

INTERSTELLAR O₂. II. VUV OSCILLATOR STRENGTHS OF SCHUMANN-RUNGE LINES
AND PROSPECTS FOR SPACE TELESCOPE OBSERVATIONS

PETER L. SMITH, H. E. GRIESINGER, JOHN H. BLACK, K. YOSHINO, AND D. E. FREEMAN

Harvard-Smithsonian Center for Astrophysics

Received 1983 April 5; accepted 1983 August 2

ABSTRACT

Interstellar molecular oxygen should be detectable in interstellar clouds through observation of its absorption lines in the spectra of background stars. This paper describes and presents the results of measurements of oscillator strengths for some lines in the vacuum ultraviolet (VUV) spectrum of O₂. Lines of the (13, 0) through (16, 0) bands of the $B^3\Sigma_u^- - X^3\Sigma_g^-$, Schumann-Runge system between 1760 Å and 1790 Å will be the most suitable for searches for absorption by interstellar O₂ with the High Resolution Spectrograph on Space Telescope. The strongest lines in these bands have oscillator strengths of about 3×10^{-5} . The strongest interstellar cloud absorption features will be lines with $f \approx 1.5 \times 10^{-5}$ that will have equivalent widths of about 13 mÅ in dark interstellar clouds with O₂ column densities of 10^{17} cm⁻², such as that in front of HD 29647.

Subject headings: interstellar: molecules — transition probabilities — ultraviolet: spectra

I. INTRODUCTION

a) Astrophysical Considerations

Molecular oxygen is predicted to be an important constituent of the interstellar gas; however, it has not yet been detected in an interstellar cloud. The preceding paper (Black and Smith 1984, hereafter Paper I) discussed the chemistry and the level populations for interstellar O₂; predicted column densities of O₂ in both diffuse and dark clouds; and proposed radio-frequency observations of ¹⁶O¹⁸O at 234 GHz. This paper discusses searches for absorption lines of interstellar O₂ in the vacuum ultraviolet (VUV) spectra of background stars. Interpretation of such observations requires accurate oscillator strengths for the rovibronic transitions that will be studied. We present and discuss such data.

The ultraviolet spectrometer on *Copernicus* was used for absorption observations of O₂ without success (Snow 1975). In particular, the forbidden $G(0)^3\Sigma_u^+ - X(0)^3\Sigma_g^-$ band was not detected toward *o* Per. No reports of observations of the Schumann-Runge (S-R) $B^3\Sigma_u^- - X^3\Sigma_g^-$ system at 1750 Å to 2000 Å have been made. This paper presents measured oscillator strengths for possible interstellar absorption lines in these bands (§ II) and demonstrates that the High Resolution Spectrograph (HRS) on Space Telescope (Brandt *et al.* 1979) will be well suited for sensitive searches for ultraviolet absorption lines of interstellar O₂ (§ III).

b) Existing VUV Spectroscopic Data for O₂

i) Spectrum

Krupenie (1972) has critically compiled data on the spectrum of O₂. The S-R bands between 1700 and 2000 Å appear to be the most suitable for optical searches for interstellar O₂ with HRS. Other band systems, discussed at the end of this section, are weak, diffuse, and/or lack rotational analysis.

The triplet-triplet, S-R bands contain many closely spaced, rotational lines belonging to 14 branches (Krupenie 1972; Creek and Nicholls 1975; Huber and Herzberg 1979). At low rotational quantum numbers, all 14 branches may contribute

significantly to the observed absorption (Brix and Herzberg 1954; Ackerman and Biaumé 1970). The upper state of the system predissociates and the individual rotational line widths of the (*v*', 0) bands depend quite strongly on *v*'; only for the least predissociated bands of the system have the triplet fine-structure components been resolved. The predissociation in the $B^3\Sigma_u^-$ state has been studied theoretically (Julienne and Krauss 1975; Julienne 1976; Sink and Bandrauk 1977) and triplet splitting constants for the $B^3\Sigma_u^-$ state have been evaluated from available experimental data (Bergeman and Wofsy 1972). The strongest S-R bands that arise from the lowest vibrational state, *v*" = 0, are those with *v*' = 13–16 because of Franck-Condon effects.

There are other VUV transitions of O₂. The strongest are of the $E^3\Sigma_u^- - X^3\Sigma_g^-$ system at 124.4 nm (Ogawa 1975; Ogawa *et al.* 1975). Other notations exist for the upper state (e.g., $B^3\Sigma_u^-$, Yoshimine *et al.* 1976; $2^3\Sigma_u^-$, Buenker, Peyerimhoff, and Poric 1976), and there is also some confusion in the literature as to whether this is the (0, 0) or the (1, 0) band. Nevertheless, this band is very diffuse, and both a rotational analysis, which would determine the wavelength of possible interstellar absorption, and a measurement of the *f*-values appear to be impossible.

Other VUV transitions of O₂ have been analyzed by Ogawa and co-workers (Yamawaki and Ogawa 1972; Chang and Ogawa 1972, 1973; Chang 1973); however, because of the death of M. Ogawa in 1974, much of this work is preliminary and incomplete. Several lines from the lowest, *N*" = 1, levels of the ground state are resolved: the $^7R_{31}(1)$ line of the $F(0)^3\Pi_u - X(0)^3\Sigma_g^-$ band at 116.1424 nm and the $R(1)$ line of the $g(0)^1\Pi_u - X(0)^3\Sigma_g^-$ band at 115.1430 nm. These lines could possibly be suitable for searches for interstellar O₂. However, the spectra show that the lines are weak and lie near the short wavelength limit of the HRS.

ii) Oscillator Strengths

Because of the important role of molecular oxygen in the photochemistry of the terrestrial atmosphere (cf. Frederick and Hudson 1980; Nicolet and Peetermans 1980; Blake 1979;

Longmire *et al.* 1979), many quantitative studies of its absorption spectrum have been made. Our laboratory has measured cross sections and band oscillator strengths of the (1, 0) through (12, 0) S-R bands (Yoshino *et al.* 1983). These bands were shown to be sufficiently broadened by predissociation for the measured cross sections to be independent of the full width at half-maximum (FWHM) of our instrument profile, viz., 13 mÅ (cf. § IIb). This value is 4 times smaller than that used for previous quantitative studies of these absorption bands. Comparison of the band f -values of Yoshino *et al.* (1983) with previously published values of Frederick and Hudson (1979) and of Gies *et al.* (1981), hereafter referred to as the Australian group,¹ revealed discrepancies larger than the quoted uncertainties.

