Supplementary Information for:

Preferred Orientations of Organic Cations at Lead-Halide Perovskite Interfaces Revealed by Vibrational Sum-Frequency Spectroscopy

Woongmo Sung,1,2 Christian Müller,3,4 Sebastian Hietzschold,3,4 Robert Lovrinčić,3,4 Nathaniel P. Gallop,5 Artem A. Bakulin,5 Satoshi Nihonyanagi,1,2 Tahei Tahara1,2

2 Molecular Spectroscopy Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
2 Riken Center for Advanced Photonics, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
3 InnovationLab GmbH, Speyerer Str. 4, 69115 Heidelberg, Germany
4 Institute for High-Frequency Technology, TU Braunschweig, Schleinitzstrasse 22, 38106, Braunschweig, Germany
5 Department of Chemistry, Imperial College London, Molecular Sciences Research Hub, 80 Wood Lane, London, W12 0BZ, United Kingdom

Keywords: Lead Halide Perovskite; Hole Transport Layer; Methylammonium Cation; Interface; Nonlinear Optical Spectroscopy

Contents:

S1. Sample morphology characterisation
S2. Sample IR characterisation
S3. Calculation on Fresnel factors
S4. DFT calculation and second-order hyperpolarizability
S5. XRD Analysis
**S1. Sample morphology characterisation**

Film thicknesses and morphologies were determined using Scanning Electron Microscopy (SEM). A focused ion beam was used to create cross sections of MAPbX₃ and FAPbX₃ on several substrates, which were then subsequently imaged using SEM. For each sample, several film thickness values were obtained at a variety of locations along the cross section with the film thicknesses estimated as an average of these values. Estimates of the thickness of the Spiro-MeOTAD and PCBM layers could not be obtained for these samples, although earlier studies have obtained thicknesses of 150—250 nm and 60—100 nm for Spiro-MeOTAD and PCBM respectively. An example FIB cross-section is displayed in Fig. S1. SEM micrographs, illustrating the morphologies of each sample are given in Fig. S2.

Fig. S1: SEM cross-section of MAPbBr₃ deposited on NiO.
Fig S2: SEM micrographs of (A) MAPbBr₃ on TiO₂; (B) MAPbBr₃ on NiOₓ; (C) CsPbBr₃ on TiO₂; (D) CsPbBr₃ on NiO₂.

S2. Sample IR characterisation

![IR Spectrum](image)

Fig. S3: IR spectrum of Spiro-MeOTAD, including the IR fingerprint region.
S3. Calculation on Fresnel factors

For PPP polarization combination, effective second-order susceptibility, $\chi^{(2)}_{\text{eff,PPP}}$ is a linear combination of second-order susceptibility tensor components, $\chi^{(2)}_{ijk}$ in which dummy indices i, j, and k are either x or z in our laboratory coordinates as described in Fig. S6(a). For a single interface having azimuthal isotropy and showing no multiple reflection, explicit version of eq. 1 in the main text is given as $^2,$
Figure S6. Beam geometry and laboratory coordinates for HD-VSFG experiment on the perovskite multilayer sample. (b) Picture of MA cation showing Mulliken charges with hydrogens summed into heavy atoms and molecular coordinates.

\[
\chi_{\text{eff,PPP}}^{(2)} = -L_{xx}(\omega_3) L_{xx}(\omega_1) L_{xx}(\omega_2) \cos \beta_3 \cos \beta_1 \sin \beta_2 \chi_{xxz}^{(2)} \\
-L_{xx}(\omega_3) L_{xx}(\omega_1) L_{xx}(\omega_2) \cos \beta_3 \sin \beta_1 \cos \beta_2 \chi_{xxz}^{(2)} \\
+L_{xx}(\omega_3) L_{xx}(\omega_1) L_{xx}(\omega_2) \sin \beta_3 \cos \beta_1 \cos \beta_2 \chi_{xxz}^{(2)} \\
+L_{xx}(\omega_3) L_{xx}(\omega_1) L_{xx}(\omega_2) \sin \beta_3 \sin \beta_1 \sin \beta_2 \chi_{xxz}^{(2)} \\
\sim -L_{xx}(\omega_3) L_{xx}(\omega_1) L_{xx}(\omega_2) \cos \beta_3 \cos \beta_1 \sin \beta_2 \chi_{xxz}^{(2)} \\
+L_{xx}(\omega_3) L_{xx}(\omega_1) L_{xx}(\omega_2) \sin \beta_3 \sin \beta_1 \sin \beta_2 \chi_{xxz}^{(2)} \\
= -C_{xxz} \chi_{xxz}^{(2)} + C_{xxz} \chi_{xxz}^{(2)} \cdots (S1)
\]

