Mechanistic Interpretation of Bound Water in Cellulosic Fibers Using Near-Infrared Spectroscopy

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Bound water governs swelling, fiber saturation behavior, and mechanical performance in cellulosic materials. Conventional determination methods, including solvent exclusion and differential scanning calorimetry (DSC), are destructive and labor-intensive. This study shows that near-infrared diffuse reflectance (NIR-DR) spectroscopy provides a mechanistically grounded alternative based on wavelength shifts in the OH combination band near 1.92 μm (≈5210 cm^{-1}). Rather than relying solely on absorption intensity, the method tracks systematic changes in band position associated with changes in the hydrogen-bonding environment of the cellulose–water system as moisture content changes. A distinct transition in band position occurs at moisture contents consistent with bound water values reported for comparable cellulosic materials. The spectral behavior is interpreted in terms of changes in the ensemble hydrogen-bonding environment within the evolving cellulose–water system. Reinterpreted in light of modern optical transport theory and contemporary cellulose science, the results establish band-position analysis as a physically meaningful, non-destructive approach for assessing bound water in lignocellulosic fibers, with potential application to rapid at-line or in-line measurement and process control.

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INTRODUCTION

Water is not only a plasticizer in cellulose-based materials; it is also a structural component of the fiber wall. The interaction of water with cellulose governs swelling, pore development, fiber flexibility, and dimensional stability. A central parameter describing this interaction is bound water content (BWC). The precise definition of bound water remains debated. Depending on the measurement technique employed, reported values may reflect different populations of water within the fiber wall, including non-freezing water, cell-wall water, or water associated with accessible hydroxyl groups. Closely related is the fiber saturation point (FSP), the moisture content at which the cell wall is saturated but no free capillary water is present (Stone and Scallan 1968; Maloney *et al.* 1998).

Bound water has traditionally been determined using solvent exclusion techniques, differential scanning calorimetry (DSC), or nuclear magnetic resonance (Carles and Scallan 1973; Nakamura *et al.* 1981). These methods provide complementary measures of water associated with the fiber wall, but they generally require laboratory instrumentation, controlled sample preparation, or destructive sample handling. A rapid, non-destructive

spectroscopic method would therefore be advantageous for both materials characterization and process monitoring.

Aside from any *a priori* model describing water sorption in cellulose, hydrogen bonding within the cellulose–water system is expected to be ubiquitous. Both water and cellulose have been described as hydrogen-bonded networks whose structure evolves with moisture content and local molecular environment (Nissan 1977; Goring 1977; Froix and Nelson 1975). As water is sorbed, cellulose–cellulose, cellulose–water, and water–water interactions collectively alter the local environment of OH groups. Changes in this hydrogen-bond organization influence both the state of sorbed water and the physical properties of cellulosic materials.

Near-infrared (NIR) spectroscopy has long been applied to rapid moisture determination in pulp and paper systems (Osborne *et al.* 1993). Conventional NIR analysis relies primarily on changes in absorption intensity, including the strong OH combination band near 1.92 μm (≈5208 cm^{-1}). However, diffuse reflectance (DR) spectra from fibrous materials depend on both absorption and reduced scattering. Variations in fiber morphology, swelling, and sheet density can alter scattering coefficients and thereby complicate purely intensity-based calibrations (Rinnan *et al.* 2009; Workman and Weyer 2012).

An alternative approach is to examine spectral band position rather than intensity alone. Hydrogen bonding alters OH vibrational energy through changes in the local molecular environment and effective bond force constant. Consequently, changes in the hydrogen-bonding environment of the cellulose–water system can manifest themselves as measurable shifts in OH-associated spectral features. Monitoring band position therefore has the potential to provide information about changes in water–cellulose interactions that is complementary to concentration-dependent absorption intensity.

Despite decades of widespread NIR implementation in the forest products industry, relatively little attention has been directed toward extracting mechanistic information from spectral band positions. Most industrial applications continue to rely on empirical calibrations based predominantly on absorbance or reflectance intensity. Band-position measurements may offer an additional advantage for heterogeneous fibrous materials because the measured wavelength of a spectral feature is potentially less sensitive than absolute intensity to variations in optical path length and scattering. This characteristic is particularly relevant to pulp and papermaking, where rapid, non-destructive measurements capable of tracking changes in fiber-wall hydration could ultimately support at-line or in-line process monitoring and control.

