# VIBRONIC THEORY OF HETEROLIGAND SYSTEMS APPLIED TO STRUCTURAL PHASE TRANSITIONS IN SOME H-BONDED MATERIALS

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**Abstract.** An approach to H-bonded molecular crystals, such as KDP, etc. is presented, which is based on the vibronic theory of ligand substitution effects. Any redistribution of protons over their potential energy minima is treated as a substitution $O_{O-H} \rightleftarrows O_{O...H}$ in the molecular building units of a crystal. The pseudospin formalism is applied for the description of proton distributions. The Ising form of the total energy of the crystal is obtained. The Ising model parameters are expressed in terms of the MOs of the molecular building units of the crystal and can be estimated from quantum-chemical calculations. This approach allows one to give reasonable estimations of the Ising parameters and to explain the main chemical trends in ferroelectric properties for the KDP-family materials. Its application to the squaric acid is also discussed.

**Key words:** H-bonded crystals, order–disorder phase transitions.

The ferroelectric properties of H-bonded materials, such as KDP ($KH_2PO_4$), $H_2SQ$ ($H_2C_4O_4$), etc. have been thoroughly studied [1, 2]. As to the theoretical models used for their microscopic description, they cannot be regarded as fully satisfactory, mainly due to the presence of some fitting parameters [2]. Therefore, it is purposeful to develop other approaches where the major parameters of the theory can be evaluated in terms of the composition and the electronic structure of the material under study. In this connection the vibronic theory of structural phase transitions [3, 4] and its application to H-bonded crystals [5–8] should be mentioned. In the latter, the origin of order–disorder phase transitions in KDP-like crystals is assumed to involve the pseudo-Jahn–Teller effect for their tetrahedral building units. Here a different approach to H-bonded materials is discussed, which is based on the vibronic theory of heteroligand systems [9] and the results of quantum-chemical calculations (see also [10]).

The effects of the ligand substitution $ML_n \rightarrow ML_{n-k}XY...Z$ are treated in this theory, and the perturbational treatment is applied for determination of the adiabatic potential for the heteroligand system $ML_{n-k}XY...Z$. The adiabatic potential of the homoligand system $ML_n$ is regarded as a zero approximation and the perturbation operator has a form:

$$\mathcal{H} = \mathcal{H}_S + V, \qquad V = \Sigma_v \, (\partial \mathcal{H}/\partial Q_v)_0 Q_v + ... \, . \qquad (1)$$

Here $V$ is the vibronic coupling operator for $ML_n$ and $\mathcal{H}_S$ is the "substitution operator" describing the ligand replacement effect on the electronic subsystem of $ML_n$ in its equilibrium molecular geometry.

The case of closed electronic shells of $ML_n$ and $ML_{n-k}XY...Z$ is considered. Then for the lowest sheet of the adiabatic potential of $ML_{n-k}XY...Z$ we have

$$E_1(Q) = 1/2 \, \Sigma_v K_v Q_v^2 +$$

$$+ S_0 - 2 \, \Sigma_{m \neq n} (S_{nm}^2/\omega_{nm}) - 4 \, \Sigma_{m \neq n} \Sigma_v (S_{nm} A_{nm}^v/\omega_{nm}) Q_v. \qquad (2)$$

In Eq. (2), $E_1(Q)$ is the total energy of $ML_{n-k}XY...Z$ as a function of the normal (symmetry) coordinates $Q_v$ of $ML_n$, and $K_v$ and $A_{nm}^v$ are the force and orbital linear vibronic constants of $ML_n$, respectively. The $\omega_{nm}$ are the energy gaps between the occupied $(\psi_n)$ and the unoccupied $(\psi_m)$ MOs of $ML_n$, and $S_{nm}$ denotes the matrix elements of the one-electron substitution operator $H_S$ in this MOs basis set. Therefore one has

$$A_{nm}^v = \langle \psi_n | \, (\partial H/\partial Q_v)_0 \, | \psi_m \rangle, \qquad S_{nm} = \langle \psi_n | H_S | \psi_m \rangle, \qquad (3)$$