The cross section measurements, from which the band oscillator strengths and predissociation line widths of the Australian group and of Frederick and Hudson (1979) were derived, have not been published. The full width half-maximum band widths (FWHM) of the instruments employed in these measurements were about 60 mÅ and 75 mÅ (0.006 nm and 0.0075 nm), respectively. These widths are considerably larger than the intrinsic line widths for the bands studied, which range from 5 to 12 mÅ (0.0005–0.0012 nm), and than the 13 mÅ (0.0013 nm) instrument profile for our spectrometer.

In the present astrophysical context, the strongest S-R absorption bands, i.e., (13, 0) through (16, 0), are the most relevant. For the bands with $v' \geq 14$, the Australian group has published the only band oscillator strengths that are based on moderate resolution spectra. Other results, some extending to $v' = 20$, were obtained with even lower resolution (Huebner *et al.* 1975; Hudson and Mahle 1972; Ackerman and Biaumé 1970; Farmer *et al.* 1968; Bethke 1959). There are significant discrepancies.

In the Australian work the usual assumption relating a line f -value, $f_{v'v''J'J''}$, to a band f -value, $f_{v'v''}$, is made, viz.

$$f_{v'v''J'J''} = \frac{(2 - \delta_{0,\Lambda''})}{(2 - \delta_{0,\Lambda'+\Lambda''})} \frac{\lambda_{v'v''}}{\lambda_{v'v''J'J''}} \frac{S(J', J'')}{2J'' + 1} f_{v'v''} \quad (1)$$

[it is understood that $f_{v'v''J'J''}$ and $S(J', J'')$ refer to individual lines (cf. Whiting *et al.* 1980); the other quantum numbers, n , Σ , and p , have been omitted for convenience]. $S(J', J'')$ is the purely rotational, Hönl-London factor, which can be calculated (Tatum and Watson 1971; Whiting *et al.* 1980) to an accuracy governed by that of the available spin-splitting constants (Bergeman and Wofsy 1972). Unfortunately, the coupling case varies from Hund's case b for high J to an intermediate case near the band head. Thus, for the lines that will be seen in the cold interstellar clouds, the splitting factors, and the Hönl-London factors which would be needed in obtaining line f -values from the band f -values, are unreliable.

The band oscillator strengths of Gies *et al.* (1981) were found to exhibit a dependence on the rotational quantum number of the line from which the determination was made (cf. Gies *et al.* 1981). This dependence may be a consequence of the

¹ The work of Gies *et al.* (1981) partially comprises a reanalysis of many of the earlier data by Lewis *et al.* (1978, 1979, 1980) from the same laboratory. In the region of the (13, 0) and (14, 0) bands, where their instrument width is about 12 times the predissociation width, the reanalysis resulted, approximately, in 43%–100% increases in predissociation width and 18%–24% decreases in band oscillator strength.

neglect of vibration-rotation interaction implicit in the use of equation (1). In a tabulation by Fang, Wofsy, and Dalgarno (1974), of the semiempirical S-R band oscillator strengths of Allison (1972), in which the potentials and transition moments of Allison, Dalgarno, and Pasachoff (1971) were used, a similar dependence of oscillator strength on rotational quantum number was reported.

As we have seen, existing measurements of $f_{v'v''}$ for the S-R bands were made with instrumental widths many times the line widths, the results of different measurements do not agree, the band f -values show a dependence upon J'' , and the Hönl-London factors are not well defined for the lines that will be strongest in the interstellar cloud absorption spectra. We have, therefore, studied absorption by individual lines of these bands—at an instrumental width which is 4 times smaller than that for previous work on these bands—in order to provide accurate line f -values for absorption features that might be seen in interstellar clouds. Because true cross sections cannot be measured directly for these bands with line widths comparable to or smaller than the instrumental width, a parametric modeling technique has been employed to fit a computed spectrum to the measured quantities.

II. MEASUREMENTS OF VUV OSCILLATOR STRENGTHS

a) Measurement Procedure

We have extended the work of Yoshino *et al.* (1983), who measured band oscillator strengths for the (1, 0) through (12, 0) S-R bands, by determining oscillator strengths of individual lines in the (13, 0) through (16, 0) bands.

The data were obtained in conjunction with, and by essentially the same apparatus and methods as, those of Yoshino *et al.* (1983). There were several minor changes or additions to the procedure: our data were accumulated for scanning intervals of 1.25 mÅ rather than 3 mÅ; the shape of the instrument profile was considered in detail and was best approximated by a triangle with FWHM of 13 mÅ; and different pressures, appropriate to the strength of the bands, were used. In units of 10^{18} cm^{-2} , the column densities were 2.68 and 5.24 for the (13, 0) band; 1.25, 2.42, and 5.05 for the (14, 0) band; 1.57, 3.27, and 6.39 for the (15, 0) band; and 2.42 and 3.76 for the (16, 0) band. As in the work of Yoshino *et al.* (1983), the attenuated and unattenuated beams were corrected for the effects of grating ghosts and scattering by reducing each by 3% of the unattenuated continuum.

b) Analysis of Data

Our procedure for determining the oscillator strengths for the single rotational lines in the S-R system of O_2 involved comparison of a synthetic spectrum with measured data.

