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Aeronomic problems of molecular oxygen photodissociation -
V. Predissociation in the Schumann-Runge bands of oxygen

by

M. NICOLET, S. CIESLIK and R. KENNES

B E L G I S C H I N S T I T U U T V O O R R U I M T E - A E R O N O M I E

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FOREWORD

This article entitled "Predissociation in the Schumann-Runge bands of oxygen" Part V of Aeronomic Problems of Molecular Oxygen Photodissociation will be published in Planetary and Space Science.

AVANT-PROPOS

Cet article intitulé "Predissociation in the Schumann-Runge bands of oxygen" Part V of Aeronomic Problems of Molecular Oxygen Photodissociation sera publié dans Planetary and Space Science.

VOORWOORD

Het artikel "Predissociation in the Schumann-Runge bands of oxygen" Deel V van Aeronomic Problems of Molecular Oxygen Photodissociation zal verschijnen in Planetary and Space Science.

VORWORT

Der Artikel "Predissociation in the Schumann-Runge bands of oxygen" Teil V von Aeronomic Problems of Molecular Oxygen Photodissociation wird in Planetary and Space Science publiziert werden.

AERONOMIC PROBLEMS OF MOLECULAR OXYGEN PHOTODISSOCIATION -
V. Predissociation in the Schumann-Runge bands of oxygen

by

Marcel Nicolet, S. Cieslik and Robert Kennes

ABSTRACT

New independent sets of laboratory absorption data for molecular oxygen provide sufficient spectral resolution in the Schumann-Runge region to yield linewidths of the rotational lines. A definitive determination of the absorption cross-sections as a function of wavelength and temperature is possible. An analysis has been made of these new results to prepare a parameterization adapted to 500 cm^{-1} intervals for atmospheric conditions between 170 and 270 K in the mesosphere and stratosphere.

RESUME

De nouvelles données de laboratoire sur l'absorption de l'oxygène moléculaire présentées avec une résolution spectrale suffisante permettent la détermination des largeurs des raies de rotation. Une détermination de la section efficace d'absorption en fonction de la longueur d'onde est définitivement rendue possible. Une analyse de ces données est présentée en vue de la détermination de formules numériques adaptées à des intervalles de 500 cm^{-1} par des conditions atmosphériques entre 170 et 270 K correspondant aux températures de la mésosphère et de la stratosphère.

SAMENVATTING

Nieuwe laboratoriumgegevens betreffende de absorptie van moleculaire zuurstof, voorgesteld met een voldoende spectrale resolutie, laten toe de breedtes van de rotatielijnen te bepalen. Een bepaling van de werkzame absorptiedoorsnede in functie van de golflengte wordt definitief mogelijk gemaakt. Een analyse van deze gegevens wordt voorgesteld teneinde de numerieke formules aangepast aan intervallen van 500 cm^{-1} te bepalen voor atmosferische voorwaarden tussen 170 en 270 K in de mesosfeer en de stratosfeer.

ZUSAMMENFASSUNG

Neue Laboratoriumdaten über der Absorption von Molekularsauerstoff, präsentiert mit genug Spektralresolution, lassen zu den Breiten der Rotationslinien zu bestimmen. Eine Bestimmung der effektiven Absorptionquerschnitt abhängig von der Wellenlänge wird definitiv ermöglicht. Eine Analyse der Daten wird präsentiert um die numerischen Formeln, angepasst an Intervallen von 500 cm^{-1} , zu bestimmen für atmosphärische Konditionen zwischen 170 und 270 K in der Mesosphäre und der Stratosphäre.

1. INTRODUCTION

Since 1969 (Ackerman, Biaumé and Nicolet 1969 ; Hudson and Carter, 1969 ; Hudson, Carter and Breig, 1969), the number of publications on spectroscopic aspects (absorption, predissociation and photodissociation) of the ultraviolet spectrum (Herzberg systems and Schumann-Runge system) of molecular oxygen has been large. This is due to a geophysical fact, namely that the O_2 photodissociation by solar UV radiation between 175 and 242 nm is the source of ozone in the stratosphere and mesosphere, and that the O_2 absorption controls the atmospheric transmittance in this spectral region ; i.e. it determines the differences in penetration of solar UV radiation at various wavelengths.

As pointed out by Nicolet and Mange (1954) precise knowledge of the absorption cross-sections in the bands of the O_2 Schumann-Runge system is needed for a detailed study of the penetration of solar radiation ; this requires exact knowledge of the rotational line positions, with their line widths and oscillator strengths. The first detailed discussions of the implication of predissociation in the Schumann-Runge band system of O_2 were made by Ackerman and Biaumé (1970), Ackerman, Biaumé and Kockarts (1970), Biaumé (1972a and b), Hudson and Mahle (1972), Allison, Dalgarno and Pasachoff (1971) and Fang, Wofsy and Dalgarno (1974). Most recent published determinations of the predissociation line widths and the band oscillator strengths can be found in Frederick and Hudson (1979) and in various Australian papers (Lewis et al., 1978, 1979, 1980, 1985 and 1986a and b; Gies et al., 1981, 1982).

The incorporation of the cross-section data of the Schumann-Runge bands into atmospheric models has been made by different groups (Kockarts, 1971, 1976 ; Blake, 1979 ; Frederick and Hudson, 1980a, b ; Nicolet and Cieslik, 1980 ; Nicolet and Peetermans, 1980 ; Nicolet, 1981 and Allen and Frederick, 1982) in order to yield a simple parameterization of the interaction of solar radiation with O_2 and with other minor atmospheric gases in the mesosphere and stratosphere.

With regard to the Herzberg continuum, the first detailed laboratory measurements at relatively high pressures were made by Ditchburn and Young (1962), and then extrapolated to provide absorption cross-sections applicable to the stratosphere. The extension of this continuum below 200 nm into the spectral range of the bands of the Schumann-Runge systems was based on the theoretical determination of Jarman and Nicholls (1967). Their theoretical curve was calibrated in terms of absolute values through use of the experimental data of Ditchburn and Young at wavelengths greater than 200 nm. The maximum absorption cross-section obtained near 195 nm is $1.3 \times 10^{-23} \text{ cm}^2$. It is important to point out that, in their studies of atmospheric absorption in the Schumann-Runge bands all the authors (Ackerman, Biaumé and Kockarts, 1970 ; Hudson and Mahle, 1972 ; Fang, Wofsy and Dalgarno, 1974 ; Kockarts, 1976 ; Nicolet and Peetermans, 1980 ; Frederick and Hudson, 1980a, b) used the theoretical values of Jarman and Nicholls, which are too high. If a mean value based on all experimental data (Ditchburn and Young, 1962 ; Ogawa, 1971 ; Hasson and Nicholls, 1971 and Shardanand and Prasad Rao, 1977) is used, there is a difference of a factor of 2 between the minimum and the maximum values. The lowest values obtained in the region 240 nm to 200 nm are those of Shardanand and Prasad Rao (1977) ; if they are used to calibrate the theoretical curve, the maximum absorption cross-section obtained at 195 nm is 10^{-23} cm^2 . This difference has already been indicated by Blake (1979).

Balloon-borne spectrometer measurements of the solar irradiance in the stratosphere were analyzed by Frederick and Mentall (1982), Herman and Mentall (1982) and Anderson and Hall (1986). After correction for the atmospheric opacity due to ozone, they imply absorption cross-sections in the Herzberg continuum that are even smaller than those reported by Shardanand and Prasad Rao (1977).

Recent laboratory measurements made at Cambridge, Mass. (Cheung, Yoshino, Parkinson, Guberman and Freeman, 1986), at Berkeley, Cal. (Johnston, Paige and Yao, 1984), and at Reims, France (Jenouvrier, Coquart and Merienne-Lafore, 1986) show that the absorption cross-

section is less than $1 \times 10^{-23} \text{ cm}^2$ at all wavelengths, and even of the order of $7.5 \times 10^{-24} \text{ cm}^2$ at short wavelengths near 200 nm (Nicolet and Kennes, 1986). Comparison of the various experimental results reveals some disagreement which can be taken as indicative of the uncertainties in the available data. In any case, at wavelengths shorter than 200 nm, it is necessary to reduce the effect of the Herzberg continuum, particularly in the region of the (5-0) to (2-0) bands of the Schumann-Runge system. At still shorter wavelengths i.e. for the (19-0) to (10-0) bands, it is also necessary to introduce absorption due to the Schumann-Runge continuum that occurs at wavelengths greater than 175 nm ; it corresponds to an absorption by thermally excited molecules (300 K in the laboratory). After the first analysis made by Allison, Dalgarno and Pasachof (1971) and by Hudson and Mahle (1972) and developed by Blake (1979), the recent measurements made by Gies, Gibson, Blake and McCoy (1982), Lewis, Berzins, Carver, Gibson and McCoy (1985a, 1985b) must be used, because the continuum, a function of the temperature, has been divided into its constituent parts : absorption into the $B^3\Sigma_u^-$, $A^3\Sigma_u^+$ and $^3\Pi_g$ states.

With regard to laboratory work on the Schumann-Runge bands, the absorption cross-sections at 300 K that coincide with atomic silicon lines have been determined by Ackerman et al. (1970) and recently throughout the whole region 179.3 - 201.5 nm by Yoshino, Freeman, Esmond and Parkinson (1983). An Atlas of the Schumann-Runge absorption bands of O_2 in the wavelength region 175-205 nm has been published by Yoshino, Freeman and Parkinson (1984). Their rotational assignments are generally in agreement with those of Ackerman and Biauomé (1970) and Brix and Herzberg (1954).

Finally, 2 recent publications (Nicolet et al, 1987 and 1988) describe the results obtained by a theoretical determination of the rotational structure and absolute absorption cross-sections of the O_2 Schumann-Runge bands between 300 and 79 K. This determination was based on the most recent experimental results. In the present paper the various spectroscopic parameters adopted to obtain the numerical values are provided for all possible calculations.

2. EXPERIMENTAL DATA ON ABSORPTION CROSS-SECTIONS

The absorption spectrum of the Schumann-Runge bands is characterized by various spectral intervals that correspond to the twenty bands (0-0) to (19-0). The adopted spectral limits cover the region from 49000 cm^{-1} to 57035 cm^{-1} , i.e. from 204 to 175 nm.

