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VIBRATIONAL POPULATIONS OF O_2 (A $^3\Sigma_u^+$) AND SYNTHETIC SPECTRA OF THE HERZBERG BANDS IN THE NIGHT AIRGLOW

by

Vladimir Degen

Laboratory for Atmospheric and Space Physics
University of Colorado
Boulder, Colorado
80302

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ABSTRACT

The relative vibrational populations of the O_2 (A $^3\Sigma_u^+$) state in the nightglow have been determined for $0<v'\leq 10$ by matching synthetic spectra of the Herzberg bands (A $^3\Sigma_u^+$ - X $^3\Sigma_g^-$) to various published spectrograms. The synthetic spectra of the "pure" Herzberg bands obtained from this procedure are given at resolutions ranging from 1 $\overset{o}{A}$ to 25 $\overset{o}{A}$.

INTRODUCTION

The Herzberg I $(A^3\Sigma_u^+ - X^3\Sigma_g^-)$ bands of O_2 are a principal

contributor to the nightglow emission in the wavelength region

2500 to 5000 A. The relative populations of the vibrational

levels of the excited state of the transition are of some

interest, partly because the knowledge of the levels involved

is necessary for an unambiguous identification of all the bands

and of other fainter features present in the spectrum, and

partly because the knowledge of their distribution is important

in any discussion of the excitation of the system. While the

nightglow spectrum of the Herzberg bands has been studied

extensively both from the ground (Chamberlain, 1955, 1961;

Krassovsky, et al., 1962; Ingham, 1962; Broadfoot and Kendall,

1968) and using rocket techniques (Hennes, 1966), to date only

the progressions involving the levels v' = 3 through 7 have

been definitely identified in it; the identification of

the remaining progressions (the $A^3\Sigma_u^+$ state has 12 vibrational

levels in all) has been hampered by overlaps of bands from

different progressions, weak band intensities, and by the

presence of numerous faint spectral features towards the

longer wavelengths.

This paper presents, first, the relative populations of the vibrational levels $0 < v' \leqslant 10$, determined by matching calculated synthetic spectra of the Herzberg bands to the various published nightglow spectrograms, and second, as an aid to nightglow identification, the vibrationally identified "pure" Herzberg synthetic spectra at the various resolutions in the literature and as might be encountered in future observations. The calculated spectra do not include any effects due to the ozone absorption, or to emulsion sensitivity and instrument response.

Herzberg bands have been studied in the laboratory in absorption by Herzberg (1952), who also determined the vibrational and rotational constants used in this work, and in afterglows by Broida and Gaydon (1954), Barth and Kaplan (1957, 1959), Barth and Patapoff (1962), and Degen and Nicholls (1966, 1968). An atlas of the laboratory spectra of the Herzberg system is in press (Degen, et al., 1969). In the calculations of the synthetic spectra use has been made of the results obtained recently by Degen and Nicholls (1969) from afterglow measurements of the band intensities.

here

No attempt has been made to identify in the nightglow

spectrum any of the features not belonging to the Herzberg I

system.

PROCEDURE

The relative vibrational populations of the $A^3\Sigma_u^+$ state

were determined by constructing by means of a computer program

the synthetic spectra of Herzberg bands with various assumed

distributions of the vibrational levels, and by comparing

them to the existing spectrograms in the literature

(described in the next section).

The relevant equations and quantities necessary for

the computation of molecular band profiles may be found

in Herzberg (1950) and Nicholls (1964). The final expression

for the emission rate, I_K, in a rotational line with the

rotational quantum number K (i.e., the J-components due to

electron spin unresolved) is given by

$$I_K(\text{photons.sec}^{-1}) = \text{constant} \times$$

$$N_{v'} \, \nu_K^3 \, S_{v'v''} \, S_K[\exp(-B_{v'}K(K+1)hc/kT)]/Q_{v'}^{rot} \qquad (1)$$

where the constant depends on the units and geometry,

$N_{v'} = \sum_K N_{K,v'}$ is the population of the vibrational level v',

ν_K is the frequency of the rotational line K,

$S_{v'v''} = R_e^2(\nu_{v'v''})\, q_{v'v''}$, where R_e is the electronic transition moment, $\nu_{v'v''}$ is the average, or "band" frequency, and $q_{v'v''}$ is the Franck-Condon factor for the transition v'-v''.