A molecular line oscillator strength, $f_{v'v''J'J''}$, is related to the absorption cross section of the line, $\sigma(\lambda)$, by

$$f_{v'v''J'J''} = \frac{mc^2}{\pi e^2 \lambda^2} \frac{1}{\eta(v'', J'')} \int_{\text{line}} \sigma(\lambda) d\lambda \equiv f_{\text{line}} \quad (2)$$

where m , c , e , and λ have their usual meanings and $\eta(v'', J'')$ is the fractional population of the absorbing level. We assumed that the rotational lines had Voigt profiles and, following Frederick and Hudson (1979), expressed the cross section $\sigma(\lambda)$ for a single line in a form dependent upon only two parameters,

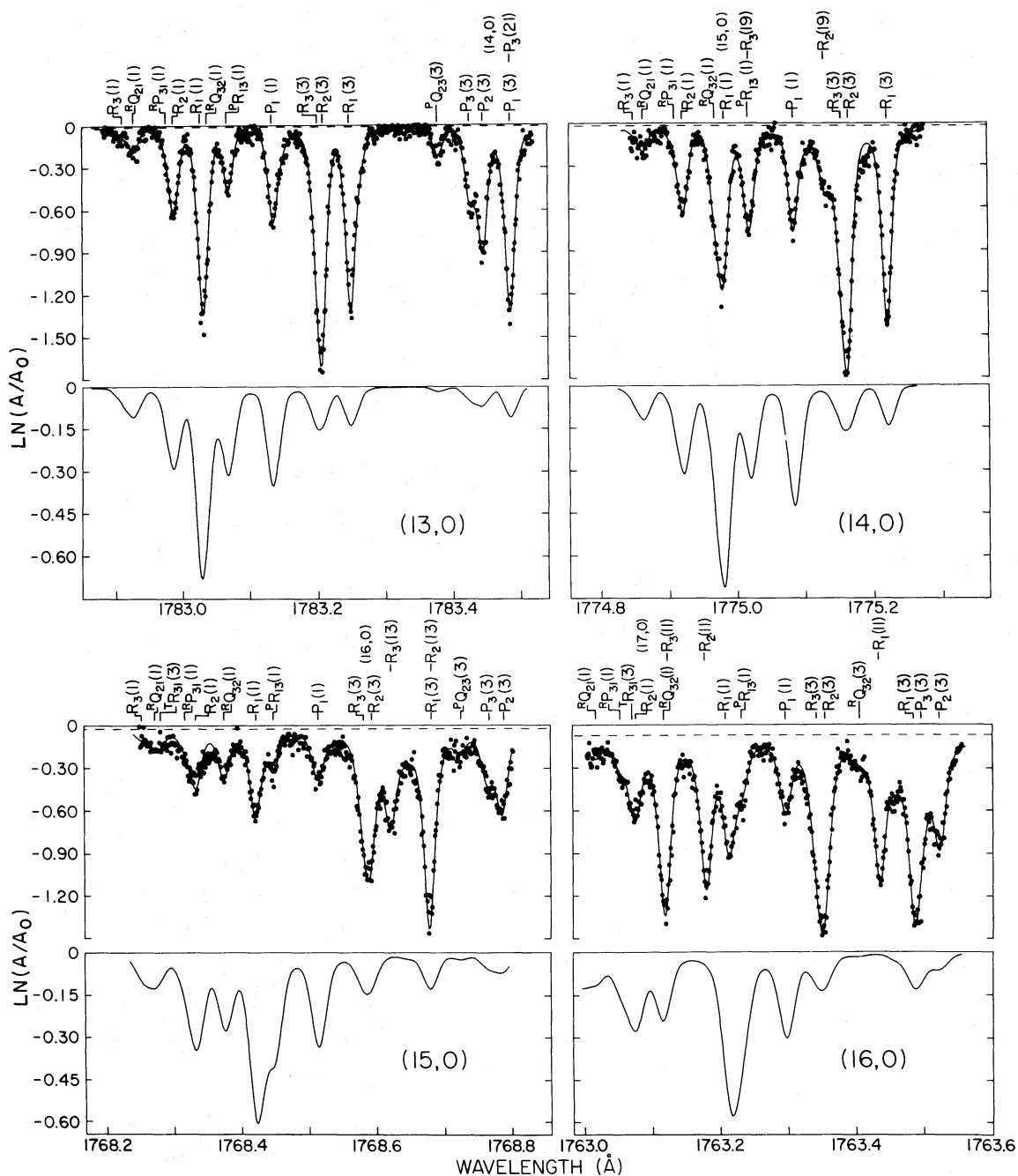


FIG. 1.—The 300 K laboratory absorption spectra and the predicted 10 K interstellar cloud absorption spectra of the band origin regions for the (13, 0) through (16, 0) bands of the Schumann-Runge system of O₂. Solid circles show the measurements; the line shows the synthetic spectra. The interstellar cloud spectrum has been broadened by a 20 mÅ rectangular instrument profile in order to represent a high-resolution-mode HRS spectrum. Locations of the unrevealed satellites are not indicated. Column densities of the (13, 0) through (16, 0) laboratory spectra were 2.68 , 2.42 , 1.57 , and $2.42 \times 10^{18} \text{ cm}^{-2}$, respectively; that for the interstellar cloud spectrum was 10^{17} cm^{-2} .

f_{line} , and a Lorentz line width (FWHM), $\Delta\lambda_L$, which is presumed to arise from predissociation:

$$\sigma(\lambda) = \frac{2}{\sqrt{\pi}} \frac{e^2}{mc^2} \eta(v'', J'') f_{\text{line}} \lambda^2 \Delta\lambda_L \times \int \frac{\exp(-t^2) dt}{(\Delta\lambda_L)^2 + [2(\lambda_0 - \lambda) - t\Delta\lambda_D/(\ln 2)^{1/2}]^2}, \quad (3)$$

where $\Delta\lambda_D$ is the calculated Doppler width (FWHM).

