

## Theoretical Analysis of Chemical Bonding Behaviors and Dielectric Properties of Different Phases of Ice

by

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**Summary.** From the chemical bond viewpoint, the chemical bond parameters, linear optical properties and geometrical characteristics of constituent chemical bonds (i.e., O–H and H...O bonds) in the single-crystalline ice phases I, II, III, VI, VII and VIII have been quantitatively studied. At the same time, the chemical bonding situations of constituent H(D) atoms in different phases of ice have been numerically scaled. The calculated results show that the different lengths and directions of the hydrogen bonding O–H(D)...O (including two parts: H(D)–O and H(D)...O bonds) in the different phases of ice cause a large variation in the linear optical properties. Their characteristics found in single-crystalline phases of ice can be used as a guideline for the application of this special kind of functional chemical bond as linkage in materials design.

Hydrogen bonds play an important role in a wide variety of materials including crystalline, liquid, supramolecular and biological substances. One of the simplest hydrogen-bonded molecules is H<sub>2</sub>O, in the liquid phase or crystalline as ice. Although ice generally has a simple crystal structure, its hydrogen bonding results in unique properties. It can be regarded as a prototype system for other hydrogen-bonded materials, thus its structural and physical properties continue to be a major subject of active research in chemistry and physics. Applying different temperatures and pressures, more than 10 crystalline phases of ice have been found in a temperature range

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down to 77 K [1, 2]. This interesting polymorphism is mainly due to the hydrogen bonding and the structural versatility of H<sub>2</sub>O molecules. In the last decades, many efforts have been made to understand ice; some physical properties of these polymorphisms, e.g., dielectric properties [3–5], elastic properties [6], infrared absorption spectra [7] and Fermi resonance [8] have been measured, and most of the structures of ice are well established [9–14]. However, the macroscopic physical properties of these different phases of ice are not yet comprehensively correlated to their microscopic structural characteristics. Especially, the crystal structures of ice **VII** and **VIII** are very closely related [12–14]: the former has a cubic structure (space group  $Pn_3m$ ) and proton disorder whereas the latter is proton-ordered with a tetragonal structure ( $P4_2/nmc$ ), therefore, of the known phases, ice **VII** and **VIII** are particularly important for understanding the nature of the hydrogen bonding. Since these polymorphic forms of ice are constructed by the arrangement of the water molecules and by the hydrogen bonds between them, it is of interest to compare them on the basis of their dielectric properties. In this work, we therefore study dielectric properties of single-crystalline ice phases **I**, **II**, **III**, **VI**, **VII** and **VIII** from the chemical bond viewpoint, with the hope to present workers in this field more information towards a sound understanding of ice.

In addition, recent calculations of second harmonic generation coefficients of crystals with H–O and H...O bonds [15] have shown us that the hydrogen bonding O–H...O has special influence on these coefficients, therefore, its linear and nonlinear optical properties as well as bonding geometries should be paid distinct attention in nonlinear optical crystal designing [16]. Because of this important influence on the optical nonlinearities of inorganic crystals [16], it is helpful and necessary to investigate the dielectric properties of these hydrogen bonds in a prototype hydrogen-bonded system, i.e., the different phases of ice with their different structural characteristics. We believe that this task will contribute useful information for the application of hydrogen bonds in the field of crystal engineering.

For the quantitative calculations of the dielectric properties of the different phases of ice the chemical bond method [17] is applied which is based on the Phillips-Van Vechten (PV) dielectric theory of solids [18, 19] and the Levine bond charge model [20]. This method has been proven useful in numerous calculations of various physical properties of crystals, especially optical phenomena [21–23].

### Theory

Starting from the energy viewpoint of the bonding and antibonding states [24], Phillips found the relation  $E_g = E_h + iC$ , therefore, the en-

energy gap  $E_g$  between the bonding and the antibonding states can be written as [18]

$$(1) \quad E_g^2 = E_h^2 + C^2$$

which means that the total average energy gap may be separated into homopolar and heteropolar parts,  $E_h$ , and  $C$ . Figuratively speaking,  $E_h$  and  $C$  measure the average energy gaps due to covalent and ionic effects.

