Chemical Bond Analysis on Second Order Nonlinear Optical Properties of Na₂SeO₄·H₂SeO₃·H₂O

by

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Summary. Second order nonlinear optical properties of Na₂SeO₄·H₂SeO₃·H₂O crystals with hydrogen bonds have been quantitatively studied from the chemical bond viewpoint. Contributions of all constituent chemical bonds to the total linear and nonlinear optical properties of this crystal at λ = 0.8716 μm have been determined. The chemical bond method quantitatively expresses those contributions. The current calculation shows that hydrogen bonds play a very important role in contributing to the total linear and nonlinear optical properties of Na₂SeO₄·H₂SeO₃·H₂O. Our results show that the coordination environments of the hydrogen bonds strongly affect their contributions to the optical response of the host crystal. Therefore, a successful selection of the excellent coordination environment of hydrogen bonds would help us to find good materials suitable for efficient second harmonic generation.

The comprehensive understanding of the origin of the optical nonlinearity of nonlinear optical (NLO) crystalline materials has been one of the most interesting subjects in the area of nonlinear optics which has been intensively pursued by many groups in this area. Various theoretical methods starting from Miller’s empirical rule up to the current first-principles calculations – at different approximation levels and from different starting-points [1-6] – have been applied to this interesting subject.

Hydrogen bonds in general exist widely in solids, not only in almost all organic but also in many inorganic crystals. Previous studies have shown that the hydrogen bonds are a robust motif which can serve as an important constituent part of solids but nevertheless offers considerable geometrical di-

Key words: theoretical analysis, SHG, NLO, hydrogen bond, Na₂SeO₄·H₂SeO₃·H₂O.
versity [7]. The combination of robustness and geometrical flexibility offers a wide scope for the construction of a range of different "molecular" packing arrangements based on the hydrogen bonds. The previous works concerning the calculation of second harmonic generation coefficients of crystals with hydrogen bonds, such as HIO₃, NH₄H₂PO₄, K[B₅O₆(OH)₄]·2H₂O and K₂La(NO₃)₅·2H₂O, have shown us that the hydrogen bonding is a special kind of functional chemical bonds, whose linear and nonlinear optical properties as well as chemical bonding geometries should be paid much attention in the NLO crystal designing [7]. At the same time, we also quantitatively explained the important effect of the hydrogen bonds on optical nonlinearities of some inorganic crystals [7]. Therefore, it is quite helpful and necessary for us to investigate the behaviors of these hydrogen bonds in different hydrogen-bonded systems, especially for the inorganic crystallized solids.

In previous works, inorganic molecular crystals Na₂SeO₄·H₂SeO₃·H₂O with high optical quality have been grown and experimentally studied at different wavelengths [8-10]. Experimental results show that such a molecular crystal exhibits various excellent features, such as a high transparency between 0.400 and 1.100 μm, a short cut-off wavelength, suitable mechanical hardness and good optical damage resistance, etc. [9, 10]. Thus, it is very interesting to study the optical behaviors of hydrogen bonds in such an inorganic molecular crystal with potential applications. We also believe that the current work can provide us some helpful information on the successful search for new practically applicable inorganic molecular crystals with hydrogen bonds.

The Chemical Bond Method

Chemical bond and related chemical bond terms are one of the explicit languages that have been preferred to express the interaction of two atoms or ions (e.g., A and B), which are separated from each other by about the sum of their atomic or ionic radii (i.e., \( r_A + r_B \)), where \( r_A \) and \( r_B \) can be regarded as their covalent radii or ionic radii, respectively). The dielectric theory of solids proposed by Phillips and van Vechten (also called as PV theory) [11, 12], the bond-charge model found by Levine [2, 13], as well as the bond-valence model perfected by Brown [14], show us that chemical bonding behaviors and related bond parameters of a crystal are the important indices that allow us to properly express complicated interactions among all constituent atoms or ions. Chemical bond is thus one of the effective starting-points to understand the complex relationship between the composition, crystallographic structure, chemical and physical properties of condensed matters. Therefore, to study the properties of constituent chemical bonds in a crystal is one of the most fundamental methods to understand
its various macroscopic properties. The method is also well applicable to the prediction of properties of new crystals and the designing of new types of functional crystal materials.