where $H$ is the one-electron Hamiltonian of $ML_n$ and $\psi_n$, $\psi_m$ are its eigenfunctions. It is easy to obtain the difference between the total energies of $ML_{n-k}XY...Z$ and $ML_n$ in their equilibrium configurations $Q^f$ and $Q^0 = 0$, respectively. Using the conditions $\partial E_1(Q)/\partial Q_v = 0$, one has from Eq. (2)

$$E_1(Q^f) - E(0) =$$

$$= S_0 - 2 \, \Sigma_{m \neq n} S_{nm}^2/\omega_{nm} - 4 \, \Sigma_v K_v^{-1} (\Sigma_{m \neq n} S_{nm} A_{nm}^v/\omega_{nm})^2. \qquad (4)$$

The analysis of the H-bonded molecular crystals under study is based on Eq. (4). Let us consider, for instance, the KDP-family crystals (Fig. 1). The $AO_4$ tetrahedra (A = P, As) in their lattices are bounded via H-bonds. Each oxygen atom of any tetrahedron exists in one of the two states because the proton's potential curve has two equivalent minima: these states are $O_{O-H}$ and $O_{O...H}$. Any proton redistribution over their equilibrium sites on H-bonds can be treated as an $O_{O-H} \rightleftarrows O_{O...H}$ replacement in the apices of these $AO_4$ tetrahedra. This "substitution" has a cooperative character because the $O_{O-H} \rightleftarrows O_{O...H}$ transformation in a

given apex of any tetrahedron results in reverse transformation in the neighbouring tetrahedron:

$$\diagup A—O—H\ldots O—A\diagdown \rightleftharpoons \diagup A—O\ldots H—O—A\diagdown$$
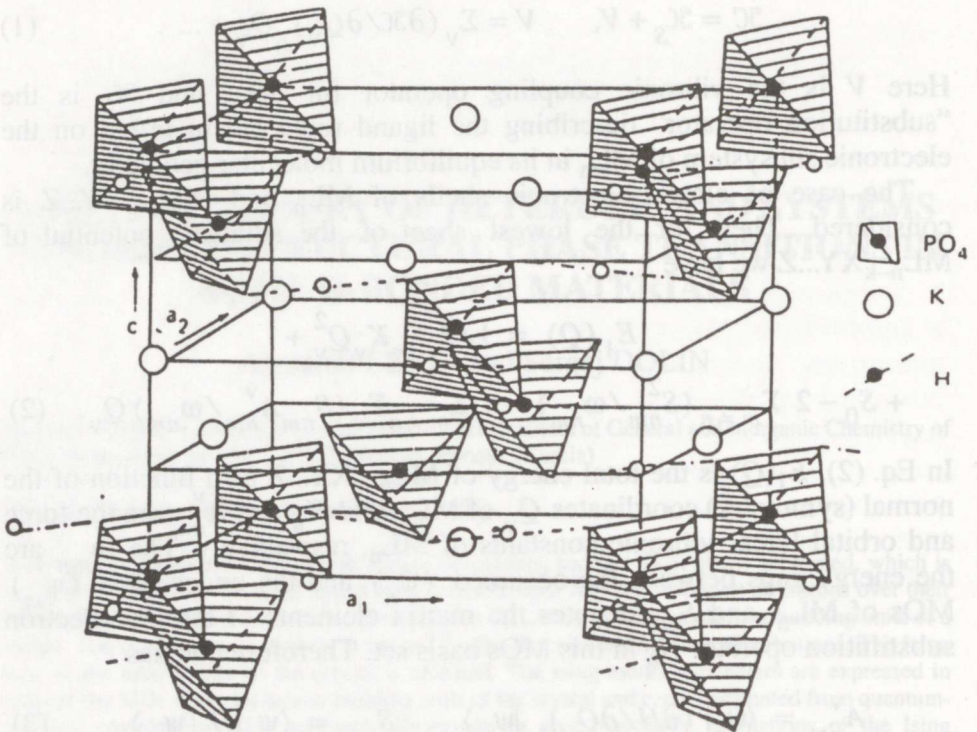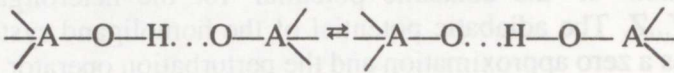


Fig. 1. The structure of a KDP crystal.

