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Temperature dependence of light absorption by water

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ABSTRACT

A model is described that relates the temperature coefficient of the optical absorption spectrum of pure water to the frequency derivative of that spectrum and two parameters that quantify the dependence of a peak's amplitude and its position on temperature. When applied to experimental temperature coefficients, it provides a better understanding of the process than the analysis currently in use.

1. Introduction

Understanding the temperature dependence of optical absorption takes on increasing importance as more accurate spectra become available. A high quality absorption spectrum from the infrared to the blue for water at 22 °C can be obtained by combining the data of Kou et al. [1] with that of Pope and Fry [2]. Kou et al. studied the range from 666 to 2400 nm with a Fourier-transform infrared spectrometer. They derived absorption coefficients from the ratio of transmittances obtained with different path lengths. This exactly cancels reflection losses at the air–window and window–water interfaces and absorption by the cell windows. Only transmittance values between 20% and 60% were used to avoid saturation and base line uncertainties. Absorption coefficients from 380 to 727.5 nm were obtained by Pope and Fry using a novel integrating cavity absorption meter (ICAM). In the ICAM, optical power loss from a water-filled highly reflective cavity is measured as a function of wavelength. Scattering, which is important at the lower end of this wavelength range, does not cause a loss of power, hence the ICAM measures absorption.

The absorption coefficient of water decreases by some six decades from the infrared through the blue. The infrared spectra in Fig. 1 from Kou et al. [1] show a general exponential decrease vs frequency that is modulated by various peaks, valleys, and shoulders indicating absorption by discrete states or groups of states. The amplitude of these features decreases relative to the background continuum with increasing frequency. The use of frequency (in wavenumbers) emphasizes the approximately uniform spacing of these features.

The vibrational level spectrum of an isolated water molecule can be described in terms of harmonics or combinations of three normal modes: a symmetric and an asymmetric stretch, and a bending or scissors mode. Single levels are broadened by rotational structure. In condensed phases, formation and breaking of hydrogen bonds further broadens levels and may introduce additional modes. The result is not a continuum for low excitations: Spectra in Fig. 1 retain various discrete features. Patel and Tam [3] have identified absorption peaks in the liquid with the band structure of two anharmonic oscillators. The first was based on a single (degenerate) stretching mode. The second, a parallel series of states, was upshifted by a bending excitation. We will refer to these as the stretching band and the combination band, respectively. The frequency in wavenumbers of levels in terms of stretching and bending numbers, (n_s,n_b), is given by

$$\begin{aligned} v(n_s,0) &= n_s(3620-63n_s) \\ v(n_s,1) &= v(n_s,0)+1645. \end{aligned} \tag{1}$$

The peaks and shoulders in Fig. 1 are labeled with their (n_s,n_b) assignments.

The 22 °C absorption spectrum of Pope and Fry [2] at has a minimum in the vicinity of 420 nm. Recent data from Abe and the Super-Kamiokande Collaboration [4] at 13 °C, and from Griskevich et al. [5] at 15 °C, suggest that this minimum is appreciably deeper and shifted to a higher frequency. The present paper is an outgrowth of a study of scattering and absorption by water in the vicinity of the minimum. When comparing various measurements, it was desirable to separate the influence of temperature from those due to other systematic effects. The classical treatment of temperature dependence is to fit the absorption spectrum

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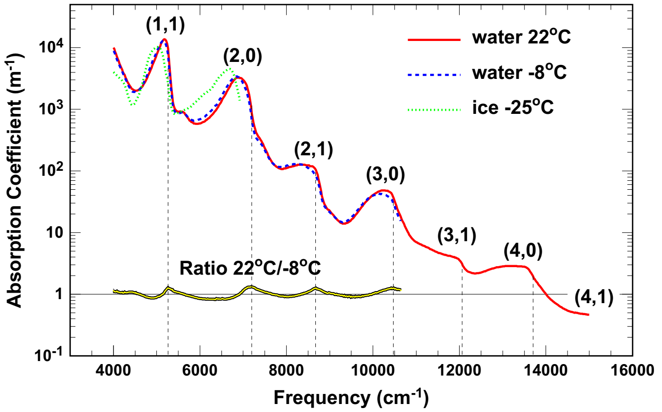

Fig. 1. Absorption spectra of water, supercooled water, and ice from Kou et al. [1]. Oscillator assignments are shown in parentheses above the peaks, see text. The ratio of the 22 °C spectrum to the −8 °C spectrum is shown in the lower part of the figure. Vertical dashed lines mark inflection points on the high frequency side of each 22 °C peak.

to an appropriate set of Gaussians and then to determine a unique temperature coefficient for each peak from experimental data. An example of this sort of analysis due to Jonasz and Fournier [6] is described in Section 3. Measurements of Buiteveld et al. [7], of Pegau et al. [8], and of Langford et al. [9] indicate that absorption peaks in the visible not only shift upward, but also move to higher frequencies with increasing temperature. The model developed below predicts that shifts of peak position may result in apparent positive and negative temperature coefficients for a given peak. A variety of experimental observations are a natural consequence of this model.

