Contents

1 Dielectric constant - experimental

	H2O	D2O	ref
ice 1h $\varepsilon(0)$ (-25 C)	≈ 98	≈ 96	(Auty & Cole, 1952 [1])
	103	110	(Johari, 1976 [10])
	103	107	(Kawada, 1979 [14])
liquid $\varepsilon(0)$ (25 C)	78.39	78.06	(Vidulich, et. al. 1967) [24]
	78.39	78.06	(Kawada et. al. 1979) [14]

	H2O	D2O	ref
gas phase μ (D)	1.8546 ± 0.0004	1.8545 ± 0.0004	Stark effect, 1973 **??**
	1.857		**??**

The dielectric constant of Ice 1h has been measured many times over the years. The first published measurements were performed by the Soviet physicist J. Errera in 1924.[1] Early experiments (1924-1965) report a wide range of values. The value one measures varies greatly depending on the crystal quality (polydispersity, the presence of voids, dislocations, etc) and presence of conducting impurities. Care must be taken to avoid complex surface charge and polarization effects which can contaminate the measurement. Because of the difficulties of adding an electrode to ice, some experimenters use "blocking electrodes" which are seperated from the ice by an insulating layer. When blocking electrodes are used, ionic defects build up in near the surface of the material and create a counteracting field which must be taken into account by solving the a Poisson-Boltzmann like equation. For our purposes we can glean enough information from standard experiments so we will not discuss blocking electrode experiments here.

It has been found that if ice is cooled in a sufficiently high electric field, it can act as an electret - meaning that it develop long lived surface and bulk polarization.[5][2] This indicates that both dipolar order and spatial charge separation can become 'frozen' in.

The dielectric constant of ice is anisotropic and is always greater in the direction parallel to the c-direction which is denoted as $\varepsilon_{\|}$.[15] When a single value is reported in the literature, this is understood to be $\varepsilon = 1/3\varepsilon_{\|} + 2/3\varepsilon_{\perp}$. This value corresponds to the effective dielectric constant in polycrystaline ice, which is how ice is most commonly found in nature.

Measurements of $\varepsilon(\omega)$ must all be corrected for the contribution of conductivity to the polarization at low frequency. Since these dielectric constant measurements are always done at finite frequency, the results must be carefully extrapolated to zero frequency using a Cole-Cole plot.

The first reported measurements to compare the dielectric constants of H2O and D2O was performed by Auty & Cole (1952).[1] They found that the dielectric constant of D2O was somewhat smaller than H2O at all temperatures ($\approx 3\%$ smaller at -20 C). The next measurement comparing H2O and D2O was performed by Johari & Jones in 1976 which found values of the dielectric constant for D2O to be about 8% larger than those measured by Auty & Cole.[10] The data of Auty & Cole was called into question, since their values for H2O ice were systematically lower than other authors by 3% to 5% (the other authors agreed within 1%). Contrary to the findying of Auty & Cole, Johari & Jones found that D2O ice has a dielectric constant which is

7% higher, which may “indicate a 4% higher effective dipole moment in D2O ice compared with H2O ice”.

Johari & Jones found that the high frequency dielectric constant of D2O is about 3% smaller at all temperatures.[10] This indicates weaker dielectric loss in the infrared frequencies.

The next study undertaken by Kawada in 1979.[14] Kawada criticised the measurements of Jahari & Jones as being “polydispersive”, since their Cole-Cole semi-circles do not have centers on the x-axis. This indicates the presence of non-Debye relaxation, likely related to the polycrystaline nature of their samples.

To a good approximation the temperature dependence of the dielectric constant follows the Curie-Weiss law:

$$\varepsilon - \varepsilon_\infty = \frac{A_c}{T - T_c} \tag{1.1}$$

The data of Kawada shows the isotopic effects found in other hydrogen-bonded systems - an increase in the Curie temperature and dielectric constant. More specifically, T_C was raised from 46 K to 55 K, or in other words $T_C(D)/T_C(H) = 1.2$.[14] This value can be compared with normal order-disorder ferroelectrics, which typically have $T_C(D)/T_C(H) = 1.02 - 1.08$ and KDP materials, which have $T_C(D)/T_C(H) = 1.6 - 1.7$.[14]

Early experimental data indicated a wide range of values for T_c, ranging from -146 to 30 K. (A T_c below 0 indicates there is no ferroelectric transition.) According to the review by Hobbs in his monograph “Ice Physics” (1974),[7] the best experiments available at that time indicated $T_c \approx 35$ K. Similar studies on H2O by Wörz & Cole[25] and Gough & Davidson[6] found $T_C \approx 38$ and $T_C \approx 32$. Johari and Whalley (1973) confirm these findings with data stretching to 133 K, finding $T_C \approx 35$. The data of Johari and Jones (1976) yield $T_c = 27 \pm 1$ K for D2O.[11] A later study by Johari & Whalley (1981) found $T_C = 6.2 \pm 1.7$ K for H2O and their review of previous experiments up to 1981 found an average of $T_C = 15 \pm 11$.[12]

Significantly, since Kawada used single crystal samples, he was able to observe significant anisotropy in the dielectric constant. They found that upon isotopic substitution $\varepsilon_\perp$ does not change but $\varepsilon_\parallel$ increases, resulting in an increase in anisotropy. They argue convincingly that this anisotropy must be due to long range dipole-dipole correlations.

The presence of a dopant, such as KOH, is known to catalyze the phase transition from proton disorder to proton order in ice. When a small amount of dopant is introduced, polarization in an electric field is drastically sped up - the dielectric relaxation time increases by a factor of 30.[16] The phase transition was discovered by Kawada in 1972.[13] The same experiment was repeated for D2O by Kawada in 1989.[17] Kawada found a transition temperature of 70 K for H2O and 76 K for D2O. The same transition temperature of 70 K was reproduced by Kawada & Shimura with RbOH doping.[18] Additionally both the D2O and H2O phase transition temperatures were exactly reproduced in a calormetric measurement.[19] It is important to note that the phase transition from proton disorder to order does not appear as a conventional ferroelectric phase transition in plots of $\varepsilon(0)$ vs T. No Curie-Weiss like increase in $\varepsilon(0)$ is observed near the critical point, instead, a discontinuous drop in $\varepsilon(0)$ is observed.

2 Dielectric anisotropy

The dielectric anisotropy has important implications in glaciology, where microwave and millimeter wave radar are used to probe ice. Change in the c-axis orientation of ice as a function of depth leads to reflection of electromagnetic radiation.[4][3][23] The degree to which this is due to dielectric anisotropy is controversial however, with some evidence suggesting that anisotropy in conductivity plays a larger role.[21]

Dielectric anisotropy at high frequencies (Ghz to visible) has been measured several times, a review can be found in.[20]

temp	$\varepsilon_\perp$	$\varepsilon_\parallel$	$\frac{\varepsilon_\parallel - \varepsilon_\perp}{\varepsilon_\perp}$	ref
266	95.7	95.8	0	(Johari & Jones, 1978 [9])
263	98	107	10	(Kawada, 1978 [15])
253	119	98	12	(Humbel, et. al., 1953 [8])
252	120	100	20*	(Fujita, et. al., 2000 [23])

Table 1: *glacial ice

Oguro and Whitworth 1991 also report anisotropy in single crystals above the ice XI phase transition.[22]

3 Other differences

The dielectric relaxation time of D2O ice is about 40% slower than H2O ice.[11]

The structure of D2O ice vs H2O ice has been studied by neutron diffraction in numerous experiments.

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