The relative band intensities depend strongly on the quantity $S_{v'v''}$, also called the band strength. The frequency dependence of the electronic transition moment has been determined by Degen and Nicholls (1969) to be of the form

$$R_e(\nu) = \text{const.} \times \nu^{.86},$$

for 40,000 cm^{-1} < ν < 20,000 cm^{-1}, or 2500 Å < λ < 5000 Å, using the Franck-Condon factors computed by Jarmain (1968) appropriate to Klein-Dunham potentials. The uncertainty in the exponent is about 10%. The change in intensity due to the electronic transition moment alone is some 75%.

S_K, the Hönl-London factors for the transition, are given by (Present, 1935; Degen and Nicholls, 1966),

$$S_K = (12K^3 + 18K^2 - 2K-4)/(2K+3)(2K-1)$$

for the Q ($\Delta K = 0$) branch. Faint S and O ($\Delta K = \pm 2$) branches
are also associated with the transition (theoretically one
sixth the intensity of the Q branch); since, however, they
are not observed in practice, they are omitted in this work.
Trial band profiles computed with and without the S and O
branches showed no discernible differences.

$B_{v'}$, the rotational constants in the Boltzmann factor,
are those given by Herzberg (1952). The temperature, T, was
taken as the lower thermospheric temperature of 200 °K (U. S.
Standard Atmosphere, 1965) . $Q_{v'}$, the rotational partition
function of the level v', is given to a good approximation
by

$$Q_{v'} = kT/2hcB_{v'}$$

(The factor 1/2 arises from the fact that a half of the
rotational levels are missing in the homonuclear oxygen
molecule.)

In order to comply with the revised vibrational assign-
ment by one unit for the $A^3\Sigma_u^+$ state, suggested by Broida
and Gaydon (1954) and confirmed by Degen and Nicholls (1968),
the origin of the band system, v_{oo}, was extrapolated from
Herzberg's data to 35005.8 cm^{-1}. Similarly, the rotational

constant $B_{v'=0}$ was extrapolated to 0.907 cm^{-1}.

The inputs to the spectrum-generating program for the array $0 \leqslant v' \leqslant 11$, $0 \leqslant v'' \leqslant 12$ were the rotational frequencies computed from Herzberg's (1950, 1952) data and the line intensities calculated from (1). A triangular slit-function of a constant half-width was applied to the rotational lines. At least ten points per line were calculated. The intensity profiles were plotted out from tape by means of a Calcomp plotter. A Deslandres array of the band origins is given in Table I.

The relative vibrational nightglow populations, $N_{v'}$, of the $A^3\Sigma_u^+$ state, obtained by matching the observed and computed spectra, are tabulated in Table II. It should be recognized, however, that these numbers represent only the averages of the vibrational populations which may actually vary somewhat with altitude.

Other points noted in the calculations regarding the appearance of the synthetic spectra were, that the choice between the Morse (Nicholls, 1965) and the Klein-Dunham (Jarmain, 1968) Franck-Condon factors did not lead to any significant differences, and that the spectrum is not sensitive to temperature variations of 20 °K.

DESCRIPTION OF FIGURES AND COMMENTS

The resolutions covered in the Figures 1 through 5 are 1, 2.3, 5.5, 11, and 25 Angstroms, respectively. The intensity is in photons.sec^{-1} on an arbitrary scale. The magnitude of this scale has been preserved between the five figures, to give an idea of the relative exposures or scanning intervals required at the different resolutions.

In each figure the spectrum is arranged in sections with somewhat different intensity scales to offset the overall decrease in the intensity of the Herzberg spectrum toward the longer wavelengths. The sections are provided with common wavelength intervals of about 200 A.

The Herzberg nightglow spectrum is very rich in bands from many progressions, and it was found more convenient to arrange the identification according to the v'' = constant progressions instead of the more usual v' = constant progressions appropriate to emission. Bands in brackets belong to the Condon locus minima.

Figure 4 is a low resolution spectrum with a line half-width of 11 A, intended to match the rocket photographic spectrum obtained by Hennes (1966). The rocket spectrum is presented in intensity units, with emulsion sensitivity and instrument

response removed, and furthermore, the exposure was made above the ozone ultraviolet-absorbing layer; hence, it may be compared directly with the synthetic spectrum. The agreement at the short-wavelength end is very good up to about 3200 A, and this region was used to determine the relative vibrational populations for the levels v' = 3 through 10. These results show that levels with v' > 7 are indeed excited in the nightglow, though there is a marked drop-off in the vibrational populations toward the high v'.

It may be noted in Hennes' spectrum that the 5-2 band is depressed, apparently by the adjacent strong atomic oxygen line at 2972 A. Such effects are encountered in photographic spectrometry.

