VIBRATIONAL SPECTROSCOPY OF NEGATIVE IONS BY STIMULATED RAMAN PUMPING

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We have been developing methods for studying the vibrational spectroscopy of Raman-active modes of gas-phase negative ions. Several years ago, we demonstrated that C_2^- could be vibrationally excited by stimulated Raman pumping (SRP); in that study, we monitored the excitation by resonant two-photon detachment of the anion^{*a*}. Since then, we have been investigating other, more general methods by which we could monitor the success of SRP. Recently we have demonstrated that anion photoelectron spectroscopy can be used in conjunction with SRP for vibrational spectroscopy of C_2^{-b} . Currently, we are attempting to couple SRP with the vibrational predissociation of a weakly-bound reporter species; in particular, we are focusing on the ArBrHI⁻ and ArNCO⁻ systems. Together, these methods constitute a quite general method for studying the vibrational spectroscopy of gas-phase negative ions. Ultimately, we hope to use the vibrationally excited ions produced by SRP to extend our studies of the transition states of neutral bimolecular reactions by the photodetachment of anion precursors^c; for instance, by exciting the hydrogen-atom stretch in BrHI⁻, we should be able to reach the transition state of the HI + Br \rightarrow HBr + I reaction by photodetachment.

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