HIGH RESOLUTION VACUUM ULTRA-VIOLET
PHOTOABSORPTION IN THE SCHUMANN-RUNGE
SYSTEM OF MOLECULAR OXYGEN

By

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Extensive measurements of the photoabsorption spectrum of the Schumann-Runge system ($B^3\Sigma_u^- - X^3\Sigma_g^-$) of molecular oxygen have been made in the wavelength region from 140 nm to 200 nm. This region includes the complex vibrational-rotational line structure of the Schumann-Runge bands and extends to the comparatively featureless, Schumann-Runge continuum. The measurements were performed using a 6.65 metre vacuum ultraviolet monochromator with light intensity recorded by photoelectric detectors. A variety of thermodynamic conditions for the gas were selected to reveal the maximum information concerning the absorption process. These include absorption cells of various path lengths and gas temperatures in the range 90K to 600K.

In the Schumann-Runge bands the equivalent widths of more than 200 rotational lines of the ($v'-0$) band progression ($v' = 2, 3, 11$ to $19$) were measured with an instrument resolution of 0.006 nm. The high $v'$ bands have been measured line by line for the first time. A detailed curve of growth analysis was developed and applied to each rotational line to obtain the equivalent band oscillator strength and predissociation line width parameters necessary for the construction of an accurate synthetic spectrum. It is found the line parameters exhibit a significant rotational variation arising from the centrifugal distortion of the molecule.

The variation of the rotational line parameters with both band (vibrational quantum number) and centrifugal distortion (rotational quantum number) is accurately reproduced by an empirical model. This model involves the calculation of the overlap between wavefunctions that
describe the initial and final vibrational rotational states of the molecule. The wavefunctions are the solutions of the Schrödinger equation describing the vibrational motion of the nuclei, under the influence of the centrifugal distortion. The ground \(X^3\Pi_g\) and upper \(B^3\Sigma_u^-\) potential states being calculated from a Rydberg-Klein-Rees procedure.

The photoabsorption spectrum in the Schumann-Runge continuum varies uniformly with wavelength, showing some weak structure due to contributions to the continuum transitions to other electronic states. The continuum is temperature dependent because of the relative ground state populations for the molecule. This temperature dependence has been carefully measured, for the first time, for various wavelengths down to 140 nm and temperatures between 90K and 600K. With the empirical wavefunction model extended into the continuum, these measurements enable the separate determination of the repulsive part of the \(B^3\Sigma_u^-\) potential and the transition moment.

The Schumann-Runge continuum extends above the 175 nm dissociation limit, underlying the high Schumann-Runge bands. Measurements of the absorption at several window regions between rotational lines has enabled the underlying continuum to be estimated by subtraction of the band wing contribution to the cross-section. These measurements are reproduced by the wavefunction model that reveals more clearly the step-like structure of this continuum.

The model calculations are used to deduce a full set of parameters suitable for the construction of a synthetic absorption spectrum. This is applied to the absorption of solar radiation in the Earth's atmosphere. Excellent agreement is found with rocket and balloon
measurements of the solar transmittance. Dissociation rates for molecular oxygen are calculated.