For the protons on the H-bonds of a crystal it is useful to apply pseudospin formalism. In this formalism two values $\sigma_j = \pm 1$ of the pseudospin $\sigma_j$ correspond to two equilibrium proton positions on the $j$th H-bond. Then one can obtain the Ising form of the total energy expression of a crystal, i.e.

$$E = C - 1/2 \sum_{i \neq j} J_{ij} \sigma_i \sigma_j \tag{5}$$

By using Eq. (4) the Ising model parameters $J_{ij}$ from Eq. (5) can be expressed in terms of the electronic structure of the material.

Let us consider the $AO_4$ tetrahedron MOs in the basis of the valence ns, np(A) AOs and σ AOs of oxygen atoms (Fig. 2). The MO scheme is shown for the hypothetical proton positions at the H-bond centres (this scheme takes into account the realistic $S_4$ symmetry of the $AO_4(H)_4$ moiety in the crystal rather than the $T_d$ one. The b–e splitting is assumed to be small as compared with the gap ($2\Delta$) between the highest occupied b, e MOs (HOMO) and the lowest unoccupied a* MO (LUMO).
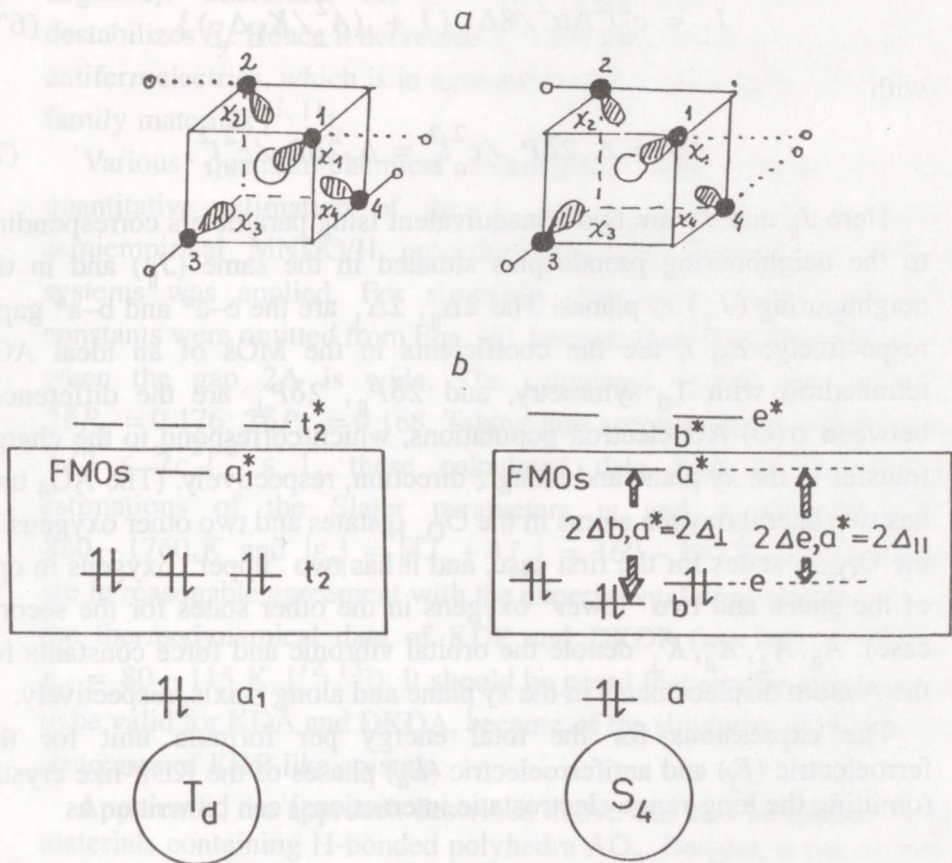
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The proton transfers from the hypothetical positions to the actual ones change the orbital energies ($\alpha$) of the $\sigma(O)$ AOs participating in the A–O bonds. These changes are $\pm\Delta\alpha$ depending on the oxygen final state: $O_{O-H}$ or $O_{O...H}$. In such way each distribution of pseudospins determines the $\sigma(O)$ orbital energies of all $AO_4$ tetrahedra, i.e. the (diagonal) substitution operator matrix in the AOs basis set of these tetrahedra.