where the subscripts 1, 2, and 3 stand for incident visible, IR, and emitted SF, respectively, and \( L_{ii}(\omega_m) \) is a Fresnel factor of laboratory coordinate (I = x, z) for \( \omega_m \) beam (m = 1, 2, 3), and \( \beta_m \) is angle of incident/emission for \( \omega_m \) beam. In this expression, Fresnel factors \( L_{xx}(\omega_m) \) and \( L_{zz}(\omega_m) \) are given by\(^2\),

\[
L_{xx}(\omega_m) = \frac{2n_1(\omega_m) \cos \gamma_m}{n_1(\omega_m) \cos \gamma_m + n_2(\omega_m) \cos \beta_m} \\
L_{zz}(\omega_m) = \frac{2n_2(\omega_m) \cos \beta_m}{n_1(\omega_m) \cos \gamma_m + n_2(\omega_m) \cos \beta_m} \left( \frac{n_1(\omega_m)}{n(\omega_m)} \right)^2 \cdots (S2)
\]
where $n_1$ and $n_2$ are the refractive indices for two mediums forming the interface, and $n'$ is the refractive index of the interface lies between $n_1$ and $n_2$, and $\beta_m$ is the refraction angle of beam having an incidence angle of $\beta_m$ in the medium 1. In this analysis, we took $n'$ as an average value between $n_1$ and $n_2$. The coefficients $C_{xxz}$ and $C_{zzz}$ are product among the Fresnel factors, thus positive. As discussed in the following section, multiple reflection effect gives additional phase rotation on the Fresnel factors.

In our experiment, incident angles of $\omega_1$ and $\omega_2$ are $\sim 50^\circ$ and $\sim 40^\circ$, respectively. Then, refraction angle at air/Spiro-MeOTAD interface is $\sim 27^\circ$ for $\omega_1$, and $\sim 26^\circ$ for $\omega_3$. At the second interface of Spiro-MeOTAD/MAPbBr$_3$, the refraction angles are $\sim 23^\circ$ for $\omega_1$, and $\sim 22^\circ$ for $\omega_3$. For $\omega_2$, refraction angle either for air/Spiro-MeOTAD and Spiro-MeOTAD/MAPbBr$_3$ depends on frequency since there exists large dispersion in refractive index of Spiro-MeOTAD as shown in Fig. S6(b). Therefore, $C_{xxz}$ and $C_{zzz}$ in eq. 1 in the main text are functions of $\omega_2$ frequency. Since extinction coefficient $\kappa$ of Spiro-MeOTAD and MAPbBr$_3$ at the probing IR region are not negligible, we use complex refractive indices for Fresnel factor calculation. In cases of $\omega_1$ and $\omega_3$, the refractive indices of Spiro-MeOTAD and MAPbBr$_3$ are almost real, and dispersion is small. So, we set $n(\omega_1) \sim n(\omega_3) = 1.96$ for MAPbBr$_3$ and $n(\omega_2) \sim n(\omega_3) = 1.70$ for Spiro-MeOTAD$^3$.

We now consider multiple reflections of beams occurring each side of Spiro-MeOTAD film. For simplicity, we calculated modified Fresnel factors for three-layer system consisting of air, Spiro-MeOTAD, and MAPbBr$_3$, and neglect contribution from other layers underneath. According to the previous investigations of VSFG spectroscopy on three-layer system, equations for effective second-order susceptibility in eq. S1 can be modified as below,

$$
\chi_{eff,ppp}^{(2)} \sim -L^1_z (\omega_2) L^1_z (\omega_1) L^1_z (\omega_2) \cos \beta_3 \cos \beta_1 \sin \beta_2 \chi_{xxz}^{(2),I} \\
+L^1_z (\omega_2) L^1_z (\omega_1) L^1_z (\omega_2) \sin \beta_3 \sin \beta_1 \sin \beta_2 \chi_{xxz}^{(2),I} \\
-L^2_z (\omega_2) L^2_z (\omega_1) L^2_z (\omega_2) \cos \beta_3 \cos \beta_1 \sin \beta_2 \chi_{xxz}^{(2),II} \\
+L^2_z (\omega_2) L^2_z (\omega_1) L^2_z (\omega_2) \sin \beta_3 \sin \beta_1 \sin \beta_2 \chi_{xxz}^{(2),II} \cdots \quad (S3)
$$