The experimental absolute cross-section data have been determined at 300 K and at 79 K with a bandwidth of 0.4 cm^{-1} in the wavelength region 179-201 nm corresponding to the $v' = 1$ to 12 bands by Yoshino et al. (1983 and 1987). These detailed measurements have been adopted for our aeronomic determination.

The positions of the lines within the Schumann-Runge bands have been calculated by using experimentally determined molecular constants, classical formulas yielding the energies of the quantum levels and sublevels and the selection rules for a $^3\Sigma_u^- - ^3\Sigma_g^-$ transition in a homonuclear molecule. The energies of the spin-split rotational levels of $^3\Sigma$ states can be expressed by the formulas of Miller and Townes (1953)

$$E_1(v, J) = T_v + B_v X - D_v X^2 - (\lambda_v - B_v + \frac{1}{2} \gamma_v) \\ - [(\lambda_v - B_v + \frac{1}{2} \gamma_v)^2 + 4X(B_v - \frac{1}{2} \gamma_v)^2]^{1/2}$$

$$E_2(v, J) = T_v + B_v X - D_v X^2$$

$$E_3(v, J) = T_v + B_v X - D_v X^2 - (\lambda_v - B_v + \frac{1}{2} \gamma_v) \\ + [(\lambda_v - B_v + \frac{1}{2} \gamma_v)^2 + 4X(B_v - \frac{1}{2} \gamma_v)^2]^{1/2}$$

for each component of the triplet. The meaning of the symbols is as follows :

$X = J(J + 1)$, where J is the total angular momentum quantum number ;

T_v is the vibrational term value ;

B_v is the rotational constant ;

Table 1 - Adopted spectroscopic constants for the upper state of the Schumann-Runge bands of O_2 to compute line positions

Band	ν_0 (cm ⁻¹)	B_v	D_v	λ_v	γ_v
			-6		-2
0-0	49357.96	0.8132	4.50 x 10	1.69	- 2.80 x 10
1-0	50045.53	0.7993	4.20	1.70	- 2.60
2-0	50710.68	0.7860	5.80	1.69	- 2.90
3-0	51351.94	0.7705	5.20	1.70	- 2.60
4-0	51969.36	0.7550	5.97	1.81	- 3.00
5-0	52560.94	0.7377	5.80	1.75	- 2.20
6-0	53122.65	0.7187	5.00	1.79	- 2.10
7-0	53655.95	0.7010	8.60	1.82	- 2.10
8-0	54156.22	0.6770	6.70	1.91	- 2.30
9-0	54622.50	0.6514	6.30	2.04	- 2.10
10-0	55051.16	0.6263	9.90	2.10	- 4.10
11-0	55439.23	0.5956	9.40	2.17	- 3.80
12-0	55784.58	0.5626	1.37 x 10 ⁻⁵	2.37	- 5.40
13-0	56085.44	0.5242	1.63	2.51	- 8.40
14-0	56340.42	0.4832	2.09	2.81	- 1.16 x 10 ⁻¹
15-0	56550.62	0.4391	2.54	3.30	- 1.64
16-0	56719.62	0.3934	3.08	4.11	- 2.41
17-0	56852.45	0.3457	3.34	5.18	- 3.48
18-0	56951.60	0.2872	5.50	6.51	- 4.94
19-0	57025.80	0.2649	6.00	7.63	- 6.04

ν_0 = band origin = $T + \frac{2}{3} \lambda - \gamma$ as given by Cheung et al. (1986)

B_v and D_v = rotational constants for vibrational levels

λ_v and γ_v splitting constants for vibrational levels.

For 18-0 and 19-0, see Fang, Wofsy and Dalgarno (1974).

D_v is the centrifugal distorsion constant ;
 λ_v is the interaction constant between the spins of the unpaired electrons ;
 γ_v is the interaction constant between the resultant electron spin and the magnetic moment produced by the rotation of the molecule.

The numerical values listed previously (Nicolet *et al.*, 1988) for these molecular constants are reproduced in Table 1 for the $v'' = 0$ of the $X^3\Sigma_g^-$ ground state and for the $v' = 0$ to $v' = 19$ levels of the $B^3\Sigma_u^-$ excited state.

For calculation of the level energies, we have used the Hund's case (b) representation, in which these energies are expressed in terms of the quantum number N instead of J , because the electronic states involved in the transition through Hund's intermediate coupling case are closer to the (b) than to the (a) case. The quantum numbers J and N are related by $J = N + S$, yielding $N = J - 1$, J and $J + 1$ for the spin components to triplet states.

Since O_2 is a homonuclear molecule (we restricted this study to the normal $^{16}O - ^{16}O$ form), only symmetrical rotational levels exist, characterized by odd values of N ($=1, 3, 5, \dots$) for the lower state, and by even values of N ($=2, 4, 6, \dots$) for the upper state, as shown in the rotational analysis of the Schumann-Runge system performed by Brix and Herzberg (1954). Tatum and Watson (1971) showed that 14 branches may theoretically exist in a $^3\Sigma_g^- - ^3\Sigma_g^-$ transition : 6 are the so-called principal branches, with $\Delta J = \Delta N$ ($P_{11}, P_{22}, P_{23} ; R_{11}, R_{22},$ and R_{33}) ; the others 8 are the satellite branches with $\Delta J \neq \Delta N$ ($R_{P_{31}}, N_{P_{13}}, P_{Q_{12}}, P_{Q_{23}}, R_{Q_{32}}, R_{Q_{21}}, P_{R_{13}}$ and $T_{R_{31}}$).

3. LINE INTENSITIES

For simplicity, we use the term "line intensity" in designating the quantity which should correctly be termed the "line integrated absorption cross-section", and which is defined by

$$S_L = \int_0^{\infty} \sigma_L(\nu) d\nu$$

where ν is the frequency (cm^{-1}) and σ_L is the contribution of the L-labelled line to the total absorption cross section.

A dimensionless parameter, the line oscillator strength f , is introduced, and is related to S_L by

$$S_L = \frac{\pi e^2}{mc^2} \cdot f_L \cdot F(\nu'', N'')$$

where e and m are the electric charge and the mass, respectively, of the motionless electron, c is the velocity of light, and $F(\nu'', N'')$ is the relative population of the lower state of the transition. In the case of a rotational line within a triplet-triplet band, the line oscillator strength is given by

$$f_L = f_{N'N''} = f_{\nu', \nu''} \cdot \frac{S_{N'N''}}{3(2N'' + 1)}$$

where $f_{\nu', \nu''}$ is the band oscillator strength and $S_{N'N''}$ is the rotational line strength factor, also known as the Hönl-London factor. The denominator is a normalization factor arising from degeneracy of the states.

4. BAND OSCILLATOR STRENGTH

The band oscillator strength $f_{\nu', \nu''}$ can be determined experimentally, and considerable work has been devoted to the determination of those of the Schumann-Runge bands. These bands, analyzed many times, are best resolved by the recent wavenumber measurements of Yoshino et al. (1984). Their comprehensive analysis based on Yoshino et al. (1983) yields a determination of mean band oscillator strengths from (0-0) to (12-0). Another approach by Lewis et al. (1986) that reveals a variation of the oscillator strength with the rotational lines, is, however, in agreement with the high resolution measurements, when a mean value is adopted for the oscillator strength. Since it is practically impossible to adopt an

Table 2 - Adopted mean absorption oscillator strengths $f_{v''v'}$, for the Schumann-Runge bands of O_2 deduced from absorption spectra.

v'	$f_{ov'}$	$f_{lv'}$
0	2.8×10^{-10}	7.6×10^{-9}
1	3.0×10^{-9}	8.2×10^{-8}
2	1.9×10^{-8}	4.6×10^{-7}
3	8.2×10^{-8}	1.8×10^{-6}
4	2.7×10^{-7}	5.0×10^{-6}
5	7.4×10^{-7}	1.3×10^{-5}
6	1.6×10^{-6}	2.7×10^{-5}
7	3.4×10^{-6}	5.0×10^{-5}
8	6.2×10^{-6}	8.6×10^{-5}
9	1.0×10^{-5}	1.2×10^{-4}
10	1.5×10^{-5}	1.7×10^{-4}
11	1.9×10^{-5}	2.1×10^{-4}
12	2.4×10^{-5}	2.6×10^{-4}
13	2.7×10^{-5}	2.6×10^{-4}
14	2.8×10^{-5}	2.9×10^{-4}
15	2.7×10^{-5}	2.7×10^{-4}
16	2.6×10^{-5}	2.0×10^{-4}
17	2.2×10^{-5}	1.6×10^{-4}
18	1.7×10^{-5}	1.3×10^{-4}
19	1.3×10^{-5}	1.6×10^{-4}

exact oscillator strength for each line, equivalent values for each vibration level must be determined. The mean band oscillator strengths adopted here are based on the results of the Cambridge and Canberra groups and are used to generate a consistent set of data given in Table 2. These mean band oscillator strengths can therefore be used for the determination of the linewidths of the rotational lines in the various Schumann-Runge bands. It seems that the oscillator strengths are generally accurate to about 5 %, at least for bands with v' less than 15; attempts which have been made to study the possible errors have not produced more accurate oscillator strengths within the appropriate uncertainty.

5. ROTATIONAL DISTRIBUTION

The $S_{N'N''}$ -factors, which govern the rotational intensity distribution in a band, have different algebraic forms for the branches of the band ; they depend also on the type of transition. For the $^3\Sigma^+ - ^3\Sigma^+$ transitions, the explicit formulas for the $S_{N'N''}$ derived by Tatum and Watson (1971) are used here.

The relative populations of the lower states are given by the Boltzmann distribution :

$$F(v'', N'') = 3(2N'' + 1) \cdot \frac{e^{-\frac{hc E(v'', N'')}{kT}}}{\sum_{v''} \sum_{N''} e^{-\frac{hc E(v'', N'')}{kT}}}$$

where h and k are the Planck and Boltzmann constants, respectively, and T is the temperature. The sum (sum of state or partition function) which appears in the denominator can be limited to $v'' = 0$ and 1 for the vibration and to $N'' < 30$ for the rotation, since the temperature does not exceed 300 K in our calculations.

