Collisions of oxygen or nitrogen molecules with laser-excited high vibrational levels of \( \text{O}_2(\text{A}^3\Sigma^+ \text{g}) \) produce a longer lived excited state, whose resonant multiphoton ionization (REMPI) spectrum cannot be assigned to any known singlet or triplet system [1]. We attribute the lower state of this new transition to the predicted [2,3] but previously unobserved \( ^5\Pi \text{g} \) valence state of \( \text{O}_2 \). The regular sequence of vibrational bands observed suggests that the upper state is an ion-pair state of \( \text{O}_2 \), dissociating to \( \text{O}^+ + \text{O}^- \). Two vibrational levels have been observed in the lower state and ten in the upper state, the latter in the range 97,000 to 100,000 cm\(^{-1}\).

\textit{Ab initio} calculations [2,3] indicate that, although quite weakly bound, at large internuclear distances the \( ^5\Pi \text{g} \) valence state should be the lowest of the states dissociating to ground state atoms. Because of its high degeneracy it could be a key intermediate state in \( \text{O} + \text{O} \) recombination [4,5]. We are developing a more detailed and quantitative theoretical model of \( \text{O} + \text{O} + \text{M} \) collisions. In addition to the experimental spectroscopy and kinetics results, we will also present preliminary work on spin-orbit resolved long-range potential curves for \( \text{O}_2 \) and implications for oxygen atom recombination and the role of \( \text{O}_2(\text{g}^5\Pi \text{g}) \) in predicting atmospheric nightglow emissions [6].

References:


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