



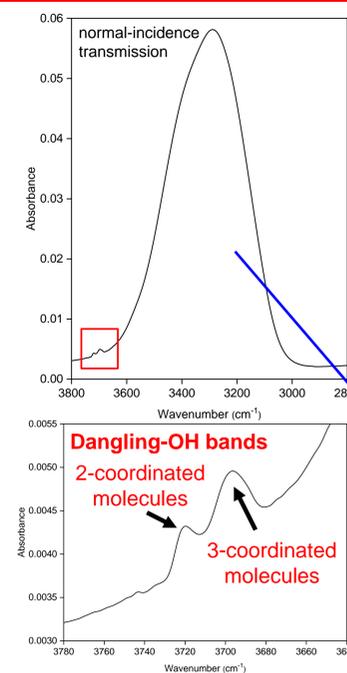
東京大学
THE UNIVERSITY OF TOKYO

Experimental measurement of the absorption cross section of dangling OH bonds in water ice

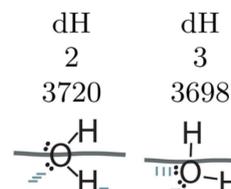
T. Hama, T. Nagasawa, T. Hasegawa, and N. Numadate, Komaba Inst. Sci., UTokyo.

Introduction: Dangling-OH bonds in water

Conclusions: Band strengths for water



H₂O is the most abundant solid of interstellar clouds.

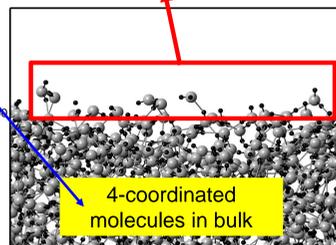


IR spectrum of amorphous water at 10 K

→ Weak dangling-OH features at 3696 and 3720 cm⁻¹

→ Free OH-stretching of 3-, and 2-coordinated molecules

→ Reflect the porosity of ice and serve as catalytic sites for adsorption and chemical reactions.



The absorption cross section of dangling OH bonds remains unknown (as explained below).

Quantification of dangling OH bonds is not possible from IR spectra of ice.

Discussion: Dipole moment of 3-coordinated molecules can be enhanced by surrounding water. Mono.→1.9, Di.→2.1, Tri.→2.3, Tet.→2.5, Pen.→2.6, Hex.→2.7 (D) Gregory et al., Science, 275, 814 (1997).

→Larger band strength of 3-coordinated dangling-OH bonds than H₂O monomers

Future work: Band strength of the 2-coordinated dangling-OH bonds

Species	Band strength [cm molecule ⁻¹] (wavenumber range)
Three-coordinated dangling OH at 90 K (This study)	1.4 ± 0.3 × 10⁻¹⁷ (3710–3680)
Dangling OH (Calculation) (Maté et al. 2021)	1.2 × 10 ⁻¹⁷ (3700–3640)
Amorphous water at 80 K (Mastrapa et al. 2009)	2.9 × 10 ⁻¹⁶ (4320–2956)
Crystalline ice at 267–273 K (Schaaf & Williams 1973)	2.3 × 10 ⁻¹⁶ (3900–2700)
H ₂ O monomer in solid O ₂ at 10 K (Ehrenfreund et al. 1996)	3.3 × 10 ⁻¹⁸ (3732)

Challenges in measuring the absorption cross section, σ (cm²)

Disappearance of dangling-OH bonds on amorphous water at 90 K by CH₃OH deposition to estimate the number density of dangling-OH bonds



A green laser lighting in a solution of Rhodamine 6G dye. It becomes weaker as it progresses inward.

$$\text{Beer-Lambert law: } A = \frac{\sigma N}{\ln 10} = \frac{4\pi d k_2}{\lambda \ln 10}$$

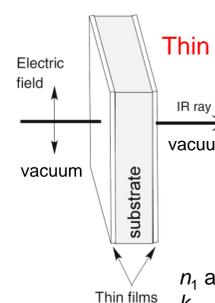
IR wavelength λ (μm)
Sample thickness d (μm)
Column density N (molecules cm⁻²)

Sample's absorbance (A) is a function of its complex refractive index (n₂ + ik₂).

Beer's law neglects optical interfaces (e.g., sample-substrate interface); it holds only for a bulk sample thicker than the IR wavelength (d ≥ λ).

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However, the thickness of vapor-deposited ice is less 1 μm, i.e., d << λ. Substrate thickness: > 1 mm
Thin sample's absorbance is induced by the electric field at optical interfaces.