The original PV theory can successfully deal with chemical bond properties of binary crystals, e.g., \( A^N B^{8-N} \) type crystals [11, 12] formed from \( A \) and \( B \) atoms with valencies \( N \) and \( 8-N \), respectively. Levine improved this theory and made it applicable for multibond crystals [2, 13]. Yet, Levine's bond charge model can successfully deal only with \( ABX_2 \) type semiconductors, but is not applicable to other multibond crystals. As shown in our previous work [6, 15], the method can be generalized. The chemical bond method regards a complex crystal as the combination of all constituent chemical bonds. That is to say, a multibond crystal can be theoretically decomposed into various single bonds corresponding to all constituent atoms or ions, according to their detailed chemical bonding structures. Any kind of chemical bond like \( A-B \) in the multibond crystal \( A_a B_b D_d G_g \ldots \) can be expressed as

\[
\frac{N(B-A)a}{N_{CA}} AB \frac{N(A-B)b N_{CA}}{N(B-A)a N_{CB}}
\]

where \( A, B, D, G, \ldots \) represent different elements or different sites of an element in the crystal formula, and \( a, b, d, g, \ldots \) represent the quantities of the corresponding element, \( N(B-A) \) represents the number of \( B \) ions in the coordination group of the \( A \) ion, and \( N_{CA} \) represents the total number of ions that can be considered as the bonded ions in the first coordination sphere of ion \( A \). On the basis of this idea, the physical property of an assigned multibond crystal is ascribed to contributions from all contained chemical bonds, which is also what Levine's model shows us. During the decomposition of a multibond crystal into its constituent single chemical bonds, the charge-neutrality principle in any crystal formula should be obeyed, and each atom shares its valence as equally as possible among the bonds that it forms [14]. Therefore, the following two network equations (the same meaning as what Brown proposed [14]) should be always kept:

\[
\sum_B s_{AB} = V_A, \quad \sum_{\text{loop}} s_{AB} = 0
\]

where each atom \( A \) in the corresponding lattice is assigned a formal charge equal to its atomic valence or oxidation state \( (V_A) \) and each bond between atoms \( A \) and \( B \) is assigned a bond valence \( (s_{AB}) \). The sum of the bond valences around any loop (taking into account the direction of the bonds) is zero.

The above idealization makes PV theory and Levine's model successfully applicable to any kind of multi-bond crystals. As shown in the previous publications [6, 15], the chemical bond method regards certain macroscopic
physical properties of a crystal as the combination of the contributions of all constituent chemical bonds. Therefore, the linear and nonlinear optical properties of any crystal can be calculated using the appropriate geometric sum of the respective properties of its constituent chemical bonds.

In a multi-bond crystal, its linear optical property $\chi$ can be ascribed to contributions $\chi^\mu$ from the various types of bonds

$$\chi = \sum_\mu F^\mu \chi^\mu = \sum_\mu N_b^\mu \chi_b^\mu$$

where $F^\mu$ is the fraction of bonds of type $\mu$ composing the actual crystal. $N_b^\mu$ is the number of chemical bonds of type $\mu$ per cm$^3$. $\chi_b^\mu$ is the susceptibility of a single bond of type $\mu$.

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

where $\Omega_p^\mu$ is the plasma frequency, $E_g^\mu$ is the average energy gap between the bonding and the antibonding states, $(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2$ (Refs. [2, 6, 13, 15]). Furthermore, the fractions of ionic and covalent characteristics of the individual bonds, $f_i^\mu$ and $f_c^\mu$, are defined by