where the first and the second terms represent SF response from the first interface (air/Spiro-MeOTAD: I) and the remaining two terms correspond to SF from the second interface (Spiro-MeOTAD/MAPbBr$_3$: II). From HD-VSFG measurement on Spiro-MeOTAD film deposited on glass substrate, we found that the SF signal from the air/Spiro-MeOTAD interface is negligibly small.
comparing to that from Spiro-MeOTAD/MAPbBr₃ interface. Therefore, we can neglect first two terms in equation S3. Modified Fresnel factors at Spiro-MeOTAD/MAPbBr₃ interface which include multiple reflections are described as follows⁴,⁵,

\[
L_{ss}^{II} (\omega_m) = \exp(i\Delta_2 (\omega_m)) \frac{t_{p,12}(\omega_m)(1-r_{p,23}(\omega_m))}{1+r_{p,12}(\omega_m)r_{p,23}(\omega_m)\exp(i\Delta_1(\omega_m))} \cos \beta_m \\
L_{zz}^{II} (\omega_m) = \exp(i\Delta_2 (\omega_m)) \frac{t_{p,12}(\omega_m)(1+r_{p,23}(\omega_m))}{1+r_{p,12}(\omega_m)r_{p,23}(\omega_m)\exp(i\Delta_1(\omega_m))} \frac{n_1(\omega_m)n_2(\omega_m)}{(n_{2,3}(\omega_m))^2} \cdots (S4)
\]

where \(n_1, n_2, n_3\) are complex refractive indices for medium 1 (air), 2 (Spiro-MeOTAD), and 3 (MAPbBr₃), and \(n_{2,3}'\) is refractive index of Spiro-MeOTAD/MAPbBr₃ interface. \(t_{p,jk}\) and \(r_{p,jk}\) are transmission and reflection coefficients at interface of medium \(j\) and \(k\). \(\beta_m\) and \(\beta_m'\) correspond to incident angle of the \(\omega_m\) beam at the first and second interface, respectively. \(\Delta_1\) corresponds to change in phase of SF signal caused by multiple reflection. An equation for \(\Delta_1\) is given by,

\[
\Delta_1(\omega_m) = \frac{2\omega_m}{c} n_2(\omega_m) d \cos \beta_m' \cdots (S5)
\]

where \(d\) is ~200 nm for the Spiro-MeOTAD layer. \(\Delta_2\) stands for relative phase difference between two SF signals generated from two different interfaces. As the air/Spiro-MeOTAD interface gives almost no SF response, \(\Delta_2\) can be assumed to be zero. Then, eq. S3 is further simplified as below⁴,⁵,

\[
\chi_{eff,ppp}^{(2)} \sim -L_{ss}^{II} (\omega_3)L_{ss}^{II} (\omega_1)L_{zz}^{II} (\omega_2) \cos \beta_3 \cos \beta_1 \sin \beta_1 \chi_{xz}^{(2),II} + L_{zz}^{II} (\omega_1)L_{zz}^{II} (\omega_2) \sin \beta_3 \sin \beta_1 \sin \beta_2 \chi_{zzz}^{(2),II} \\
= -C_{xz}^{II} \chi_{xz}^{(2),II} + C_{zzz}^{II} \chi_{zzz}^{(2),II} \cdots (S6)
\]

For simplicity we omitted superscript \(\text{II}\) in the equations of the main text. Using the refractive indices shown in Fig. S7, the values of \(C_{xz}^{II}\) and \(C_{zzz}^{II}\) are calculated and these values are shown in Fig. S8. In Fig. S8(a) and S8(b), the values between 1509 and 1517 cm⁻¹ are missing since refractive index of the Spiro-MeOTAD film goes below 1, and the \(\omega_2\) beam at air/Spiro-MeOTAD interface shows total external reflection. Phase of the coefficient \(C_{xz}^{II}\) and \(C_{zzz}^{II}\) is ~4° for the frequency corresponding to
δas mode and ~6° to ~27° for the δs mode region as shown in Fig. S8(b). Thus, the real parts of the coefficients are almost same as the amplitude in Fig. S8(a), and the Cxx and Czz in the main text have positive sign for the ω2 frequencies of δs mode and δas mode. We used the amplitudes of the coefficients at 1480 and 1580 cm⁻¹ for calculating χ(2)eff,PPP of δs and δas modes, respectively. For ammonium moiety having C₃ᵥ symmetry, χxyz(2),Ⅱ and χzzz(2),Ⅱ are given as⁵,⁶,