Thin sample's absorbance in a five-layer system deduced from Maxwell's equations. (when measured by normal incidence transmission using linearly polarized IR light)

Itoh, Y., Kasuya, A., & Hasegawa, T. 2009, J Phys Chem A, 113, 7810

$$A_{\text{thin}}^{\theta=0} = \frac{8\pi da}{\lambda \ln 10} (2n_2 k_{2xy}) \quad 2n_2 k_{2xy}: \text{transverse optic (TO) function}$$

$$\text{Optical interface effects: } a = \frac{1}{n_1 + n_3} + \left(\frac{n_1 - n_3}{n_1 + n_3} \right)^4 \left\{ 1 - \left(\frac{n_1 - n_3}{n_1 + n_3} \right)^4 \right\}^{-1} \left(\frac{2n_3}{n_3^2 - n_1^2} \right)$$

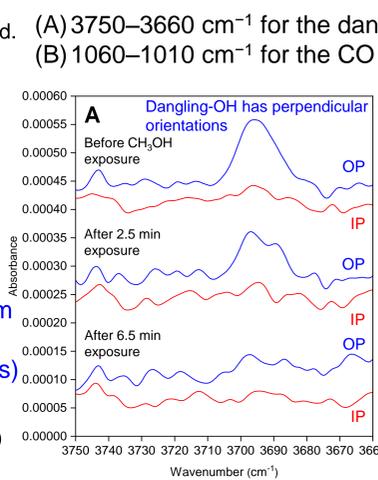
n₁ and n₃ are the refractive indices of vacuum and the substrate.

k_{2xy} is the x- and y- (surface-parallel) components of optically isotropic k₂. k₂ = $\frac{2k_{2xy} + k_{2z}}{3}$

σ requires the isotropic k₂.

A_{thin}^{θ=0} is influenced by n₁, n₂, and n₃, and only the surface-parallel (in-plane, IP) vibration is observed by k_{2xy}, without the surface-perpendicular (out-of-plane, OP) vibration given by k_{2z}

To measure σ for dangling OH bonds, we need to measure both k_{2xy} and k_{2z}, correct the optical interface effects expressed by n₁, n₂, and n₃, and obtain the isotropic k₂.



Overlap of the two dangling OH peaks complicates measurement of σ. Dangling-OH bonds vanishes after 6.5 min of CH₃OH deposition.

→ Number density of dangling-OH bonds: N = 3.3 ± 0.6 × 10¹³ cm⁻²

Analytical expressions for the IP and OP spectra

$$A_{\text{IP}} = A_{\text{thin}}^{\theta=0} = \frac{8\pi da}{\lambda \ln 10} (2n_2 k_{2xy}) \quad k_{2xy} = \frac{A_{\text{IP}} \lambda \ln 10}{16\pi d a n_2}$$

$$A_{\text{OP}} = \frac{8\pi da}{H \lambda \ln 10} \frac{(2n_2 k_{2z})}{(n_2^2 + k_{2z}^2)^2} \approx \frac{8\pi da}{H \lambda \ln 10} \frac{(2n_2 k_{2z})}{n_2^4}$$

Longitudinal optic (LO) energy-loss function k_{2z} ≈ $\frac{n_2^4 H A_{\text{OP}} \lambda \ln 10}{16\pi d a n_2}$
H: substrate-parameter (0.33 for Si)

k₂ < n₂ for amorphous water at 3750–3650 cm⁻¹ (two-order difference)
(Mastrapa et al., 2009, Astrophys J, 701, 1347)

$$\sigma = \frac{4\pi d k_2}{\lambda N} = \frac{4\pi d}{\lambda N} \left(\frac{2k_{2xy} + k_{2z}}{3} \right) = \left(\frac{2A_{\text{IP}} + n_2^4 H A_{\text{OP}}}{3} \right) \frac{\ln 10}{4a n_2 N}$$

CO band of CH₃OH has a perpendicular orientation by hydrogen-bonding with the dangling OH bonds

Bahr et al., JCP, 128, 134712 (2008).

Dawes et al., PCCP, 18, 1245 (2016).

Luna et al. A and A, 617, A116 (2018)

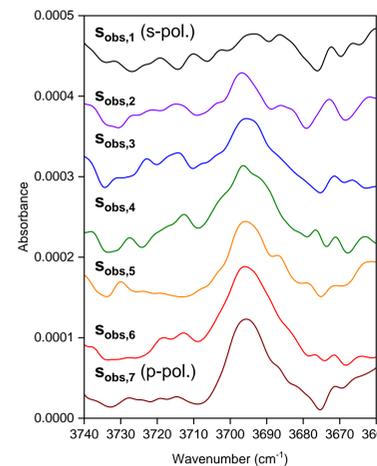
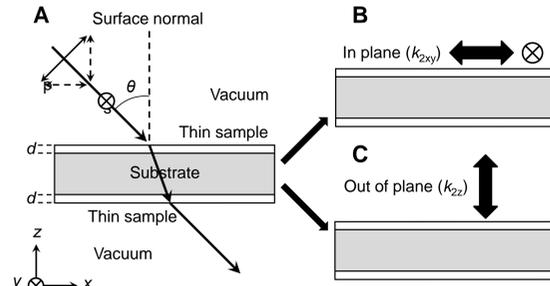
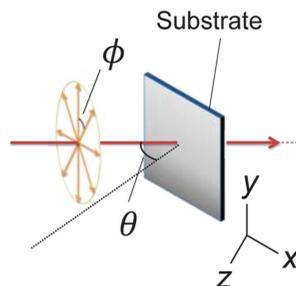
Infrared multiple-angle incidence resolution spectrometry (IR-MAIRS) [by Prof. T. Hasegawa (Kyoto Univ.)]