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

Chemical bond nonlinearities are evaluated on the basis of linear results by means of a geometrical addition of nonlinear contributions $d_{ij}^\mu$ of all bonds $\mu$ [2]. The corresponding macroscopic property is the NLO tensor coefficient $d_{ij}$ that can be expressed as

$$d_{ij} = \sum_\mu \left\{ \frac{G_{ij}^\mu N_b^\mu (0.5) \left\{ [(Z_A^\mu)^* + n(Z_B^\mu)^*] / [(Z_A^\mu)^* - n(Z_B^\mu)^*] \right\} f_i^\mu (\chi_b^\mu)^2}{d^\mu q^\mu} + \frac{G_{ij}^\mu N_b^\mu s(2s - 1) [r_0^\mu / (r_0^\mu - r_c^\mu)]^2 f_c^\mu (\chi_b^\mu)^2 \rho^\mu}{d^\mu q^\mu} \right\},$$

where $G_{ij}^\mu$ is the geometrical contribution of chemical bonds of type $\mu$

$$G_{ij}^\mu = 1 / n_b^\mu \sum_\lambda \alpha_i^\mu(\lambda) \alpha_i^\mu(\lambda).$$

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

$q^\mu$ is the bond charge of the $\mu$th bond

$$q^\mu = (n_e^\mu)^* [1 / (\chi^\mu + 1) + K f_c^\mu] e$$

$$K = 2 F_c - 1.1 \quad \text{and} \quad F_c = \sum_\mu N_b^\mu f_c^\mu$$

where $n_e^\mu$ is the effective valence electrons per $\mu$ bond.
$\rho^\mu$ is the difference in the atomic sizes, and $r^\mu_c$ is the core radius.

All of the above parameters can be quantitatively deduced from the detailed chemical bonding structures of all constituent atoms, as described in previous publications [6, 15].

Results and Discussion

Na$_2$SeO$_4$·H$_2$SeO$_3$·H$_2$O crystals crystallize in the orthorhombic space group $Cmce_{21}$ with unit cell dimensions $a = 6.915$ Å, $b = 11.193$ Å, and $c = 9.615$ Å. Each unit cell contains four molecules [8]. Structurally, the Na$_2$SeO$_4$·H$_2$SeO$_3$·H$_2$O crystal is built up of sodium cations Na$^+$, selenate anions (SeO$_4$)$^{2-}$, molecules of selenious acid H$_2$SeO$_3$ and crystal water H$_2$O. From the crystallographic data of the Na$_2$SeO$_4$·H$_2$SeO$_3$·H$_2$O single crystal [8], we can see that the Na$^+$ cations occupy general positions 8b, whereas the (Se(1)O(1,2,3,3))$^{2-}$ (i.e., (SeO$_4$)$^{2-}$) anions, H(4)$_2$Se(2)O(4,4,5)$_3$ (i.e., H$_2$SeO$_3$) molecules and H(6,61)O(6) (i.e., H$_2$O) crystal water lie in the symmetry planes perpendicular to the $a$ crystallographic axis of the crystal. The atomic stacking situation is sketched in Fig. 1. Different from the Na$^+$ cations, the (Se(1)O$_4$)$^{2-}$ anions and H(4)$_2$Se(2)O$_3$ molecules occupy $C_s$ sites and form infinite chains through hydrogen bonds, O(4)·H(4)·O(3). H(6,61)O(6) crystal water molecules on $C_s$ sites are attached to the H(4)$_2$Se(2)O(4,4,5)$_3$ molecules by hydrogen bonds, O(6)·H(6)·O(5). Structurally, these hydrogen bonds play a very important role in the linkage of constituent groups. Therefore, it is interesting to study their optical behavior in Na$_2$SeO$_4$·H$_2$SeO$_3$·H$_2$O.

From the complete crystal structure [8], the chemical bonding situations of all constituent atoms or ions in Na$_2$SeO$_4$·H$_2$SeO$_3$·H$_2$O can be derived, as stated above. On the basis of this structural information the decomposition formula of Na$_2$SeO$_4$·H$_2$SeO$_3$·H$_2$O can be written as

