

Sensing Vase-to-Kite Switching of Cavitands by Sum-Frequency Vibrational Spectroscopy

Pasquale Pagliusi,^{#,†} François Lagugné-Labarhet,^{‡,*} Devanand K. Shenoy,[§] Enrico Dalcanale,[⊥] and Y. Ron Shen^{†,*}

LiCryL-INFM/CNR and Dipartimento di Fisica, Università della Calabria, 87036, Italy, Department of Physics, University of California-Berkeley, Berkeley, California, 94720, LPCM, UMR 5803 CNRS, Université Bordeaux I, 33405 Talence, France, Center for Bio/molecular Science and Engineering, Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, D.C. 20375, and Dipartimento di Chimica Organica e Industriale, Università di Parma and INSTM, Udr Parma, Viale G. Usberti 17/A, 43100 Parma, Italy

Received June 13, 2006; E-mail: f.lagugne@lpcm.u-bordeaux1.fr; yrshen@calmail.berkeley.edu

Quinoxaline-bridged cavitands (QxCav)¹ are molecular receptors for aromatic guests in solution,² in the gas phase,³ and at the solid–gas interfaces.⁴ They present the peculiar property of a thermally driven reversible switching between a closed vase conformation, presenting a deep cavity for guest complexation, and an open kite conformation with a flat extended surface.⁵ It has been shown that the conformational switch could be induced by a change of the surrounding pH or temperature,^{6,7} as well as by interactions with metal ions.⁸ Decreasing the pH converts the cavitand molecules from the vase to the kite structure, a function that could be considered as an action of grabbing and releasing a guest molecule.⁹ In this context and considering the possible applications of such molecules as sensors,⁴ it is of pivotal interest to monitor in situ these conformational changes at a molecular scale for cavitands deposited at an interface with their cavities oriented toward air or water. Second-harmonic generation (SHG) and sum frequency generation (SFG) spectroscopy have the unique capability to probe a monolayer at an interface with relatively short acquisition times. They can play a key role in probing static molecular conformations and dynamical changes of interfacial cavitand molecules.

In a previous work, SHG and surface tension measurements were used to monitor the molecular orientation of cavitand monolayers on water and their possible conformational switching as the bulk pH varied.¹⁰ It was found that a quinoxaline-bridged cavitand (QxCav, Figure 1a) monolayer on water switched from a vase to kite conformation at sufficiently low pH. Coulombic repulsion between protonated wings of the cavitand molecules was responsible for the switching to the open kite conformation. The SHG response derived from electronic contributions of the molecules, does not provide direct information on the molecular structure and the conformational change. Sum-frequency vibrational spectroscopy (SFVS), however, can provide direct structural and therefore conformational information, such as average orientations of selected moieties within the molecular monolayer through their vibrational spectra.¹¹

This paper reports an SFVS study of a C₁₁H₂₃-footed QxCav monolayer on water with two different pH values that ensure the two different configurations, vase and kite, respectively.¹⁰ In our experiment, the SF signal is generated in reflection from two input beams at ω_{vis} (18800 cm⁻¹) and ω_{IR} (2700–3200 cm⁻¹) that overlap at the water/vapor interface covered by a QxCav monolayer. (See Figure 1b.) The SF signal is given by¹¹

$$S(\omega_{\text{SF}}) \propto |(\hat{\epsilon}_{\text{SF}} \cdot \vec{L}_{\text{SF}}) \vec{\chi}^{(2)} : (\hat{\epsilon}_{\text{vis}} \cdot \vec{L}_{\text{vis}}) (\hat{\epsilon}_{\text{IR}} \cdot \vec{L}_{\text{IR}})|^2 I_{\text{vis}} I_{\text{IR}} \quad (1)$$

where $\hat{\epsilon}_i$, \vec{L}_i and I_i denote the polarization, the transmission Fresnel coefficients at the interface, and the beam intensity at ω_i , respectively, and $\vec{\chi}^{(2)}$ is the surface nonlinear susceptibility that can be expressed as

$$\vec{\chi}^{(2)} = \vec{\chi}_{\text{NR}}^{(2)} + N_s \int \vec{\alpha}^{(2)}(\Omega) f(\Omega) d\Omega$$

$$\vec{\alpha}^{(2)} = \sum_q \frac{\vec{A}_q}{\omega_{\text{IR}} - \omega_q + i\Gamma_q} \quad (2)$$