6. ABSORPTION CROSS-SECTION

The absorption cross-section at a given wavenumber is theoretically given by

$$\sigma(\nu) = \sigma_c(\nu) + \sum \sigma_L(\nu)$$

where $\sigma_c(\nu)$ is the contribution of the underlying continuum and the sum extends over all the lines of the spectrum. Obviously, only a part of the lines is used, excluding those for which the line center ν_L is too far from the wavenumber ν . In our calculation, a given line is used in the preceding formula if it satisfies the condition

$$|\nu - \nu_L| < \Delta$$

where Δ is a spectral interval to be defined. Particular attention was paid to the choice of Δ since the lines may be quite broad in certain parts of the Schumann-Runge band spectrum ; in the final computation we used values of Δ of 500 cm^{-1} .

In fact, to determine the exact contribution of the lines to the cross-section, a number of runs were made with increasing values of Δ (ranging from 100 to 500 cm^{-1}). When the result does not depend on Δ , this means that the exact contribution of the lines is known ; 500 cm^{-1} was adopted for the spectral interval Δ at each 0.1 cm^{-1}

The contributions $\sigma_L(\nu)$ of the individual lines have been calculated using the Voigt profile approximated by a formula established by Whiting (1968) :

$$\frac{\sigma_L(\nu)}{\sigma_L(\nu_L)} = \left(1 - \frac{\Delta\nu_L}{\Delta\nu_V}\right) e^{-2.772 \left(\frac{\nu - \nu_L}{\Delta\nu_V}\right)^2} + \frac{(\Delta\nu_L/\Delta\nu_V)^{2.25}}{1 + 4\left(\frac{\nu - \nu_L}{\Delta\nu_V}\right)^2}$$

$$+ 0.016 \left(1 - \frac{\Delta\nu_L}{\Delta\nu_V}\right) \left(\frac{\Delta\nu_L}{\Delta\nu_V}\right) \cdot \left[e^{-0.4 \frac{\nu - \nu_L}{\Delta\nu_V}^{2.25}} - \frac{10}{10 + \frac{\nu - \nu_L}{\Delta\nu_V}} \right]$$

where $\sigma_L(\nu_L)$ is the absorption cross-section at the centre of the line and is given by

$$\sigma_L(\nu_L) = \frac{S_L}{\Delta\nu_V \left[1.065 + 0.447 \left(\frac{\Delta\nu_L}{\Delta\nu_V} \right) + 0.058 \left(\frac{\Delta\nu_L}{\Delta\nu_V} \right)^2 \right]}$$

$\Delta\nu_V$ is the Voigt line width, given by

$$\Delta\nu_V = \frac{\Delta\nu_L}{2} + \left[\frac{\Delta\nu_L^2}{4} + \Delta\nu_D^2 \right]^{1/2}$$

where $\Delta\nu_L$ is the Lorentz line width and $\Delta\nu_D$ is the Doppler line width. The Doppler line width can be calculated by

$$\Delta\nu_D = 7.1623 \cdot 10^{-7} \nu_L \left(\frac{T}{M} \right)^{1/2}$$

where $M = 32$ is the molecular weight.

7. ROTATIONAL PREDISSOCIATION LINEWIDTHS

The mean predissociation linewidths (Table 3) were determined after a detailed comparison between calculated absorption cross sections and the experimental results published by Yoshino et al. (1983) in the spectral region corresponding to the $v' = 1$ to 12 bands. Furthermore, the absorption cross sections throughout this region also depend on the underlying continuum that corresponds near 50000 cm^{-1} to the O_2 Herzberg continuum. At wavenumbers greater than 55000 cm^{-1} , the O_2 Schumann-Runge continuum (Lewis et al. 1985a, b) plays a role that is dependent on temperature. These two underlying continua are described in an atlas on the "Rotational Structure and Absorption Cross-Sections from 300 K to 190 K of the Schumann-Runge Bands" of O_2 by M. Nicolet, S. Cieslik, and R. Kennes, Aeronomica Acta A - N°318, 340 pages, 1987. In this publication, Tables and Figures of calculated absorption cross sections are given for molecular oxygen as a function of wavenumber over the spectral interval 49000 - 57000 cm^{-1} for temperatures between 190 and 300 K.

Table 3 - Adopted mean rotational linewidths

v'	cm^{-1}	v'	cm^{-1}
0	0.1	10	1.0
1	0.9	11	1.4
2	0.6	12	0.8
3	1.8	13	0.5
4	3.6	14	0.5
5	2.0	15	0.5
6	1.8	16	0.5
7	1.9	17	0.5
8	2.1	18	0.3
9	1.2	19	0.3

8. THE 500 cm^{-1} SPECTRAL INTERVALS

Various calculations were made for the different spectral intervals, but as usual the 500 cm^{-1} wavenumber grid was adopted finally. Such an interval corresponds to a constant energy range and is the most appropriate ; it is very practical for atmospheric modeling because the solar irradiance is not known with high accuracy and its spectral resolution is generally inadequate for a study with detailed structure. Thus, it seems useful to describe the principal features in each of 17 intervals between 49000 and 57000 cm^{-1} . Such description provides a first indication of the strong variation of the absorption from 200 to 175 nm, and the relative effects of the underlying continuum.

8.1. The spectral interval 49000 - 49500 cm^{-1}

This interval corresponds mainly to the spectral region of the 0-0 and 2-1 bands with minimum absorption cross-sections less than 10^{-26} cm^2 , and even less than 10^{-27} cm^2 at low temperature. Thus, the averaged cross-section depends strongly on the underlying continuum. The Herzberg continuum absorption cross-section must be known with great accuracy and

can be determined experimentally at low temperature in the spectral region of $v' = 1$ bands. It is of the order of $7 \times 10^{-24} \text{ cm}^2$.

8.2. The spectral interval 49500 - 50000 cm^{-1}

The 1-0 and 3-1 bands are the principal bands within this spectral interval, with minimum cross-sections at low temperature less than 10^{-26} cm^2 between 49500 and 49500 cm^{-1} , and less than 10^{-25} cm^2 between 49750 and 50000 cm^{-1} . The Herzberg continuum makes the principal contribution to determination of the averaged cross-section, particularly in the 49500 - 49750 spectral interval, because its own cross-section is not less than $7 \times 10^{-24} \text{ cm}^2$.

A first comparison between the experimental and theoretical absorption cross-sections at 300 K can be made in the 49750 - 50000 cm^{-1} region, particularly with the peaks of the rotational lines of the 1-0 band. It is clear, however, that experimental noise persists at cross-sections of the order of 10^{-23} cm^2 so that a comparison with the Herzberg continuum cannot be made between the rotational lines.

8.3. The spectral interval 50000 - 50500 cm^{-1}

This region is characterized by the presence of the rotational lines ($R \geq 19$) of the 2-0 band and ($R \leq 9$) of the 1-0 band with almost all the rotational lines of the 4-1 band. Such an overall pattern of absorption results in a structure very sensitive to temperature. No comparison is possible between the experimental and theoretical cross-sections for the continuum or for the line wings below $2 \times 10^{-23} \text{ cm}^2$. It can be seen that the Herzberg continuum could be measured at low temperature between 50100 and 50300 cm^{-1} . Finally, it is pointed out that the 50000 - 50500 cm^{-1} interval depends strongly on temperature ; hence, the averaged absorption cross-section is related to the behaviour of the 4-1 band with the predissociation linewidth of its rotational lines.

8.4. The spectral interval 50500 - 51000 cm⁻¹

Absolute experimental and theoretical absorption cross-sections in this interval correspond mainly to the 2-0 and 5-1 bands. Again the experimental structure for absorption less than $2 \times 10^{-23} \text{ cm}^2$ arises from laboratory noise. The effect of the underlying continuum is still important in the region of the 2-0 band ; it is easily detected, for example, between 50500 and 50550 cm⁻¹. In the 50750 - 51000 cm⁻¹ interval corresponding to the 5-1 band (P3 to P17) the temperature effect is extremely important. It should be pointed out that the absorption cross-section of the Herzberg continuum could be measured at low temperature between 50750 and 50850 cm⁻¹, i.e. near 197 nm. In that interval, where the window region between the rotational lines of the 5-1 band reaches $2 \times 10^{-25} \text{ cm}^2$ at 190 K, there is, therefore, a notable difference and the absorption cross-section is dependent on the Herzberg continuum, and cannot be less than $5 \times 10^{-24} \text{ cm}^2$.

8.5. The spectral interval 51000 - 51500 cm⁻¹

In this interval where the linewidths of the rotational lines of the 3-0 band play an increasing role in the overall pattern of absorption, the accuracy required for the underlying continuum is less critical than in the region of wavenumbers less than 51000 cm⁻¹. It is clear that the wings of many lines give a detectable contribution to the effective absorption cross-section of the whole interval. Nevertheless, the role of the underlying continuum is far from negligible. Between 51350 and 51500 cm⁻¹ the importance of the 6-1 band is dependent on its variation with temperature and on the increasing relative importance of the Herzberg continuum with decreasing temperature. The mean absorption cross-section at 190 K near 51400 - 51500 cm⁻¹ is of the order of 10^{-23} cm^2 where the pseudocontinuum between the P13 - R15 and P11 - R13 lines of the 6-1 band is only $2 \times 10^{-24} \text{ cm}^2$ near 51450 cm⁻¹.

8.6. The spectral interval 51500 - 52000 cm⁻¹

This spectral region corresponds to the 4-0 band and also to portions of the 7-1 and 6-1 bands. The role of the Herzberg continuum is practically almost negligible between 52000 and 51750 cm⁻¹ where the wings of the rotational lines contribute to the total absorption cross section. Between 51750 and 51500 cm⁻¹ for the (R ≥ 19) lines of the 4-0 band and the first rotational lines of the 6-1 band, the variation with temperature must still be compared with an effect from the Herzberg continuum. For example, at 51750 cm⁻¹ if T = 190 K, the effective continuum, of the order of 10⁻²³ cm² between the P21 and P23 lines of the 4-0 band, is associated with a pseudo-continuum of 3 x 10⁻²⁴ cm² and corresponds to the wings of these two lines. At T = 270 K, the pseudo-continuum corresponds to an equivalent cross-section of about 7 x 10⁻²³ cm², because the rotational population increases with temperature.

