water whose peak occurs near 2100 cm^{-1} was previously examined by Raman [1] and infrared [2] spectroscopy. This band is structured and displays a high-frequency shoulder near 2300 cm^{-1}. It has generally been assigned as a two-phonon sum band, $\nu_2 + \nu_L$, where ν_2 refers to the intramolecular $\nu_2 A_1$ bending fundamental at 1650 cm^{-1}, and ν_L refers to one, or more, of the three intermolecular librations of water [3].

The previous infrared study involved temperatures from 5° to 75°C, [1] but the Raman investigation was conducted at room temperature. [2] Hence, it was desirable to extend the Raman work to include a similar range of temperatures, 3° to 95°C. However, other recent Raman investigations of water [4,5] involved absolute intensity measurements, and thus such absolute measurements were also carried out here. In addition, Raman measurements were performed for the depolarized and polarized geometries, X(ZX)Y and X(ZZ)Y, respectively.

The results of the new Raman investigations follow.

EXPERIMENTAL PROCEDURES

Procedures employed to obtain absolute Raman intensities were described in Refs. [4,5]. The same procedures, which involved the use of Newton's rings for cell alignment, were employed here with the J. Y. HG2S double monochromator. However, a new Raman cell was used with a much more rigorous method of water purification.

The new three-window Raman cell was constructed of brass, instead of stainless-steel [4,5]. The interior surfaces were sand-blasted and then blackened by oxidation. This procedure virtually eliminated the possibility of optical reflections from the cell walls. The in-line windows of this new cell were also placed farther apart (18 cm), which moved the blaze of the laser beam far from the vicinity of the 90-degree viewing window.

The more rigorous water purification involved distilling the water (already highly purified) directly into the Raman cell. The water was purified by two methods prior to distillation into the cell: (1) triple-distillation in an all-quartz still, and (2) passage under pressure through three columns; the first containing activated carbon, the second de-ionizing materials, and the third 0.5 μm millipore filters. The second method was

found to be preferable for removing dust.

Distillation into the Raman cell was accomplished using an all-glass entrapment line 1 meter in length. This line sloped upward at 45 degrees to the Raman cell and contained two steam traps in series. The traps and the upward slope effectively removed dust from the water. However, precautions also had to be taken to prevent dust-laden air from leaking into the Raman cell. (The Raman cell and all of its parts were washed in detergent solution and then boiled in triple-distilled water for 3 days prior to use. This procedure prevented fluorescence by removing plasticizers from the "O" rings.)

The quality of the water in the Raman cell was tested by viewing the focussed laser beam in the filled cell through the 90-degree window. After 15 consecutive distillations into the cell, one dust particle was observed to fall through a 2-cm length of the horizontal laser beam in 5 minutes. Under these conditions the green 514.5 nm Rayleigh light plus the red Raman light from the OH-stretching vibration were visually superimposed on the cell background, which was black.

A duPont 310 Curve Resolver (a special purpose analog computer) was employed for Gaussian analysis of the structured 2100 cm^{-1} contour.

RESULTS

Raman spectra corresponding to depolarized X(ZX)Y and polarized X(ZZ)Y orientations are shown for the $1000 < \bar{\Delta v} < 2600$ cm^{-1} region in Figs. 1 and 2, respectively. Each figure contains two spectra, obtained at 3° and 95°C, which are comparable in terms of absolute intensities.

The following effects are evident from examination of the figures: (1) the X(ZX)Y and X(ZZ)Y spectra cross at 2060 cm^{-1} and at 2025 cm^{-1}, respectively, in the $v_2 + v_L$ combination region, (2) the $v_2 + v_L$ peak frequencies and total contour intensities decrease with increasing temperature, (3) the v_2 bending intensity at 1650 cm^{-1} increases with temperature rise for the depolarized X(ZX)Y case, whereas just the opposite temperature dependence, i.e., a decrease in intensity, is evident for the polarized X(ZZ)Y case, and (4) the Raman intensity at 1300 cm^{-1} decreases (for both polarizations) with increase of temperature, and is larger, relative to the 1650 cm^{-1} intensity, in the X(ZZ)Y spectrum, thus indicating polarization.

The crossings evident in Figs. 1 and 2 at 3° and 95°C are shown in more detail in Figs. 3 and 4, where all of the $v_2 + v_L$ spectra of the 3°-95°C series are shown.

From examination of Figs. 3 and 4 it is evident that the crossings of Figs. 1 and 2 are part of a more general phenomenon, namely, exact isosbestic points at 2060 cm^{-1} and 2025 cm^{-1} for the X(ZX)Y and X(ZZ)Y geometries. Other exact isosbestic points were reported recently for the OH-stretching region [4,5].

Peak frequencies obtained from the X(ZX)Y and X(ZZ)Y spectra of Figs. 3 and 4 for the $\nu_2+\nu_L$ contour are plotted versus temperature in Fig. 5. These data are adequately represented by a linear least squares equation, and the peak frequency is seen to decrease with increasing temperature according to: $\bar{\Delta\nu}(cm^{-1})$ = -0.87 t(°C) + 2141. Draegert et al. also observed a decrease in the $\nu_2+\nu_L$ peak frequency in the infrared spectrum with rising temperature [2]. They reported a slope, $\Delta\nu/\Delta T$, of -0.9 $\pm$ 0.14 cm^{-1}/°C, in excellent agreement with the present slope of -0.87 cm^{-1}/°C.

The $\nu_2+\nu_L$ Raman contours corresponding to the X(ZX)Y and X(ZZ)Y orientation were next decomposed by means of the duPont 310 analog computer using Gaussian components. Three Gaussian components were required to obtain acceptable fits, whereas unacceptably large residuals of 10-20% resulted when only two components were used. The peak frequencies employed for the three components were: (1) 2050 $\pm$ 10 cm^{-1}, (2) 2150 $\pm$ 5-10 cm^{-1}, and (3) 2300 $\pm$ 25 cm^{-1}. The component half-widths for the X(ZX)Y case were, respectively, 200 cm^{-1}, 250 cm^{-1} and 250 cm^{-1}. All half-widths for the X(ZZ)Y case were 200 cm^{-1}. A typical decomposition is shown in Fig. 6.

