

Probing Environment-Induced Vibrational Stark Effects in Benzyl Alcohol Derivatives in Gas Phase

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Understanding how local electric fields influence molecular systems and their spectroscopy provides a valuable approach for characterizing chemical systems. The Stark effect describes the modification of a molecule's spectroscopic properties under the influence of an electric field, whether externally applied or generated by its surrounding environment [1]. Such fields can arise in both gas-phase and condensed-phase systems, leading to spectral changes such as shifts or broadening.

This phenomenon can be explored in electronic transitions (referred to as the electronic Stark effect (ESE)) which is particularly valuable for studying UV–Vis chromophores. ESE has been widely used to probe charge migration processes [1], guide the design of fluorescent sensors [2], and, more recently, enable detailed conformational analysis through field-induced shifts in electronic transitions [3]. Complementarily, the vibrational Stark effect (VSE), defined as the shift in vibrational frequencies of a molecular probe in response to an electric field, provides a highly sensitive measure of the local chemical environment [4]. As such, VSE offers a powerful route to elucidate conformational preferences by correlating structure-dependent electric fields with vibrational frequency shifts.

In this work, we investigate the vibrational Stark effect in a series of benzyl alcohol (BA) derivatives (Figure 1). The hydroxyl group is used as a vibrational probe to evaluate the influence of neutral and charged substituents on the phenyl ring. By combining molecular mechanics with high-level quantum chemical calculations, we rationalize the relationship between molecular conformation, local electric fields, and vibrational response. Overall, this study demonstrates that VSE analysis provides a robust and sensitive approach to probing subtle environmental effects and their influence on conformational preferences in isolated molecular systems.

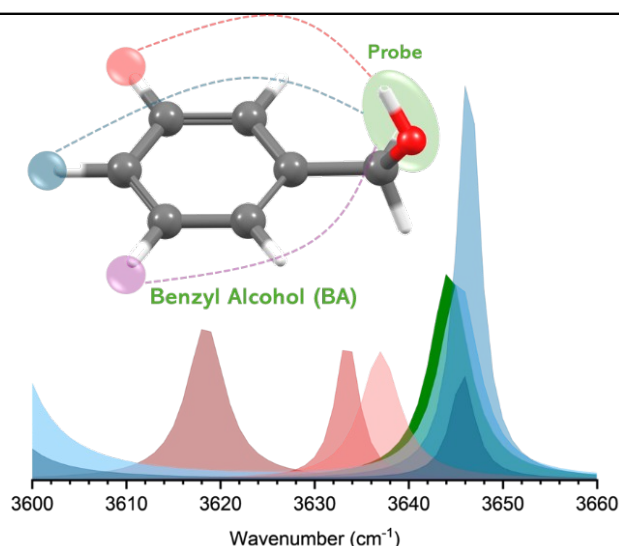


Figure 1 : Vibrational shifts of Benzyl Alcohol (BA) derivatives.

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