8.7. The spectral interval 52000 - 52500 cm⁻¹

The differences with and without an underlying continuum are small, practically negligible, in the spectral range 52500 - 52250 cm⁻¹ that corresponds mainly to the P9 - R11, ..., P19 - R21 rotational lines of the 5-0 band with a mean predissociation linewidth of 2 cm⁻¹. Since the wings of the lines contribute to the absorption with a pseudocontinuum of about 10⁻²² cm² at 300 K, an underlying continuum even of the order of 7 x 10⁻²⁴ cm² cannot play a consequential role. But in the spectral region corresponding to the 52100 - 52250 cm⁻¹ interval, where the minimum cross-sections at 300 K reach 2 x 10⁻²³ cm² between the peaks of the P21 - R23 and P25 - R27 lines of the 5-0 band, the contribution of the Herzberg continuum to the absorption cross-section, especially at low temperature, is not negligible. On the other hand, in the same spectral region, the effect of temperature on the rotational structure is particularly significant because it corresponds to the lines of the 7-1 band and to the last rotational lines of the 5-0 band.

8.8. The spectral interval 52500 - 53000 cm⁻¹

Within this interval there is an addition of rotational lines belonging to various bands : the 6-0 band with $P \geq 13$, the 5-0 band with $R \leq 9$, the 9-1 band with $P \geq 9$ and the 8-1 band with $R \leq 1$ to $R \leq 11$. The Herzberg continuum plays a minor or negligible role because the minimum absorption cross-sections seem to coincide with a pseudocontinuum associated with a normal contribution of the wings of the various lines. The variation of the absorption cross-sections of this pseudocontinuum are closely associated with the variation of temperature.

8.9. The spectral interval 53000 - 53500 cm⁻¹

The contributions of the 6-0 band, R1 to R13, of the 7-0 band, P15 to P29, of the 9-1 band, R1 to R9, and of the 10-1 band, R1 to R25, determine the structure of the absorption cross-sections. The variation of the averaged absorption cross-section is explained by the alteration of the vibrational and rotational structures between 300 K and 170 K. An effect of the Herzberg continuum is outside the range of detection.

8.10. The spectral interval 53500 - 54000 cm⁻¹

The various structures that correspond to the 7-0 band (R1 to R15) with the 8-0 band (R15 to R29) and to the 11-1 band (R1 to R21) with the 12-1 band ($R \geq 17$) indicate that the principal variation of the averaged absorption cross-section depends on temperature ; this variation is particularly apparent in the spectral region 53700 - 53900 cm⁻¹ where the minimum cross-section may vary by a factor of 10, between 10⁻²² and 10⁻²¹ cm² for $T = 190$ K and $T = 300$ K, respectively.

8.11. The spectral interval 54000 - 54500 cm⁻¹

The two main bands of this 500 cm⁻¹ interval are the 8-0 band from R1 to R13 and the 9-0 band from R13 to R29. Three bands from the vibrational level $v'' = 1$ belong to the same interval, namely the 12-1

band from R1 to R15, the 13-1 band from P5 to R23, and the 14-1 band from P17 to R27. The averaged absorption cross-section at 300 K is greater than 10^{-20} cm^2 , and the variation of the structure is associated only with the rotational and vibrational populations dependent on temperature (300 K to 170 K), particularly in the $54150 - 54350 \text{ cm}^{-1}$ region.

8.12 The spectral interval $54500 - 55000 \text{ cm}^{-1}$

The 10-0 band (P7 to P23) and the 9-0 band (R1 to P9) are the two main bands of this interval, along with the addition of at least 6 bands starting from $v'' = 1$. The structure of the following bands has been measured and calculated : 14-1 from R1 to P17, 15-1 from R1 to R21, 16-1 from R13 to R25, 17-1 from R17 to P25, 18-1 from P19 to P27 and 19-1 from P19 to R27.

The variation of the absorption cross-sections at 300 K is of the order of 10^4 , from about $4 \times 10^{-22} \text{ cm}^2$ near 182.9 nm, corresponding to P17 of the 15-1 band, to $4 \times 10^{-18} \text{ cm}^2$ at the peak of the R9 - P7 lines of the 10-0 band near 181.8 nm, i.e. only for the 1 nm interval.

8.13. The spectral interval $55000 - 55500 \text{ cm}^{-1}$

This interval is characterized by almost all the rotational lines (R1 to R23) of the 11-0 band, along with the first lines (R1 to R7) of the 10-0 band, and the last lines (P17 to R29) of the 12-0 band. Four bands with vibrational levels $v'' = 1$ are also present in the same spectral region. They are : the 16-1 band from R1 to P11, the 17-1 band from R1 to P15, the 18-1 band from R1 to R17 and the 19-1 band from R1 to R19.

The effect of the Schumann-Runge continuum can be detected. However, because the absorption cross-section of this continuum is related to the vibrational and rotational populations, it is a complicated function of temperature. The effect of temperature decreases from 300 K to 170 K. The averaged absorption cross-section for this 500 cm^{-1}

interval reaches almost $5 \times 10^{-20} \text{ cm}^2$, while the minimum cross-section at 190 K is only $4 \times 10^{-22} \text{ cm}^2$ between the P19 and R19 lines of the 11-0 band ; the associated maximum cross-section comes to $6 \times 10^{-19} \text{ cm}^2$ near 55400 cm^{-1} at the peak of the R7 line of the 10-0 band.

8.14. The spectral interval 55500 - 56000 cm^{-1}

This spectral region is the last interval where a direct comparison can be made between the experimental and theoretical values. This comparison ends with the 12-0 band at 55785 cm^{-1} (179.26 nm). The rotational structure of the 12-0 band in the $55785 - 55500 \text{ cm}^{-1}$ interval corresponds to the rotational lines between R1 and R17. However, the 13-0, 14-0 and 15-0 bands also contribute in this 500 cm^{-1} interval from various portions of their rotational structure. The 13-0 band makes an important contribution from rotational lines between P9 and R25, but the experimental data only begin at P17. The 14-0 band with rotational lines between R19 and R29 has only been measured in the laboratory between P25 and R29. The 15-0 band with its lines between P23 and R29 is practically beyond the present detailed laboratory measurements.

This spectral interval has a distinctive peculiarity : the absence of rotational lines from the vibrational level $v'' = 1$, since the calculation ended with 19-1 in the preceding interval near 55468 cm^{-1} at the rotational line R1.

The temperature effect is the result of the combination of a variation due to the Schumann-Runge continuum (increase with temperature) and a variation related to the rotational structure of various bands. The averaged absorption cross-section in this 500 cm^{-1} interval reaches $7 \times 10^{-20} \text{ cm}^2$ at 300 K, and the extreme low and high values are 10^{-21} cm^2 and 10^{-18} cm^2 , respectively.

8.15. The spectral interval 56000 - 56500 cm^{-1}

Seven bands lie in this interval, namely the 13-0 band from R1 to P7, the 14-0 band from R1 to P17, the 15-0 band from R7 to R23, the 16-0

band from R15 to P25, the 17-0 band from P17 to R27, the 18-0 band from P19 to P27 and the 19-0 band from P21 to P27.

Among all these bands the 14-0 and 15-0 bands are most important in this 500 cm^{-1} interval where the averaged absorption cross section is greater than 10^{-19} cm^2 . It is expected that the individual structures of all the components cannot be very accurate, but the number of possible errors due to various causes does not permit classification of all the uncertainties.

8.16. The spectral interval $56500 - 57000 \text{ cm}^{-1}$

In this last 500 cm^{-1} interval illustrated in our atlas we must consider at least all the first rotational lines of the 15-0 to 19-0 bands, namely 15-0 from R1 to R7, 16-0 from R1 to P13, 17-0 from R1 to R17, 18-0 from R1 to P19, and 19-0 from P3 to P19. The effect of the Schumann-Runge continuum must be introduced into the calculation with its temperature dependence.

Because of various uncertainties, detailed characterization of the theoretical results is difficult. The adopted equivalent linewidths depend essentially on the analysis of rotational lines from vibrational levels $v'' = 1$ which may be equivocal. The total uncertainty which is difficult to quantify could perhaps reach several tens of per-cent.

9. *AERONOMIC PARAMETERS FOR THE SCHUMANN-RUNGE BANDS*

The various parameters to be used for the calculation of the O_2 transmittance and its photodissociation frequency for the 16 spectral intervals of 500 cm^{-1} described in parag. 8 are given in Table 4, where the individual absorption cross-sections are listed and where the solar irradiances deduced from the SUSIM observations (see Nicolet and Kennes, 1988) are used to determine the photodissociation frequencies at optical depth, $\tau_{\text{O}_2} = 0$.