The sum of the integrated intensities of components 2 and 3, I_2+I_3, was divided by the integrated intensity of component 1, I_1, and the ratio $(I_2+I_3)/I_1$ was plotted logarithmically versus T^{-1}. The results for the two polarizations are shown in Fig. 7.

The data of Fig. 7 were treated by linear least squares (heavy lines), i.e., $\ln[(I_2+I_3)/I_1]$ = $-(\Delta H°/RT)$ + constant. The X(ZX)Y and X(ZZ)Y data yielded slopes corresponding to $\Delta H°$ values of -2.4_8 and -2.4_7 kcal/mol OHO, respectively.

The error bars shown in Fig. 7 refer to analog decompositions involving both linear and curved (upwardly concave) baselines. The use of an upwardly concave baseline, as opposed to a straight baseline, however, only produced a general vertical displacement of the data, but no significant change in slope. Hence, no change in the $\Delta H°$ values resulted from the two types of baselines employed, and the error bars shown do not represent the

errors in the slopes. A value of -2.5 ± 0.1 kcal/mol OHO was obtained from analysis of the individual data sets, and is considered to represent the data of Fig. 7 adequately. This value is in excellent agreement with enthalpy values presented recently, see Table II of Ref. (5).

INTERPRETATION

A. Spectral Effects.

The isosbestic points observed in the X(ZX)Y and X(ZZ)Y spectra indicate that the $\nu_2 + \nu_L$ contour contains sub-structure involving HB and NHB components [4,5]. The decrease in the peak frequency with temperature rise is also indicative of an increase in the intensity of the 2050 cm^{-1} NHB Gaussian component (as revealed by computer analysis), relative to the sum of the 2150 and 2300 cm^{-1} HB components. The concomitant decrease in the total contour intensity with temperature rise is similar to that seen previously for the OH-stretching contour [5,6] and occurs when an HB component is replaced by an NHB component having a smaller molar intensity. Because the total contour intensity is a linear combination of the HB and NHB component intensities involved, a plot of the total contour intensity is not very informative and was not shown here, although such data were available.

The opposite temperature dependences of the X(ZX)Y and X(ZZ)Y spectra at 1650 cm^{-1} is a new effect. Here, the polarized HB bending component is unresolved from the more highly depolarized NHB bending component. Previously published computer analysis indicated that the component peak frequencies, that is, the peak frequencies of the two bending components, differ by only ≈ 15 cm^{-1} [1]. However, the opposite temperature dependences now observed provide much more compelling evidence for two bending components than the previous Gaussian decomposition of

spectra corresponding to a single temperature.

The mechanism which gives rise to two spectral classes of components, HB and NHB, is discussed next.

B Mechanistic Considerations.

Consider that an H_2O molecule is tetrahedrally surrounded by four nearest-neighbor H_2O molecules to which it has formed four equal (in length, angle, etc.) hydrogen bonds, one for each of its two protons, and one for each of its two lone electron pairs. Under these circumstances the point group symmetry of the central H_2O molecule is C_{2v} and its $\nu_2 A_1$ bending vibration is strongly polarized, Figs. (1) and (2), and Ref. [7]. However, the point group symmetry must decrease when one of the four hydrogen bonds is broken (e.g., severely bent and/or stretched), Refs [5,8]. (Further, a broken hydrogen bond which involves one of the protons of the central H_2O molecule is more important, for the present discussion, than the hydrogen bonds formed by the lone pair electrons, because that breakage decouples the OH stretches of the central H_2O molecule and lowers the symmetry to C_s.) The ν_2 vibration for a C_s H_2O molecule must still be polarized, of course, but now the ν_2 depolarization ratio for the C_s molecule can be different from the ν_2 depolarization ratio for the C_{2v} molecule. For example, ρ can increase, provided that it remains less than 3/4. (The depolarization ratio, ρ, is equal to $I[X(ZX)Y] / I[X(ZZ)Y]$.) Hence, hydrogen bond rupture is clearly capsable of producing two unresolved ν_2 vibrations whose properties, i.e., depolarization ratios, peak frequencies, and half-widths, are different [1].

When separate 4-bonded and 3-bonded structures exist in liquid water, it is obvious that the polarized $\nu_2 A_1$ HB bend will only couple strongly with its corresponding 4-bonded HB librations, or which there are three. The more highly depolarized (but still polarized) $\nu_2 A'$ bend (the prime refers to the plane of the C_s H_2O molecule) will only couple strongly with its 3-bonded librations, again 3 in terms of degrees of freedom. (These librational bands may be unresolved.) Hence the two couplings described provide the mechanism for producing pure HB and pure NHB two-phonon combination or sum bands. Stated alternatively, one would expect to see two classes of librations, with three broad components for each class, two classes of intramolecular bends, and two classes of two-phonon combination tones, with one class referring to HB or 4-bonded interactions, and the other class to NHB, i.e., 3-bonded (or fewer), interactions. Furthermore, one would also expect to find opposite temperature dependences of the intensities of these two classes.

An important mechanism leading to the formation of 4-bonded and 3-bonded structures in liquid water has recently been proposed by Giguère and Pigeon-Gosselin [8]. In the Giguère model, an H_2O molecule is surrounded tetrahedrally by four H_2O molecules to which it is fully hydrogen bonded by linear hydrogen bonds. A partial rotation of the central H_2O molecule then occurs such that a bifurcated structure results between one proton of the central H_2O molecule and two oxygen atoms of the neighboring H_2O molecules. The O-H-O angle deviates markedly

from 180° for the hydrogen bond in the bifurcated structure. The
other proton is unaffected and remains hydrogen bonded. (The two
hydrogen bonds involving the two lone electron pairs of the
central oxygen atom could also be bent. But the strain from this
bending could be relieved, e.g., by change in the sp^3
hybridization.) The bifurcated structure is considered to
correspond to a shallow potential minimum between two adjoining
deeper minima, and it is thought to result in equal $HO_{(2)}$ and
$HO_{(3)}$ distances in the $O_{(1)}-H \cdot\substack{\cdot O_{(2)} \\ \cdot O_{(3)}}$ structure. The $HO_{(2)} = HO_{(3)}$
distance of this structure is 2.4A, and this value agrees exactly
with the HO distance inferred by Walrafen et al. [5], who
estimated NHB O-H O distances and angles for liquid water from
vibrations of vicinal surface silanol groups [5]. The O-H···O
angle in the bifurcated structure may be as small as 150° [5],
which is equivalent to producing a 3-bonded structure because
such a small angle is equivalent to breaking the hydrogen bond.

