ANISOTROPY-INDUCED POLARIZATION EFFECTS IN DEGENERATE FOUR-WAVE MIXING SPECTROSCOPY: A NEW PROBE FOR MOLECULAR ORIENTATION AND ALIGNMENT

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The influence of angular momentum (rotational) anisotropy on the nonlinear optical technique of Degenerate Four-Wave Mixing (DFWM) has been investigated theoretically by incorporating a state-multipole expansion for the zero-order density operator into a perturbative treatment for resonant matter-field interactions. The weak-field response evoked from a rovibronically-resolved DFWM process is found to be affected strongly by the presence of molecular orientation and/or alignment, thereby leading to the formation of "anomalous" polarization components in the emerging signal field that are absent in the case of rotationally isotropic samples. Experimental verification of this behavior was obtained through use of the doubly-resonant Stimulated Emission Pumping (SEP) scheme. In particular, polarized ultraviolet excitation of jet-cooled CS_2 molecules enabled the selective preparation of gas-phase ensembles having well-defined angular momentum anisotropy in an electronically-excited intermediate state [*e.g.*, V $^1B_2$ ($^1\Delta_u$)], as quantified by the distribution and correlation of probability amplitude among the magnetic sublevels comprising an isolated rovibronic line. Before the transient population/coherence created in this intermediate manifold could decay through radiative or nonradiative channels, polarization resolved DFWM spectroscopy was employed to probe transitions terminating on highly excited vibrational levels of the $\tilde{X}\ ^1\Sigma_g^+$ ground electronic potential surface. Recorded data sets are in excellent agreement with theoretical predictions, thus suggesting an entirely new class of resonant four-wave mixing measurements designed to permit the extraction of spatial (angular momentum) information in a manner that is both background-free and insensitive to isotropic contributions.