More recent studies have substantially refined the understanding of cellulose–water interactions. Neutron scattering, nuclear magnetic resonance (NMR), calorimetry, and molecular-dynamics simulations indicate that cellulose-associated water occupies heterogeneous environments differing in mobility, confinement, and proximity to cellulose surfaces and interfibrillar regions (O'Neill *et al.* 2017; Paajanen *et al.* 2019; Zou *et al.* 2023; Maloney *et al.* 2023). Contemporary NIR studies likewise indicate that water–cellulose interactions can influence not only spectral intensity but also band position and spectral shape (Watanabe *et al.* 2006; Ma *et al.* 2020; Cichosz *et al.* 2023). These findings provide a contemporary framework for reassessing the moisture-dependent shift of the OH combination band near 1.92 μm observed in the present work.

The present work revisits a foundational NIR-DR study conducted at the Pulp and Paper Research Institute of Canada (Paprican, now FPInnovations), in which systematic moisture-dependent shifts in the OH combination band near 1.92 μm were observed and

compared with independently measured bound water contents. Advances in cellulose science and photon transport theory now allow these observations to be interpreted more rigorously in terms of the evolving cellulose–water hydrogen-bond network and the optical behavior of heterogeneous fibrous materials.

The objective of this paper is to present the band-shift methodology in full technical context, integrate the observations with modern understanding of hydrogen bonding and optical transport, and evaluate the physical basis for using spectral band position as a non-destructive indicator of bound water in cellulosic fibers.

THEORETICAL BACKGROUND

Vibrational Origin of the 1.92 µm Band

The NIR region (0.8 to 2.5 µm) contains overtone and combination bands of fundamental molecular vibrations. The broad water-associated feature near 1.92 µm is principally a combination band involving O–H stretching and H–O–H bending vibrations rather than a simple overtone of the fundamental O–H stretching vibration. Its position is influenced by vibrational anharmonicity and the local hydrogen-bonding environment (Fig. 1).

For an anharmonic oscillator, vibrational frequency depends on the effective bond force constant and the molecular environment. Hydrogen bonding generally lengthens and weakens the donor OH bond, lowering its vibrational frequency and shifting the associated absorption toward longer wavelengths. Such hydrogen-bond-induced frequency shifts have been widely observed in hydrogen-bonded liquids and polymers and provide a spectroscopic probe of local molecular structure (Symons and Eaton 1985; Graener and Laubereau 1991; Fengel 1993). Accordingly, changes in band position can reflect changes in the hydrogen-bonding environment. In the NIR region, overtone and combination transitions are influenced by anharmonicity and therefore retain sensitivity to hydrogen-bond-induced changes in OH vibrational behavior.

In cellulose, sorbed water interacts with accessible hydroxyl groups, particularly within less ordered regions of the fiber wall. As moisture content increases from the dry state toward the FSP, the hydrogen-bonding environment evolves as cellulose–water interactions are supplemented by increasingly cooperative water–water interactions. These changes alter the ensemble of OH environments contributing to the spectral feature near 1.92 µm and can therefore produce measurable shifts in its position.

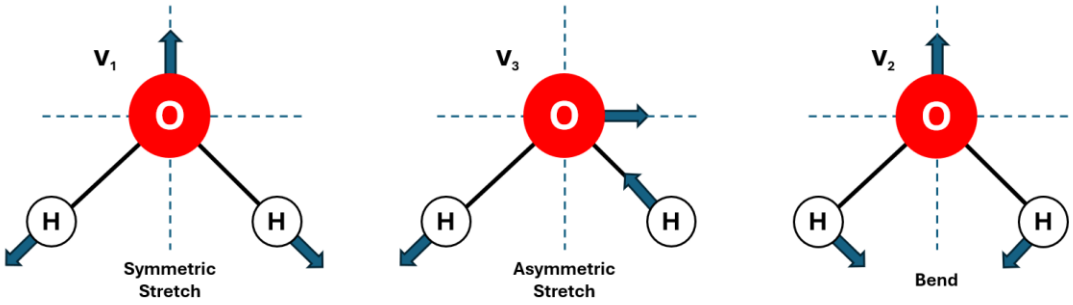

Fig. 1. Fundamental vibrational modes of the water molecule adapted from standard molecular vibration theory. The symmetric stretch (v_1), asymmetric stretch (v_3), and bending mode (v_2) give rise to overtone and combination bands observed in the near-infrared region. Absorption near 1.92 µm arises primarily from combination vibrations involving OH stretching and bending modes.