The relevance of the Giguère model to the present data is
obvious. A rotation giving rise to a bifurcated structure, with
its corresponding potential minimum, would lead to a libration in
which one proton of the central H_2O molecule would be in an
entirely new and greatly weakened force field. Only three
hydrogen bonds would restrain the rotation, as opposed to the
original four. Hence, a lowering of all three librational
frequencies would be expected. The model is also very relevant
to the restricted translations of liquid water, i.e., to O-O
stretching of hydrogen-bonded O-H O units.

The partial covalency of, r large transfer within, linear

hydrogen bonds, decreases when the O-H···O angle decreases below 180° [5]. Therefore, oscillations of the H atom about the equilibrium $HO_{(2)}$ = $HO_{(3)}$ distance of the bifurcated structure would preclude the type of Raman scattering produced by the partially covalent harmonic force field of linear O-H···O units.

C. Anharmonicity, and Estimation of the 3-Bonded Librational Frequency.

A weak Raman band is evident in Figs. (1) and (2) near 1300 cm^{-1}, see also Ref. (1). The qualitative polarization of this band requires that it be reassigned (1) to the overtone of the 720-740 cm^{-1} HB libration. (The 720-740 cm^{-1} feature refers to the out-of-plane libration of B_1 symmetry. Note that B_1 x B_1 = A_1, which requires the overtone to be polarized. The libration around the C_2 axis, A_2, occurs at 425-450 cm^{-1}. The in-plane libration occurs at 550 cm^{-1} and its species is B_2 [9].) The overtone assignment of the 1300 cm^{-1} band corresponds to an anharmonicity of about 12%, which is shown to agree with the anharmonicity of the fundamental 3-bonded libration.

The Gaussian component at 2150 cm^{-1}, component (2), adjoins component (1) at 2050 cm^{-1}. Component (2) almost certainly corresponds to the sum of the two HB fundamentals, the $v_2 A_1$ bend at 1650 cm^{-1}, and the B_2 libration at 550 cm^{-1}. The anharmonicity for this intramolecular-intermolecular sum combination is 2.3%. The value of 2.3% is then assumed to apply to component (1) at 2050 cm^{-1}, because of its nearness to component (2). On the basis of this assumption, component (1) must correspond to the sum of the observed frequency, 1650 cm^{-1}, plus the calculated frequency, 447 cm^{-1}. But the difference between the observed frequencies of 2050 cm^{-1} and 1650 cm^{-1} is only 400 cm^{-1}. Hence, the 3-librational anharmonicity is 12%, in agreement with the overtone value.

Next consider that component (3), the $\nu_2+\nu_L$ HB component at 2300 cm^{-1} arises from the sum of the 1650 cm^{-1} $\nu_2 A_1$ and 720-740 cm^{-1} B$_2$ fundamentals. Here, the anharmonicity is $\sim$ 3.5%. However, the difference between 2300 cm^{-1} and 1650 cm^{-1} is 650 cm^{-1}, whereas the observed librational value is $\sim$ 730 cm^{-1}, thus corresponding to 12% anharmonicity.

Finally, a similar calculation for the 2150 cm^{-1} HB component assuming that it is the sum of the 1650 cm^{-1} and 550 cm^{-1} fundamentals yields an anharmonicity of 10% for the in-plane B$_2$ libration.

The most important conclusion of the preceding considerations is that a frequency value of $\sim$ 450 cm^{-1} results for the 3-bonded libration. This frequency agrees with the theoretical value of 450 cm^{-1} obtained by Curnutte and Williams [10]. Moreover, the 450 cm^{-1} 3-bonded libration almost certainly refers to the in-plane B$_2$ motion of an H$_2$O molecule restrained by a hydrogen bond to one of its protons, and by two hydrogen bonds to its two lone electron pairs.

ADDENDUM

Absolute Raman intensity measurements were conducted in the frequency region of $\sim$ 3725-6000 cm^{-1}, _i.e._, at the high-frequency foot of the intense OH-stretching region and above. A weak, broad Raman contour was observed whose maximum intensity occurs near 4000 $\pm$ 10 cm^{-1} at 3°C, _cf._, Ref. [1]. This intensity maximum is preceded by a minimum, or at least a region of sharp upward concavity near 3900 cm^{-1}. High-frequency asymmetry is also present extending at least to 4600 cm^{-1}.

When the temperature of the water is increased to 93°C, a filling-in of Raman intensity occurs near 3910-3930 cm^{-1}. This effect causes the contour to appear to be broadened, and this filling-in was confirmed by Raman difference spectra. An upward frequency shift of about 50 cm^{-1} is also present in the contour maximum.

The 4000 cm^{-1} contour was previously decomposed into two Gaussian components at 3990 $\pm$ 25 cm^{-1} and at 4170 $\pm$ 50 cm^{-1} (1). The 3990 cm^{-1} component was assigned to the combination $v_1 + v_L$ (B_2), _i.e._, to 3450 + 550 cm^{-1}, and the 4170 cm^{-1} component was assigned to $v_1 + v_L$ (B_1) or 3450 + 730 cm^{-1} (1). Both assignments involved HB components.

The filling-in near 3910-3930 cm^{-1} observed from difference spectra, indicates that a high-temperature component may exist whose frequency is about 70 cm^{-1} less than that of the Gaussian (peak) component at 3990 cm^{-1}. This component, however, cannot be assigned to the sum of the 3450 cm^{-1} HB component and the 450 cm^{-1} NHB librational component because such an assignment would not allow for anharmonicity. However, an assignment involving only NHB components is reasonable, _e.g._, 3620 + 450 cm^{-1}, where the 3620 cm^{-1} component refers to NHB OH-stretching (dangling OH group) (3), and the value of 450 cm^{-1} refers to the 3-bonded or NHB libration of B_2 type.

