Supporting Information

for

Second Harmonic Generation Responses of KH$_2$PO$_4$: Importance of K and Breaking down of Kleinman Symmetry

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Computational Details

1. First-principles calculation

The structural and electronic properties of paraelectric and ferroelectric phases of KH$_2$PO$_4$ (P-KDP and F-KDP, respectively) were calculated within the framework of density functional theory (DFT) by using the Vienna ab-initio simulation package (VASP) with the projector augmented wave (PAW) method. The generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) type exchange-correlation potentials was used throughout this work. The employed PAW-PBE pseudopotentials of elements K, H, P and O treat $3s^23p^4$, $1s$, $3s^23p$ and $2s2p$ as the valence states, respectively. The plane wave cutoff energy for the expansion of wave functions was set at 700 eV and the tetrahedron method with Blöchl corrections was used for integrations in the $k$ spaces with the $k$-meshes, 13 $\times$ 13 $\times$ 18 and 13 $\times$ 13 $\times$ 13 for P-KDP and F-KDP, respectively. Excellent convergence of the energy differences (0.1 meV) and stress tensors (0.001 eV/Å) were achieved. The quasi-Newton algorithm as implemented in the VASP code was used in all structural relaxations. In this work, both the cell volume and the atomic positions were allowed to relax to minimize the internal forces.

The electronic structures of P-KDP and F-KDP were also calculated by using the ABINIT package with the Optimized Norm-Conserving Vanderbilt (ONCV) pseudopotentials. The plane-wave cutoff energy of 55 Ha and 5×5×5 Monkhorst-Pack $k$-point set are found to be enough to reach the convergence of the calculations.

The SHG tensors were calculated with two different methods based on the “sum over states (SOS)” methods: 1) the optical module implemented in ABINIT, and 2) our own local code based on the calculated electronic structures from ABINIT and VASP calculations. The SOS formalism for second order susceptibility was derived by Aversa and Sipe and later modified by Rashkeev et al. and Sharma et. al. As the DFT electronic structure calculations underestimate bandgaps, the scissor operation was used to correct this deficiency. All atom response theory related calculations were done using our own code.

2. Partial response functional (PRF) method

The contribution of a certain occupied energy region between $E_B$ and valence band maximum (VBM), $\zeta_r(E_B)$, to each SHG coefficient $\chi_{ijk}^{(2)}$ is determined by considering only those excitations from all occupied states between $E_B$ and VBM to all the unoccupied states of the conduction bands (CBs), and the contribution, $\delta\zeta_r(E_B)$, of specific occupied states of energy $E_B$ to each $\chi_{ijk}^{(2)}$ by the excitations from that energy to all unoccupied states of the CBs.

$$\delta\zeta_r(E_B) = -\frac{d\zeta_r(E_B)}{dE_B}$$

Similarly, the contribution, $\zeta_c(E_B)$, of a certain unoccupied region between conduction band minimum (CBM) and $E_B$ to each $\chi_{ijk}^{(2)}$ is determined by the excitations from all occupied states of the VBs only to all unoccupied states between CBM and $E_B$, and the contribution, $\delta\zeta_c(E_B)$, of specific unoccupied states of energy $E_B$ to each $\chi_{ijk}^{(2)}$ by the excitations from all occupied states of the VBs only to that energy.

$$\delta\zeta_c(E_B) = \frac{d\zeta_c(E_B)}{dE_B}$$

3. Atom response theory (ART) analysis

To evaluate the individual atom contributions to the SHG components, $d_{ij}$, it is computationally more convenient to express the corresponding PRFs in terms of the band index $I_B$, $\zeta(I_B)$, where the band index $I_B$ runs from 1 to $N_{tot}$ (i.e., the total
number of band orbitals) with increasing energy, $E_\text{r}$, from $E_{\text{min}}$ to $E_{\text{max}}$. Here, $\zeta_\text{r}(I_\text{r})$ and $\zeta_\text{c}(I_\text{r})$ are denoted as $^\text{VB}\zeta_j$ and $^\text{CB}\zeta_j$, respectively, with IB replaced by a subscript $j$.