\[ \chi_{xyz}^{(2),Ⅱ} = \frac{1}{2} N_s [-β_{xyy}^{(2)}(\langle \cos θ \rangle - \langle \cos^3 θ \rangle) + β_{xyy}^{(2)}((1 + r)\langle \cos θ \rangle - (1 - r)\langle \cos^3 θ \rangle)] \]

\[ \chi_{zzz}^{(2),Ⅱ} = N_s [β_{yzz}^{(2)}(\langle \cos θ \rangle - \langle \cos^3 θ \rangle) + β_{yzz}^{(2)}(r\langle \cos θ \rangle + (1 - r)\langle \cos^3 θ \rangle)] \]

\[ r = \beta_{xx}^{(2)} / \beta_{yy}^{(2)} \cdots (S7) \]

where \( N_s \) is surface number density of ammonium moiety, \( β_{xyy}^{(2)} \) and \( β_{yzz}^{(2)} \) are second-order hyperpolarizability tensor components, \( θ \) is polar angle between C-N dipole of methyl ammonium ion and the surface normal (z-axis) of the perovskite film as described in Fig. S6. The brackets mean average over orientational distribution of ammonium moieties in the detection area of the HD-VSFG measurement. As shown in the section S4, \( β_{xyy}^{(2)} \) and \( β_{yzz}^{(2)} \) are mainly contributed to δs and δas modes, respectively. So, at each of resonance conditions, \( χ_{xyz}^{(2),Ⅱ} \) and \( χ_{zzz}^{(2),Ⅱ} \) are approximated to,

For \( ω_2 = ω_δs \), \( \chi_{xyz}^{(2),Ⅱ} \approx \frac{1}{2} N_s β_{xyy}^{(2)}((1 + r)\langle \cos θ \rangle - (1 - r)\langle \cos^3 θ \rangle) \]

\[ \chi_{zzz}^{(2),Ⅱ} \approx N_s β_{yzz}^{(2)}(r\langle \cos θ \rangle + (1 - r)\langle \cos^3 θ \rangle) \cdots (S8) \]

For \( ω_2 = ω_δas \), \( \chi_{xyz}^{(2),Ⅱ} \approx -\frac{1}{2} N_s β_{xyy}^{(2)}(\langle \cos θ \rangle - \langle \cos^3 θ \rangle) \]

\[ \chi_{zzz}^{(2),Ⅱ} \approx N_s β_{yzz}^{(2)}(\langle \cos θ \rangle - \langle \cos^3 θ \rangle) \cdots (S9) \]

By substituting eq. S8 and S9 into eq. S6, the effective second-order susceptibility is given as,

\[ \chi_{eff,PPP}^{(2)} \approx -\frac{1}{2} C_{xyz}^{(2)} N_s β_{xyy}^{(2)}((1 + r)\langle \cos θ \rangle - (1 - r)\langle \cos^3 θ \rangle) \]

\[ + C_{zzz}^{(2)} N_s β_{yzz}^{(2)}(r\langle \cos θ \rangle + (1 - r)\langle \cos^3 θ \rangle), \text{ at } ω_2 = ω_δs \cdots (S10) \]

\[ \chi_{eff,PPP}^{(2)} \approx \frac{1}{2} C_{xyz}^{(2)} N_s β_{xyy}^{(2)}(\langle \cos θ \rangle - \langle \cos^3 θ \rangle) \]

\[ + C_{zzz}^{(2)} N_s β_{yzz}^{(2)}(\langle \cos θ \rangle - \langle \cos^3 θ \rangle), \text{ at } ω_2 = ω_δas \cdots (S11) \]
Eqs. S10 and S11 correspond to Eqs. 2 and 3 in the main text.