The familiar expression,

$$I_0(\lambda)/I(\lambda) = \exp[\sigma(\lambda)N], \quad (4)$$

for the ratio of the incident intensity of strictly monochromatic radiation, $I_0(\lambda)$, to that transmitted through a medium containing a column density, N , of molecules with absorption cross section, $\sigma(\lambda)$, must be modified to account for the finite bandpass of the instrument function, $G(\lambda', \lambda)$, of the spectrometer. The resultant expression for the measured flux ratio is (Hudson 1971)

$$\frac{A_0(\lambda)}{A(\lambda)} = \frac{\int G(\lambda, \lambda') d\lambda'}{\int G(\lambda, \lambda') \exp[-\sum \sigma(\lambda')N] d\lambda'}, \quad (5)$$

where the sum is over all lines and A_0 and A are the measured background and signal fluxes, respectively.

The line f -values and predissociation line widths were determined by comparing measured and calculated values of $\ln(A_0/A)$. The latter were determined by using a modified form of the computer program of Frederick and Hudson (1979). Scans of A_0 before and after the absorption measurements showed it to vary linearly with wavelength and to decrease by about 3% while the spectra were being obtained. Linear

functions of wavelength and time were used to interpolate the appropriate values of A_0 . The synthetic spectra used wavelengths from a preliminary version of Yoshino, Freeman, and Parkinson (1983) that dealt with the main branch lines only. The satellite line positions were calculated from the triplet splitting factors of Bergeman and Wofsy (1972). For some blends, adjustment of the wavelengths by 2.4 mÅ, or 10% of the observed FWHM, resulted in a better fit.

Absorption measurements were made in regions of minimal attenuation between the lines, and interpolation formulae were used to determine the continuum contributions to the spectra, σ_c (cf. Fig. 1 and Table 1) which arise from dissociative transitions from vibration-rotation levels with $v'' \geq 1$. We have made no allowances for the contribution from the wings of lines, and, therefore, our values are upper limits to the continuum cross sections. Our values are, however, significantly smaller than the results of Gies *et al.* (1982). Consequently, we conclude that the latter are too large.

The low signal levels associated with high optical depth produced data with a poor signal-to-noise ratio. Consequently, we limited the fit to points for which the optical depth was less than 2. This meant that for many lines, only spectra at the lowest two pressures were suitable for f -value determinations, although, for portions of some bands, a third spectrum was studied for comparison purposes. Examples of the absorption data and the spectral syntheses which fit them are shown in Figure 1. The final values of f_{line} and $\Delta\lambda_L$ are given in Table 1. In Table 2, our f -values are compared with other measured values for the lines that will be the strongest in the interstellar absorption spectrum of O₂ (cf. § III). The difference between our work and that of Frederick and Hudson (1979) and of Hudson and Mahle (1972) is usually within the

TABLE 1
LINE OSCILLATOR STRENGTHS FOR SOME LOW N'' , ROVIBRONIC LINES OF THE (13, 0) THROUGH (16, 0) SCHUMANN-RUNGE BANDS OF OXYGEN^a

| Band | (13, 0) | (14, 0) | (15, 0) | (16, 0) | | | | |
|---------------------------|---------------------|--------------|---------------------|--------------|---------------------|--------------|---------------------|--------------|
| $\Delta\lambda_L^b$ | 5.1 ± 0.5 | 5.7 ± 0.5 | 10.3 ± 0.3 | 12.4 ± 0.3 | | | | |
| σ_c^c | 3.7 | 7.3 | 15.1 | 30.5 | | | | |
| | $\lambda(\text{Å})$ | $f(10^{-5})$ | $\lambda(\text{Å})$ | $f(10^{-5})$ | $\lambda(\text{Å})$ | $f(10^{-5})$ | $\lambda(\text{Å})$ | $f(10^{-5})$ |
| $R_3(1)$ | {1782.909 | 0.32 wb | {1774.847 | 0.27 wb | {1768.254 | 0.78 wb | | |
| $^RQ_{21}(1)$ | {1782.927 | 0.20 wb | {1774.863 | 0.24 wb | {1768.273 | 0.23 wb | | |
| $^TR_{31}(3)$ | | | | | {1768.282 | 0.11 wb | | |
| $^RP_{31}(1)$ | {1782.975 | 0.10 wb | {1774.909 | 0.14 wb | {1768.319 | 0.24 wb | {× 1763.072 | 0.10 wb |
| $R_2(1)^*$ | {1782.986 | 1.31 b | {1774.922 | 1.46 b | {1768.334 | 1.73 b | {× 1763.054 | 0.32 wb |
| $^RQ_{32}(1)^*$ | {× 1783.035 | 1.11 b | {1774.968 | 1.30 b | {1768.376 | 1.46 | {1763.076 | 1.47 b |
| $R_1(1)^*$ | {× 1783.026 | 1.39 b | {1774.982 | 1.62 b | {1768.422 | 1.64 b | {1763.116 | 1.43 b |
| $^PR_{31}(1)^*$ | 1783.067 | 2.73 | 1775.020 | 2.91 b | {1768.449 | 3.38 b | {1763.214 | 1.46 b |
| $P_1(1)^*$ | 1783.133 | 0.89 | 1775.084 | 1.15 | {1768.514 | 0.90 | {1763.234 | 2.80 b |
| $R_3(3)$ | {1783.199 | 1.17 b | {1775.155 | 1.47 b | {1768.581 | 1.38 b | {1763.298 | 0.85 |
| $R_2(3)$ | {1783.208 | 1.17 b | {1775.167 | 1.49 b | {1768.593 | 1.45 b | {1763.344 | 1.28 b |
| $R_1(3)^*$ | 1783.248 | 1.29 | 1775.223 | 1.33 b | {1768.679 | 1.45 b | {1763.356 | 1.40 b |
| $^PQ_{23}(3)$ | 1783.378 | 0.25 w | | | {1768.725 | 0.34 w | {1763.486 | 1.39 b |
| $P_3(3)$ | {1783.425 | 0.68 b | | | {1768.765 | 0.93 b | {1763.500 | 0.62 b |
| $P_2(3)$ | {1783.445 | 0.95 b | | | {1768.787 | 1.18 b | {1763.524 | 1.06 |
| $P_1(3)$ | 1783.486 | 1.01 b | | | 1768.881 | 1.19 b | | |

^a Lines are listed in the expected order with the wavelength used in the synthesis; inversions from the expected order are marked ×. The alphabetic indicators of uncertainty, w and b, are explained in § IIc. Blended lines, b, in the same band are indicated by a left-hand brace. An asterisk denotes the lines most relevant to interstellar cloud absorption spectra (see Table 2).

