

Supporting information for: Orientation of Methylguanidinium Ions at the Water-Air Interface

S. Strazdaite,^{*,†} J. Versluis,[†] N. Ottosson,^{†,‡} and Huib J. Bakker^{*,†}

*Institute for Atomic and Molecular Physics AMOLF, Science park 102, Amsterdam
1098 XG, The Netherlands, and Advanced Research Center for Nanolithography ARCNL,
Science park 110, Amsterdam 1098 XG, The Netherlands*

E-mail: strazdaite@amolf.nl; bakker@amolf.nl

In Figure S1 we show calculated $\chi_{\text{eff}}^{(2)}$ values for the SS and AS methyl stretch vibrations in SSP, SPS and PPP polarization combinations. We do not include SPS polarization combination in our orientational analysis, because it has been found that the intensities of the asymmetric CH_3 stretching modes of methanol, acetone and acetonitrile, measured with the SPS polarization combination do not correspond with the values predicted by the bond additivity model.^{S1} For the SSP and PPP polarization combinations, the experimental findings are in excellent agreement with the predicted polarization dependence.^{S2-S4}

^{*}To whom correspondence should be addressed

[†]Institute for Atomic and Molecular Physics AMOLF, Science park 102, Amsterdam 1098 XG, The Netherlands

[‡]Advanced Research Center for Nanolithography ARCNL, Science park 110, Amsterdam 1098 XG, The Netherlands

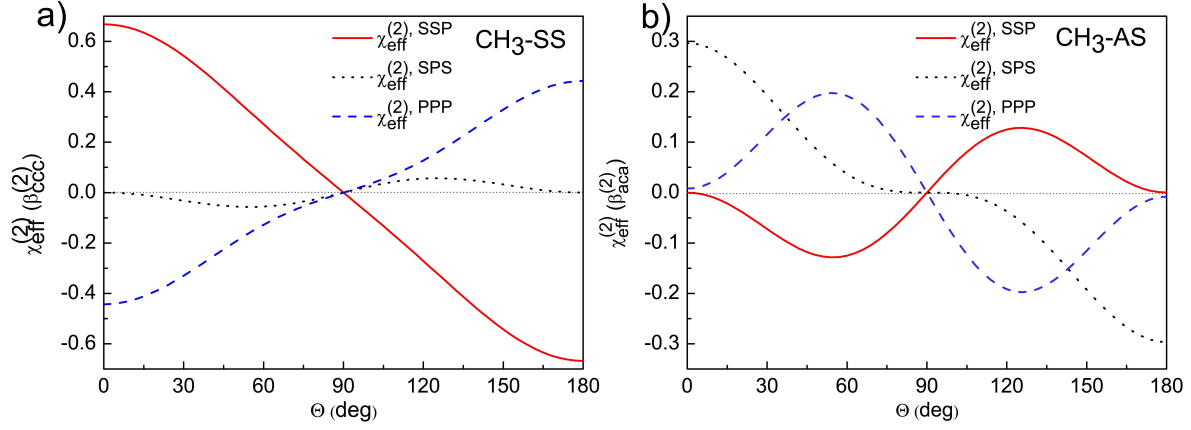


Figure S1: Calculated $\chi_{\text{eff}}^{(2)} (\beta_{\text{ccc}})$ as a function of the orientational angle θ for the symmetric methyl vibration (a) and $\chi_{\text{eff}}^{(2)} (\beta_{\text{aca}})$ for the asymmetric methyl vibration (b). The functions are plotted for SSP, SPS and PPP polarization combinations. The details of the calculation are given in the manuscript.

Fitting Results

The SSP and PPP spectra were globally fitted with three Gaussian peaks and 11 parameters:

$R, S, D, x_1 = 0.5N_s\beta_{\text{ccc}}\langle\cos\theta\rangle, x_2 = \text{ratio between FR and SS,}$

ω_{SS} and σ_{SS} – frequency and width of SS,

ω_{FR} and σ_{FR} – frequency and width of FR,

ω_{AS} and σ_{AS} – frequency and width of AS.

The expressions for $\chi_{\text{eff}}^{(2)}$ of each of the resonance in SSP and PPP are:

For SSP

$$\begin{aligned}
 \chi_{\text{eff}}^{(2),\text{SS}} &= 0.334x_1((1+R) - (1-R)D) \exp\left(\frac{-(\omega - \omega_{\text{SS}})^2}{2\sigma_{\text{SS}}^2}\right) \\
 \chi_{\text{eff}}^{(2),\text{FR}} &= 0.334x_1x_2((1+R) - (1-R)D) \exp\left(\frac{-(\omega - \omega_{\text{FR}})^2}{2\sigma_{\text{FR}}^2}\right) \\
 \chi_{\text{eff}}^{(2),\text{AS}} &= 0.334 \times 2x_1S(1-D) \exp\left(\frac{-(\omega - \omega_{\text{AS}})^2}{2\sigma_{\text{AS}}^2}\right)
 \end{aligned} \tag{1}$$

Table S1: Parameters determined from a global fit of the SSP and PPP spectra of a solution of M-Gdm⁺ in water.