For simplicity the frontier MOs (b, e, a*) approximation is used to evaluate $E_1(Q^f)$ for each $AO_4$ tetrahedron from Eq. (4). Thus the total energy of the crystal is the sum of these quantities over all crystal tetrahedra. Here the "cooperative" coupling of the $O_{O-H}/O_{O...H}$ states should be taken into account for the neighbouring tetrahedra. Then the sum of the $S_0$ terms vanishes, while the sum of the other terms has the Ising form (Eq. (5)), and the Ising parameters are

$$J_{\parallel} = c_a^2 l_t^2 \Delta\alpha^2 / 8\Delta_{\perp} \times$$

$$\times \{1 + (A_{\perp}^2/K_{\perp}\Delta_{\perp}) - 2(\Delta_{\perp}/\Delta_{\parallel}) - 2(A_{\parallel}^2\Delta_{\perp}/K_{\parallel}\Delta_{\parallel}^2)\}, \qquad (6')$$

$$J_\perp = c_a^2 l_t^2 \Delta\alpha^2 / 8\Delta_\perp \{1 + (A_\perp^2 / K_\perp \Delta_\perp)\} \qquad (6'')$$

with

$$\Delta\alpha = \Delta_\perp 2\delta P_\perp / c_a^2 l_t^2 = \Delta_\parallel 2\delta P_\parallel / c_a^2 l_t^2. \qquad (7)$$

Here $J_\parallel$ and $J_\perp$ are two nonequivalent Ising parameters corresponding to the neighbouring pseudospins situated in the same ($J_\parallel$) and in the neighbouring ($J_\perp$) $xy$ planes. The $2\Delta_\parallel$, $2\Delta_\perp$ are the e–a* and b–a* gaps, respectively; $c_a$, $l_t$ are the coefficients in the MOs of an ideal $AO_4$ tetrahedron with $T_d$ symmetry, and $2\delta P_\parallel$, $2\delta P_\perp$ are the differences between $\sigma(O)$ AO electron populations, which correspond to the charge transfer in the $xy$ plane and along $z$ direction, respectively. (The $AO_4$ unit has two lateral oxygen atoms in the $O_{O...H}$ states and two other oxygens in the $O_{O-H}$ states for the first case, and it has two "upper" oxygens in one of the states and two "lower" oxygens in the other states for the second case). $A_\parallel$, $A_\perp$, $K_\parallel$, $K_\perp$ denote the orbital vibronic and force constants for the A atom displacements in the $xy$ plane and along $z$-axis, respectively.

The expressions for the total energy per formula unit for the ferroelectric ($E_f$) and antiferroelectric ($E_a$) phases of the KDP-like crystal (omitting the long-range electrostatic interactions) can be written as

$$E_f = -2J_\perp - \varepsilon_0/2, \qquad E_a = -2J_\perp + \varepsilon_0/2. \qquad (8)$$

Here $\varepsilon_0 = 4J_\parallel + 4J_\perp$, ($|\varepsilon_0|$ is about 0,1 $J_\perp$ in accordance with quantum-chemical calculations; see below).

Equations (6–8) permit us to give a qualitative explanation for some of the main trends in the behaviour of KDP-like materials. It is well known that the $R_{O-D} < R_{O-H}$ and $R_{O...D} > R_{O...H}$ inequalities are valid for the H- and D-bonds. Hence we have $\delta P(D) > \delta P(H)$ and $J_\perp(D) > J_\perp(H)$. Thus, $|E_f|$ and $|E_a|$ increase for a deuterated material, which is in agreement with experimental data that show the increasing of $T_c$ for both deuterated ferroelectrics and antiferroelectrics [1, 11]. We are also able to explain the effect of the P $\rightarrow$ As replacement. The energy gaps in molecules and crystals usually become narrower when the atomic numbers of the constituent atoms increase. The quantum-chemical calculations of different $AO_4$-containing clusters (A = P, As), in particular, $H_4AO_4^+$, reproduce this trend. The decreasing of the HOMO–LUMO gap leads to the increasing of the quantities $\Delta_\perp / \Delta_\parallel$, $A_\perp^2 / K_\perp \Delta_\perp$, and $(\Delta_\parallel^2 / K_\parallel \Delta_\parallel) : (A_\perp^2 / K_\perp \Delta_\perp)$. As a result, the value of $|\varepsilon_0|$ increases ($\varepsilon_0$ is