^b $\Delta\lambda_L$ (in mÅ) is the predissociation line width (FWHM).

^c σ_c (in 10^{-21} cm²) is the continuum cross section (cf. § IIc).

combined limits of uncertainty. On the other hand, we frequently disagree with the work of Gies *et al.* (1981) by more than the combined uncertainties.

c) Uncertainties

The uncertainties in our f -values derive from the imprecision of the fitting procedure as well as from the uncertainties in the quantities σ_c , temperature, N , G , A , and A_0 .

The imprecision of the fitting procedure has two parts. First, the precision of matching the synthesis to the data on isolated spectral features was estimated to be 2%; i.e., for most lines, changes in f -value by this amount produced synthetic spectra which did not match the data. Second, there is uncertainty in the sum in the denominator of equation (5) of about 4%. This is a consequence of the blending of $N'' = 3$ satellites and of high N'' lines from other bands with the $N'' = 1$ and 3 main branch lines. We noted that the predicted intensities of

unblended satellites could disagree with the observations by as much as 20% and that the blended satellites could add 10% to the strength of main branch lines. The predicted intensities of high N'' , main-branch lines from other bands were more accurate but their contribution to the uncertainty of our f -values was similar. Thus, the contribution to the uncertainty of the f -values that derives from the fitting of the synthetic spectrum is 4.5% for optimum cases. Uncertainty in the fit for either isolated, weak lines (denoted w in Table 1) or strong, blended lines (denoted b) are a factor of two larger. The fitting of weak, blended lines (denoted wb) is uncertain by about 20% (cf. Table 3).

The fractional uncertainty in the line f -value that would result from uncertainties in the measured quantities is given by

$$\frac{\Delta f}{f} = \left[\sum_i \left(\frac{1}{f} \frac{df}{dp_i} \Delta p_i \right)^2 \right]^{1/2}, \quad (6)$$

TABLE 2
OSCILLATOR STRENGTHS OF INDIVIDUAL SCHUMANN-RUNGE LINES RELEVANT TO INTERSTELLAR CLOUD ABSORPTION SPECTRA^a

| WAVELENGTH (Å) | LINE | EQUIVALENT WIDTH (mÅ) ^b | LINE OSCILLATOR STRENGTH, f (in 10^{-5}) ^c | | | | | |
|-------------------|----------------------------------|---------------------------------------|--|---------------------|-------------------|---------------------|----------------------|----------------------|
| | | | This Work ^d | Hudson ^e | Gies ^f | Bethke ^g | Huebner ^h | Allison ⁱ |
| (13, 0) band: | | | | | | | | |
| 1782.986 | R ₂ (1) | 0.13 | 1.31 | 1.35 | 1.50 | 1.59 | 1.71 | 1.53 |
| 1783.026 | R ₁ (1) | 0.32 | 1.38 | 1.49 | 1.66 | 1.76 | 1.89 | 1.69 |
| 1783.035 | ^R Q ₃₂ (1) | 0.11 | 1.11 | 1.19 | 1.33 | 1.40 | 1.51 | 1.36 |
| 1783.067 | ^P R ₁₃ (1) | 0.12 | 2.73 | 2.38 | 2.65 | 2.81 | 3.02 | 2.72 |
| 1783.133 | P ₁ (1) | 0.21 | 0.89 | 0.85 | 0.95 | 1.00 | 1.08 | 0.97 |
| 1783.248 | R ₁ (3) | 0.10 | 1.29 | 1.44 | 1.60 | 1.70 | 1.83 | 1.63 |
| (14, 0) band: | | | | | | | | |
| 1774.922 | R ₂ (1) | 0.15 | 1.46 | 2.50 | 1.82 | 1.62 | 1.89 | 1.62 |
| 1774.968 | ^R Q ₃₂ (1) | 0.13 | 1.30 | 2.28 | 1.66 | 1.48 | 1.72 | 1.48 |
| 1774.982 | R ₁ (1) | 0.37 | 1.62 | 2.73 | 1.99 | 1.77 | 2.06 | 1.77 |
| 1775.020 | ^P R ₁₃ (1) | 0.13 | 2.91 | 4.56 | 3.14 | 2.96 | 3.44 | 2.97 |
| 1775.084 | P ₁ (1) | 0.26 | 1.14 | 1.53 | 1.05 | 0.99 | 1.15 | 1.00 |
| 1775.223 | R ₁ (3) | 0.11 | 1.33 | 2.66 | 1.93 | 1.73 | 2.01 | 1.71 |
| (15, 0) band: | | | | | | | | |
| 1768.334 | R ₂ (1) | 0.16 | 1.73 | 1.55 | 1.67 | 1.63 | 1.87 | 1.58 |
| 1768.376 | ^R Q ₃₂ (1) | 0.14 | 1.46 | 1.46 | 1.57 | 1.54 | 1.76 | 1.49 |
| 1768.422 | R ₁ (1) | 0.37 | 1.64 | 1.65 | 1.77 | 1.73 | 1.98 | 1.68 |
| 1768.499 | ^P R ₁₃ (1) | 0.15 | 3.38 | 2.92 | 2.94 | 3.07 | 3.51 | 2.99 |
| 1768.514 | P ₁ (1) | 0.20 | 0.90 | 0.90 | 0.91 | 0.95 | 1.09 | 0.93 |
| 1768.679 | R ₁ (3) | 0.11 | 1.45 | 1.63 | 1.74 | 1.71 | 1.96 | 1.64 |
| (16, 0) band: | | | | | | | | |
| 1763.076 | R ₂ (1) | 0.14 | 1.47 | 1.25 | 1.55 | 1.58 | 1.77 | 1.46 |
| 1763.116 | ^R Q ₃₂ (1) | 0.14 | 1.43 | 1.20 | 1.48 | 1.52 | 1.69 | 1.40 |
| 1763.214 | R ₁ (1) | 0.33 | 1.46 | 1.29 | 1.59 | 1.63 | 1.82 | 1.50 |
| 1763.234 | ^P R ₁₃ (1) | 0.12 | 2.80 | 2.40 | 2.73 | 3.03 | 3.39 | 2.81 |
| 1763.298 | P ₁ (1) | 0.19 | 0.85 | 0.70 | 0.80 | 0.89 | 0.99 | 0.82 |
| 1763.486 | R ₁ (3) | 0.11 | 1.39 | 1.28 | 1.58 | 1.62 | 1.81 | 1.48 |