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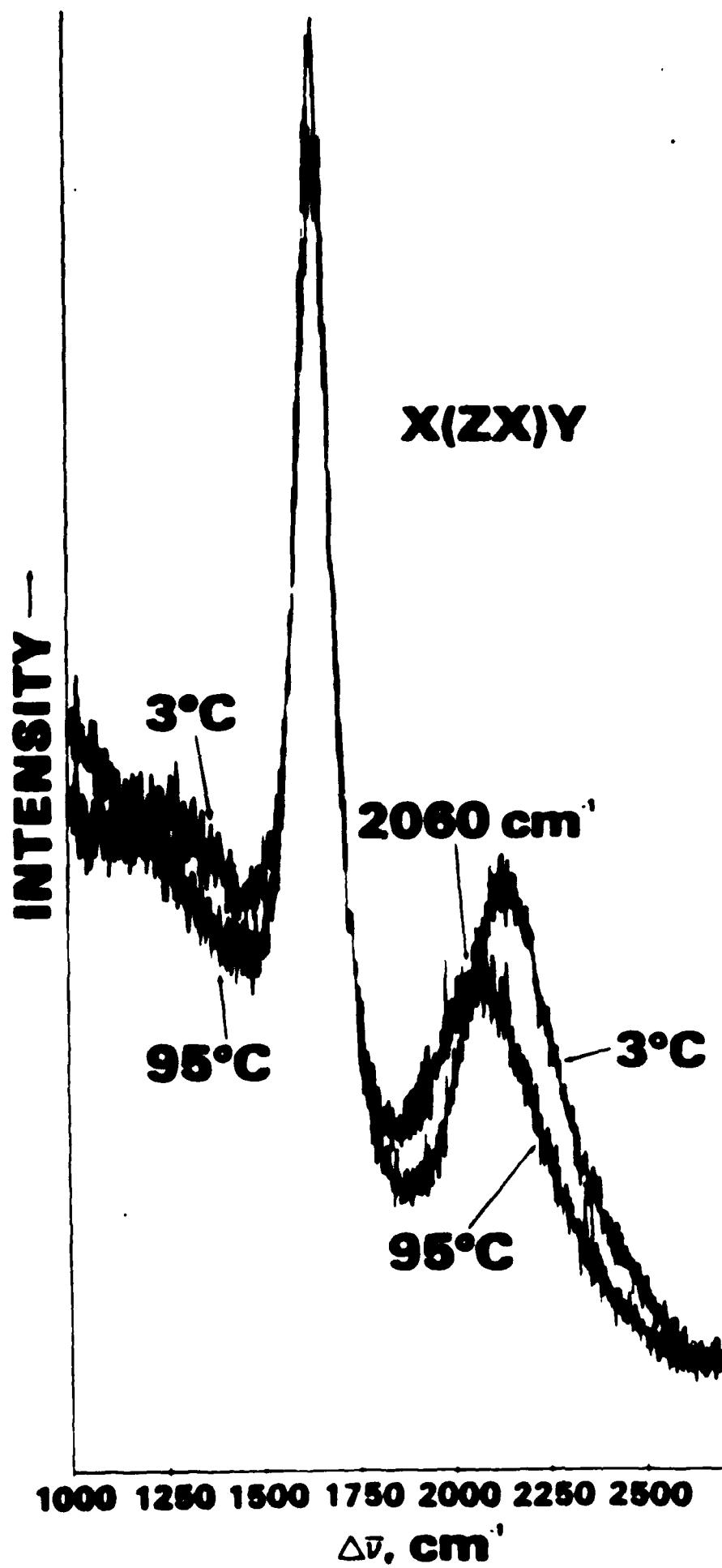
ACKNOWLEDGMENTS

Fig. 1. Absolute Raman spectra, depolarized, X(ZX)Y orientation, for liquid water in the region from 1000 cm^{-1} to 2500 cm^{-1} at 3° and 95°C. The intense bending peak has a larger amplitude at 95°C than at 3°C, see the upper of the two superimposed peaks at 1650 cm^{-1}. Also the 95°C spectrum crosses the 3°C spectrum at 2060 cm^{-1} (and near 1175 cm^{-1}). A filling-in of the minimum near 1850 cm^{-1} thus results with rising temperature.

Fig. 4.

