LIFETIME-MEDIATED POLARIZATION EFFECTS IN NONLINEAR SPECTROSCOPY: DEGENERATE FOUR-WAVE MIXING STUDIES OF PREDISSOCIATED S_2O IN A SLIT-JET EXPANSION

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Transient S_2O molecules were entrained in a pulsed slit-jet expansion ($T_{rot} < 10$ K) and interrogated through use of sub-Doppler Degenerate Four-Wave Mixing (DFWM) spectroscopy. High-resolution scans have been acquired for the 2_o^v (v=3-10) vibronic bands of the intense $\tilde{C}\ ^1A' \leftarrow \tilde{X}\ ^1A'$ ($\pi^* \leftarrow \pi$) absorption system, where increasing excitation of the ν_2 S-S stretching mode is known to promote predissociation of the $\tilde{C}$ state.

For bands involving moderately-predissociated states (*e.g.*, 2_0^4 where $\tau_{\tilde{c}} \simeq 63$ ps), the recorded pattern of rovibronic line intensities exhibits a pronounced dependence upon DFWM polarization geometry, a situation not encountered in analogous studies performed for features terminating on long-lived levels of the $\tilde{C}$ manifold (*e.g.*, 2_0^3 where $\tau_{\tilde{c}} \simeq 22$ ns). This behavior can be reproduced quantitatively through detailed weak-field analyses of the resonant DFWM response, however, a qualitative understanding follows from the selective dissipation of optically-induced transient gratings as incurred by unimolecular relaxation pathways. In strongly-predissociated members of the 2_0^v progression (i.e., $v \geq 5$), additional polarization specificity is introduced by the presence of strong depopulation pumping processes which lead to the creation of net orientation and/or alignment of the molecular ensemble on a timescale commensurate with that of the pulsed four-wave mixing experiment

Owing to its absorption-based response and laser-limited spectral resolution, DFWM is often applied to target species where rapid nonraditive relaxation channels preclude successful exploitation of detection techniques based upon secondary matter-field interactions (e.g., fluorescence or ionization). Therefore, a detailed understanding of the role which molecular lifetime plays as a mediator for resonant nonlinear response is of central importance for the quantitative application of this optical scheme.

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