In addition, we checked that multiple reflection between the two interfaces of Spiro-MeOTAD/MAPbBr$_3$ and MAPbBr$_3$/TiO$_2$ gives only small modulation in phase of the Fresnel factors. For the $\omega_1$ visible probe beam ($\lambda$~795 nm) and the $\omega_3$ SF signal ($\lambda$~706 nm) at the resonance of $\delta_{\text{as}}$ mode, corresponding refractive index of TiO$_2$ is ~2.52 and ~2.55, respectively. Therefore, refractive index difference between MAPbBr$_3$ (n~1.96) and TiO$_2$ is ~0.6, and reflection coefficient $r_p$ is ~0.11 at MAPbBr$_3$/TiO$_2$ interface. On the other hand, refractive index of MAPbBr$_3$ at IR frequency ($\omega_2$) of 1580 cm$^{-1}$ (n~2.15) is well-matched with TiO$_2$ refractive index (~2.06), and reflection coefficient is close to zero. Considering three-layer thin film system consisting of Spiro-MeOTAD, MAPbBr$_3$, and TiO$_2$, the modified Fresnel factors for Spiro-MeOTAD/MAPbBr$_3$ interface are, $L_{xx}(\omega_1) = 1.05-0.01i$, $L_{xx}(\omega_2) = 0.79$, $L_{zz}(\omega_2) = 0.97-0.1i$, $L_{zz}(\omega_3) = 0.82+0.01i$, $L_{zz}(\omega_3) = 0.78$, and $L_{zz}(\omega_3) = 0.87+0.09i$. From these values, coefficients for $\chi^{(2)}_{xxz}$ and $\chi^{(2)}_{zzz}$ are 0.29-0.03i and 0.05+0.005i, respectively. The corresponding phase change is about 6°.

Figure S7. Complex refractive indices (Red: $n$ and black: $k$) of (a) MAPbBr$_3$ calculated from complex dielectric constant listed in Ref. 1 and (b) Spiro-MeOTAD obtain from an IR absorption spectrum of 20 nm Spiro-MeOTAD film.
Figure S8. (a) Amplitude and (b) phase of complex coefficients $C_{xxz}$ and $C_{zzz}$ including multiple reflection effect.

**S4. DFT calculation and second-order hyperpolarizability**

From DFT calculation (Gaussian09, B3LYP/6-311++G(d,p)) of a methylammonium cation in vacumm, we obtained polarizability and dipole derivatives for calculating second-order hyperpolarizability tensor components. Table S1 and S2 show lists of dipole and polarizability derivatives for ammonium bending modes.

**Table S1. Dipole derivatives for $\delta_s$ and $\delta_{as}$ modes**

| Frequency (cm$^{-1}$) | Mode   | $\delta \mu / \delta \xi$ (a.u.) | $\delta \mu / \delta \eta$ (a.u.) | $\delta \mu / \delta \zeta$ (a.u.) |
|-----------------------|--------|----------------------------------|----------------------------------|----------------------------------|
| 1536                  | $\delta_s$ | 0.02                             | 0.00                             | $-1.04 \times 10^1$             |
| 1671                  | $\delta_{as}$ | -6.42                            | 0.02                             | 0.00                             |
| 1671                  | $\delta_{as}$ (degenerated) | 0.00                             | 6.41                             | 0.00                             |
Table S2(a). Polarizability derivative tensor components (a. u.) for $\delta_s$ mode

| Coordinate | $\xi$ | $\eta$ | $\zeta$ |
|------------|-------|--------|--------|
| $\xi$      | 0.73x10^{-1} | 0.00  | 0.00  |
| $\eta$     | 0.00   | 0.71x10^{-1} | 0.00  |
| $\zeta$    | 0.00   | 0.00   | -0.49 |

Table S2(b). Polarizability derivative tensor components (a. u.) for $\delta_{ss}$ mode

| Coordinate | $\xi$ | $\eta$ | $\zeta$ |
|------------|-------|--------|--------|
| $\xi$      | 0.31  | 0.00   | -0.49 |
| $\eta$     | 0.00  | -0.31  | 0.00   |
| $\zeta$    | -0.49 | 0.00   | 0.94x10^{-3} |

Table S2(c). Polarizability derivative tensor components (a. u.) for $\delta_{ss}$ (degenerate) mode

| Coordinate | $\xi$ | $\eta$ | $\zeta$ |
|------------|-------|--------|--------|
| $\xi$      | 0.00  | 0.31   | 0.00   |
| $\eta$     | 0.31  | 0.00   | 0.49   |
| $\zeta$    | 0.00  | 0.49   | 0.00   |