Suppose that a specific atom $\tau$ has $L$ atomic orbitals with a coefficient $^\text{VB}\zeta_\text{r}^j$ in the valence band $j$ at a wave vector $\vec{k}$. The total contribution $^\text{VB}A_\tau$ of an atom $\tau$ makes to the SHG coefficient from all the VB bands $j$ is written as

$$^\text{VB}A_\tau = \frac{\Omega}{(2\pi)^3} \int d\vec{k} \cdot \sum_{l,j} ^\text{VB}\zeta_j |^\text{VB}\zeta_j^k|^2$$

where $\Omega$ is the unit cell volume, $^\text{VB}\zeta_j$ is the corresponding PRFs in terms of the band index $j$. Similarly, the total contribution $^\text{CB}A_\tau$ of an atom $\tau$ makes to the SHG coefficient from all the CB bands $j$ is written as

$$^\text{CB}A_\tau = \frac{\Omega}{(2\pi)^3} \int d\vec{k} \cdot \sum_{l,j} ^\text{CB}\zeta_j |^\text{CB}\zeta_j^k|^2$$

in which we assumed that the atom has $L$ atomic orbitals with coefficient $^\text{CB}\zeta_\text{c}^j$ in the conduction band $j$ at a wave vector $\vec{k}$. To calculate the actual contribution of each constituent atom in a unit cell to the total SHG response, one needs to consider the signs of $^\text{VB}\zeta_j$ and $^\text{CB}\zeta_j$.

The total contribution, $A_\tau$, each individual atom makes to the SHG response from both the VBs and the CBs (i.e., from all the bands) is given by

$$A_\tau = \frac{^\text{VB}A_\tau + ^\text{CB}A_\tau}{2}$$

where the factor of 1/2 is applied to remove the double counting of each excitation.
Table S1. Optimized crystal structure data for the P-KDP and the F-KDP. KH₂PO₄ crystalizes in a paraelectric phase (P-KDP) with space group $I42d$, which transforms into a ferroelectric phase (F-KDP) with space group $Fd\bar{d}2$ below the Curie temperature $T_c = 123 \, K^{17-21}$. Single-crystal neutron structural analyses have been performed on KDP by Miyoshi et al.\textsuperscript{22} at several temperatures, i.e. 10, 30, 70, 110, 115, 118, 120, 125, 150, 200K. They adopt the crystal data at 10K for F-KDP because the atomic sites change little with the elevated temperature from 10 to 120 K. Besides, the crystal structure data of P-KDP at 125-200K were found in agreement with the reported single-crystal neutron diffraction data at 293K.\textsuperscript{23}

| P-KDP             | Lattice parameters(Å) | F-KDP             | Lattice parameters(Å) |
|-------------------|------------------------|-------------------|------------------------|
|                   | $a$        | $b$        | $c$        |                   | $a$        | $b$        | $c$        |
| This work         | 7.527     | 7.527     | 7.060     | This work          | 10.674    | 10.724    | 7.100     |
| Exp.a             | 7.430     | 7.430     | 6.970     | Exp.b              | 10.544    | 10.481    | 6.920     |
| Atoms             | Wyckoff sites | $x$     | $y$     | $z$            | Atoms             | Wyckoff sites | $x$     | $y$     | $z$ |
| K                 | 4b        | 0         | 0        | 0.500           | K                 | 8a        | 0         | 0        | 0.519 |
| H                 | 8d        | 0.142     | 0.250    | 0.125           | H                 | 16b       | 0.039     | 0.183    | 0.134 |
| P                 | 4a        | 0         | 0        | 0              | P                 | 8a        | 0         | 0        | 0     |
| O                 | 16e       | 0.145     | 0.089    | 0.126           | O1                | 16b       | 0.133     | 0.281    | 0.135 |
| O2                |           |           |          |                 | O2                | 16b       | 0.218     | 0.136    | 0.385 |

\textsuperscript{a}Reference\textsuperscript{23-24}

\textsuperscript{b}Reference\textsuperscript{22}
**Table S2** Normalized orbital composition of VBM and CBM for P-KDP and F-KDP.