Macroscopic dielectric constant  $\varepsilon$ , refractive index  $n_r$  and dielectric susceptibility  $\chi$  are connected by

$$(2) \quad \varepsilon = n_r^2 = 1 + \chi$$

For a crystal composed of different types of chemical bonds (labeled  $\mu$ ) the total dielectric susceptibility  $\chi$  can be resolved into contributions  $\chi^\mu$  from the various types of bonds

$$(3) \quad \chi = \sum_{\mu} F^{\mu} \chi^{\mu} = \sum_{\mu} N_b^{\mu} \chi_b^{\mu}$$

where  $\chi^\mu$  is the total macroscopic susceptibility that a crystal composed entirely of bonds of type  $\mu$  would have.  $F^\mu$  is the fraction of bonds of type  $\mu$  composing the actual crystal,  $\chi_b^\mu$  is the susceptibility of a single bond of type  $\mu$ .

According to the PV theory [18, 19], the susceptibility  $\chi^\mu$  of the bond type  $\mu$  is given by

$$(4) \quad \chi^\mu = (4\pi)^{-1} (\hbar \Omega_p^\mu / E_g^\mu)^2$$

where  $\Omega_p^\mu$  is the plasma frequency [19].

When the detailed information of the complex crystal structure is given, the bond-valence equation [17] of this crystal can be obtained according to the chemical bonding structures of all constituent atoms. Any kind of chemical bond A-B in the multibond crystal  $A_a B_b D_d G_g \dots$  can be acquired by the following formula

$$(5) \quad [N(B - A)a / N_{CA}] A [N(A - B)b / N_{CB}] B$$

In this formula, A, B, D, G, ... represent different elements or different sites of the same element in the crystal formula, and  $a, b, d, g, \dots$  represent the numbers of the corresponding element,  $N(I-J)$  represents the number of I ion in the coordination group of J ion,  $N_{CA}, N_{CB}, \dots$  represent the nearest coordination number of each element in the crystal.

According to the deduced bond-valence equation, we can calculate each type of constituent chemical bond of the multibond crystal by using the chemical bond method [17]. Any bond of the type  $\mu$  assumed in a complex crystal consists of A and B ions, the number of valence electrons of A and B are  $Z_A^\mu$  and  $Z_B^\mu$ , the nearest coordination numbers of A and B ions are  $N_{CA}^\mu$



and  $N_{CB}^\mu$ , and the effective charge of each valence electron of A and B ions are  $q_A^\mu$  and  $q_B^\mu$ , respectively [17]. The effective valence electron of A and B ions may be calculated as

$$(6) \quad (Z_A^\mu)^* = Z_A^\mu q_A^\mu, \quad (Z_B^\mu)^* = Z_B^\mu q_B^\mu$$

Quantitatively, the values of  $E_h^\mu$  and  $C^\mu$  can be calculated from [17, 20]

$$(7) \quad E_h^\mu = 39.74/(d^\mu)^{2.48}$$

$$(8) \quad C^\mu = 14.4b^\mu \exp(-k_s^\mu r_0^\mu) [(1/n)(Z_A^\mu)^* - (Z_B^\mu)^*] / r_0^\mu$$

where  $n$  is the ratio of the numbers of the element B to A in Eq. (5).  $d^\mu$  is the bond length in Å,  $r_0^\mu = d^\mu/2$  is the average radius of A and B atoms,  $\exp(k_s^\mu r_0^\mu)$  the Thomas-Fermi screening factor.  $b^\mu$  is a correction factor and proportional to the  $p$ th power of the average coordination number  $N_c^\mu$ , the detailed expression of  $b^\mu$  is listed below [15]

$$(9) \quad b^\mu = \beta(N_c^\mu)^3$$

$$(10) \quad N_c^\mu = N_{CA}^\mu / (1 + n) + nN_{CB}^\mu / (1 + n)$$

The proportionality constant  $\beta$  is a parameter specific for the crystal regarded. For our calculations it is deduced using the known refractive index  $n_r$  of ice I.