Optical Transport in Fibrous Media

Diffuse reflectance spectroscopy in pulp sheets is governed by coupled absorption and scattering processes. Reflectance, $R(\lambda)$, therefore depends on both molecular absorption and photon scattering, commonly represented in Kubelka-Munk theory by the absorption and scattering coefficients, k and s, respectively. In its simplest application, the scattering coefficient is often assumed to vary slowly with wavelength over the spectral region of interest (Koukoulas and Jordan 1997).

In swelling fibers, however, scattering can change as fiber dimensions, pore structure, and refractive-index contrasts within the sheet evolve with moisture content. Modern radiative-transfer analyses that separately evaluate absorption (K) and scattering (S) indicate that intrinsic spectral features originate primarily from molecular absorption, whereas scattering strongly influences spectral intensity, baseline, and apparent band shape (Neuman *et al.* 2012). Similar conclusions emerge from broader studies of optical transport and NIR spectroscopy, which distinguish molecular absorption phenomena from scattering-induced changes in spectral amplitude and shape (Burns and Ciurczak 2007; Jacques 2013).

Intensity-based NIR moisture determination can therefore be sensitive to structural changes within the cellulose matrix as well as to water content itself. Band position provides a complementary measurement because the underlying vibrational transition energies are determined by molecular interactions rather than photon path length. Although scattering can influence the apparent shape and position of overlapping spectral features, wavelength shifts arising systematically from changes in the molecular environment are less directly dependent on absolute reflectance intensity.

Derivative spectroscopy further reduces baseline and multiplicative effects associated with scattering and facilitates localization of spectral features (Rinnan *et al.* 2009).

MATERIALS AND METHODS

Materials

Pulp samples included thermomechanical pulp (TMP), fully bleached softwood kraft (BSWK), fully bleached hardwood kraft (BHWK), and cotton linters. These materials were selected to encompass differences in fiber morphology, chemical composition, and water retention characteristics.

Prior to analysis, the pulp samples were formed into laboratory handsheets and subjected to controlled wetting and drying to obtain moisture contents ranging from water-saturated to near oven-dry conditions.

Moisture Determination

Samples were saturated in deionized water, and excess surface water was removed by blotting. Near-infrared measurements were performed immediately following sample preparation. Following NIR analysis, the samples were weighed and then oven-dried at 105 °C for 4 h to determine oven-dry mass. Moisture content was calculated gravimetrically from the difference between wet and oven-dry mass and expressed as grams of water per gram of oven-dry fiber (g/g).

Near-Infrared Diffuse Reflectance Spectroscopy

Near-infrared diffuse reflectance (NIR-DR) spectra were collected using a Lambda 19 UV/VIS/NIR spectrophotometer (PerkinElmer Corp., Norwalk, CT) equipped with a 60-mm integrating sphere. Spectra were acquired in reflectance mode over the wavelength range 0.9 to 2.5 μm. Reflectance measurements were collected at 1-nm wavelength intervals.

Reflectance data were transformed to Kubelka–Munk units according to,

$$K/S = (1 - R)^2 / 2R \quad (1)$$

where R is the measured reflectance and K/S represents the apparent absorption-to-scattering ratio; K and S were not determined independently. To enhance spectral resolution and permit accurate localization of overlapping absorption bands, second-derivative spectra were calculated numerically from the Kubelka–Munk-transformed data. Particular attention was directed toward the OH combination band near 1.92 μm. The wavelength position of the second-derivative minimum was used to monitor changes in the hydrogen-bonding environment of sorbed water as a function of moisture content. Second derivatives of the Kubelka–Munk spectra were calculated numerically using a finite-difference approximation derived from a Taylor-series expansion. No additional smoothing or polynomial fitting was applied.

Determination of Bound Water Content

Bound water content was estimated from the moisture-dependent behavior of the OH combination band near 1.92 μm (≈5210 cm^{-1}). At lower moisture contents, band position varied approximately linearly with moisture content, whereas at higher moisture contents it approached an approximately constant value. The NIR-derived bound water content was taken as the moisture content corresponding to the intersection of these two response regimes, consistent with the procedure used in the original analysis. Because replicate determinations of the transition were not available in the historical dataset, confidence intervals for the breakpoint could not be calculated retrospectively.

Published bound water values obtained using independent techniques, including differential scanning calorimetry and related methods, were used for comparison. These literature values were not obtained from the same specimens and therefore should not be regarded as independent validation of the NIR method. Rather, they provide a comparison with the range of bound water contents reported for broadly comparable cellulosic materials. Fiber saturation point values determined by solvent exclusion were also included to distinguish the NIR-derived bound water content from the broader measure of fiber-wall hydration represented by FSP.

