TORSIONAL MOTION AND ANTISYMMETRIC STRETCHING IN THE EMISSION SPECTRA OF PHOTODISSOCIATING N₂O₄ NEAR 200 NM


Dispersed emission spectra have been collected for a free jet expansion of N₂O₄ excited in the 186 nm band using 199.7, 203, 204, and 205 nm laser light. Most molecules excited in this band dissociate directly; however, a tiny fraction emit photons and return to the ground state. As the molecule begins to dissociate, it develops good Franck-Condon overlap with progressively higher vibrational levels of the ground electronic state giving a series of peaks shifted from the laser line. The observed spectra show progressions in the N-N stretch and in combination bands involving the torsion and antisymmetric stretching motions. Electronic structure calculations (CIS) of the relevant excited states aid in understanding the changes experienced by the electronic wavefunction as the molecule dissociates. A comparison is drawn between these experiments and similar work on nitromethane. Finally, we reassign the torsional frequency, \( \nu_4 \), based on several bands observed in the spectra. This result is then combined with the results of previous workers to obtain a gas phase value for the NO₂ out of phase rock, \( \nu_4 \).

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