Table 4 - Absorption cross sections (cm^2) and number of photons ($\text{cm}^{-2}\text{s}^{-1}/500\text{ cm}^{-1}$) at zero optical depth

No	Interval (cm^{-1})	Cross-section (O_2)	Temperature (K)	Herzberg Continuum	O_3 Cross-sections	Number of photons
1	49000-49500	$7.90 \pm 0.05 \times 10^{-24}$	$170 \leq T \leq 270$	7.2×10^{-24}	3.26×10^{-19}	1.92×10^{12}
2	49500-50000	$1.05 \pm 0.07 \times 10^{-23}$	$170 \leq T \leq 270$	7.4	3.14	1.69
3	50000-50500	1.34 ± 0.15	$200 \leq T \leq 270$	7.5	3.30	1.38
4	50500-51000	4.22 ± 0.25	$170 \leq T \leq 270$	7.5	3.69	1.29
5	51000-51500	$1.55 \pm 0.05 \times 10^{-22}$	$170 \leq T \leq 270$	7.5	4.11	1.14
6	51500-52000	4.83 ± 0.07	$210 \leq T \leq 270$	7.4	4.38	7.81×10^{11}
7	52000-52500	6.33 ± 0.33	$210 \leq T \leq 270$	7.2	4.80	8.07
8	52500-53000	$1.34 \pm 0.07 \times 10^{-21}$	$210 \leq T \leq 270$	7.0	5.31	6.89
9	53000-53500	3.06 ± 0.15	$180 \leq T \leq 270$	6.7	5.88	5.98
10	53500-54000	7.04 ± 0.40	$180 \leq T \leq 270$	6.4	6.40	4.81
11	54000-54500	$1.34 \pm 0.07 \times 10^{-20}$	$180 \leq T \leq 270$	6.0	6.88	4.04
12	54500-55000	2.92 ± 0.10	$170 \leq T \leq 290$	5.6	7.29	4.12
13	55000-55500	4.63 ± 0.03	$180 \leq T \leq 270$		7.63	3.72
14	55500-56000	6.24 ± 0.25	$180 \leq T \leq 250$		7.86	2.82
15	56000-56500	$1.12 \pm 0.02 \times 10^{-19}$	$180 \leq T \leq 230$		7.99	2.55
16	56500-57000	1.65 ± 0.01	$170 \leq T \leq 250$		8.11	2.01

Because the O_2 cross-sections presented in Table 4 for various temperature intervals are averaged values over the 500 cm^{-1} spectral ranges at zero optical depth, they coincide with the maximum cross-sections defined by $N(\text{O}_2) = 0$. In order to give an idea of the variations in the O_2 absorption Table 5 gives the mean cross-sections, the corresponding number of O_2 absorbing molecules $N(\text{cm}^{-2})$ and the appropriate altitudes z (km) for the optical depths $\tau = 0.1, 1.0$ and 10 . From this table it is possible to decide the best approach to arrive at correct estimates of the beginning of the absorption ($\tau = 0.1$), to the approximate maximum of the absorption ($\tau = 1.0$) and of the minimum value of the absorption cross-section ($\tau = 10$) that corresponds to a negligible

Table 5 - Aeronomic parameters for 500 cm⁻¹ intervals

49500 - 49000 cm ⁻¹ (0-0,2-1)				50000 - 49500 cm ⁻¹ (1-0,3-1)		
r	0.1	1.0	10	0.1	1.0	10
σ (cm ²)	7.8x10 ⁻²⁴	7.5x10 ⁻²⁴	7.5x10 ⁻²⁴	1.0x10 ⁻²³	8.75x10 ⁻²⁴	8.0x10 ⁻²⁴
N (cm ⁻²)	1.3x10 ²²	1.3x10 ²³	1.3x10 ²⁴	1.0x10 ²²	1.15x10 ²³	1.25x10 ²⁴
z (km)	50	25	15	50	25	15
50500 - 50000 cm ⁻¹ (1-0,2-0)				51000 - 50500 cm ⁻¹ (2-0,5-1)		
σ	1.3x10 ⁻²³	1.0x10 ⁻²³	8.0x10 ⁻²⁴	2.5x10 ⁻²³	1.4x10 ⁻²³	8.0x10 ⁻²⁴
N	8x10 ²¹	1.0x10 ⁻²³	1.25x10 ⁻²⁴	4x10 ²¹	7x10 ²²	1.2x10 ²⁴
z	50	30	15	60	30	15
51500-51000 cm ⁻¹ (3-0,6-1)				52000-51500 cm ⁻¹ (4-0,6-1,7-1)		
σ	1x10 ⁻²²	3x10 ⁻²³	1x10 ⁻²³	3x10 ⁻²²	1x10 ⁻²²	1.5x10 ⁻²³
N	1x10 ²¹	3x10 ²²	1x10 ²⁴	3.5x10 ²⁰	1x10 ²²	7x10 ²³
z	65	35	15	70	45	20
52500-52000 cm ⁻¹ (5-0,7-1,8-1)				53000-52500 cm ⁻¹ (6-0,5-0,9-1,8-1)		
σ	2x10 ⁻²²	7.5x10 ⁻²³	2x10 ⁻²³	6.5x10 ⁻²²	1.2x10 ⁻²²	3x10 ⁻²³
N	5x10 ⁻²⁰	1.3x10 ²²	5x10 ²³	1.5x10 ²⁰	7x10 ²¹	3x10 ²³
z	70	45	20	75	50	25
53500-53000 cm ⁻¹ (6-0,7-0,9-1,10-1)				54000-53500 cm ⁻¹ (7-0,8-0,11-1)		
σ	1.5x10 ⁻²¹	3x10 ⁻²²	6x10 ⁻²³	5x10 ⁻²¹	1x10 ⁻²¹	1.75x10 ²²
N	6x10 ¹⁹	3x10 ²¹	1.5x10 ²³	2x10 ¹⁹	1x10 ²¹	6x10 ²²
z	80	55	35	85	60	35
54500-54000 cm ⁻¹ (8-0,9-0)				55000-54500 cm ⁻¹ (10-0,9-0)		
σ	12x10 ²⁰	1x10 ⁻²¹	2.5x10 ⁻²²	2x10 ⁻²⁰	2x10 ⁻²¹	5x10 ⁻²²
N	1x10 ¹⁹	1x10 ²¹	4x10 ²²	5x10 ¹⁸	5x10 ²⁰	2x10 ²²
z	90	65	35	95	70	40
55500-55000 cm ⁻¹ (11-0)				56000-55500 cm ⁻¹ (12-0,13-0)		
σ	3.5x10 ⁻²⁰	5x10 ⁻²¹	1x10 ⁻²¹	5x10 ⁻²⁰	7x10 ⁻²¹	2x10 ⁻²¹
N	3x10 ¹⁸	2x10 ²⁰	10 ²²	2x10 ¹⁸	1.5x10 ²⁰	5x10 ²¹
z	100	75	45	100	75	55
56500-56000 cm ⁻¹ (15-0,14-0)				57000-56500 cm ⁻¹ (19-0 to 15-0)		
σ	1x10 ⁻¹⁹	2x10 ⁻²⁰	5x10 ⁻²¹	1.6x10 ⁻¹⁹	8x10 ⁻²⁰	2x10 ⁻²⁰
N	1x10 ¹⁸	5x10 ¹⁹	2x10 ²¹	< 10 ¹⁸	1.3x10 ¹⁹	5x10 ²⁰
z	100	80	60	> 100	90	70

transmittance of the order of 5×10^{-5} . The altitudes associated with the different optical depths indicate clearly what the atmospheric regions are that correspond to the principal behavior for each 500 cm^{-1} interval between 57000 cm^{-1} and 49000 cm^{-1} . For example, the interval between 49000 and 49500 cm^{-1} that corresponds to the 0-0 and 2-1 bands has an absorption cross-section practically identical to that of the Herzberg continuum, about $7.5 \times 10^{-24} \text{ cm}^2$.

The spectral range between 49500 and 53000 cm^{-1} is typically representative of the stratosphere while the spectral region between 54000 and 56000 cm^{-1} is particularly associated with the mesosphere. The 500 cm^{-1} interval between 56500 and 57000 cm^{-1} that corresponds to the spectral range of the 19-0 to 16-0 bands plays a role in the lower thermosphere.

It may be added that there is no practical rule that may be used to derive the decrease of the averaged absorption cross-section between the optical depths $\tau = 0.1$ to $\tau = 10$. The superposition of bands from $v'' = 0$ and $v'' = 1$ dependent on the effect of temperature with height is different for each 500 cm^{-1} interval. A detailed parameterization is required.

10. PHOTODISSOCIATION IN THE MESOSPHERE

The photodissociation frequency (s^{-1}) and the photodissociation rate ($\text{cm}^{-3} \text{ s}^{-1}$) for the Herzberg continuum have been obtained for various atmospheric conditions (Nicolet and Kennes, 1988). But the atomic oxygen production in the spectral interval of the predissociation bands of the Schumann-Runge system is a different problem. Nevertheless, when the atmospheric opacity from ozone absorption and molecular scattering is negligible, it is possible to determine the total photodissociation frequency and photodissociation rate if the solar irradiance is known. With the SUSIM data given in Table 4 we can determine the oxygen production.

Above the mesopause, the photodissociation frequency is $J(O_2)_{SRB} = 1.25 \times 10^{-7} \text{ s}^{-1}$ for the Schumann-Runge bands (57000 - 49500 cm^{-1}) and $J(O_2)_{HER} = 5.8 \times 10^{-10} \text{ s}^{-1}$ for the Herzberg continuum (49500-41250 cm^{-1}). The atmospheric optical depth $\tau_A = 0$, the molecular scattering optical depth $\tau_{MS} = 0$, and the O_3 optical depth $\tau_{O_3} = 0$.

The effect of the O_3 absorption on the transmittance, and therefore on $J(O_2)_{SRB}$ is negligible or relatively small in the mesosphere. From 60 km to 50 km, the effect of ozone is to decrease the photodissociation frequency, $10^{-10} < J(O_2)_{SRB} < 10^{-9} \text{ s}^{-1}$, from $0.02 \times 10^{-10} \text{ s}^{-1}$ to $0.04 \times 10^{-10} \text{ s}^{-1}$, respectively, i.e. less than 4 %. Thus, the adoption of a general formula from the mesopause to the stratopause can be envisaged for $J(O_2)_{SRB}$. The result is (Fig. 1)

$$J(O_2)_{SRB} = 6.55 \times 10^6 N^{-0.7567} \text{ s}^{-1}$$

for

$$5 \times 10^{18} \leq N(O_2) \leq 1 \times 10^{22} \text{ cm}^{-2}$$

i.e. up to 95 km and down to 50 km near $N = 10^{22} \text{ cm}^{-2}$, with an accuracy generally better than $\pm 5 \%$ and always better than $\pm 10 \%$. Such a result corresponds to

$$5 \times 10^{-8} \geq J(O_2)_{SRB} \geq 5 \times 10^{-10} \text{ s}^{-1}$$

If the reference solar irradiance published in WMO (1985) is adopted the preceding formula (Nicolet, 1987) becomes

$$J(O_2)_{SRB} = 3 \times 10^7 N^{-0.795} \text{ s}^{-1}$$

and the numerical results indicate a decrease of $J(O_2)$ of 15, 25, 40 and 50% at $N(O_2) = 10^{19}$, 10^{20} , 10^{21} and 10^{22} cm^{-2} , respectively. Thus, the precision in the solar irradiance values should be improved.

The addition of the photodissociation produced in the Herzberg continuum increases the total photodissociation at 95 km by 1-2 % and at 90 km by 2 to 4 %.