Fig. 2. Absolute Raman spectra, polarized, X(ZZ)Y orientation, for liquid water in the region from 1000 cm^{-1} to 2500 cm^{-1} at 3° and $95^{\circ}C$. A crossing occurs at 2025 cm^{-1} (and also near 1900 cm^{-1}, see Fig. 1). Note that the bending peak at 1650 cm^{-1} is weaker at $95^{\circ}C$ than at $3^{\circ}C$ for this orientation, whereas just the opposite effect occurs for the X(ZX)Y orientation, Fig. 1.
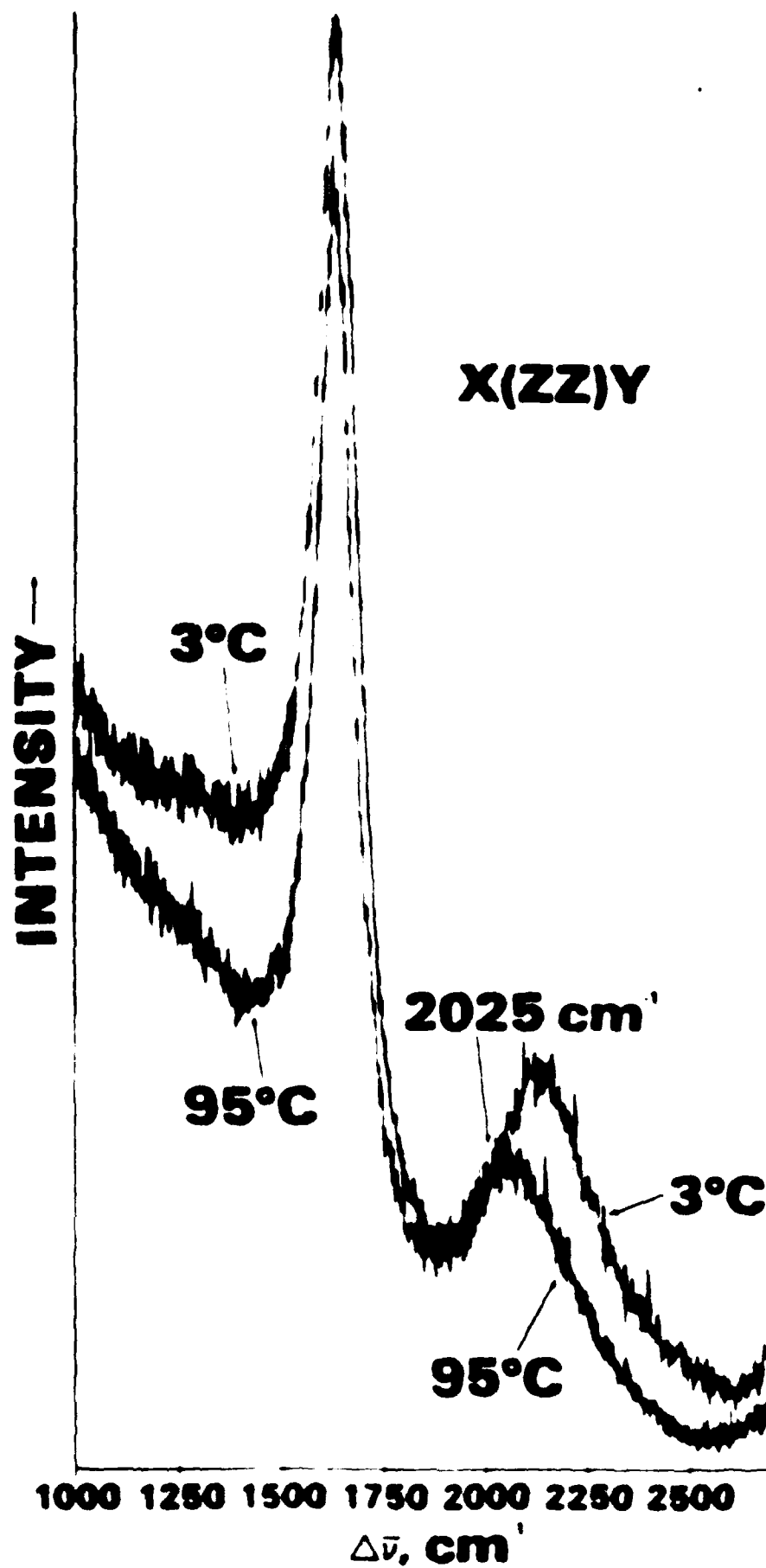
Fig. 2

Fig. 3. Absolute Raman spectra, depolarized, X(ZX)Y orientation, for liquid water in the region from 1800 cm^{-1} to 2600 cm^{-1} for five temperatures from 3° to 95°C. Note the isosbestic point at 2060 cm^{-1}.

Fig. 3.