(7)  \[
\begin{align*}
\text{Na}_2\text{SeO}_4 \cdot \text{H}_2\text{SeO}_3 \cdot \text{H}_2\text{O} & = \frac{1}{3}\text{NaO}(1)_2 + \frac{1}{3}\text{NaO}(2)_2 + \frac{1}{3}\text{NaO}(3)_2 + \frac{1}{3}\text{NaO}(4)_2 \\
& + \frac{1}{3}\text{NaO}(5)_3/2 + \frac{1}{3}\text{NaO}(6)_3/2 + \frac{1}{4}\text{Se}(1)\text{O}(1)_{4/3} \\
& + \frac{1}{4}\text{Se}(1)\text{O}(2)_{4/3} + \frac{1}{4}\text{Se}(1)\text{O}(3)_{4/3} + \text{H}(4)\text{O}(3)_{2/3} \\
& + \text{H}(4)\text{O}(4)_{2/3} + \frac{2}{3}\text{Se}(2)\text{O}(4) + \frac{1}{3}\text{Se}(2)\text{O}(5)_{3/4} \\
& + \text{H}(6)\text{O}(5)_{1/2} + \text{H}(6)\text{O}(6)_{1/2} + \text{H}(61)\text{O}(6)_{1/4}
\end{align*}
\]

which clearly describes the detailed chemical bonding structure (i.e., the structural linkage) of all constituent atoms in Na$_2$SeO$_4$·H$_2$SeO$_3$·H$_2$O. This
Fig. 1. The occupations of lattice sites of all constituent atoms of one Na$_2$SeO$_4$·H$_2$SeO$_3$·H$_2$O crystal formula in the 3D crystallographic frame, projected onto the ab plane. Large light spheres: oxygen, small light spheres: hydrogen, large dark spheres: selenium, small dark spheres: sodium.

decomposition finally leads to the empirical calculation of macroscopic optical properties of the whole crystal on the basis of microscopic contributions of the constituent chemical bonds.

Starting from the chemical bonding structures of all constituent atoms in the Na$_2$SeO$_4$·H$_2$SeO$_3$·H$_2$O single crystal, we have quantitatively calculated chemical bond parameters of all constituent chemical bonds and further their quantitative contributions to the total linear and nonlinear optical properties of the crystal. The calculated results are summarized in Table 1. In the present calculation the refractive index $n_x = 1.6006$ at 0.8716 μm [9, 10] has been introduced as a reference to quantitatively determine the related chemical bond parameters.

The restrictions imposed by the point group of the crystal (mm2) yield an NLO tensor for Na$_2$SeO$_4$·H$_2$SeO$_3$·H$_2$O crystals of the general form [16]

$$
d = \begin{pmatrix}
0 & 0 & 0 & 0 & d_{15} & 0 \\
0 & 0 & 0 & d_{24} & 0 & 0 \\
d_{31} & d_{32} & d_{33} & 0 & 0 & 0
\end{pmatrix}
$$

According to the Kleiman symmetry conditions on NLO tensors [17], the
five nonzero tensor components reduce to three independent coefficients \( d_{31}, d_{32}, d_{33} \).

**Table 1**

Chemical bond parameters of all constituent chemical bonds of \( \text{Na}_2\text{SeO}_4 \cdot \text{H}_2\text{SeO}_3 \cdot \text{H}_2\text{O} \) crystals at 0.8716 \( \mu \text{m} \) \( d_{ij}^{\mu} \) are given in pm/V