Molecular Modeling

Semi-empirical molecular orbital calculations were performed using HyperChem molecular modeling software (HyperCube Inc. 1992). Molecular geometries were initially optimized using the MM+ molecular mechanics force field (Allinger and Burkert 1982). Electronic structure calculations were then performed using the AM1 semi-empirical parameterization (Theodorou 1989).

Simple cellulose–water cluster models were constructed to examine changes in atomic charge distribution and hydroxyl bond geometry associated with hydrogen-bond formation. Energy minimization was performed using a conjugate-gradient optimization routine. The calculations were intended to provide qualitative mechanistic insight into changes in the local electronic and geometric environment of cellulose hydroxyl groups upon interaction with water. They were not used to calculate vibrational frequencies or to quantitatively predict the magnitude or direction of the observed NIR band shifts.

RESULTS

Spectral Features

All pulp types exhibited a pronounced absorption feature near 1.92 μm (Fig. 2). Second-derivative analysis resolved the band minimum with high precision (Fig. 3).

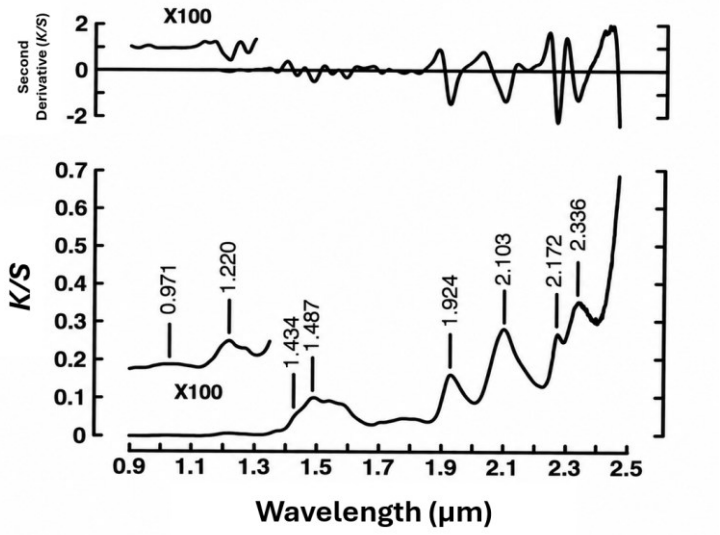

Fig. 2. NIR absorption spectrum of a fully bleached softwood kraft pulp (below) and its second derivative spectrum (above). Subtle changes in the NIR absorption bands can be identified through the second derivative spectrum.

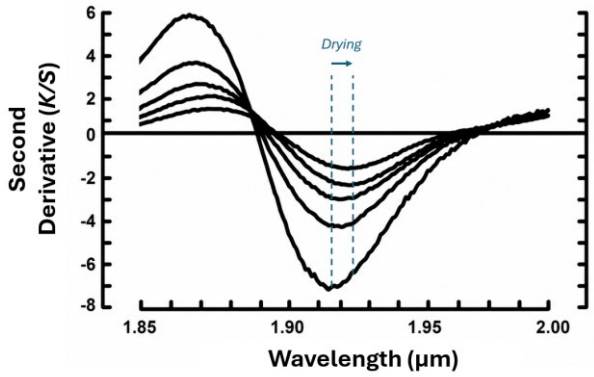

Fig. 3. Moisture-dependent OH combination-band response in fully bleached softwood kraft pulp. The position of the water-associated combination band shifts to longer wavelengths as the pulp is dried. Tracking band position as a function of moisture content provides the basis for determining the bound water transition point.

Moisture-Dependent Band Shifts

Decreasing moisture content produced a systematic shift of the OH combination band near 1.92 µm (≈5208 cm^{-1}) toward longer wavelengths (Fig. 4). A distinct change in the moisture dependence of band position was observed, with a transition in slope occurring at water contents consistent with bound water values reported in the literature for comparable pulp types.