According to Phillips' suggestion [18], one can define the fraction of ionic and covalent characteristic of the individual bonds,  $f_i^\mu$  and  $f_c^\mu$ , by

$$(11) \quad f_i^\mu = (C^\mu)^2 / (E_g^\mu)^2 \quad f_c^\mu = (E_h^\mu)^2 / (E_g^\mu)^2$$

Also, one can define the crystal covalency  $F_c$  by

$$(12) \quad F_c = \sum_{\mu} N_b^\mu f_c^\mu$$

$G_{ijk}^\mu$  is the geometrical characteristic of chemical bonds of type  $\mu$  which may be expressed as

$$(13) \quad G_{ijk}^\mu = 1/n_b^\mu \sum_{\lambda} \alpha_i^\mu(\lambda) \alpha_j^\mu(\lambda) \alpha_k^\mu(\lambda)$$

where the sum on  $\lambda$  is over all  $n_b^\mu$  bonds of type  $\mu$  in the unit cell, and  $\alpha_i^\mu(\lambda)$  is the direction cosine with respect to the  $i$ th coordinate axis of the  $\lambda$ th bond of type  $\mu$ .

## Results and Discussion

The condensed phases of ice are composed of polar H<sub>2</sub>O molecules which are hydrogen bonded by H...O bonds. As shown in Fig. 1, each H<sub>2</sub>O molecule has four nearest neighbors to which it is hydrogen bonded. Under variable pressure and temperature conditions, these molecules form single-crystalline phases of different structures. In each of these phases of ice, every oxygen

atom is surrounded by four hydrogen atoms which form a highly distorted tetrahedron around the central oxygen. Two of the hydrogen atoms can be regarded as tightly bound ( $\text{H}_2\text{O}$ ), two as loosely bound. Thus, as concerns the quasistatic bonding structure, each phase of ice consists of equal numbers of  $\text{H}-\text{O}$  and  $\text{H}\cdots\text{O}$ , i.e. short and long bonds.