^a Note that, at interstellar cloud temperatures, the blend of R₂(3) and R₃(3) will be as strong as some of the individual lines listed in this table (cf. Fig. 1).

^b Predicted value at 20 K for $N(\text{O}_2) = 2 \times 10^{15} \text{ cm}^{-2}$, i.e., for an optically thin line.

^c For work other than that reported here, the f -values were determined from published f -values by application of eq. (1) (recall that the band f -values of Gies *et al.* 1981 and of Allison 1972 are functions of J'').

^d Uncertainties for our work are given in Table 3. All lines in Table 2 are isolated or in categories w or b; i.e., the maximum uncertainty is $\pm 11\%$.

^e Frederick and Hudson 1979 for the (13, 0) band; Hudson and Mahle 1972 for the (14, 0) through (16, 0) bands; uncertainties for the (13, 0) band are $\pm 1.3\%$.

^f Gies *et al.* 1981; uncertainty $\pm 4\%$; see text note 1.

^g Bethke 1959.

^h Huebner *et al.* 1975.

ⁱ Allison 1972.

TABLE 3
UNCERTAINTIES IN LINE f -VALUES

| Lines | Narrower Bands (13, 0), (14, 0) | Wider Bands (15, 0), (16, 0) |
|---|------------------------------------|---------------------------------|
| Isolated lines | $\pm 6\%$ | $\pm 5\%$ |
| Strong, blended lines, b } Weak, isolated lines, w } | $\pm 11\%$ | $\pm 9\%$ |
| Weak, blended lines, wb | $\pm 20\%$ | $\pm 20\%$ |

where $(1/f)(df/dp_i)$ is the fractional change in f with change in quantity p_i , Δp_i is the uncertainty in p_i , and the sum is over all quantities. We did not calculate the factors in equation (6) explicitly, but used the spectral synthesis program to estimate the change in f -value resulting from changes in the p_i .

The uncertainty in σ_c contributes an uncertainty of less than $\pm 0.5\%$ to $\ln(A/A_0)$. Uncertainties in the Doppler width, fractional population, and in the column density, i.e., in temperature and pressure, contributed less than 1% uncertainty in the f -values. The uncertainty in the instrument profile width was $\pm 12\%$. Use of profiles modified by these amounts produced $\pm 6\%$ changes in f -values for lines of the (13, 0) and (14, 0) bands and $\pm 2\%$ changes for the more strongly predissociated lines of the (15, 0) and (16, 0) bands. These changes were assumed to be measures of the fitting uncertainties.

The above uncertainties, when combined in quadrature, were about the same size as the scatter in the results; for the narrower bands, (13, 0) and (14, 0), the scatter in the results from various pressures was larger than the estimated uncertainties, approaching $\pm 10\%$, and for the wider bands, (15, 0) and (16, 0), the scatter was smaller than the estimated uncertainties, approaching $\pm 3\%$. The estimated uncertainties for the narrower bands were increased to account for this slight anomaly. The combined uncertainties are given in Table 3.

III. PROSPECTS FOR OBSERVING ULTRAVIOLET ABSORPTION BY INTERSTELLAR O₂

In Paper I, the chemistry and level populations for interstellar O₂ are discussed, column densities for several types of clouds are predicted, and some ground-based observations of radio-frequency emission lines of ¹⁶O¹⁸O are suggested. The predicted column densities are 10^{10} – 10^{13} cm⁻² for diffuse clouds and as much as 10^{17} – 10^{18} cm⁻² for dark clouds.

It will be possible to search for interstellar O₂ using the High Resolution Spectrograph (HRS) on Space Telescope to observe O₂ ultraviolet absorption lines in the spectrum of a background star. The lines that will have the largest equivalent widths are those with relatively large oscillator strength that arise from the low J'' levels, which have the largest share of the population at cloud temperatures (cf. Table 2, Paper I). We used the design specifications of HRS (Bahcall and O'Dell 1979), our measured rovibronic line f -values, and the calculated level populations to predict interstellar absorption profiles for the (13, 0) through (16, 0) bands of the $B^3\Sigma_u^- - X^3\Sigma_g^-$, S-R system. The calculated interstellar absorption spectra for the case of a cloud with $N(\text{O}_2) = 1 \times 10^{17}$ cm⁻² at $T = 10$ K is shown in Figure 1.