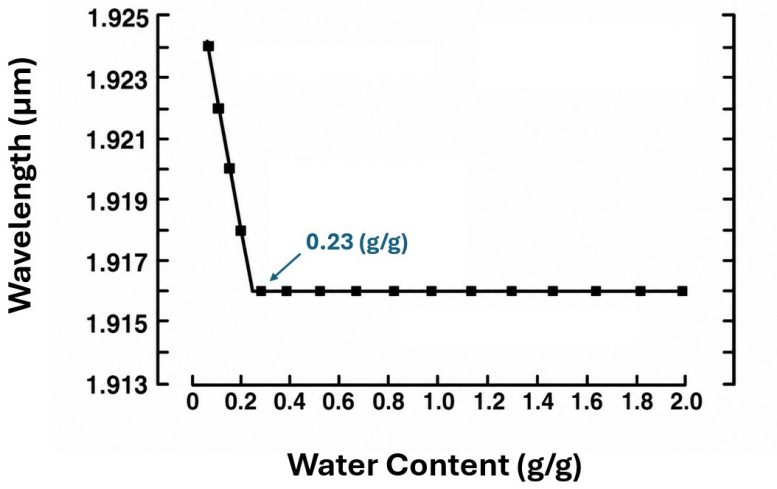

Fig. 4. Relationship between the wavelength position of the OH combination band near 1.92 µm (≈5208 cm^{-1}) and water content for a fully bleached softwood kraft pulp (BSWK). As water content decreases, the band shifts systematically toward longer wavelengths until a transition occurs at approximately 0.23 g/g. Below this moisture content, further drying produces little additional change in band position. The water content corresponding to this spectral transition is consistent with bound water contents reported in the literature for comparable cellulosic materials.

The resulting NIR-derived bound water contents fell within the range of literature values obtained using alternative measurement techniques (Table 1). Fiber saturation point values determined by solvent exclusion were consistently higher than the NIR-derived bound water contents, reflecting the distinction between these operationally defined measures of fiber-wall hydration.

Table 1. NIR-derived Bound Water Contents Compared with Literature Values Obtained Using Alternative Methods, Together with Fiber Saturation Points Determined by Solvent Exclusion (for selected pulp samples)

Pulp Type*	NIR-DR Bound Water Content (g/g)	Literature Bound Water Content (g/g)	Fiber Saturation Point (g/g)
TMP	0.39±0.03	0.40	0.89±0.02
BHWK	0.29±0.03	0.33	0.76±0.02
BSWK	0.23±0.03	0.25	0.79±0.02
Cotton Linters[3]	0.19±0.02	0.18	0.45±0.02
*Carles and Scallan 1973; Nelson 1997			

Notes: TMP = thermomechanical pulp; BHWK = bleached hardwood kraft; BSWK = bleached softwood kraft.

DISCUSSION

In quantitative spectrophotometric analysis, absorption intensity is commonly related to analyte concentration. For example, NIR-DR measurement of moisture in paper generally relies on the relationship between the intensity of OH-associated absorption and water content. In heterogeneous fibrous materials, however, strong absorption and moisture-dependent changes in scattering can introduce nonlinearities or anomalous spectral features, particularly outside the linear region of the concentration-response relationship (Koukoulas and Jordan 1997).

The systematic shift of the OH combination band near 1.92 μm (≈5210 cm^{-1}) toward longer wavelengths during drying indicates that the spectral response is not attributable solely to decreasing water concentration. Rather, the changing band position is consistent with progressive modification of the ensemble hydrogen-bonding environment within the cellulose–water system. This interpretation is consistent with early structural descriptions of water in cellulosic materials, in which water remaining at lower moisture contents becomes increasingly associated with accessible cellulose hydroxyl groups and confined regions of the fiber wall (Blackwell and Marchessault 1971; Goring 1977).

More recent experimental and computational studies provide a more heterogeneous picture of cellulose-associated water than a simple distinction between bound and free water implies. Neutron scattering, NMR, calorimetry, and molecular-dynamics simulations indicate populations of water differing in confinement, mobility, and association with cellulose surfaces and interfibrillar regions (O'Neill *et al.* 2017; Paajanen *et al.* 2019; Zou *et al.* 2023; Maloney *et al.* 2023). These findings suggest that water progressively occupies a distribution of chemically and structurally distinct environments within the fiber wall rather than forming a single, uniformly bound population.

At high moisture contents, water associated with the fibers includes populations whose molecular environment approaches that of bulk liquid water, together with water located within the swollen fiber wall. As drying proceeds, removal of more weakly constrained water changes the relative contributions of water–water and cellulose–water interactions to the observed OH spectral response. Below the FSP, removal of cell-wall water progressively alters the distribution of local hydrogen-bonding environments. The continued shift toward longer wavelength until the transition associated with bound water content is reached suggests that the OH environments contributing to the band continue to evolve well below the FSP. Below this transition, further drying produces comparatively little change in band position, indicating that the moisture-dependent spectral response has entered a different regime.