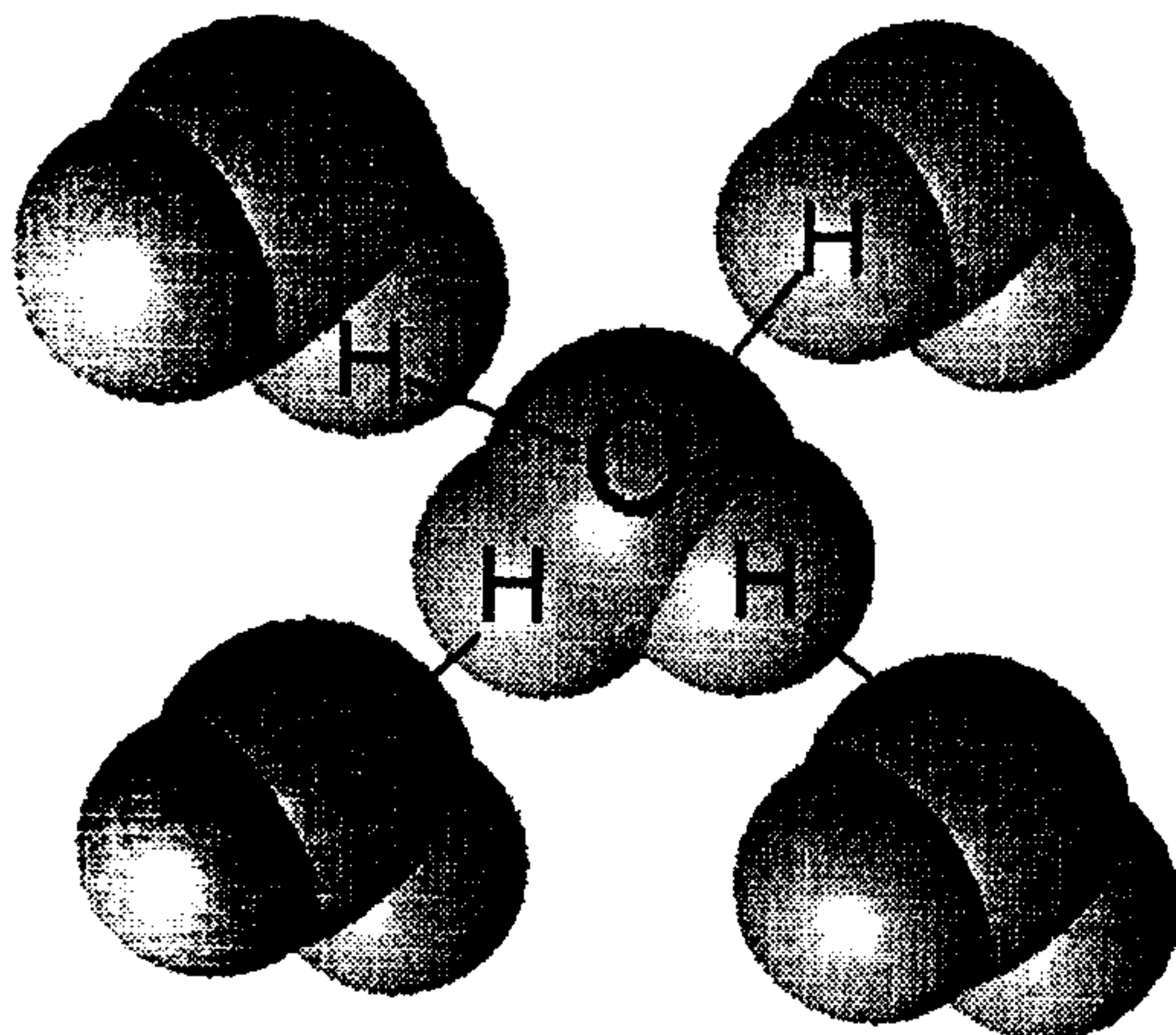
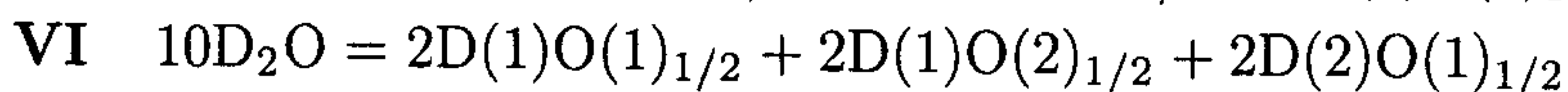
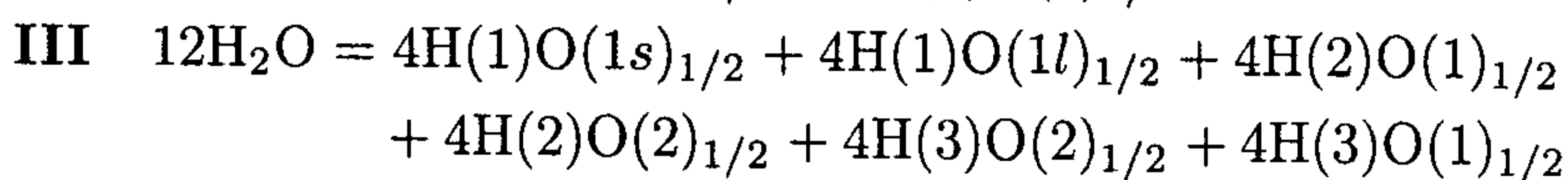
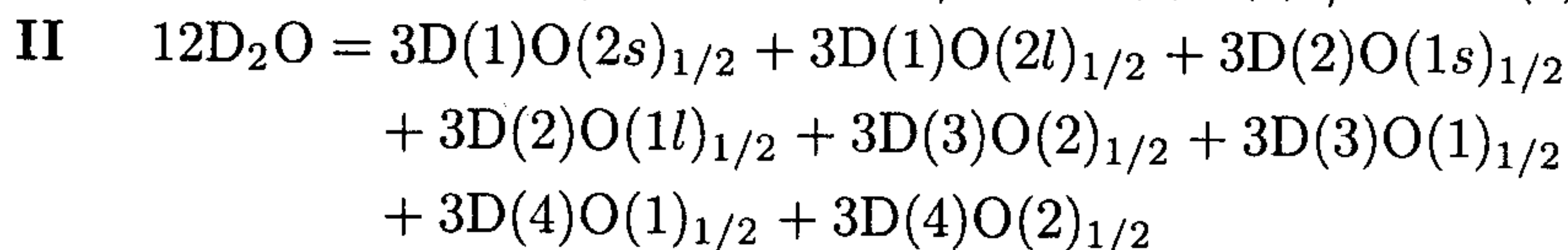
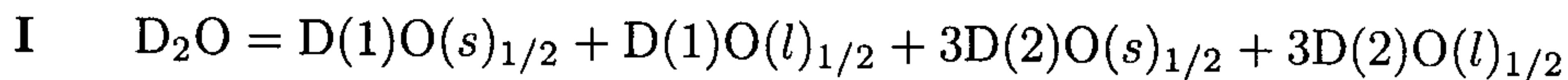