	R	1.0 ± 0.1
	S	1.1 ± 0.1
	D	0.5 ± 0.06
	x_1	-19
	x_2 FR/SS	2.1
SS	ω_{SS}	2863 cm^{-1}
	σ_{SS}	23 cm^{-1}
FR	ω_{FR}	2922 cm^{-1}
	σ_{FR}	23 cm^{-1}
AS	ω_{AS}	2950 cm^{-1}
	σ_{AS}	21 cm^{-1}

For PPP

$$\begin{aligned}
\chi_{\text{eff}}^{(2),\text{SS}} = & (-0.279x_1((1+R) - (1-R)D)) \\
& - 0.242x_1((1-R)(1-D)) \\
& + 0.250x_1((1-R)(1-D)) \\
& + 0.1372x_1(R + (1-R)D)) \exp\left(\frac{-(\omega - \omega_{\text{SS}})^2}{2\sigma_{\text{SS}}^2}\right) \\
\chi_{\text{eff}}^{(2),\text{FR}} = & (-0.279x_1x_2((1+R) - (1-R)D)) \\
& - 0.242x_1x_2((1-R)(1-D)) \\
& + 0.250x_1x_2((1-R)(1-D)) \\
& + 0.1372x_1x_2(R + (1-R)D)) \exp\left(\frac{-(\omega - \omega_{\text{FR}})^2}{2\sigma_{\text{FR}}^2}\right) \\
\chi_{\text{eff}}^{(2),\text{AS}} = & (0.558x_1S(1-D) + 0.484x_1SD - 0.50x_1SD) \\
& + 0.548x_1S(1-D)) \exp\left(\frac{-(\omega - \omega_{\text{AS}})^2}{2\sigma_{\text{AS}}^2}\right),
\end{aligned} \tag{2}$$

Where the numbers in front of each $\chi_{eff}^{(2)}$ element represents the Fresnel factors.

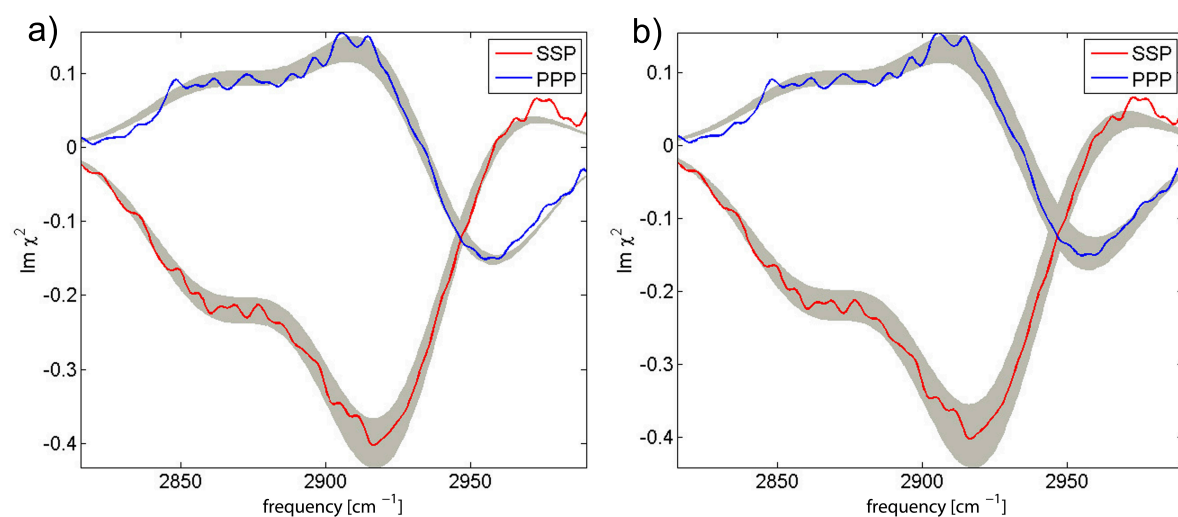


Figure S2: Imaginary $\chi^{(2)}$ spectra of a solution of methylguanidinium hydrochloride in water measured with SSP and PPP polarization combinations. The grey areas mark the region in which the R value is varied ± 0.1 from the fitted value of 1 (a) and the region in which the angle θ is varied $\pm 5^\circ$ from the fitted value of 45° (b).