The spectral transition should therefore not be interpreted as a sharp boundary between discrete populations of bulk and bound water. Rather, it identifies a change in the moisture dependence of the ensemble OH vibrational environment at a water content consistent with bound water values reported in the literature for comparable cellulosic materials. The correspondence provides evidence for the physical plausibility of interpreting the transition as a spectroscopic indicator of bound water content, but does not constitute independent validation of the method. Such validation would require application of the NIR approach and an established reference technique to the same specimens under controlled conditions.

Because the energies of the underlying vibrational transitions are determined by molecular interactions rather than spectral amplitude, band-position analysis is less directly dependent on absolute reflectance intensity than conventional intensity-based measurements. Although scattering can influence the apparent shape and position of broad,

overlapping NIR features, the systematic wavelength shift observed here provides a mechanistically grounded complement to empirical intensity-based or chemometric moisture measurements.

Conceptual Molecular Modeling Support

To provide qualitative insight into the molecular changes accompanying cellulose–water interactions, semi-empirical molecular orbital calculations were performed on cellulose–water cluster models. The calculations indicated changes in atomic charge distribution and OH bond geometry associated with hydrogen-bond formation between water and cellulose hydroxyl groups.

These qualitative observations are consistent with more recent molecular simulations of cellulose–water systems. Molecular-dynamics studies have shown that hydration modifies the hydrogen-bonding and electrostatic environment of cellulose surface hydroxyl groups and that interfacial water can assume distinct, energetically favorable configurations within cellulose fibril structures (Chen *et al.* 2022; Barrios *et al.* 2024). More recent density-functional calculations on cellobiose–water complexes likewise demonstrate site-specific hydrogen bonding and associated changes in molecular geometry and interaction energy (Barrios *et al.* 2025). Collectively, these studies support the view that hydration progressively modifies the local electronic and hydrogen-bonding environment of cellulose hydroxyl groups.

Figure 5 presents a conceptual representation of these changes in the local electronic and geometric environment of a cellulose hydroxyl group upon interaction with water. The modeling supports the general interpretation that hydrogen bonding perturbs the OH environment and is therefore consistent with a molecular basis for moisture-dependent changes in the NIR spectrum. Recent spectroscopic work provides additional support for this interpretation, showing moisture-dependent changes in hydrogen-bonded water populations associated predominantly with wood polysaccharides (Majstorović and Sandak 2026).

The molecular modeling was not used to calculate vibrational frequencies and therefore does not independently predict the magnitude or direction of the observed wavelength shift. Rather, it provides qualitative evidence that cellulose–water hydrogen bonding modifies the electronic and geometric environment of the OH groups contributing to the spectral response. The experimentally observed band-position changes are interpreted in the context of these interactions and the broader evolution of the cellulose–water hydrogen-bonding network during drying.

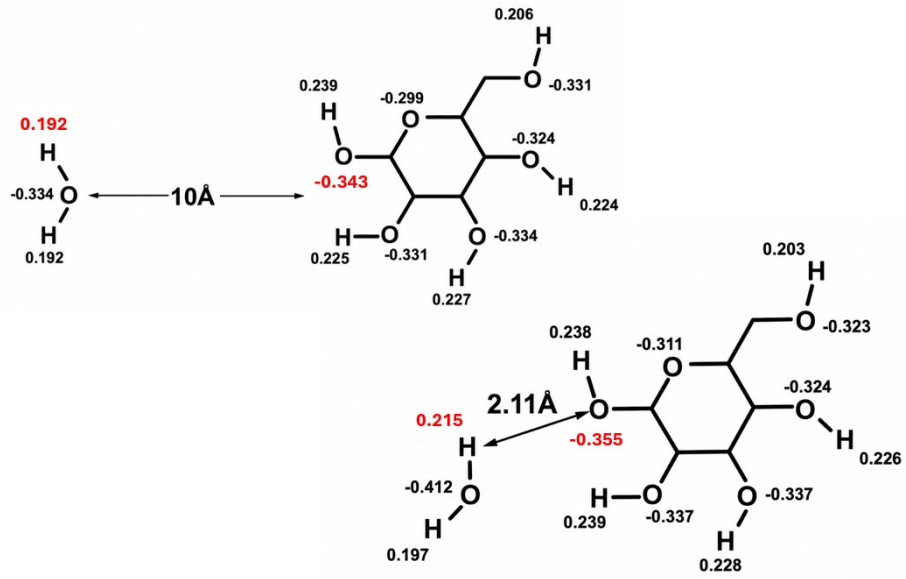

Fig. 5. Conceptual molecular model illustrating changes in OH bond geometry and atomic charge distribution associated with hydrogen-bond formation. Labels indicate the calculated net atomic charge on individual atoms of water and glucose, which represents cellulose. Water is brought from a separation distance of 10 Å (top of figure) to 2.11 Å (bottom of figure), representing the formation of a typical hydrogen-bonded arrangement between water and a cellulose hydroxyl group.