The flux of ζ Oph at the wavelengths of the S-R bands, 3×10^{-9} ergs cm⁻² s⁻¹ Å⁻¹, will permit a detection threshold

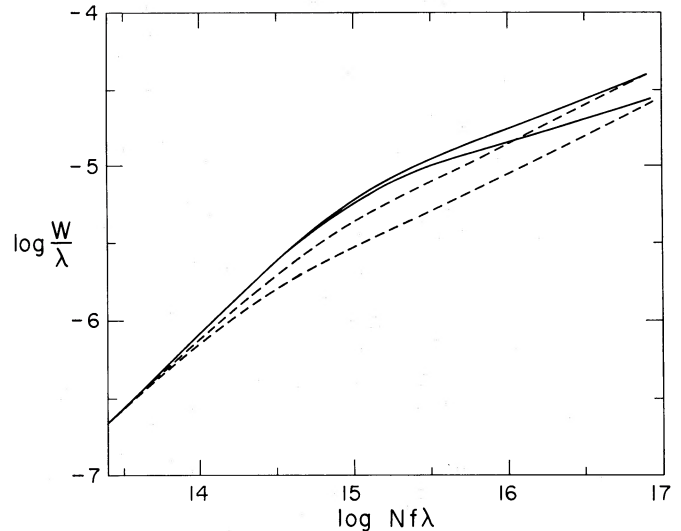


FIG. 2.—Curves of growth for lines of the (13, 0) and (16, 0) bands of O₂. These bands have the minimum and maximum, respectively, values of natural line widths of the bands studied (cf. Table 1). W is the equivalent width. $Nf\lambda$ is in units of cm⁻² Å. The dashed curves are for $b = 0.1$ km s⁻¹; the solid curves for $b = 1.0$ km s⁻¹. The upper curve for each value of b is for the (16, 0) band.

of 0.06 mÅ at the level of 3 standard deviations in a 2000 s exposure with HRS. A column density $N(\text{O}_2) = 3 \times 10^{14}$ cm⁻² would be required to produce this equivalent width in the strongest O₂ lines. The column density of O₂ toward ζ Oph is expected to be several orders of magnitude smaller than the above value (cf. Paper I, § IIc) and, therefore, if O₂ is formed by gas phase processes alone, it is unlikely to be detected by VUV observations of diffuse clouds.

Alternatively, one might observe in the direction of a more highly reddened star that lies behind a much larger column of O₂. Observable O₂ absorption lines in such clouds will show curve of growth effects. The natural widths of the lines (cf. Table 1), the Doppler broadening parameter, b , and the physical properties of the cloud, i.e., temperature and pressure, must be included in any interpretation of observed spectra. Curves of growth for the (13, 0) and (16, 0) bands, i.e., those with the largest and smallest natural widths in our study, for two values of the Doppler broadening parameter, $b = 0.1$ km s⁻¹ and $b = 1.0$ km s⁻¹, are given in Figure 2.

The late B star HD 29647 lies behind one of the darkest parts of the Taurus molecular cloud and has a flux at 1750 Å of 5×10^{-14} ergs cm⁻² s⁻¹ Å⁻¹ (Snow and Seab 1980). Column densities of foreground interstellar C₂ (Hobbs, Black, and van Dishoeck 1983) and CN (Crutcher 1983) are known to be large toward this star. The interstellar extinction of ultraviolet light from this star is known to be abnormally low, relative to the column density of the gas. Thus there will be few—if any—other locations as favorable as this for ultraviolet absorption line studies of interstellar molecules. A column density $N(\text{O}_2) \geq 10^{17}$ cm⁻² would not be unexpected in front of HD 29647; $N(\text{OH}) \approx 10^{15}$ cm⁻² over much of the Taurus cloud complex (Baud and Wouterloot 1980) and $n(\text{O}_2)$ could be 100 $n(\text{OH})$ (cf. Paper I, § II d). If O₂ level populations at $T = 10$ K appropriate for the Taurus cloud (cf. Table 2 in Paper I) and a value $b = 1.0$ km s⁻¹ are adopted, then a

column density $N(\text{O}_2) = 1.0 \times 10^{17} \text{ cm}^{-2}$ would produce an equivalent width of 13 mÅ in the strongest line, the $R_1(1)$ line of the (15, 0) band. Such a spectral feature should be detectable in the UV spectrum of this star in a 2000 s exposure with HRS. If $n(\text{O}_2) \approx n(\text{CO})$, then $N(\text{O}_2)$ could be as large as 10^{18} cm^{-2} (cf. Paper I), and the equivalent width would be 28 mÅ.

Searches for interstellar O₂ using the HRS will be considerably more sensitive than the ground-based observations at the 234 GHz line of ¹⁶O¹⁸O discussed in Paper I. The VUV observations could detect O₂ at column densities of 10^{17} cm^{-2} , albeit in a very few locations such as that in front of HD 29647. Detection of several VUV lines of O₂ would permit assessment of the predicted level populations and of

the assumed properties of the cloud, such as temperature, density, and Doppler broadening. The ground-based, radio-frequency observations will be limited to regions of larger column density, $N(\text{O}_2) \approx 10^{18} \text{ cm}^{-2}$. However, it is possible that such column densities exist in many locations so that O₂ abundances could be studied in a number of clouds.

The authors gratefully acknowledge the generous assistance and advice of W. H. Parkinson and R. D. Hudson, and thank J. R. Esmond, N. Galluccio, and A. Morrell for their technical support. This work was supported in part by NASA grants NSG-7304 and NSG-5176 and NSF grant AST 81-14718 to Harvard College.