Fig. 1. Schematic drawing of the constituent chemical bonds of single-crystalline ice. Each  $\text{H}_2\text{O}$  molecule has four nearest neighbors and is hydrogen bonded to those (-). The oxygen atom of the  $\text{H}_2\text{O}$  molecule is coordinated to four hydrogen atoms (H), these hydrogen atoms form a highly distorted tetrahedron around the central oxygen atom

In the measured physical properties, no difference between  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  has been found in **VI** and **VII** phases of ice [6]. Therefore, in understanding the behavior of hydrogen bonds in these crystalline phases of ice, a distinction between  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  would not lead to pronounced differences. Also restricted by the available crystal structural data, only six phases are studied in the current work, i.e., the  $\text{D}_2\text{O}$  phases **I**, **II**, **VI**, **VII**, **VIII** and the  $\text{H}_2\text{O}$  phase **III**.

Based on the given crystal structural data [9–14] and the chemical bond method [17], the bond-valence equations of different phases of ice are listed as



$$+ 2D(2)O(2)_{1/2} + 2D(3)O(2s)_{1/2} + 2D(3)O(2l)_{1/2} \\ + 4D(4)O(2s)_{1/2} + 4D(4)O(2l)_{1/2}$$

$$\text{VII } 2D_2O = 2DO(s)_{1/2} + 2DO(l)_{1/2}$$

$$\text{VIII } 8D_2O = 8DO(s)_{1/2} + 8DO(l)_{1/2}$$

where  $s$  and  $l$  denote chemical bonds with short and long bond length, respectively.

TABLE 1

Chemical bond parameters, geometrical characteristics and linear optical properties of each type of bonds in different phases of ice. Numbers in parenthesis indicate the number of respective bonds per unit cell (at  $\pm$  values for each of the two cases).