X(ZX)Y

3°
26°
49°
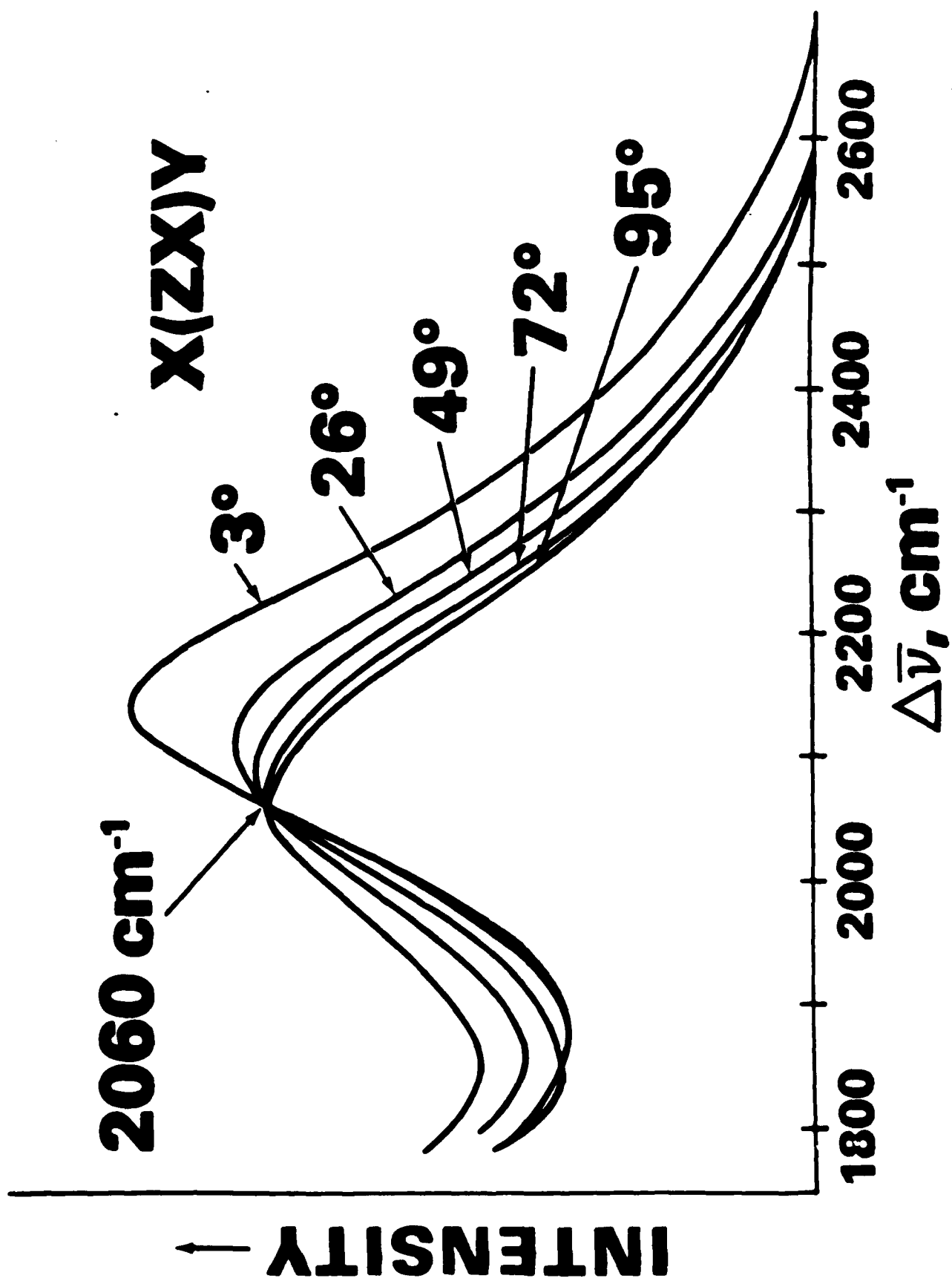72°
95°

2060 cm⁻¹

INTENSITY

Δν̄, cm⁻¹

1800 2000 2200 2400 2600

Fig. 4. Absolute Raman spectra, polarized, X(ZZ)Y orientation, for liquid water in the region from 1800 cm^{-1} to 2600 cm^{-1} for five temperatures from $3°$ to $95°C$. An isosbestic point occurs at 2025 cm^{-1} which is 45 cm^{-1} below the X(ZX)Y isosbestic point, Fig. 3. A subsidiary point also occurs near 1900 cm^{-1}.
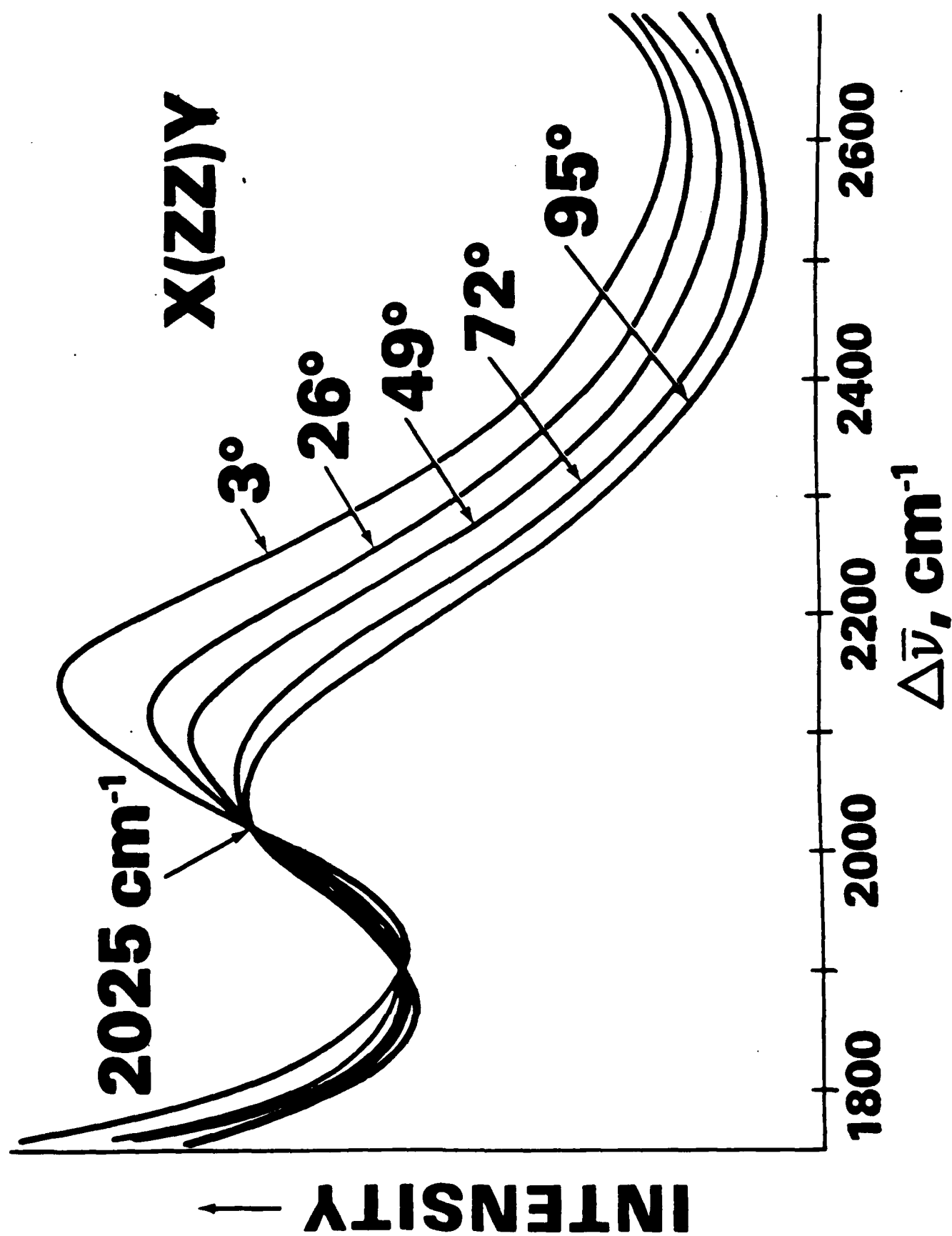
Fig. 4.

Fig. 5. Shift in the position of the peak of the two-phonon, bending plus librational Raman contour from liquid water as a function of temperature from 3° to 95°C. Least square equation shown on the figure. Diamonds, X(ZX)Y, and circles, X(ZZ)Y, orientations.