IR-MAIRS combines oblique incidence transmission measurements and multivariate analysis to retrieve both pure IP (k_{2xy}) and OP (k_{2z}) spectra

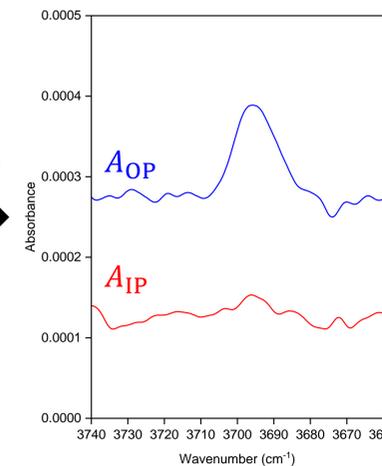
Originally developed for quantitative molecular orientation analysis of organic thin films. Ref: Hasegawa and Shioya, Bull. Chem. Soc. Jpn. (2020) 93, 1127.



Si(111) substrate (40 × 40 × 1 mm) connected to a 4 K He refrigerator. Indium solder is used to cool the Si substrate down to 6 K.



CLS



(1) Seven oblique incidence transmission measurements were taken at θ = 45° at different polarization angles from φ = 0° (s-pol.) to 90° (p-pol.) in 15° steps.

These spectra (s_{obs,1-7}) are expressed as a linear combination of the IP (s_{IP}) and OP (s_{OP}) components

r_{IP,1-7}: weighting coefficients for s_{IP}
r_{OP,1-7}: weighting coefficients for s_{OP}
u₁₋₇: Nonlinear noises (e.g., reflected IR light)

$$s_{\text{obs},1} = r_{\text{IP},1} s_{\text{IP}} + r_{\text{OP},1} s_{\text{OP}} + u_1 \text{ (s-pol.)}$$

$$s_{\text{obs},2} = r_{\text{IP},2} s_{\text{IP}} + r_{\text{OP},2} s_{\text{OP}} + u_2$$

$$s_{\text{obs},3} = r_{\text{IP},3} s_{\text{IP}} + r_{\text{OP},3} s_{\text{OP}} + u_3$$

$$s_{\text{obs},4} = r_{\text{IP},4} s_{\text{IP}} + r_{\text{OP},4} s_{\text{OP}} + u_4$$

$$s_{\text{obs},5} = r_{\text{IP},5} s_{\text{IP}} + r_{\text{OP},5} s_{\text{OP}} + u_5$$

$$s_{\text{obs},6} = r_{\text{IP},6} s_{\text{IP}} + r_{\text{OP},6} s_{\text{OP}} + u_6$$

$$s_{\text{obs},7} = r_{\text{IP},7} s_{\text{IP}} + r_{\text{OP},7} s_{\text{OP}} + u_7 \text{ (p-pol.)}$$

(2) Seven single-beam spectra, s_{obs,j}, forms the matrix, S. The linear combination part can be tied up using the weighting matrix R for r_{IP,j} and r_{OP,j} (classical least-squares (CLS) regression).

$$S = \begin{pmatrix} s_{\text{obs},1} \\ s_{\text{obs},2} \\ \vdots \\ s_{\text{obs},7} \end{pmatrix} = \begin{pmatrix} r_{\text{IP},1} & r_{\text{OP},1} \\ r_{\text{IP},2} & r_{\text{OP},2} \\ \vdots & \vdots \\ r_{\text{IP},7} & r_{\text{OP},7} \end{pmatrix} \begin{pmatrix} s_{\text{IP}} \\ s_{\text{OP}} \end{pmatrix} + U \equiv R \begin{pmatrix} s_{\text{IP}} \\ s_{\text{OP}} \end{pmatrix} + U$$

U is a "garbage matrix". Non-linear noise factors are pooled in U as an error term.

(3) s_{IP} and s_{OP} can be calculated as the least-squares solution of the classical least-squares regression equation as

$$\begin{pmatrix} s_{\text{IP}} \\ s_{\text{OP}} \end{pmatrix} = (R^T R)^{-1} R^T S$$

For details of r_{IP,1-7}, r_{OP,1-7}, and R, see, Itoh et al., JPC A 2009, 113, 7810. Shioya et al., JPC A 2019, 123, 7177.

The IP and OP absorbance spectra: A_{IP} = -log₁₀ $\frac{s_{\text{IP}}^b}{s_{\text{IP}}^s}$ A_{OP} = -log₁₀ $\frac{s_{\text{OP}}^b}{s_{\text{OP}}^s}$
Superscripts b and s indicate background and sample measurements.