Relevance to Contemporary Cellulose Materials

Water-state characterization remains relevant to nanocellulose systems, high-consistency refining, barrier materials, and studies of drying and hornification. The band-position approach provides a non-destructive spectroscopic probe that may also be adaptable to modern diode-array, fiber-optic, and process-scale NIR instrumentation.

An important next step is to establish the robustness of the spectral response under conditions representative of commercial pulping and papermaking. Dissolved and fiber-associated ions, including Na^{+}, Ca^{2+}, and Al^{3+}, as well as pH and temperature, may affect fiber swelling, hydration, and local hydrogen-bonding environments and thereby influence the NIR response. These effects should be quantified before band position can be established as a reliable process measurement. If sufficiently robust, rapid measurement of the OH-associated spectral feature could potentially provide an at-line or in-line indicator of fiber-wall hydration for process monitoring and control.

SUMMARY AND CONCLUSIONS

1. The OH combination band near 1.92 μm (≈5210 cm^{-1}) shifts systematically with moisture content below the fiber saturation point. A transition in the moisture dependence of band position occurs at water contents consistent with bound water values reported in the literature for comparable cellulosic materials.
2. The systematic band shift is consistent with progressive changes in the ensemble hydrogen-bonding environment of the cellulose–water system during drying. As moisture content decreases, changes in the relative contributions of water–water and cellulose–water interactions alter the average OH vibrational environment sampled by

the NIR measurement. The transition in band-position response should therefore not be interpreted as a sharp boundary between discrete populations of bound and free water, but rather as a change in the distribution of cellulose-associated water environments occurring in the bound-water region.

3. The spectral behavior is consistent with modification of the local electronic, geometric, and hydrogen-bonding environments within the cellulose–water system. Band-position analysis therefore provides a physically meaningful, non-destructive approach for assessing bound water in cellulosic fibers and complements conventional intensity-based NIR methods by providing information related to changes in the molecular environment of sorbed water.

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REFERENCES CITED

Allinger, N. L., and Burkert, U. (1982). *Molecular Mechanics*, ACS Monograph 177, American Chemical Society, Washington, DC.

Barrios, N., Parra, J. G., Venditti, R. A., and Pal, L. (2024). "Elucidation of temperature-induced water structuring on cellulose surfaces for environmental and energy sustainability," *Carbohydr. Polym.* 329, 121799. https://doi.org/10.1016/j.carbpol.2024.121799

Blackwell, J., and Marchessault, R. H. (1971). "Investigation of the structure of cellulose and its derivatives," in: *Cellulose and Cellulose Derivatives*, Vol. 6, Part IV, N. Bikales and L. Segal (eds.), Wiley-Interscience, New York, NY, pp. 1-37.

Burns, D. A., and Ciurczak, E. W. (eds.) (2007). *Handbook of Near-Infrared Analysis*, 3rd Ed., CRC Press, Boca Raton, FL. https://doi.org/10.1201/9781420007374

Carles, J. E., and Scallan, A. M. (1973). "The determination of the amount of bound water within cellulosic gels by NMR spectroscopy," *Journal of Applied Polymer Science* 17(1), 173-186. https://doi.org/10.1002/app.1973.070170618

Chen, P., Wohlert, J., Berglund, L., and Furó, I. (2022). "Water as an intrinsic structural element in cellulose fibril aggregates," *J. Phys. Chem. Lett.* **13**(24), 5424–5430. https://doi.org/10.1021/acs.jpclett.2c00781

Fengel, D. (1993). "Influence of water on the OH valency range in deconvoluted spectra of cellulose," *Holzforschung* 47(2), 103-108. https://doi.org/10.1515/hfsg.1993.47.2.103

Froix, M., and Nelson, R. (1975). "The interaction of water with cellulose from nuclear magnetic resonance relaxation times," *Macromolecules* 8(6), 726-730. https://doi.org/10.1021/ma60048a011

Goring, D. A. I. (1977). "The effect of cellulose on the structure of water," in: *Fibre-Water Interactions in Paper-Making*, Vol. 1, Fundamental Research Committee, British Paper and Board Industry Federation, London, UK, pp. 43-59.

Graener, H., and Laubereau, A. (1991). "Structural information on a hydrogen-bonded polymer from nonlinear infrared spectroscopy," *Journal of Physical Chemistry* 95(9), 3447-3451. https://doi.org/10.1021/j100162a001

HyperCube, Inc. (1992). *HyperChem Molecular Modeling Software*, Version 2.0, HyperCube, Inc., Gainesville, FL.