At the mesopause, the contribution to the total photodissociation of O_2 by the Herzberg continuum increases from (Fig. 2)

3 % for $\sec \chi = 1$ and $N(O_2) = 1.8 \times 10^{19} \text{ cm}^{-2}$
to 9 % for $\sec \chi = 4$ and $N(O_2) = 7.1 \times 10^{19} \text{ cm}^{-2}$.

In the region of 60-65 km, the role of the Herzberg continuum in the total production of atomic oxygen increases up to more than 50 % when $N(O_2) = 2 \times 10^{21} \text{ cm}^{-2}$. The following table provides the details of the calculation at 60 km for $\sec \chi = 1, 1.414, 2, 3$ and 4, respectively.

$N(O_2)$	$J(O_2)$	% Herzberg	$n(O_2)J(O_2)$
1×10^{21}	1.4×10^{-9}	40	1.9×10^6
1.4	1.2	47	1.6
2	1.1	54	1.4
3	9.0×10^{-10}	62	1.2
4	8.2	67	1.1

Consequently, the atomic oxygen production therefore lies between 4 and 2×10^6 atoms $\text{cm}^{-3} \text{ s}^{-1}$ for solar zenith angles between 0° and 70° (Fig.3).

The stratospheric conditions were described by Nicolet and Kennes (1988b) between 55 and 15 km.

11. CONCLUDING REMARK

The combination of high resolution absorption cross-section measurements with a parallel theoretical calculation adapted to the atmospheric conditions provide the means of determining the molecular oxygen photodissociation in the spectral range of the Schumann-Runge region with excellent accuracy. The parameterization of the O_2 transmit-

tance and of the photodissociation frequency will be given in a subsequent paper.

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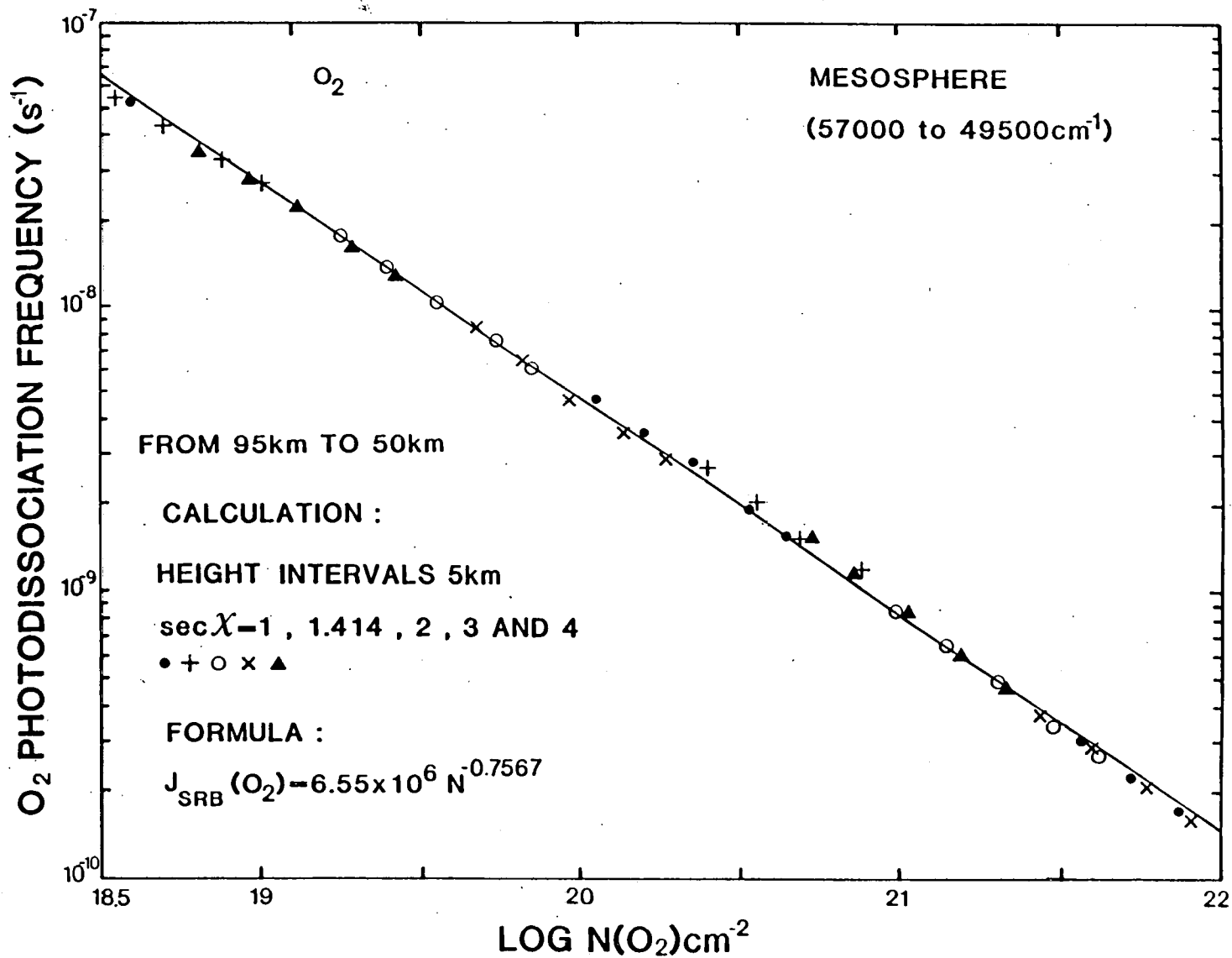


Fig. 1 - Photodissociation frequency of O₂ in the mesosphere for the spectral interval 175-202 nm that corresponds to the Schumann-Runge band predissociation.

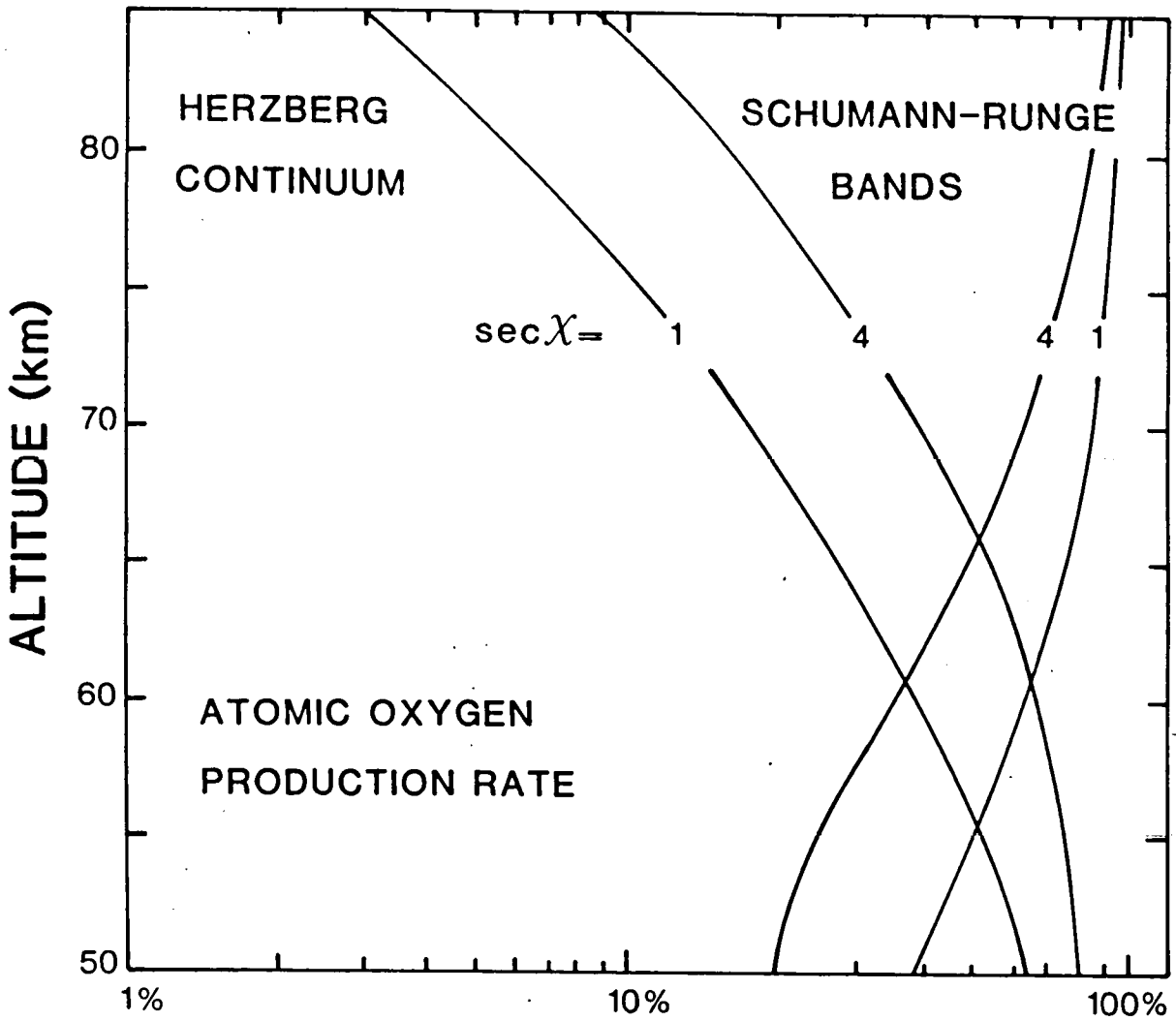


Fig. 2 - Relative production rate of oxygen atoms by direct photodissociation of O_2 in the spectral ranges of the Schumann-Runge bands and of the Herzberg continuum between 85 and 50 km.

