

O₂(⁵Π_g), ION-PAIR STATES, AND OXYGEN ATOM RECOMBINATION

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Collisions of oxygen or nitrogen molecules with laser-excited high vibrational levels of O₂(A³Σ_u⁺) 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 ⁵Π_g valence state of O₂. The regular sequence of vibrational bands observed suggests that the upper state is an ion-pair state of O₂, dissociating to O⁺ + 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.

Ab initio calculations [2,3] indicate that, although quite weakly bound, at large internuclear distances the ⁵Π_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 O + O recombination [4,5]. We are developing a more detailed and quantitative theoretical model of O + O + 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 O₂ and implications for oxygen atom recombination and the role of O₂(⁵Π_g) in predicting atmospheric nightglow emissions [6].

References:

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