Ice	A-B	$d^\mu/\text{\AA}$	$G_{33}^\mu$	$E_h^\mu/\text{eV}$	$C^\mu/\text{eV}$	$f_c^\mu$	$\chi^\mu$	$F_c$
I	D1-O	1.003	1.0000(2)	39.7105	17.8923	0.8312	0.5376	0.8320
	D1...O	1.7520	-1.0000(2)	9.8915	4.4057	0.8345	0.8926	
	D2-O	1.0071	0.0348(4)	39.0488	17.6807	0.8299	0.5439	
	D2...O	1.7581	$\begin{cases} 0.0391(2) \\ -0.03991(4) \end{cases}$	9.8066	4.3813	0.8336	0.8994	
II	D1-O2	0.9370	$\begin{cases} \pm 0.0885(1) \\ \pm 0.0542(1) \\ \pm 0.0047(1) \end{cases}$	46.6997	19.0094	0.8579	0.7764	
	D1...O2	1.8439	$\begin{cases} \pm 0.1076(1) \\ \pm 0.0411(1) \\ \pm 0.0079(1) \end{cases}$	8.7136	3.4327	0.8657	1.4523	
	D2-O1	0.9565	$\begin{cases} \pm 0.0314(1) \\ \pm 0.0007(1) \\ \pm 0.3428(1) \end{cases}$	44.3741	18.3052	0.8546	0.8038	
	D2...O1	1.8644	$\begin{cases} \pm 0.0084(1) \\ \pm 0.0299(1) \\ \pm 0.1349(1) \end{cases}$	8.4780	3.3772	0.8630	1.4928	
	D3-O2	1.0140	$\begin{cases} \pm 0.2028(1) \\ \pm 0.4398(1) \\ \pm 0.0005(1) \end{cases}$	38.3932	16.3157	0.8470	0.8787	
	D3...O1	1.8448	$\begin{cases} \pm 0.2909(2) \\ \pm 0.0001(1) \end{cases}$	8.7031	3.5342	0.8584	1.5149	
	D4-O1	0.9749	$\begin{cases} \pm 0.3933(1) \\ \pm 0.8578(1) \\ \pm 0.6138(1) \end{cases}$	42.3260	17.4607	0.8546	0.8178	

Table I contnd.

	D4...O2	1.8114	$\begin{cases} \pm 0.4787(1) \\ \pm 0.9409(1) \\ \pm 0.3696(1) \end{cases}$	9.1065	3.6582	0.8611	1.4631	
								0.8578
<b>III</b>	H1-O1	0.9149	$\begin{cases} 0.1573(4) \\ -0.1572(4) \end{cases}$	49.5475	20.0610	0.8592	0.7229	
	H1...O1	1.8478	$\begin{cases} 0.2834(4) \\ -0.2833(4) \end{cases}$	8.6681	3.4066	0.8662	1.3825	
	H2-O1	0.9397	$\sim 0.0000(8)$	46.3676	18.9736	0.8566	0.7499	
	H2...O2	1.8275	$\pm 0.0029(4)$	8.9088	3.5439	0.8634	1.3890	
	H3-O2	0.9584	$\begin{cases} 0.3103(4) \\ -0.3102(4) \end{cases}$	44.1562	18.3461	0.8528	0.7774	
	H3...O1	1.8502	$\begin{cases} 0.3578(4) \\ -0.3577(4) \end{cases}$	8.6402	3.4626	0.8616	1.4221	0.8600
<b>VI</b>	D1-O2	0.9675	0.7405(4)	43.1334	17.2143	0.8715	1.8748	
	D1...O1	1.8823	-0.3660(4)	8.2794	3.1798	0.8626	0.9943	
	D2-O1	0.9855	-0.2826(4)	41.2050	16.6712	0.8593	1.0285	
	D2...O2	1.8571	0.6100(4)	8.5608	3.2630	0.8731	1.8269	
	D3-O2	0.9786	-0.0007(4)	41.9302	16.5622	0.8650	0.9924	
	D3...O2	1.7532	-0.0001(4)	9.8747	3.7608	0.8733	1.7110	
	D4-O2	0.9230	$\pm 0.1020(4)$	48.4761	18.9355	0.8676	0.9273	
	D4...O2	1.8757	$\pm 0.0846(4)$	8.3519	3.1215	0.8774	1.7976	0.8695
<b>VII</b>	D-O	0.9607	$\pm 0.0793(1)$	43.8945	16.3880	0.8777	1.4404	
			$\pm 0.0792(1)$					
	D-O	1.9615	$\pm 0.2665(2)$	7.4750	2.5938	0.8925	2.8399	0.8851
<b>VIII</b>	D-O	0.9733	$\pm 0.2351(8)$	42.4987	16.0551	0.8751	1.3873	
	D...O	1.9196	$\pm 0.1882(8)$	7.8862	2.7880	0.8889	2.6437	0.8820