<table>
<thead>
<tr>
<th>Chemical bond</th>
<th>( d_{ij}^{\mu} (\text{Å}) )</th>
<th>( f_{ij}^{\mu} )</th>
<th>( \chi^{\mu} )</th>
<th>( q^{\mu}/\epsilon )</th>
<th>( G_{31}^{\mu} )</th>
<th>( d_{31}^{\mu} )</th>
<th>( G_{32}^{\mu} )</th>
<th>( d_{32}^{\mu} )</th>
<th>( G_{33}^{\mu} )</th>
<th>( d_{33}^{\mu} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-O(1)</td>
<td>2.407</td>
<td>0.324</td>
<td>0.880</td>
<td>0.386</td>
<td>0.256</td>
<td>-0.125</td>
<td>0.101</td>
<td>-0.049</td>
<td>0.088</td>
<td>-0.043</td>
</tr>
<tr>
<td>Na-O(2)</td>
<td>2.339</td>
<td>0.329</td>
<td>0.845</td>
<td>0.393</td>
<td>-0.314</td>
<td>0.149</td>
<td>-0.062</td>
<td>0.029</td>
<td>-0.269</td>
<td>0.127</td>
</tr>
<tr>
<td>Na-O(3)</td>
<td>2.472</td>
<td>0.318</td>
<td>0.914</td>
<td>0.379</td>
<td>0.006</td>
<td>-0.003</td>
<td>0.365</td>
<td>-0.185</td>
<td>0.114</td>
<td>-0.058</td>
</tr>
<tr>
<td>Na-O(4)</td>
<td>2.481</td>
<td>0.318</td>
<td>0.919</td>
<td>0.378</td>
<td>-0.007</td>
<td>0.004</td>
<td>-0.328</td>
<td>0.167</td>
<td>-0.063</td>
<td>0.032</td>
</tr>
<tr>
<td>Na-O(5)</td>
<td>2.388</td>
<td>0.189</td>
<td>0.444</td>
<td>0.480</td>
<td>-0.276</td>
<td>0.004</td>
<td>-0.091</td>
<td>0.001</td>
<td>-0.106</td>
<td>0.002</td>
</tr>
<tr>
<td>Na-O(6)</td>
<td>2.418</td>
<td>0.187</td>
<td>0.451</td>
<td>0.477</td>
<td>0.305</td>
<td>-0.004</td>
<td>0.065</td>
<td>-0.0009</td>
<td>0.299</td>
<td>-0.004</td>
</tr>
<tr>
<td>Se(1)-O(1)</td>
<td>1.628</td>
<td>0.129</td>
<td>1.939</td>
<td>2.393</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.329</td>
<td>-0.043</td>
<td>-0.058</td>
<td>-0.008</td>
</tr>
<tr>
<td>Se(1)-O(2)</td>
<td>1.601</td>
<td>0.130</td>
<td>1.889</td>
<td>2.432</td>
<td>0.000</td>
<td>0.000</td>
<td>0.004</td>
<td>0.0004</td>
<td>0.995</td>
<td>0.124</td>
</tr>
<tr>
<td>Se(1)-O(3)</td>
<td>1.656</td>
<td>0.161</td>
<td>2.120</td>
<td>1.833</td>
<td>-0.203</td>
<td>-0.058</td>
<td>-0.071</td>
<td>-0.020</td>
<td>-0.027</td>
<td>-0.008</td>
</tr>
<tr>
<td>H(4)-O(3)</td>
<td>1.776</td>
<td>0.444</td>
<td>2.448</td>
<td>0.708</td>
<td>0.008</td>
<td>0.055</td>
<td>0.222</td>
<td>1.573</td>
<td>0.626</td>
<td>4.439</td>
</tr>
<tr>
<td>H(4)-O(4)</td>
<td>0.988</td>
<td>0.614</td>
<td>1.006</td>
<td>1.174</td>
<td>-0.296</td>
<td>-0.482</td>
<td>-0.065</td>
<td>-0.106</td>
<td>-0.329</td>
<td>-0.536</td>
</tr>
<tr>
<td>Se(2)-O(4)</td>
<td>1.740</td>
<td>0.361</td>
<td>5.279</td>
<td>1.127</td>
<td>0.271</td>
<td>-1.266</td>
<td>0.101</td>
<td>-0.473</td>
<td>0.117</td>
<td>-0.545</td>
</tr>
<tr>
<td>Se(2)-O(5)</td>
<td>1.666</td>
<td>0.160</td>
<td>1.611</td>
<td>2.166</td>
<td>0.000</td>
<td>0.000</td>
<td>0.349</td>
<td>0.024</td>
<td>0.077</td>
<td>0.005</td>
</tr>
<tr>
<td>H(6)-O(5)</td>
<td>2.170</td>
<td>0.254</td>
<td>1.247</td>
<td>0.642</td>
<td>0.000</td>
<td>0.000</td>
<td>0.251</td>
<td>0.156</td>
<td>0.586</td>
<td>0.364</td>
</tr>
<tr>
<td>H(6)-O(6)</td>
<td>0.964</td>
<td>0.239</td>
<td>0.483</td>
<td>1.889</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.238</td>
<td>-0.017</td>
<td>-0.016</td>
<td>-0.001</td>
</tr>
<tr>
<td>H(61)-O(6)</td>
<td>0.968</td>
<td>0.789</td>
<td>2.828</td>
<td>1.499</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.279</td>
<td>-1.669</td>
<td>-0.531</td>
<td>-3.182</td>
</tr>
</tbody>
</table>

