Vibrational Structure in the Photo-electron Spectrum of $O_2^+ \, ^2\Sigma_g^-$ ($\sigma_g 2s$)

J. L. Gardner and James A. R. Samson
Behlen Laboratory of Physics
University of Nebraska
Lincoln, Nebraska 68508 U.S.A.

Abstract

Discrete vibrational structure has been observed in the photo-electron spectrum of oxygen at an ionization potential of 40.33 eV. Two levels, attributed to the $O_2^+ \, ^2\Sigma_g^-$ ($\sigma_g 2s$) final state, have been detected with a vibrational spacing of 0.071 eV.

We have previously reported a photoelectron spectrum of O_2 recorded with dispersed 304 Å He I radiation [1], in which the statistics were poor and the resolution was broadened by drift in the scanning electronics over the long period required to record the spectrum. We have recently re-recorded a much improved spectrum with a drift-free digital scanning system and with better trapping of scattered electrons in the ionization region. The low electron energy region (ie ionization potentials near the incident photon energy of 40.8 eV), reproduced in fig. 1, contains two peaks corresponding to ionization potentials of 40.33 and 40.40 eV in addition to a broad continuum. After considering the effects discussed below, we believe that the discrete structure corresponds to the $^2\Sigma_g^-$ final state and the broad continuum at lower ionization potentials to the $^4\Sigma_g^-$ final state, both arising upon removal of a $\sigma_g 2s$ electron from O_2 [2].

Three experimental effects which could account for the discrete structure are impurities in the gas, scattered light from the monochromator grating and inelastic scattering of the photoelectrons by the gas. The dominant impurity in the target gas is He from the light source; ionization of this gas was observed in the spectrum, but no other impurities could be detected at ionization potentials away from the two peaks in question. Further, the 0.071 eV separation of the new peaks does not agree with energy separations in any likely contaminant.

Replacing the grating with one giving an order of magnitude increase in the scattered light did not alter the population of the new peaks, relative to the c $^4\Sigma_u^-$ peaks [1,3]. Also, the peaks were not present in a spectrum recorded with scattered light (mostly 584 Å radiation) adjacent to the 304 Å line. Thus scattered light could not be responsible for the two peaks.

The most likely cause of spurious results is inelastic scattering of primary photoelectrons into the solid angle accepted by the analyzer; such effects have been observed previously in Xe [4] and in N_2 and CO [5]. However, the 0.071 eV separation of the peaks does not correspond to any known vibrational spacings in the O_2, O_2^+ or O_2^- molecules [6]. Further, the number of scattering events will depend quadratically on the pressure in the ionization region; such a pressure dependence is difficult to measure directly because of the low count rates and because the signal detected in general does not depend linearly (for the primary photo-electrons) on the pressure in the analyzer [4]. Thus spectra including the new peaks and the peaks from transitions to O_2^+ c $^4\Sigma_u^-$ were recorded at pressures of 1×10^{-4} and 3×10^{-4} Torr (measured at the detector). The ratio of the intensity of the new peaks at the two pressures, normalized to the intensity of the c $^4\Sigma_u^-$ peaks, was 1.21±.26, confirming that the intensity of the 40.33 and 40.40 eV peaks show the same pressure dependence as the rest of the known photo-electron spectrum.