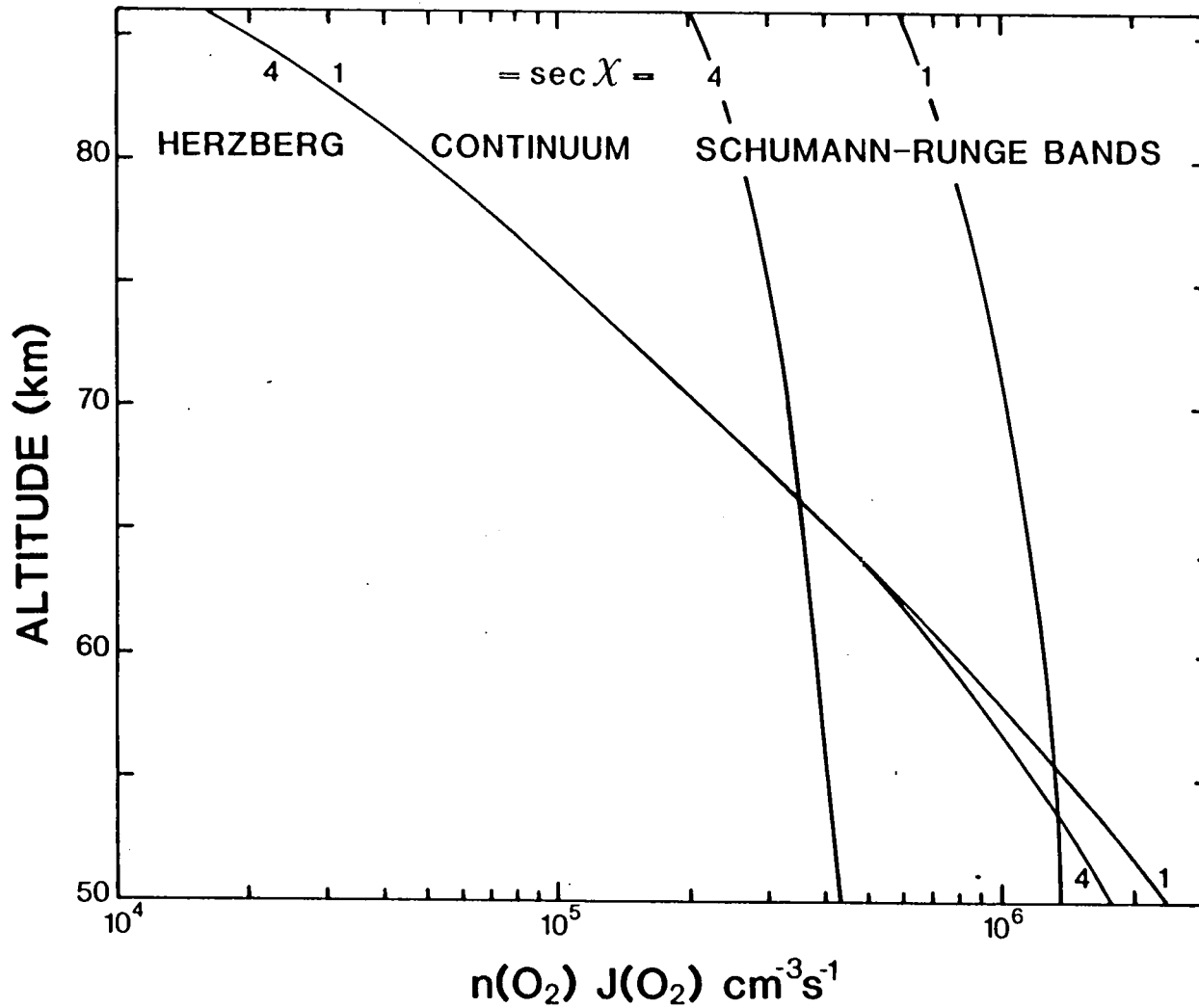


Fig. 3 - Photodissociation rates of O_2 ($cm^{-3} s^{-1}$) in the mesosphere for 2 solar zenith angles : $\sec \chi = 1$ and 4. Comparison between the effects of the Herzberg continuum and of the photodissociation of the Schumann-Runge bands.

APPENDIX

Absorption cross-sections

Summary

Figures of calculated and experimental absorption cross-sections are given for molecular oxygen as a function of wavenumber over the spectral interval 49000-57000 cm^{-1} at 300 K. The spectrum corresponds to the domain of the rotational lines of the various bands of the $B^3\Sigma_u^- - X^3\Sigma_g^-$ Schumann-Runge system with their underlying continua ; it is presented for the range of the (0-0) to (19-0) bands in 32 intervals of 250 cm^{-1} . Calculated absorption cross-sections have been determined for each band after comparison with the most recent laboratory measurements made at 300 K. The calculations required knowledge of the line wavenumbers of the (0-0) to (19-0) and (2-1) to (19-1) bands with their mean oscillator strengths and determination of the associated equivalent linewidths of the rotation lines with their underlying continuum.

Basic data

The present figures are intended to serve those who require detailed information about the ultraviolet absorption of molecular oxygen in the predissociation region of the O_2 Schumann-Runge system. This inventory makes use of the recent experimental data on the rotational lines and underlying continua after analysis of the extensive literature on oxygen absorption coefficients.

After the first detailed analyses, such as those determining wavelength assignments, for $v' \geq 12$, of Brix and Herzberg (1954) and, for $v' \leq 13$, of Ackerman and Biauomé (1970) and Biauomé (1972), extensive wavenumber measurements of the rotation lines of the O_2 Schumann-Runge absorption bands were provided by Yoshino, Freeman and Parkinson (1984). These sets of data are also the most accurate, and are almost complete, since the cross-sections are absolute, the linewidths being in excess of

the instrument resolution for the various bands studied.

Rotational constants of the upper electronic state of the Schumann-Runge system have also been published recently by Cheung, Yoshino, Parkinson and Freeman (1986). These constants open the possibility of calculating the wavenumbers of the rotational lines. The same spectroscopic constants have also been determined by Lewis, Berzins and Calver (1986) from the wavenumber measurements of Yoshino et al. (1984).

The band oscillator strengths of the ($v',0$) and ($v',1$) bands adopted here are based on the various results of Yoshino, Freeman, Esmond and Parkinson (1983), of Cheung, Yoshino, Parkinson and Freeman (1984), of Yoshino, Freeman, Esmond and Parkinson (1987), of Lewis, Bergins and Carver (1986), and also of Allison, Dalgarno and Pasachoff (1971).

The predissociation linewidths have been determined after detailed comparison between calculated absorption cross-sections and the experimental results published by Yoshino et al. (1983) in the spectral region corresponding to the $v' = 1$ to 12 bands. However, the absorption cross-sections throughout this region may also depend on the underlying continuum that corresponds near 50000 cm^{-1} to the O_2 Herzberg continuum (see Nicolet and Kennes, 1986, and 1988). At wavenumbers greater than 55000 cm^{-1} , the O_2 Schumann-Runge continuum (see Lewis, Bergins and Carver, 1985a,b) plays a role that is dependent on temperature.

The rotational structure of the bands

The Schumann-Runge bands of O_2 arise from the transition $\text{B } ^3\Sigma_u^- - \text{X } ^3\Sigma_g^-$ in the $49000 - 57000 \text{ cm}^{-1}$ spectral region containing the rotational lines from bands with $v' = 0$ to 19 and $v'' = 0$ and 1 in absorption when the temperature is not more than 300 K. From 2-0 to 19-0, the intervals decrease from 665 cm^{-1} to 75 cm^{-1} ; these values correspond to a variation from 2.62 nm to 0.23 nm. The absorption occurs mostly in the six principal branches, P and R. The final results of the calculations

illustrate that the distribution of the intensity varies greatly in each interval. However, at low temperature, the structure is different, because the rotational lines of the bands with $v'' = 1$ do not play any role at low temperature; the rotational structure represents at low temperature only the bands from $v'' = 0$. The maximum averaged cross-sections for 500 cm^{-1} intervals vary from about $8 \times 10^{-24} \text{ cm}^2$ between $49000 - 49500 \text{ cm}^{-1}$ (practically the underlying continuum) to almost $2 \times 10^{-19} \text{ cm}^2$ between $56500 - 57000 \text{ cm}^{-1}$, the spectral range of the 15-0 to 19-0 bands. The variation of 10^4 in the absorption cross-sections (10^{-23} to 10^{-19} cm^2) requires that atmospheric absorption be taken into account from the mesopause to the lower stratosphere, for temperatures from 270 K to less than 190 K.

The O_2 Herzberg continuum

The absorption cross-sections of the O_2 Herzberg continuum at wavelengths greater than 200 nm that were used before 1980 must now be replaced by experimental and observational results obtained recently (1984-1986). An analysis by Nicolet and Kennes (1986, and 1989) leads to the adoption of an empirical formula for the absorption cross-section, $\sigma_{\text{HER}}(\text{O}_2) \text{ cm}^2$,