2. The model

Ratios of absorption coefficients at 22 °C to those at −8 °C are plotted in the lower part of Fig. 1. Although the individual absorption spectra show considerable structure, the ratio takes a simple form; a series of cusps where the ratio is greater than one, separated by regions where it drops below unity. Vertical dashed lines in Fig. 1 indicate that the cusps correspond with inflection points on the high frequency sides of peaks in the 22 °C spectrum, not their centers. This suggested a connection between temperature dependence and the shape of the absorption spectrum.

Consider part of an absorption spectrum, $a(\nu,T)$, in the vicinity of some spectral feature located at frequency ν_0 where the absorption coefficient is a_0. We assume that a is separable:

$$a(\nu,T)=a_0(T)f(\nu-\nu_0(T)). \tag{2}$$

Differentiating Eq. (2) with respect to T and substituting $df/d\nu_0=-df/d\nu$ leads to

$$\frac{1}{a}\frac{da}{dT}=\frac{1}{a_0}\frac{da_0}{dT}-\frac{1}{a}\frac{da}{d\nu}\frac{d\nu_0}{dT}. \tag{3}$$

The temperature coefficient[1] is the sum of two terms. The first is the trivial "classical" interpretation: If a temperature change of +1 °C increases the intensity of an absorbing peak by +1%, then the temperature coefficient is +1% per °C across the whole peak.

The second term on the right side of Eq. (3) has more interesting properties. If the region of interest contains a peak, $da/d\nu$ is zero at the peak position. The temperature coefficient will change sign in scanning across that peak. That maximum temperature changes match the inflection points on the high frequency side of the peaks in Fig. 1, indicates that $d\nu_0/dT$ is positive in the infrared. Experimental data presented in Section 3 indicate this is true in the visible as well. As a consequence, temperature coefficients will be negative on the low frequency side of a peak and positive on its high side.

Isotopic labeling can provide insight into the source of the spectral shift. Corcelli and Skinner [10] have used a combined electronic structure/molecular dynamics approach to calculate the temperature dependence of the first OH or OD stretching absorption of dilute HOD in D_2O or H_2O, respectively. These correspond to the fundamental member of the Tam and Pantel stretching band, $\nu(1,0)$, offscale to the left in Fig. 1. Both the calculated and experimental (*e.g.*, Palamarev and Georgiev [11]) peak positions increase linearly with temperature. Corcelli and Skinner have divided their calculated configurations into events where the H atom of the OH bond was involved in a hydrogen bond (HB) with a solvent D_2O molecule and those where it was not (non-HB). The non-HB events fell on the extreme high-frequency side of HB distribution. Corcelli and Skinner conclude that the net temperature shift of the OH absorption line is due to a blue shift and narrowing of the HB contribution combined with an increase in the relative contribution from non-HB configurations. The position of the latter was relatively temperature independent. The fraction of non-HB atoms increased from 0.10 to 0.25 as the temperature increased from 10 to 90 °C. Although the Corcelli and Skinner treatment is not a two component model, their calculated OH spectra show over a limited temperature range, approximate isosbestic points characteristic of such models.

If the region of interest in Eq. (3) is a decreasing continuum, the derivative is negative throughout, and temperature coefficients will be positive. Consider then the progressive transition from a spectral region dominated by individual peaks to one of a decreasing continuum. In the first region, temperature coefficients should show a bipolar oscillation, with some upwards bias due to the underlying continuum and any contribution from the classical term of Eq. (3). Moving up in frequency, the relative contribution of peaks decreases and that of the continuum increases. The amplitude of the oscillations will decrease, and the upward bias will increase. At some point, the negative lobes will be balanced out by the bias, and an absorption peak will appear to have only a positive temperature coefficient peak. However, this will not be centered at the peak position but on the inflection point on its high frequency side. With further increases in frequency, the envelopes of the upper and lower coefficient oscillations will converge to the continuum value.

3. Experimental data

The logarithmic frequency derivative, $(1/a)(da/d\nu)$, is compared with the fractional temperature coefficient, $(1/a)(da/dT)$, in Fig. 2. The derivative of the 22 °C spectrum in Fig. 1 is shown as a hollow curve in Fig. 2(a). The solid curve is from the absorption spectrum of Pope and Fry [2], also at 22 °C. Peak positions of the stretching and combination band absorptions are shown by (n_s,n_b) labels. Each of the oscillator states is marked by a sharp negative derivative spike on its high frequency side. Positive excursions are less pronounced due to, in part, the overall decreasing trend of the spectrum. These derivative oscillations damp down in moving into the visible. Negative excursions corresponding to each state persist, but the positive excursions transform into a small negative background between the larger

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[1] We will use "temperature coefficient" for the fractional temperature coefficient, reserving "absolute temperature coefficient" for da/dT.