Acknowledgement

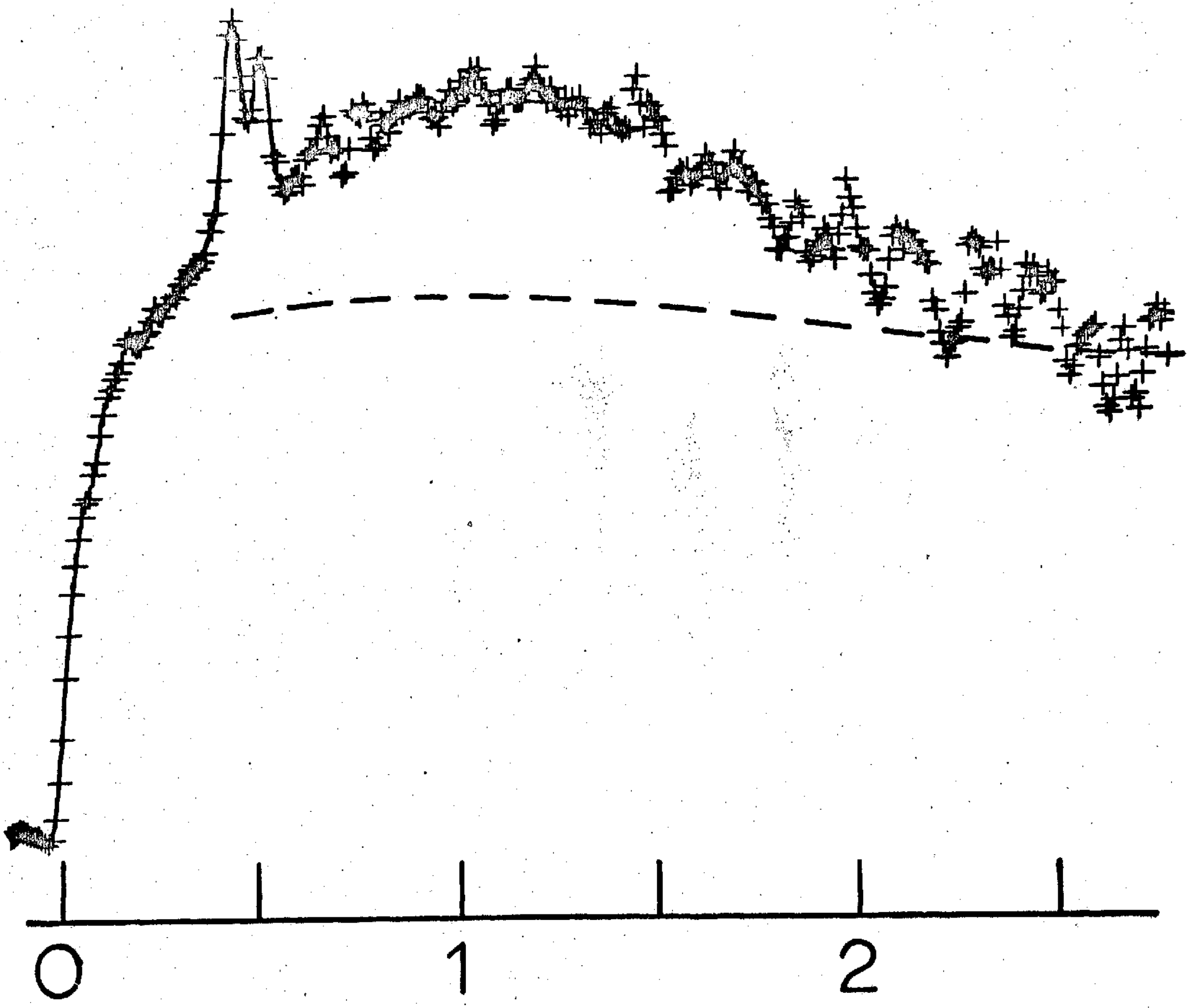
This research was supported in part by the National Aeronautics and Space Administration and by the Atmospheric Sciences Section of the National Science Foundation.

References

1. J. L. Gardner and J. A. R. Samson, J. Electron Spectrosc. 2, 259 (1973).
2. K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, ESCA Applied to Free Molecules, North Holland, 1969, p. 70.
3. O. Edqvist, E. Lindholm, L. E. Selin and L. Åsbrink, Phys. Scripta 1, 25 (1970).
4. J. L. Gardner and J. A. R. Samson, J. Electron Spectrosc. 2, 267 (1973).
5. D. G. Streets, A. W. Potts and W. C. Price, Int. J. Mass Spectrom. Ion Phys. 10, 123 (1972).
6. P. H. Krupenie, J. Phys. Chem. Ref. Data 1, 423 (1972).

Figure Caption

Fig. 1 Low electron energy region of the 304 Å O_2 photoelectron spectrum. The corresponding ionization potentials are 40.8 eV minus the electron energy. The spectrum has been corrected for the analyzer transmission; as a consequence, the relative error in the intensity near 0.5 eV is one half that near 2.5 eV.



ELECTRON ENERGY (eV)