Here, $\vec{\chi}_{\text{NR}}^{(2)}$ denotes the nonresonant background, N_s and $f(\Omega)$ are the number density of the surface molecules and the orientational distribution of the selected moiety, and $\vec{\alpha}^{(2)}$ is the resonant molecular hyperpolarizability, in which \vec{A}_q , ω_q , and Γ_q are the amplitude, resonant frequency, and damping coefficient of the q th vibrational mode, respectively.

The QxCav monolayer on water is azimuthally isotropic, and its nonvanishing $\vec{\chi}^{(2)}$ elements are $\chi_{zzz}^{(2)}$, $\chi_{zxz}^{(2)} = \chi_{zyy}^{(2)} \approx \chi_{xzx}^{(2)} = \chi_{yzy}^{(2)}$, and $\chi_{xzz}^{(2)} = \chi_{yyz}^{(2)}$, with z referring to the direction of the surface normal. They can be deduced from measurement with various input/output polarization combinations, namely, SSP (referring to S-, S-, and P-polarizations for SF output, visible input, and IR input, respectively), SPS, and PPP. The S-polarization is parallel to the surface and perpendicular to the incidence plane. Therefore, the SPS polarization combination can only excite vibrational modes with a component along the surface and perpendicular to the incidence plane, while SSP can excite modes with a component in the incidence plane.

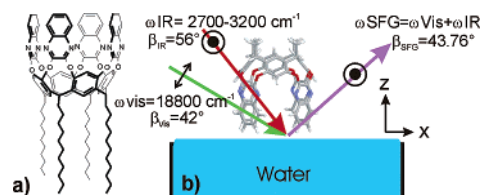


Figure 1. (a) Molecular structure of quinoxaline-bridged cavitand (QxCav) having four C₁₁H₂₃ alkyl chains at the lower rim; (b) schematic of the setup for SFVS on QxCav on water with SPS polarization combination.

Shown in Figure 2 are the SFG spectra of a QxCav monolayer on water at a surface pressure of 50 mN/m for the three polarization combinations in the spectral range from 2750 to 3150 cm⁻¹ at pH = 5.7 and pH = 0.2. The observed peaks between 2800 and 3000 cm⁻¹ arise from CH stretches of the alkyl chains pointing toward

[#] Università della Calabria.

[†] University of California Berkeley.

[‡] Université Bordeaux I.

[§] Naval Research Laboratory

[⊥] Università di Parma.

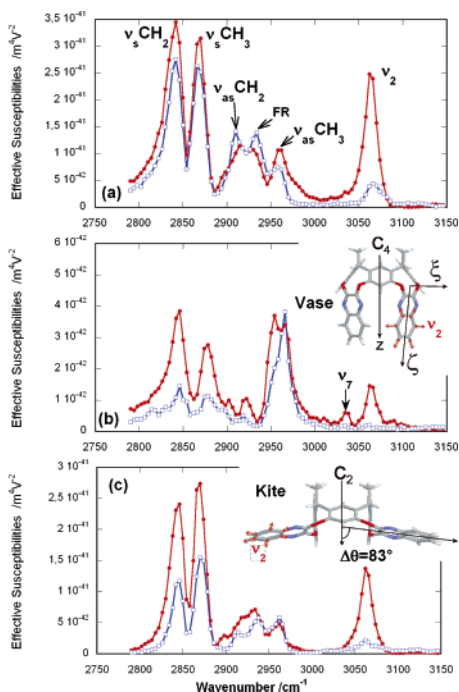


Figure 2. SFG spectra of a QxCav monolayer on water at pH = 5.7 and pH = 0.2 with polarization combinations (a) SSP, (b) SPS, and (c) PPP. Spectra at pH = 0.2 are multiplied by 4. The insets of panels b and c depict the closed and totally open QxCav molecular structure.