REFERENCES

- Ackerman, M., and Biaumé, F. 1970, *J. Molec. Spectrosc.*, **39**, 73.
 Allison, A. 1972, unpublished, except for examples given in Table 3 of Fang, Wofsy, and Dalgarno (1974).
 Allison, A. C., Dalgarno, A., and Pasachoff, N. W. 1971, *Planet. Space Sci.*, **19**, 1463.
 Bahcall, J. N., and O'Dell, C. R. 1979, in *IAU Colloquium 54, Scientific Research with the Space Telescope*, ed. M. S. Longair and J. W. Warner, NASA CP-211, p. 31.
 Baud, B., and Wouterloot, J. G. A. 1980, *Astr. Ap.*, **90**, 297.
 Bergeman, T. H., and Wofsy, S. C. 1972, *Chem. Phys. Letters*, **15**, 104.
 Bethke, G. W. 1959, *J. Chem. Phys.*, **31**, 669.
 Black, J. H., and Smith, P. L. 1984, *Ap. J.*, **277**, 562 (Paper I).
 Blake, A. J. 1979, *J. Geophys. Res.*, **84**, 3272.
 Brandt, J. C., et al. 1979, *High Resolution Spectrograph for the Space Telescope, Proc. Soc. Photo-Opt. Engr.*, **172**, Instrumentation in Astronomy III.
 Brix, P., and Herzberg, G. 1954, *Canadian J. Phys.*, **32**, 110.
 Buenker, R. J., Peyerimhoff, S. D., and Poric, M. 1976, *Chem. Phys. Letters*, **42**, 383.
 Chang, H. C. 1973, Ph.D. thesis, University of Southern California.
 Chang, H. E., and Ogawa, M. 1972, *J. Molec. Spectrosc.*, **44**, 405.
 ———. 1973, Internal Technical Report USC-VAC-UV-140, University of Southern California.
 Creek, D. M., and Nicholls, R. W. 1975, *Proc. Roy. Soc. London A*, **341**, 517.
 Crutcher, R. M. 1983, *Ap. J.*, submitted.
 Fang, T. M., Wofsy, S. C., and Dalgarno, A. 1974, *Planet. Space Sci.*, **22**, 413.
 Farmer, A. J., Fabian, W., Lewis, B. R., Lokan, K. H., and Haddad, G. N. 1968, *J. Quant. Spectrosc. Rad. Transf.*, **8**, 1739.
 Frederick, J. E., and Hudson, R. D. 1979, *J. Molec. Spectrosc.*, **74**, 247.
 ———. 1980, *J. Atmos. Sci.*, **37**, 1088.
 Gies, H. P. F., Gibson, S. T., Blake, A. J., and McCoy, D. G. 1982, *J. Geophys. Res.*, **87**, 8307.
 Gies, H. P. F., Gibson, S. T., McCoy, D. G., Blake, A. J., and Lewis, B. R. 1981, *J. Quant. Spectrosc. Rad. Transf.*, **26**, 469.
 Hobbs, L. M., Black, J. H., and van Dishoeck, E. F. 1983, *Ap. J. (Letters)*, **271**, L95.
 Huber, K. P., and Herzberg, G. 1979, *Molecular Spectra and Molecular Structure. IV: Constants of Diatomic Molecules* (New York: van Nostrand Reinhold).
 Hudson, R. D. 1971, *Rev. Geophys. Space Phys.*, **9**, 305.
 Hudson, R. D., and Mahle, S. H. 1972, *J. Geophys. Res.*, **77**, 2902.
 Huebner, R. H., Celotta, R. J., Mielczarek, S. R., and Kuyatt, C. E. 1975, *J. Chem. Phys.*, **63**, 241.
 Julienne, P. S. 1976, *Molec. Spectrosc.*, **63**, 60.
 Julienne, P. S., and Krauss, M. 1975, *J. Molec. Spectrosc.*, **56**, 270.
 Krupenie, P. H. 1972, *J. Phys. Chem. Ref. Data*, **1**, 423.
 Lewis, B. R., Carver, J. H., Hobbs, T. I., McCoy, D. G., and Gies, H. P. 1978, *J. Quant. Spectrosc. Rad. Transf.*, **20**, 191.
 ———. 1979, *J. Quant. Spectrosc. Rad. Transf.*, **22**, 213.
 ———. 1980, *J. Quant. Spectrosc. Rad. Transf.*, **24**, 364.
 Longmire, M. S., Bartoe, J. D., Brown, C. M., Brueckner, G. E., and Tousey, R. 1979, *J. Geophys. Res.*, **86**, 5203.
 Nicolet, M., and Peetermans, W. 1980, *Planet. Space Sci.*, **28**, 85.
 Ogawa, M. 1975, *Canadian J. Phys.*, **53**, 2703.
 Ogawa, M., Yamawaki, K. R., Hashizume, A., and Tanaka, Y. 1975, *J. Molec. Spectrosc.*, **55**, 425.
 Sink, M. L., and Bandrauk, A. D. 1977, *J. Chem. Phys.*, **66**, 5313.
 Snow, T. P. 1975, *Ap. J. (Letters)*, **201**, L21.
 Snow, T. P., Jr., and Seab, C. G. 1980, *Ap. J. (Letters)*, **242**, L83.
 Tatum, J. B., and Watson, J. K. G. 1971, *Canadian J. Phys.*, **49**, 2693.
 Whiting, E. E., Schadee, A., Tatum, J. B., and Hougen, J. T. 1980, *J. Molec. Spectrosc.*, **80**, 249.
 Yamawaki, K., and Ogawa, M. 1972, Internal Technical Report USC-VAC-UV-130, University of Southern California.
 Yoshimine, M., Tanaka, K., Tatewaki, H., Obara, S., Sasaki, F., and Ohno, K. 1976, *J. Chem. Phys.*, **64**, 2254.
 Yoshino, K., Freeman, D. E., Esmond, J. R., and Parkinson, W. H. 1983, *Planet. Space Sci.*, **31**, 339.
 Yoshino, K., Freeman, D. E., and Parkinson, W. H. 1983, *J. Phys. Chem. Ref. Data*, **13**, in press.

JOHN H. BLACK: Steward Observatory, University of Arizona, Tucson, AZ 85721

DARYL E. FREEMAN, HARRIET E. GRIESINGER, PETER L. SMITH, and KOUICHI YOSHINO: Harvard College Observatory, 60 Garden Street, Cambridge, MA 02138