Figure 2 is a fairly high resolution spectrum with a half-width of 2.3 A which may be compared with the ground-based photographic spectrograms recorded by Chamberlain (1955) and Ingham (1961). These spectrograms provided a means of determining the vibrational populations for v' = 1 and 2, by comparing neighbouring band-pairs in the wavelength region above 3000 A. While it appears that the levels v' = 2 and v' = 1 are definitely excited in the nightglow, the presence

of numerous faint spectral features already mentioned permits only a rough estimate of the vibrational populations for these levels. The value quoted for $N_{v=0}$ is somewhat arbitrary.

Figure 3 is a two section spectrum of intermediate resolution with a 5.5 Å half-width, comparable to that of Broadfoot and Kendall (also ground-based). Similar comments as for Figures 2 and 4 apply.

Figures 1 and 5 cover the extreme resolutions of 1 Å and 25 Å, respectively. The former has not yet been attained observationally, and the latter is of a magnitude which might be used with a fast scanning photoelectric spectrometer.

Figure 6 gives, explicitly, the relative contribution of each single band to the spectrum, arranged such that each $v' =$ constant progression occupies one compartment in the figure. The line width is 10 Å.

On the whole the agreement between the observed and the calculated spectra tends to be better at the shorter wavelengths. The necessity of using bands from the primary and secondary Condon loci in some of the comparisons, particularly towards the longer wavelengths, may be responsible for some of the discrepancies in the band intensities which could not be removed by further adjusting the relative populations, $N_{v'}$.

TITLES OF FIGURES

Fig. 1.   1 A resolution.

Fig. 2.   2.3 A resolution.

Fig. 3.   5.5 A resolution.

Fig. 4.   11 A resolution.

Fig. 5.   25 A resolution.

Fig. 6.   Resolved spectrum of the Herzberg bands.

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12
0	2855.8*	2988.7	3132.3	3287.7	3456.7	3640.8	3842.4	4063.8	4308.0	4578.7	4880.4	5218.5	5599.7
1	2794.0	2921.1	3058.1	3206.1	3366.5	3541.0	3731.3	3939.8	4168.9	4421.9	4702.7	5015.7	5367.0
2	2737.1	2859.0	2990.0	3131.4	3284.3	3450.1	3630.5	3827.6	4043.5	4281.1	4543.7	4835.3	5160.9
3	2684.9	2802.0	2927.8	3063.2	3209.3	3367.5	3539.2	3726.1	3930.5	4154.6	4401.4	4674.5	4978.2
4	2637.0	2749.9	2871.0	3001.1	3141.2	3292.6	3456.5	3634.6	3828.8	4041.2	4274.3	4531.4	4816.2
5	2593.5	2702.6	2819.5	2944.8	3079.6	3225.0	3382.1	3552.5	3737.7	3939.9	4161.2	4404.5	4673.0
6	2554.3	2660.1	2773.2	2894.3	3024.5	3164.5	3315.7	3479.3	3656.8	3850.0	4061.1	4292.5	4547.1
7	2519.3	2622.2	2732.0	2849.6	2975.6	3111.1	3257.1	3414.8	3585.6	3771.2	3973.5	4194.7	4437.6
8	2488.9	2589.2	2696.2	2810.7	2933.2	3064.8	3206.3	3359.0	3524.2	3703.3	3898.2	4111.0	4343.9
9	2463.2	2561.5	2666.2	2778.0	2897.7	3026.0	3163.9	3312.5	3473.0	3646.9	3835.7	4041.5	4266.5
10	2443.0	2539.6	2642.5	2752.3	2869.7	2995.6	3130.7	3276.1	3433.0	3602.8	3786.9	3987.4	4206.2
11	2429.2	2524.7	2626.3	2734.8	2850.6	2974.7	3107.9	3251.2	3405.7	3572.7	3753.7	3950.6	4165.3

*Computed from Herzberg's 1950, 1952 data.

Table I.

Legend

Table I. Band origins (Å) of the O_2 $\left(A^3\Sigma_u^+ - X^3\Sigma_g^- \right)$ Herzberg I system.

v'	$N_{v'}$
0	(.10)
1	.20
2	.33
3	.57
4	1.00
5	.95
6	.88
7	.75
8	.35
9	.14
10	.13

Table II.

Legend

Table II. Vibrational populations of $O_2(A^3\Sigma_u^+)$ in the nightglow relative to $N_{v'=4} = 1$.

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