negative). Therefore, the $P \rightarrow As$ replacement stabilizes $E_a$ and destabilizes $E_f$. Hence it decreases $T_c$ for ferroelectrics and increases $T_c$ for antiferroelectrics, which is in agreement with experimental data for KDP-family materials [1, 11].

Various quantum-chemical calculations were carried out for a quantitative estimation of the $J_{\parallel}$ and $J_{\perp}$ values. In particular, a semiempirical MNDO/H procedure specially adapted for H-bonded systems was applied. For simplicity, the terms containing vibronic constants were omitted from Eqs. (6), because their contributions are small when the gap $2\Delta$ is wide. The calculated values are $2\Delta = 12 \text{ eV}$, $2\delta P_{\parallel} = 0.176$, $2\delta P_{\perp} = 0.168$. Taking into account the obvious inequality $1/2 \leq 2c_a^2 l_t^2 \leq 1$, these calculated data lead to the following estimations of the Slater parameters $w$ and $\varepsilon_0 : w = 2J_{\parallel} + 4J_{\perp} = 880 - 1760 \text{ K}$ and $|\varepsilon_0| = |4J_{\parallel} + 4J_{\perp}| = 160 - 320 \text{ K}$. These estimates are in reasonable agreement with the experimental ones obtained by using the thermodynamical data of KDP and DKDP ($w = 800 - 1100 \text{ K}$ and $\varepsilon_0 = 80 - 115 \text{ K}$, [12, 13]). It should be noted that similar estimates seem to be valid for KDA and DKDA, because of the similarity of the electronic structures of KDP-like crystals.

Apparently, the approach described above can also be applied to other materials containing H-bonded polyhedra $AO_n$. Besides, it can as well be applied to some different systems such as squaric acid ($H_2SQ$). The latter is a layered molecular crystal (Fig. 3), which is usually referred to as a two-dimensional analogue of KDP. We shall consider the "$C_4$-core" of the $H_2SQ$ molecule as a pseudoatom surrounded by four O(H) ligands. The valence orbitals of this pseudoatom are the $\sigma$ and $\pi$ MOs of the $C_4$-core containing $\sigma(C)$ and $\pi(C)$ AOs which participate in the C–O bonds. It is easy to obtain the expression for the total energy of the $H_2SQ$ layer in a form of Eq. (5). As earlier, we omit the vibronic contributions for simplicity. Then, for the independent Ising parameters we have

$$J_{cis} = -c_{a_g}^2 l_{b_g}^2 \Delta\alpha_\sigma^2/8\Delta_{b_g a_g^*} - c_{a_u}^2 c_{b_u}^2 \Delta\alpha_\pi^2/8\Delta_{a_u b_u^*},$$

$$J_{tr} = J_{cis} + c_{a_g}^2 l_{e_u}^2 \Delta\alpha_\sigma^2/4\Delta_{e_u a_g^*} + c_{e_u}^2 l_{b_g}^2 \Delta\alpha_\sigma^2/4\Delta_{b_g e_u^*} +$$

$$+ c_{a_u}^2 c_{e_g}^2 \Delta\alpha_\pi^2/4\Delta_{a_u e_g^*}. \qquad (9)$$
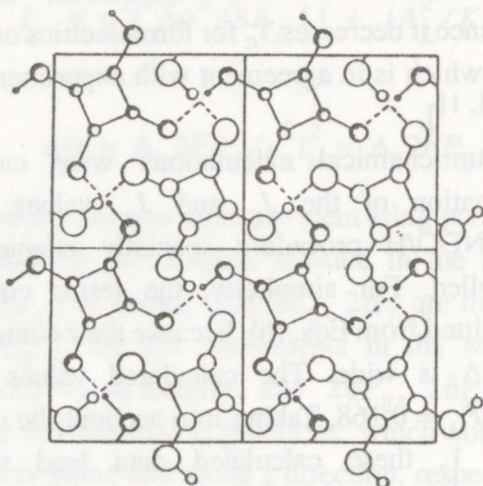
Fig. 3. The layer structure in the $H_2SQ$ crystal (low-temperature phase).