air. They are attributed to symmetric (2845 cm^{-1}) and antisymmetric stretch modes of CH_2 (2910 cm^{-1}) and symmetric (2870 cm^{-1}), antisymmetric (2940 cm^{-1}), and Fermi resonance (2960 cm^{-1}) modes of CH_3 stretches. The relatively strong CH_2 modes are an indication that the alkyl chains had appreciable gauche defects. The peaks at 3036 and 3064 cm^{-1} are attributed to the ν_7 and ν_2 mode of the aromatic rings of the wings. The ν_2 mode is much more prominent than ν_7 , and at pH = 5.7, is ~ 20 times stronger in SSP than in SPS, indicating that the aromatic rings were oriented with their axes close to the surface normal.

At a pH of 0.2 however, the overall intensity of the SSP spectra is weaker by a factor of ~ 4 , and the relative intensities of the all CH_2 and CH_3 modes remain roughly the same, indicating that the alkyl chains on the cavitand bowl extending out of the surface had their orientation and conformation nearly unchanged. The SPS spectra are much weaker, and therefore reveal less information on conformation even though the observed change is more significant. From eqs 1 and 2, we can conclude that the reduction of the SFG intensity by 4 corresponds to a reduction of the surface molecular density by 2, which is seen directly from the surface-pressure/molecular area measurement.¹⁰ This change is due to vase-to-kite switching of the cavitand molecules induced by protonation at low pH.

Figure 2 shows that even after taking the reduction of the surface molecular density into account, the ν_2 mode of the aromatic rings is still much weaker at pH = 0.2 in all spectra. This indicates that the average orientation of the aromatic rings, and hence the wings, of cavitand molecules must now lie close toward the surface plane, a consequence of vase-to-kite switching of the molecules. We can analyze the ν_2 spectral peaks and deduce more quantitative information about the conformational change.

From fitting of the SFG spectra using eqs 1 and 2, the nonvanishing $|\chi_{S,ijk}^{(2)}|$ of the ν_2 mode in the lab coordinates can be deduced. For the ν_2 mode, only two hyperpolarizability elements, $\alpha_{\zeta\zeta\zeta}^{(2)}$, and $\alpha_{\xi\xi\xi}^{(2)}$, in the molecular coordinates with $\hat{\zeta}$ being along the main molecular axis and $\hat{\xi}$ in the molecular plane, are nonvanishing. From

eq 2, the relations between $\chi_{S,ijk}^{(2)}$ and $\alpha_{lmn}^{(2)}$ for an azimuthally isotropic surface are

$$\chi_{XXZ}^{(2)} = \frac{1}{8} N_s \alpha_{\xi\xi\xi}^{(2)} \langle \cos \theta [3 + \cos 2\theta + 2 \sin^2 \theta (2r - \cos 2\psi)] \rangle$$

$$\chi_{XZX}^{(2)} = -\frac{1}{4} N_s \alpha_{\xi\xi\xi}^{(2)} \langle \cos \theta \sin^2 \theta (1 - 2r + \cos 2\psi) \rangle$$

$$\chi_{ZZZ}^{(2)} = N_s \alpha_{\xi\xi\xi}^{(2)} \langle \cos \theta (\cos^2 \psi \sin^2 \theta + r \cos^2 \theta) \rangle \quad (3)$$