Fig. 5.
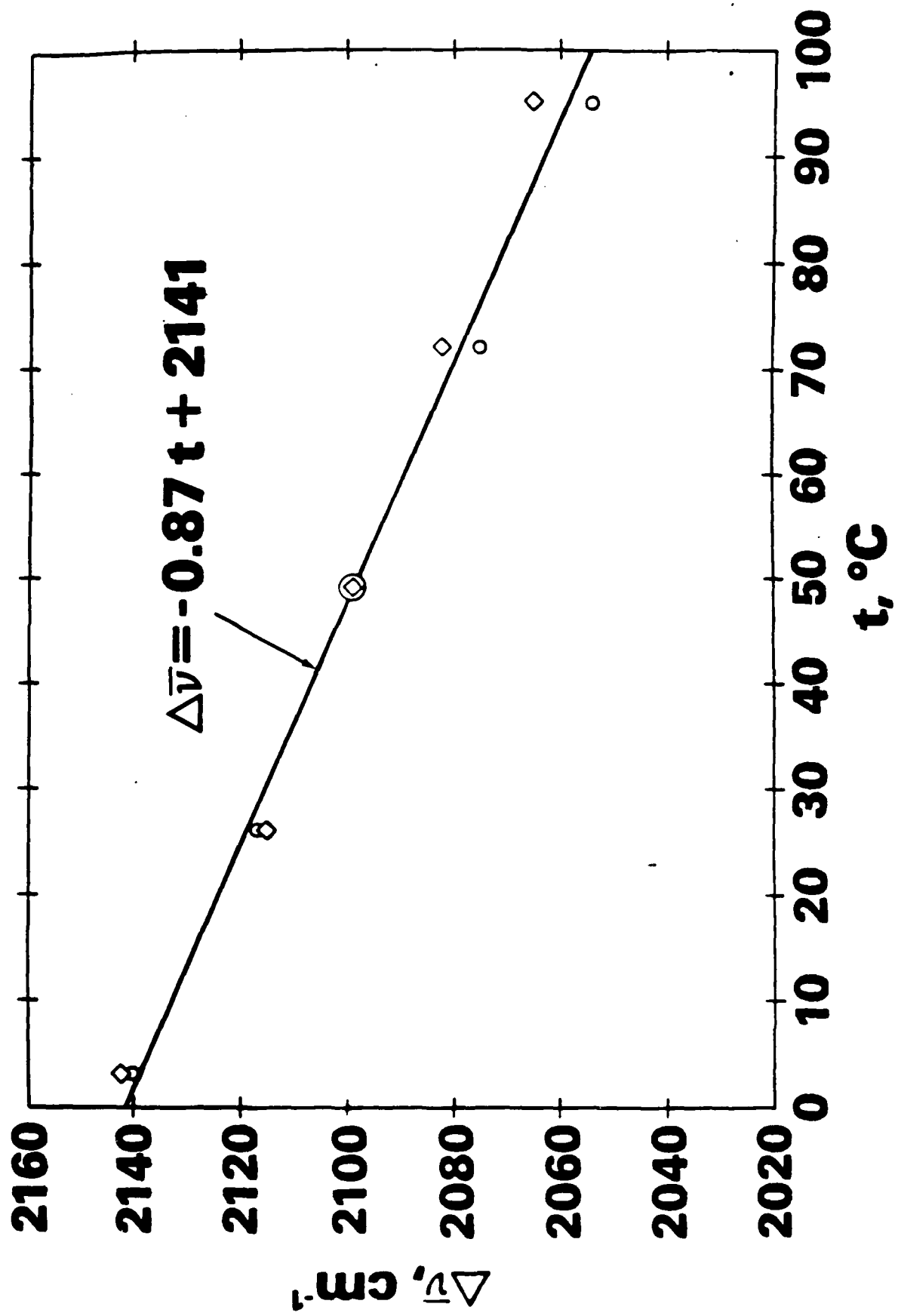
$\Delta\bar{v} = -0.87\,t + 2141$

Fig. 6. Typical 3-Gaussian analysis of the two-phonon, bending plus librational Raman contour for liquid water using a baseline (dashed) which is upwardly concave. Component 1 is a NHB component whose intensity rises with increasing temperature, whereas the HB components 2 and 3, show the opposite temperature dependence. Polarized, X(ZZ)Y orientation, 49°C.
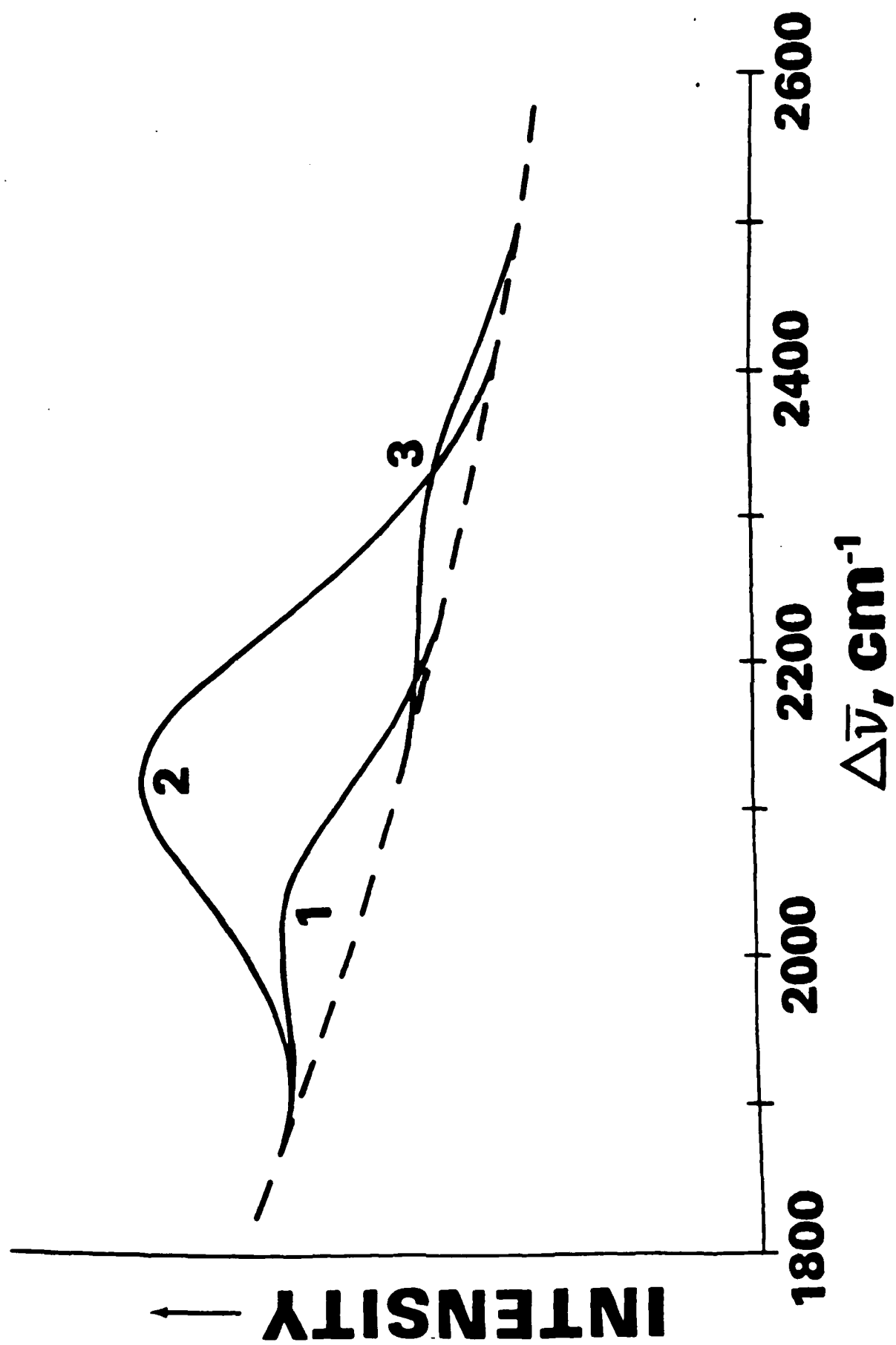
Fig. 6.