|       | VBM          |       | CBM          |       |
|-------|--------------|-------|--------------|-------|
|       | P-KDP        |       | Total        |       |
|       | s  p  d      |       | s  p  d      |       |
| K     | 0.26% 0.00% 0.00% | 0.26% | 17.84% 0.00% 0.74% | 18.59% |
| H     | 0.00% 3.07% 0.00% | 3.07% | 2.97% 0.00% 0.00% | 2.97% |
| P     | 0.00% 0.00% 0.00% | 0.00% | 14.87% 0.00% 0.00% | 14.87% |
| O     | 0.00% 96.29% 0.00% | 96.29% | 59.48% 2.97% 0.00% | 62.45% |
|       | F-KDP        |       | Total        |       |
|       | s  p  d      |       | s  p  d      |       |
| K     | 0.00% 0.55% 0.00% | 0.55% | 17.10% 0.00% 0.00% | 17.10% |
| H     | 0.55% 0.55% 0.00% | 1.10% | 2.97% 1.49% 0.00% | 4.46% |
| P     | 0.00% 0.28% 0.00% | 0.28% | 14.87% 0.00% 0.00% | 14.87% |
| O     | 0.00% 97.79% 0.00% | 97.79% | 59.48% 2.98% 0.00% | 62.46% |
Table S3. Contributions (in %) of the atoms to the SHG coefficients $d_{14}$ and $d_{36}$ of P-KDP calculated by VASP. $W_A$ refers to the number of the same type of atoms (on the same Wyckoff site) in a unit cell; $A_A$, $C_A$, $^{VB}A_A$, $^{CB}A_A$ refer to the contributions (in %) of a single atom, total of the same type of atoms, and all from the valence bands (conduction bands) for a single atom, respectively.

| $d_{14}$ | Atom | $W_A$ | $A_A$ | $C_A$ | $^{VB}A_A$ | $^{CB}A_A$ |
|----------|------|------|-------|-------|-----------|-----------|
| P-KDP    | K    | 2    | 8.94  | 17.88 | 0.50      | 8.44      |
|          | H    | 4    | 1.15  | 4.62  | 0.27      | 0.89      |
|          | P    | 2    | 2.92  | 5.84  | 0.63      | 2.29      |
|          | O    | 8    | 8.96  | 71.67 | 7.60      | 1.35      |

| $d_{36}$ | Atom | $W_A$ | $A_A$ | $C_A$ | $^{VB}A_A$ | $^{CB}A_A$ |
|----------|------|------|-------|-------|-----------|-----------|
| P-KDP    | K    | 2    | 5.77  | 11.54 | -1.34     | 7.12      |
|          | H    | 4    | 1.75  | 7.02  | 0.43      | 1.32      |
|          | P    | 2    | 2.05  | 4.10  | 0.17      | 1.88      |
|          | O    | 8    | 9.67  | 77.34 | 8.08      | 1.59      |
Table S4. Contributions (in %) of the atoms to the SHG coefficients $d_{14}$ and $d_{36}$ of P-KDP calculated by ABINIT. $W_A$ refers to the number of the same type of atoms (on the same Wyckoff site) in a unit cell; $A_A$, $C_A$, $^{VB}A_A$, $^{CB}A_A$ refer to the contributions (in %) of a single atom, total of the same type of atoms, and all from the valence bands (conduction bands) for a single atom, respectively.

|        | Atom | $W_A$ | $A_A$ | $C_A$ | $^{VB}A_A$ | $^{CB}A_A$ |
|--------|------|-------|-------|-------|------------|------------|
| $d_{14}$ P-KDP | K    | 2     | 7.68  | 15.36 | 1.19       | 6.49       |
|        | H    | 4     | 1.26  | 5.06  | 0.17       | 1.09       |
|        | P    | 2     | 3.37  | 6.74  | 0.73       | 2.64       |
|        | O    | 8     | 9.11  | 72.84 | 6.81       | 2.30       |
| $d_{36}$ P-KDP | K    | 2     | 6.00  | 12.00 | 0.78       | 5.22       |
|        | H    | 4     | 1.75  | 7.01  | 0.57       | 1.18       |
|        | P    | 2     | 2.84  | 5.68  | 0.90       | 1.94       |
|        | O    | 8     | 9.41  | 75.30 | 7.43       | 1.99       |
Table S5. Contributions (in %) of the atoms to the SHG coefficients $d_{15}$, $d_{31}$, $d_{24}$, and $d_{32}$ of F-KDP calculated by VASP. $W_A$ refers to the number of the same type of atoms (on the same Wyckoff site) in a unit cell; $A_r$, $C_A$, $^{\text{VB}}A_r$, $^{\text{CB}}A_r$ refer to the contributions (in %) of a single atom, total of the same type of atoms, and all from the valence bands (conduction bands) for a single atom, respectively.