Then, second-order hyperpolarizability tensor component is proportional to product between dipole and polarizability derivatives$^8$. The calculated tensor components for $\delta_s$ mode are $\beta^{(2)}_{\xi\xi\zeta} = -0.76$, $\beta^{(2)}_{\zeta\zeta\zeta} = 5.10$, $\beta^{(2)}_{\xi\zeta\zeta} = 0$, $\beta^{(2)}_{\zeta\xi\zeta} = 0$ and for $\delta_{ss}$ mode $\beta^{(2)}_{\xi\xi\zeta} = 0$, $\beta^{(2)}_{\zeta\zeta\zeta} = 0$, $\beta^{(2)}_{\xi\zeta\zeta} = 3.15$, $\beta^{(2)}_{\zeta\xi\zeta} = 3.15$. 
S5. XRD Analysis

To confirm the phase purity of samples produced using our synthesis method, we performed X-ray Diffraction (XRD) on a set of films produced under an identical procedure to those subjected to HD-vSFG spectroscopy. XRD analysis was performed using a benchtop diffractometer (D2 Phaser, Bruker Inc.). The diffraction pattern was scanned in the range \(2\theta = 10—50^\circ\) with a resolution of 0.05°, using the Cu-K\(_\alpha\) line (1.5406 Å) as the X-ray source. Fig. S8 displays the obtained XRD pattern. Comparison of the obtained XRD pattern with standard patterns for the cubic and orthorhombic phases, obtained from the Inorganic Crystal Structure Database (ICSD # 29073 and ICSD # 97851, respectively) is provided in Fig. S9. Our obtained XRD pattern matches well with the standard pattern for the cubic phase. We also note that the peak splitting at \(2\theta \approx 30^\circ\), characteristic of the orthorhombic phase of CsPbBr\(_3\), is absent. On this basis, we conclude that the dominant phase in our samples is the cubic phase.

Fig. S8: Representative XRD pattern for the as-synthesised CsPbBr\(_3\) films.

Fig. S9: Comparison of XRD pattern displayed in Fig. S8 with standard patterns for the orthorhombic and cubic phases of CsPbBr\(_3\), obtained from the Inorganic crystal structure database.
References

(1) Glaser, T.; Müller, C.; Sendner, M.; Krekeler, C.; Semonin, O. E.; Hull, T. D.; Yaffe, O.; Owen, J. S.; Kowalsky, W.; Pucci, A.; et al. Infrared Spectroscopic Study of Vibrational Modes in Methylammonium Lead Halide Perovskites. J. Phys. Chem. Lett. 2015, 6, 2913–2918.

(2) Zhuang, X.; Miranda, P.; Kim, D.; Shen, Y., Mapping molecular orientation and conformation at interfaces by surface nonlinear optics. Phys. Rev. B 1999, 59, 12632.

(3) Brittman, S.; Garnett, E. C. Measuring n and k at the Microscale in Single Crystals of CH$_3$NH$_3$PbBr$_3$ Perovskite. J. Phys. Chem. C 2015, 120, 616-620.

(4) Tong, Y.; Zhao, Y.; Li, N.; Osawa, M.; Davies, P. B.; Ye, S., Interference effects in the sum frequency generation spectra of thin organic films. I. Theoretical modeling and simulation. J. Chem. Phys. 2010, 133, 034704.

(5) Backus, E. H.; Garcia-Araez, N.; Bonn, M.; Bakker, H. J., On the role of Fresnel factors in sum-frequency generation spectroscopy of metal–water and metal-oxide–water interfaces. J. Phys. Chem. C 2012, 116, 23351-23361.

(6) DeVore, J. R.; Refractive indices of rutile and sphalerite J. Opt. Soc. Am. 1951, 41, 416-419.

(7) Kischkat, J.; et al. Mid-infrared optical properties of thin films of aluminum oxide, titanium dioxide, silicon dioxide, aluminum nitride, and silicon nitride. Appl. opt. 2012, 51, 6789-6798.

(8) Ishiyama, T.; Imamura, T.; Morita, A. Theoretical studies of structures and vibrational sum frequency generation spectra at aqueous interfaces. Chem. Rev. 2014, 114, 8447-8470.