where θ is the angle between $\hat{\zeta}$ and \hat{z} , $r \equiv \alpha_{\zeta\zeta\zeta}^{(2)}/\alpha_{\xi\xi\xi}^{(2)}$, and the angular brackets denote an orientational average with $f(\Omega) = f(\theta) \delta(\psi - \pi/2)$ as the distribution function. We assume a truncated flat distribution $f(\theta) = \text{constant}$ for $\theta_{\min} < \theta < \theta_{\max}$, and $f(\theta) = 0$ elsewhere. Then using eq 3 and the experimental values of $\chi_{S,XXZ}^{(2)}$, $\chi_{S,XZX}^{(2)}$ and $\chi_{S,ZZZ}^{(2)}$, we can deduce $\Delta\theta = (\theta_{\min}, \theta_{\max})$ for pH = 5.7 and pH = 0.2. Following the above procedure to analyze the spectra in Figure 2, we found $r \cong 2.4$, $\Delta\theta = (0^\circ, 29^\circ)$ and $\Delta\theta = (65^\circ, 112^\circ)$ for the case of pH = 5.7 and pH = 0.2, respectively. This set of parameters describes that in the vase configuration of QxCav, the aromatic rings of quinoxaline wings were oriented more or less along the surface normal, but in the kite configuration, nearly flat on the surface. In conclusion, we have demonstrated that SF vibrational spectroscopy is a noninvasive probe of cavitand monolayer conformation. Specifically, we showed unambiguously that the QxCav monolayer undergoes a vase to kite conformational change by changing the pH of the water subphase from 5.7 to 0.2. The spectra of the CH stretch modes of the alkyl chains showed that at a fixed surface pressure of 50 mN/m, the conformational transition decreased the surface molecular density by a factor of 2 because of the larger effective area of the kite compared to that of the vase. In addition, the spectra of the breathing mode of the quinoxaline rings on the wings showed that the orientation of the quinoxaline wings changed from nearly perpendicular to nearly parallel to the water surface. The results reported here provide the first quantitative molecular-level description of a vase-kite conformational change of a cavitand monolayer, showing that SFVS is a valuable technique and ideal for monitoring the conformational behavior of molecular receptors at interfaces.

Acknowledgment. This work was supported by a grant from the Naval Research Laboratory.

Supporting Information Available: Details of sample preparation and compression isotherms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Cram, D. J. *Science* **1983**, *219*, 1177.
- (2) Soncini, P.; Signore, S.; Dalcanale, E.; Ugozzoli, F. *J. Org. Chem.* **1992**, *57*, 4608–4612.
- (3) Vincenti, M.; Dalcanale, E.; Soncini, P.; Guglielmetti, G. *J. Am. Chem. Soc.* **1990**, *112*, 445–446.
- (4) Feresenbet, E. B.; Dalcanale, E.; Dulcey, C.; Shenoy, D. K. *Sens. Actuators B* **2004**, *97*, 211–220.
- (5) Moran, J. R.; Karbach, S.; Cram, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 5826–5828.
- (6) Azov, V. A.; Diederich, F.; Lill, Y.; Hecht, B. *Helv. Chim. Acta* **2003**, *86*, 2149–2155.
- (7) Azov, V. A.; Jaun, B.; Diederich, F. *Helv. Chim. Acta* **2004**, *87*, 449–462.
- (8) Frei, M.; Marotti, F.; Diederich, F. *Chem. Commun.* **2004**, 1362–1363.
- (9) Azov, V. A.; Schlegel, A.; Diederich, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 4635–4638.
- (10) See the π -A curves in Supporting Information. The pH = 5.7 curve in Figure 3 of Lagugn -Labarthe, F.; An, Y. Q.; Yu, T.; Shen, Y. R.; Dalcanale, E.; Shenoy, D. K. *Langmuir* **2005**, *21*, 7066–7070 was not properly plotted.
- (11) Zhuang, X.; Miranda, P. B.; Kim, D.; Shen, Y. R. *Phys. Rev. B* **1999**, *59*, 12632–12640.

JA064158G