On the basis of the geometrical sum of all nonlinear contributions \( d_{ij}^{\mu} \) of constituent chemical bonds, the three independent second order NLO tensor coefficients have been quantitatively calculated. The final results and available experimental data are listed in Table 2, from which we can see the current work reasonably explain us the optical behavior of \( \text{Na}_2\text{SeO}_4 \cdot \text{H}_2\text{SeO}_3 \cdot \text{H}_2\text{O} \) crystals.

**Table 2**

Comparison between experimental and theoretical results on second order NLO tensor coefficients of \( \text{Na}_2\text{SeO}_4 \cdot \text{H}_2\text{SeO}_3 \cdot \text{H}_2\text{O} \) crystals at 0.8716 \( \mu \text{m} \) \( d_{ij} \) are given in pm/V

<table>
<thead>
<tr>
<th>NLO tensors ( d_{ij} )</th>
<th>Expt.</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{31} )</td>
<td>0.62</td>
<td>-1.726</td>
</tr>
<tr>
<td>( d_{32} )</td>
<td></td>
<td>-0.612</td>
</tr>
<tr>
<td>( d_{33} )</td>
<td>0.71</td>
<td>0.709</td>
</tr>
</tbody>
</table>
It should be noted that in the present calculation scheme, an assumption introduced by Levine [2] is still used: $\beta_{||} \gg \beta_{\perp}$ and $\beta_{\perp} = 0$. Applying this assumption, certain contributions from bonds, which are oriented parallel to one of the crystallographic planes, are neglected. In this case, electric field directions perpendicular to the respective plane are also perpendicular to the bond, resulting in a vanishing second harmonic polarization. This case can be found in our calculation for the $d_{31}$ tensor. As shown in Table 1, when $E_\omega \parallel a$ axis (i.e., $E_\omega \perp bc$ plane), the geometrical factors $G_{31}$ for bonds lying in the $bc$ plane are zero, and the polarization due to the $\beta_{||}$ part vanishes. The contributions from the $\beta_{\perp}$ part are not included following Levine's assumption. This can be regarded as the reason for the large difference between the calculated $d_{31}$ and the observed one.

From Table 1 we can see that various H–O bonds play an important role in contributing to the total linear and nonlinear optical properties of the Na$_2$SeO$_4$·H$_2$SeO$_3$·H$_2$O crystal, though the Se–O bonds deliver the dominant contributions to the total linear optical properties and the $d_{31}$ NLO tensor element. It is obvious that hydrogen bonds play a very important role not only in the structural linkage but in contributions to the optical behaviors of the host crystal. Unfortunately, there are strong cancellations among contributions from various H–O bonds. If such cancellations can be suppressed, strong second order NLO responses may be expected from such a molecular crystal. This problem shows that one has to pay much attention to the coordination environment of all hydrogen atoms. The interactions between different H$^+$ ions and other anionic groups will finally determine the spatial characteristics of constituent hydrogen bonds. In order to successfully explore the excellent features of hydrogen bonds, the key is to construct an ideal coordination environment for these functional chemical bonds.

Conclusion

From the chemical bond viewpoint, we have analyzed second order nonlinear optical responses of the Na$_2$SeO$_4$·H$_2$SeO$_3$·H$_2$O single crystal at $\lambda = 0.8716$ $\mu$m. The previous experimental measurements and the current calculations show that such a compound may be a potential inorganic molecular crystal material for nonlinear optical applications. Constituent hydrogen bonds in such a crystal have been studied, the calculations on their optical contributions to the optical behavior of this crystal show us their important role in the host crystal. The present work also shows that the spatial characteristics of constituent hydrogen bonds is one of the important factors that restrict the contributions from these functional bonds to the total optical response of the host crystal. Therefore, we expect to modify existing practical NLO crystalline solids with hydrogen bonds by modeling their coordination
environments, so that large NLO-SHG responses can be finally expected. The current work is a good example in this regard.

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