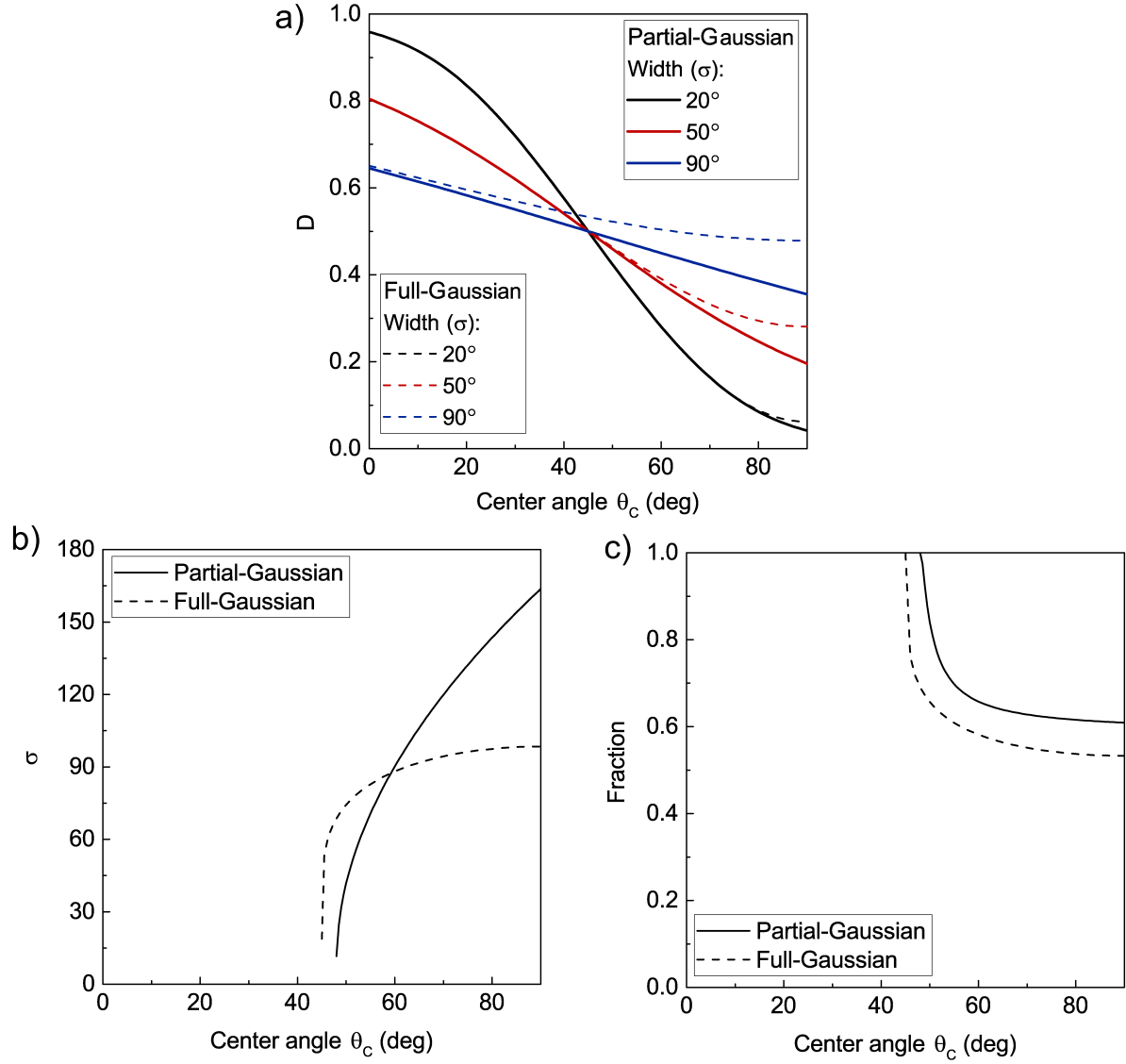


Figure S3: A comparison of partial and full-Gaussian distributions: (a) dependence of D on the angle θ_c of the maximum of the distribution for three different widths. θ is the angle with respect to the surface normal, i.e. $\theta=0^\circ$ corresponds to ions with their main axis perpendicular to the surface, and $\theta=90^\circ$ to ions with their main axis parallel to the surface; (b) the width of the distribution required to get a D value of 0.5, as a function of θ_c . For $\theta_c < 45^\circ$ D is always larger than 0.5, which implies that there is no width for which D acquires the experimentally observed $D=0.5$; (c) the fraction of molecules with their main axis at an angle $\theta > 20^\circ$ with respect to the surface plane for different values θ_c . At each value of θ_c , the fraction is calculated using a distribution width that yields $D=0.5$.

References

- (S1) Wu, H.; Zhang, W.-k.; Gan, W.; Cui, Z.-f.; Wang, H.-f. An Empirical Approach to the Bond Additivity Model in Quantitative Interpretation of Sum Frequency Generation Vibrational Spectra. *J. Chem. Phys.* **2006**, *125*, 133203–13.
- (S2) Superfine, R.; Huang, J. Y.; Shen, Y. R. Nonlinear optical studies of the pure liquid/vapor interface: Vibrational spectra and polar ordering. *Phys. Rev. Lett.* **1991**, *66*, 1066–1069.
- (S3) Yeh, Y. L.; Zhang, C.; Held, H.; Mebel, A. M.; Wei, X.; Lin, S. H.; Shen, Y. R. Structure of the acetone liquid/vapor interface. *The Journal of Chemical Physics* **2001**, *114*, 1837–1843.
- (S4) Lu, R.; Gan, W.; hua Wu, B.; Zhang, Z.; Guo, Y.; Wang, H.-f. C-H Stretching Vibrations of Methyl, Methylene and Methine Groups at the Vapor/Alcohol (n = 1 - 8) Interfaces. *J. Phys. Chem. B* **2005**, *109*, 14118–14129.