

HIGH VIBRATIONAL LEVELS OF O₂(*b*¹Σ_g⁺) AND O₂(*a*¹Δ_g)

K. S. KALOGERAKIS, D. L. HUESTIS, P. C. COSBY, T. G. SLANGER, R. A. COPELAND , *Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025*; A. TOTTH, *Bowdoin College, Brunswick, Me.*

Relaxation of laser-excited O₂(*A*³Σ_u⁺, *v* = 6 – 10) in collisions with O₂ populates high vibrational levels of O₂(*b*¹Σ_g⁺) and O₂(*a*¹Δ_g). Previous work on the spectroscopy of O₂ emissions from the Earth's night atmosphere has enabled us to assign the Q-branches of thirteen (*v'*, *v''*) bands in the (2+1) REMPI spectra of O₂(*b*¹Σ_g⁺, *v''* = 10 – 15) and O₂(*a*¹Δ_g, *v''* = 16 – 19), through the intermediate Rydberg levels 3*d*π ¹Σ_g⁺(*v'* = 2 – 5) and ¹Δ_g(*v'* = 4, 5), respectively.

The derived spectroscopic constants for O₂(*b*¹Σ_g⁺, *v''* = 10 – 13) agree with our previous work. Improved values are obtained for *v''* = 14, 15. Our constants for 3*d*π ¹Σ_g⁺(*v'* = 5) are the first available. Our spectra are better calibrated and our constants for the *v'* = 2 – 4 levels significantly more precise than the 1988–1992 work in the groups of Chupka and Houston.

The energies of O₂(*a*¹Δ_g, *v''* = 16 – 19) were known previously only to within about 80 cm⁻¹ from the 1995 electron scattering work of Allan. The highest level known accurately from nightglow spectra is *v''* = 11. Our spectral analysis gives precise rotational constants and ΔG values for these vibrational levels and for 3*d*π ¹Δ_g(*v'* = 4, 5). The absolute term energies are uncertain by about 5 cm⁻¹ based on earlier work in the groups of Chupka and Houston.

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