|       | Atom | $W_A$ | $A_r$ | $C_A$ | $^{\text{VB}}A_r$ | $^{\text{CB}}A_r$ |
|-------|------|-------|-------|-------|-------------------|-------------------|
| $d_{15}$ |       |       |       |       |                   |                   |
| F-KDP | K    | 2     | 6.67  | 13.33 | -0.34             | 7.00              |
|       | H    | 4     | 1.31  | 5.24  | 0.65              | 0.66              |
|       | P    | 2     | 4.49  | 8.98  | 2.34              | 2.15              |
|       | O    | 8     | 9.06  | 72.45 | 7.89              | 1.17              |
| $d_{31}$ |       |       |       |       |                   |                   |
| F-KDP | K    | 2     | 5.51  | 11.01 | -3.68             | 9.19              |
|       | H    | 4     | 1.48  | 5.90  | 0.04              | 1.44              |
|       | P    | 2     | -0.42 | -0.85 | -2.83             | 2.41              |
|       | O    | 8     | 10.49 | 83.93 | 8.62              | 1.87              |
| $d_{24}$ |       |       |       |       |                   |                   |
| F-KDP | K    | 2     | 9.34  | 18.68 | 1.03              | 8.31              |
|       | H    | 4     | 0.27  | 1.09  | -0.55             | 0.82              |
|       | P    | 2     | -0.68 | -1.37 | -2.51             | 1.83              |
|       | O    | 8     | 10.20 | 81.60 | 9.22              | 0.98              |
| $d_{32}$ |       |       |       |       |                   |                   |
| F-KDP | K    | 2     | 7.30  | 14.61 | -0.34             | 7.65              |
|       | H    | 4     | 2.02  | 8.10  | 0.77              | 1.25              |
|       | P    | 2     | 5.65  | 11.30 | 3.48              | 2.17              |
|       | O    | 8     | 8.25  | 65.99 | 6.66              | 1.59              |
**Table S6.** Contributions (in %) of the atoms to the SHG coefficients $d_{15}$ of F-KDP calculated by ABINIT. $W_A$ refers to the number of the same type of atoms (on the same Wyckoff site) in a unit cell; $A_r$, $C_A$, $^{VB}A_r$, $^{CB}A_r$ refer to the contributions (in %) of a single atom, total of the same type of atoms, and all from the valence bands (conduction bands) for a single atom, respectively.

| $d_{15}$ | Atom | $W_A$ | $A_r$ | $C_A$ | $^{VB}A_r$ | $^{CB}A_r$ |
|----------|------|-------|-------|-------|------------|------------|
| F-KDP    | K    | 2     | 7.05  | 14.09 | 1.01       | 6.03       |
|          | H    | 4     | 1.73  | 6.92  | 0.83       | 0.90       |
|          | P    | 2     | 4.63  | 9.26  | 2.10       | 2.53       |
|          | O    | 8     | 8.72  | 69.73 | 6.69       | 2.03       |
Fig S1. Connection of (a) PO₄ and (b) KO₈ polyhedra by hydrogen bond in P-KDP.

Fig S2. Projections of P-KDP along the (a) a-axis (b) b-axis and (c) c-axis.
Fig S3. Connection of (a) PO₄ and (b) KO₆ polyhedra by hydrogen bond in F-KDP.

Fig S4. Projections of F-KDP along the (a) a-axis (b) b-axis and (c) c-axis.
**Fig S5.** Calculated electronic band structure and DOS of P-KDP.

**Fig S6.** Calculated electronic band structure and DOS of F-KDP.
Fig S7. PDOS plots of P-KDP.

Fig S8. PDOS plots of F-KDP.
Fig S9. Calculated electronic structure and optical property of F-KDP. (a) PDOS plots calculated for the valence bands, and (b) those for the conduction bands. (c) $\zeta(E_B)$-vs-$E_B$ for valence bands, and (d) $\zeta(E_B)$-vs-$E_B$ for the conduction bands; (e) The corresponding derivative functionals $\delta\zeta(E_B)$-vs-$E_B$ for the valence bands, and (f) $\delta\zeta(E_B)$-vs-$E_B$ for the conduction bands.
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