Jacques, S. L. (2013). "Optical properties of biological tissues: A review," *Physics in Medicine and Biology* 58(11), R37-R61. https://doi.org/10.1088/0031-9155/58/11/R37

Koukoulas, A. A., and Jordan, B. D. (1997). "Effect of strong absorption on the Kubelka-Munk scattering coefficient," *Journal of Pulp and Paper Science* 23(5), J224-J232.

Maloney, T. C., Paulapuro, H., and Stenius, P. (1998). "Hydration and swelling of pulp fibers measured with differential scanning calorimetry," *Nordic Pulp and Paper Research Journal* 13(1), 31-36.

Maloney, T., Phiri, J., Zitting, A., Paajanen, A., Penttilä, P., and Ceccherini, S. (2023). "Deaggregation of cellulose macrofibrils and its effect on bound water," *Carbohydrate Polymers* 319, article 121166. https://doi.org/10.1016/j.carbpol.2023.121166

Majstorović, F., and Sandak, J. (2026). "Moisture-dependent transition from strong to weak hydrogen bonding in wood polysaccharides," *Carbohydr. Polym.* 385, 125396. https://doi.org/10.1016/j.carbpol.2026.125396

Nakamura, K., Hatakeyama, T., and Hatakeyama, H. (1981). "Studies on bound water of cellulose by differential scanning calorimetry," *Textile Research Journal* 51(9), 607-613. https://doi.org/10.1177/004051758105100909

Nelson, R. A. (1977). "The determination of moisture transitions in cellulosic materials using differential scanning calorimetry," *Journal of Applied Polymer Science* 21(7), 1797-1808. https://doi.org/10.1002/app.1977.070210306

Neuman, M., Coppel, L., and Edström, P. (2012). "A partial explanation of the dependence between light scattering and light absorption in the Kubelka-Munk model," *Nordic Pulp & Paper Research Journal* 27(2), 426-430.

Nissan, A. H. (1977). "The science of paper," in: *Paper Science and Technology*, Joint Textbook Committee of the Paper Industry of the United States and Canada.

O'Neill, H., Pingali, S. V., Petridis, L., He, J., Mamontov, E., Hong, L., Urban, V., Evans, B., Langan, P., Smith, J. C., and Davison, B. H. (2017). "Dynamics of water bound to crystalline cellulose," *Scientific Reports* 7, article 11840. https://doi.org/10.1038/s41598-017-12035-w

Osborne, B. G., Fearn, T., and Hindle, P. H. (1993). *Practical NIR Spectroscopy with Applications in Food and Beverage Analysis*, 2nd Ed., Longman Scientific & Technical, Harlow, UK.

Paajanen, A., Ceccherini, S., Maloney, T., and Ketoja, J. A. (2019). "Chirality and bound water in the hierarchical cellulose structure," *Cellulose* 26(10), 5877-5892. https://doi.org/10.1007/s10570-019-02525-7

Rinnan, Å., van den Berg, F., and Engelsen, S. B. (2009). "Review of the most common pre-processing techniques for near-infrared spectra," *TrAC Trends in Analytical Chemistry* 28(10), 1201-1222. https://doi.org/10.1016/j.trac.2009.07.007

Stone, J. E., and Scallan, A. M. (1968). "A structural model for the cell wall of water-swollen wood pulp fibres based on their accessibility to macromolecules," *Cellulose Chem. Technol.* 2, 343-358.

Symons, M. C. R., and Eaton, G. (1985). "Solvation of acetone in protic and aprotic solvents and binary solvent mixtures," *Journal of the Chemical Society, Faraday Transactions 1* 81(8), 1963-1975. https://doi.org/10.1039/F19858101963

Theodorou, D. N. (1989). "Semi-empirical methods: Current status and perspectives," *Tetrahedron* 44(24), 7393-7404. https://doi.org/10.1016/S0040-4020(01)86235-9

Workman, J., Jr., and Weyer, L. (2012). *Practical Guide and Spectral Atlas for Interpretive Near-Infrared Spectroscopy*, 2nd Ed., CRC Press, Boca Raton, FL. https://doi.org/10.1201/b11894

Zou, Y., Maillet, B., Brochard, L., and Coussot, P. (2023). "Fast transport diffusion of bound water in cellulose fiber network," *Cellulose* 30(12), 7463-7478. https://doi.org/10.1007/s10570-023-05369-4

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