Here $J_{cis}$ and $J_{tr}$ refer to a pseudospin coupling in the *cis* and *trans* positions of the $C_4O_4$-fragment, respectively; $c_{a_g}$, $l_{b_g}$, etc. are the coefficients in the MOs of the $C_4O_4$-fragment, and $2\Delta_{b_g a_g^*}$, etc. are the gaps between these MOs. $\Delta\alpha_\sigma$ and $\Delta\alpha_\pi$ are the variations of the $\sigma(O)$ and $\pi(O)$ AOs energies depending upon the state of the oxygen atom ($O_{O-H}$ or $O_{O...H}$). One can express $\Delta\alpha$ in terms of the electronic populations of the $\sigma(O)$ and $\pi(O)$ AOs (on the analogy of Eq. (7)).

In conclusion, let us point out the physical meaning of Eqs. (6) and (9). These were obtained from Eq. (4) and they correspond to the change of the internal energy of the H-bonded molecular units of a crystal due to proton rearrangement on their H-bonds. Thus, a mechanism of the indirect pseudospin interaction in the crystal can be proposed, which is connected with the electronic and the geometrical reorganization of the non-hydrogen framework of a crystal. The numerical estimations for the Ising parameters of KDP-like crystals mentioned above evidence that such molecular mechanism is important and may be predominant.

## ACKNOWLEDGEMENT

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# HETEROLIGANDILISTE SÜSTEEMIDE VIBROONTEOORIA RAKENDAMINE STRUKTUURSETELE FAASISIIRETELE MÕNEDES VESINIKSIDEMEGA MATERJALIDES

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On esitatud KDP-tüüpi vesiniksidemega molekulaarkristallide käsitlus, mis põhineb ligandide asendusefektide vibroonteoorial. Prootonite ümberjaotumist potentsiaalenergia miinimumide vahel on vaadeldud asendusena $O_{O—H} \rightleftarrows O_{O...H}$ kristalli molekulaarsetes struktuuriüksustes. Prootonite jaotuse kirjeldamiseks on rakendatud pseudospinni formalismi. Kristalli koguenergia on antud Isingi kujus, kus Isingi parameetrid avalduvad kristalli struktuuriüksuste molekuliorbitaalide termineis ja on hinnatavad kvantmehaaniliste arvutuste abil. See käsitlus võimaldab anda Isingi parameetritele mõistlikud hinnangväärtused ja selgitada KDP-tüüpi materjalide senjettelektriliste omaduste põhilisi "keemilisi" tendentse.

# ВИБРОННАЯ ТЕОРИЯ ГЕТЕРОЛИГАНДНЫХ СИСТЕМ В ПРИМЕНЕНИИ К СТРУКТУРНЫМ ФАЗОВЫМ ПЕРЕХОДАМ В НЕКОТОРЫХ Н-СВЯЗАННЫХ МАТЕРИАЛАХ

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Предложен подход к Н-связанным молекулярным кристаллам типа KDP и т. п. на основе вибронной теории эффектов замещения

лигандов. Любое перераспределение протонов по минимумам их потенциальной энергии рассматривается как замещение $O_{O-H} \rightleftharpoons O_{O...H}$ в молекулярных структурных единицах кристалла. Для описания распределения протонов применен псевдоспиновый формализм. Полная энергия кристалла получена в форме Изинга, где параметры Изинга выражаются в терминах МО молекулярных структурных единиц кристалла и могут быть оценены из квантовохимических расчетов. Этот подход позволил получить разумные оценки параметров Изинга и объяснить основные "химические" тенденции в сегнетоэлектрических свойствах материалов семейства KDP. Обсуждено также применение предложенного подхода к квадратной кислоте.