INTENSITY →

$\Delta \bar{v}$, cm^{-1}

1800   2000   2200   2400   2600

Fig. 7.   The ratio $I_{\text{DD}}/I_{\text{NDD}}$ on a logarithmic scale _versus_ $10^4/T$
for liquid water from 3° to 95 oC. I_{NDD} is the integrated Raman
intensity of component 1, Fig. 6, and I_{DD} is the sum of the
integrated intensities of components 2 and 3.   The extremes of
the error bars refer to different baseline curvatures as
discussed in the text. The lines shown through the data refer to
least squares.   The $\Delta H°$ values shown refer to the enthalpy of
formation of O-H···O units.
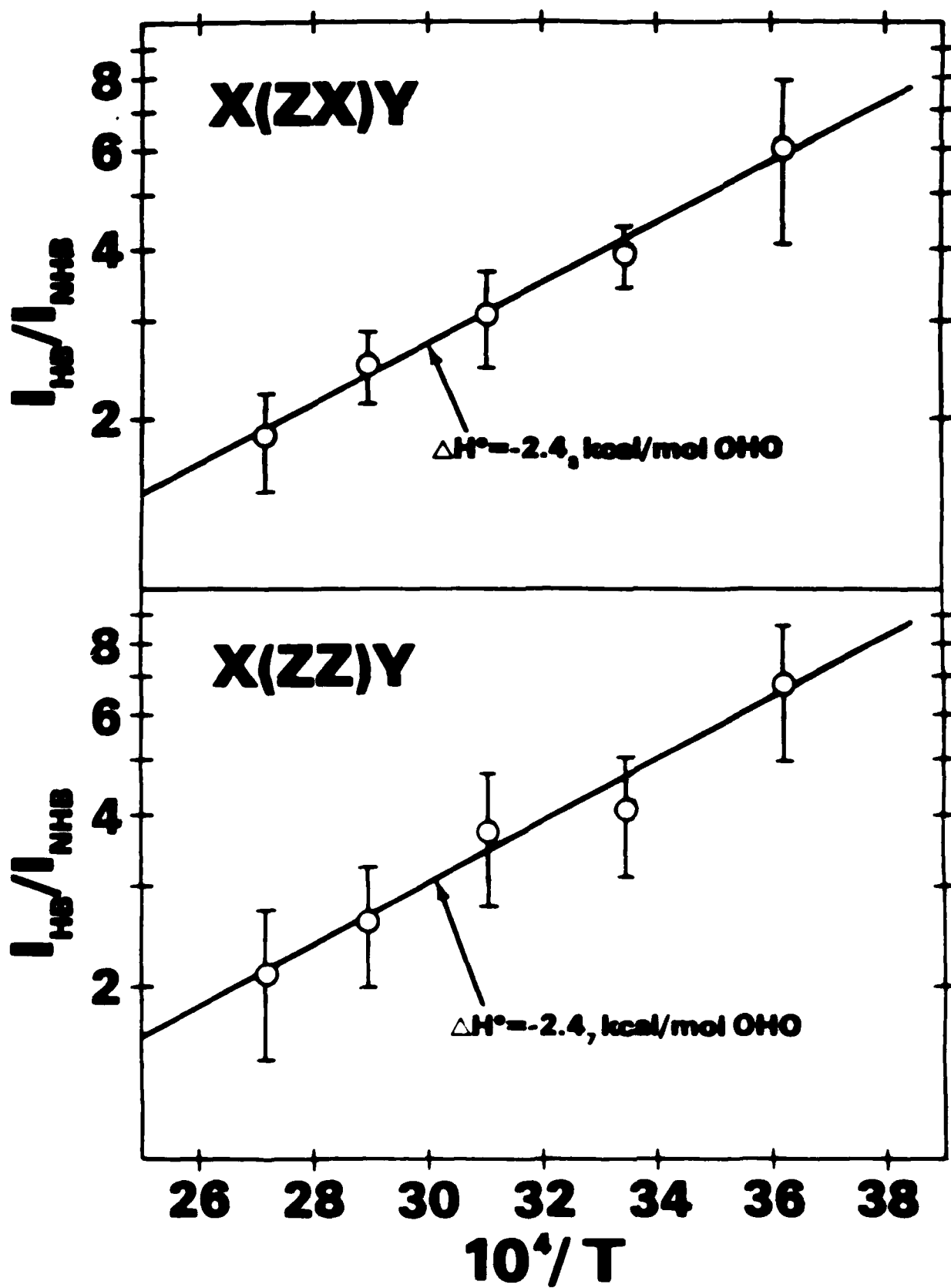
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