By using the above theories, chemical bond parameters, geometrical characteristics and linear optical properties of each type of constituent chemical bonds of the crystalline ice phases **I**, **II**, **III**, **VI**, **VII** and **VIII** are calculated and tabulated in Table 1. In these different phases of ice, the bond length  $d^\mu$  of D-O has a wide range from 0.9149 Å and to 1.0140 Å and  $d6\mu$  (D...O) from 1.7520 Å to 1.9615 Å. The geometrical characteristic  $G_{33}^\mu$  (the abbreviation for  $G_{333}^\mu$ ), which is specified as a measure for the alignment of the D-O and D...O bonds with respect to the crystalline  $z$ -axes, covers the whole possible range from -1 to +1. The fraction of covalency for the individual short bonds,  $f_c^\mu$  (D-O), ranges from 0.8299 to 0.8777, that for



the long bonds,  $f_c^\mu$  (D...O), from 0.8345 to 0.8925. These parameters and their variation determine the corresponding linear optical susceptibilities of the bonds which thus extend from 0.5376 to 1.8748 for  $\chi^\mu$  (D–O) and from 0.8926 to 2.8399 for  $\chi^\mu$  (D...O).

The interesting structure-property relationships show the versatility of the hydrogen bonding O–H(D)...O even if only one material – ice in different phases – is regarded. It is obvious that by a variation of the bond geometry, i.e. bond length and bond angle, the dielectric properties can be tuned in a relatively broad range. The various calculated values of  $G_{33}^\mu$  point out that besides straight ones also bent hydrogen bonds exist in several phases of ice proving the easily bending behavior of this type of bond.

All single-crystalline phases of ice, regarded here, are covalently bonded crystals, in other words, they belong to soft materials. According to their covalency, the phases can be ranked as

$$F_c : \text{I} < \text{II} < \text{III} < \text{VI} < \text{VIII} < \text{VII}.$$

TABLE 2  
Dielectric susceptibilities ( $n_r^2$ ) of different phases of ice

Ice	Temp./K <sup>(a)</sup>	Pressure/Kbar <sup>(a)</sup>	$n_r^2$	
			Theor. <sup>(b)</sup>	Expt.
I	223	0	1.720	1.72 <sup>(c)</sup>
II	123	0.001	2.150	
III	98	0.001	2.074	1.96 <sup>(c)</sup>
VI	225	11	2.388	2.19 <sup>(c,d)</sup>
VII	295	26	3.140	
VIII	269	28	3.015	

(a) Conditions of the crystalline ices (Refs. 9–14).

(b) This work, and  $n_r^2 = 1.72$  was used as the basis to calculate dielectric properties of the other phases of ice.

(c) References [3–5].

(d) Reference [6].

The dielectric susceptibilities of the ice phases are summarized in Table 2 together with their physical conditions (temperature and pressure). The comparison between calculated and experimental data, given for some phases, shows a reasonably good agreement. Therefore, the parameters calculated for the various bonds can be used as a meaningful basis for theoretical discussions. A ranking of the phases with respect to the magnitude of the dielectric susceptibility yields nearly the same order as for the covalency

$$n_r^2 \quad \text{I} < \text{III} < \text{II} < \text{VI} < \text{VIII} < \text{VII}.$$

hinting a close connection between these two properties for hydrogen bonds.



### Conclusions

Chemical bond properties and optical frequency dielectric constants of single-crystalline phases of ice I, II, III, VI, VII and VIII are quantitatively investigated using the chemical bond method. The optical dielectric constants ( $n_r^2$ ) are theoretically calculated, based on crystal structural data of these ice phases. The theoretical results point out that O–H...O hydrogen bonds are functional chemical bonds which have interesting characteristics variable in a wide range. Hydrogen bonds thus prove to be important building blocks in all areas of materials design. The versatile bond geometry (especially direction and angle) makes them especially useful for crystal design in the field of nonlinear optical applications.

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