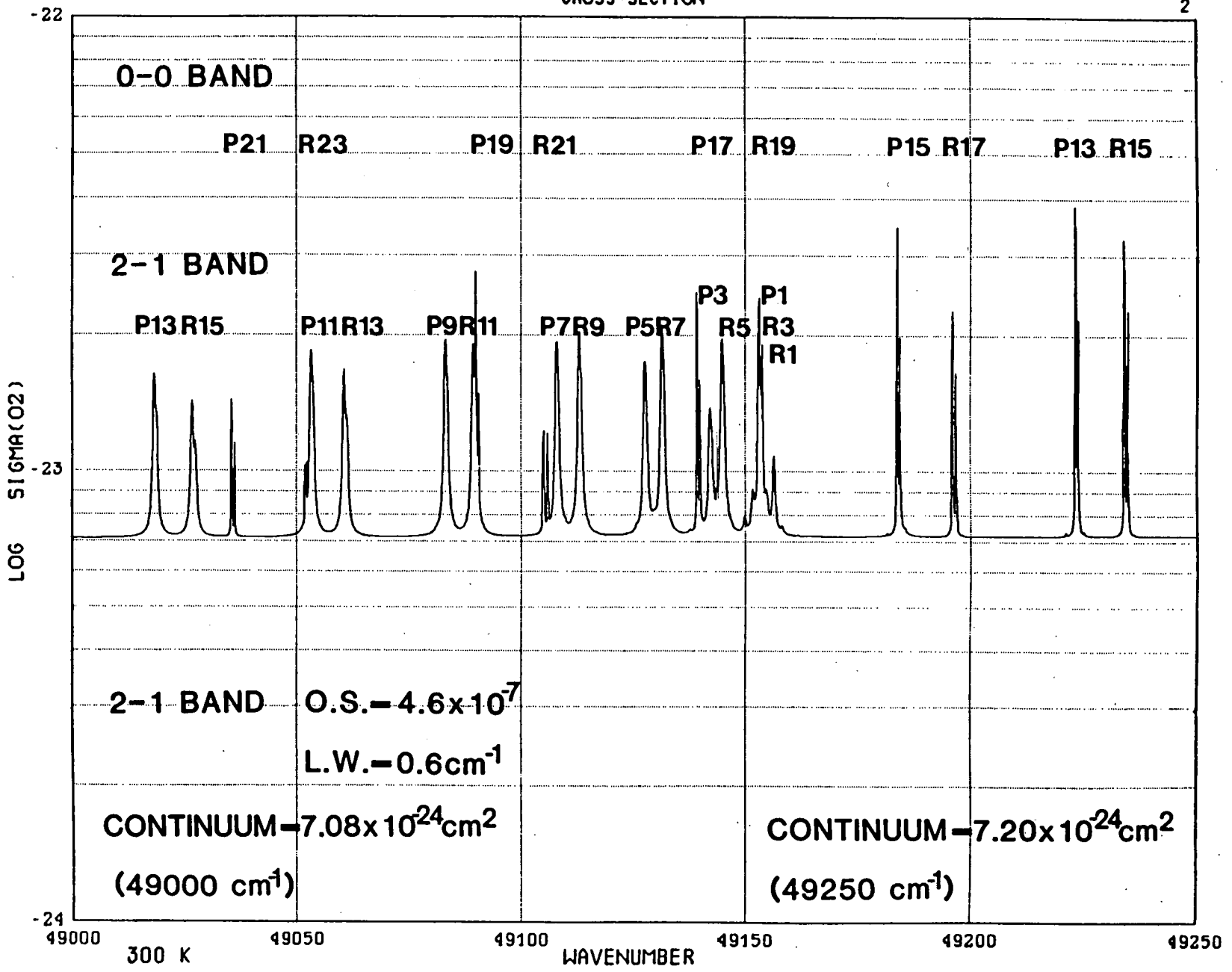
$$\sigma_{\text{HER}}(\text{O}_2) = 7.5 \times 10^{-24} (\nu/5 \times 10^4) \exp \{-50 [\ln(\nu/5 \times 10^4)]^2\}$$

The O_2 Schumann-Runge Continuum

The photoabsorption continuum underlying the Schumann-Runge bands of vibration $v' > 10$ has been deduced almost exclusively from recent analysis (Lewis et al., 1985a,b).

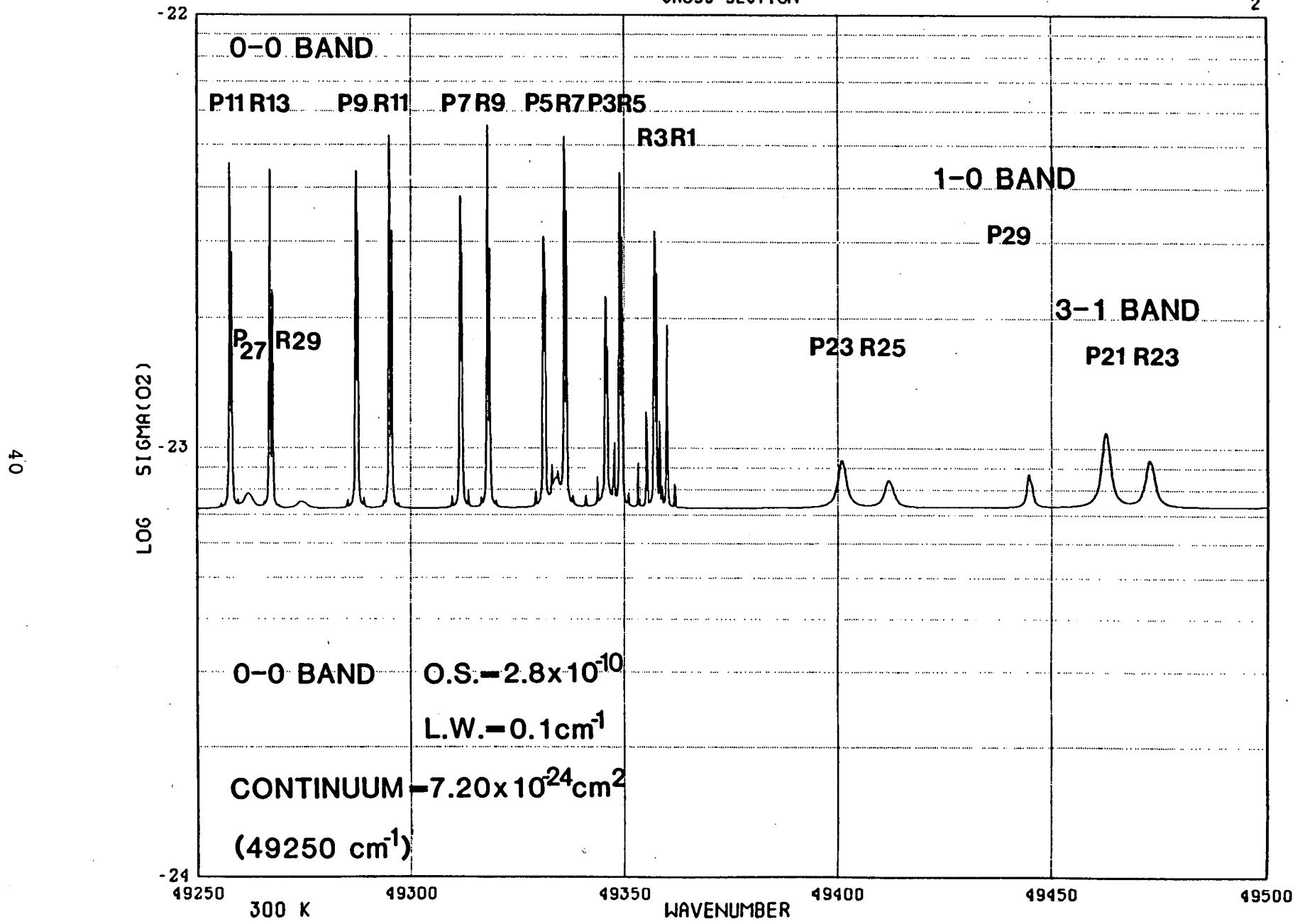
The values from our approximate determination of the cross-sections were deduced for temperatures between 170 K and 300 K, corresponding to the range of atmospheric and laboratory temperatures.

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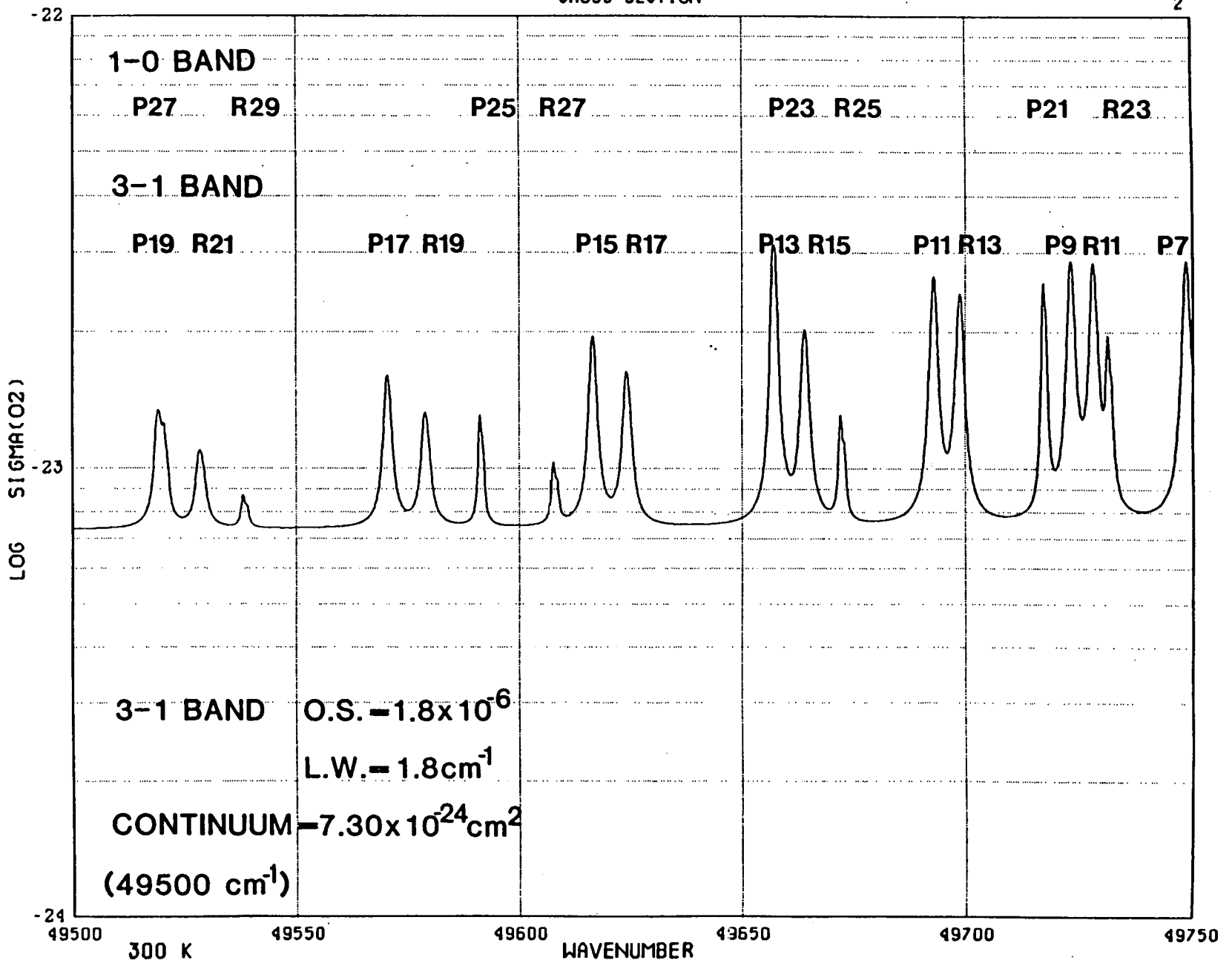


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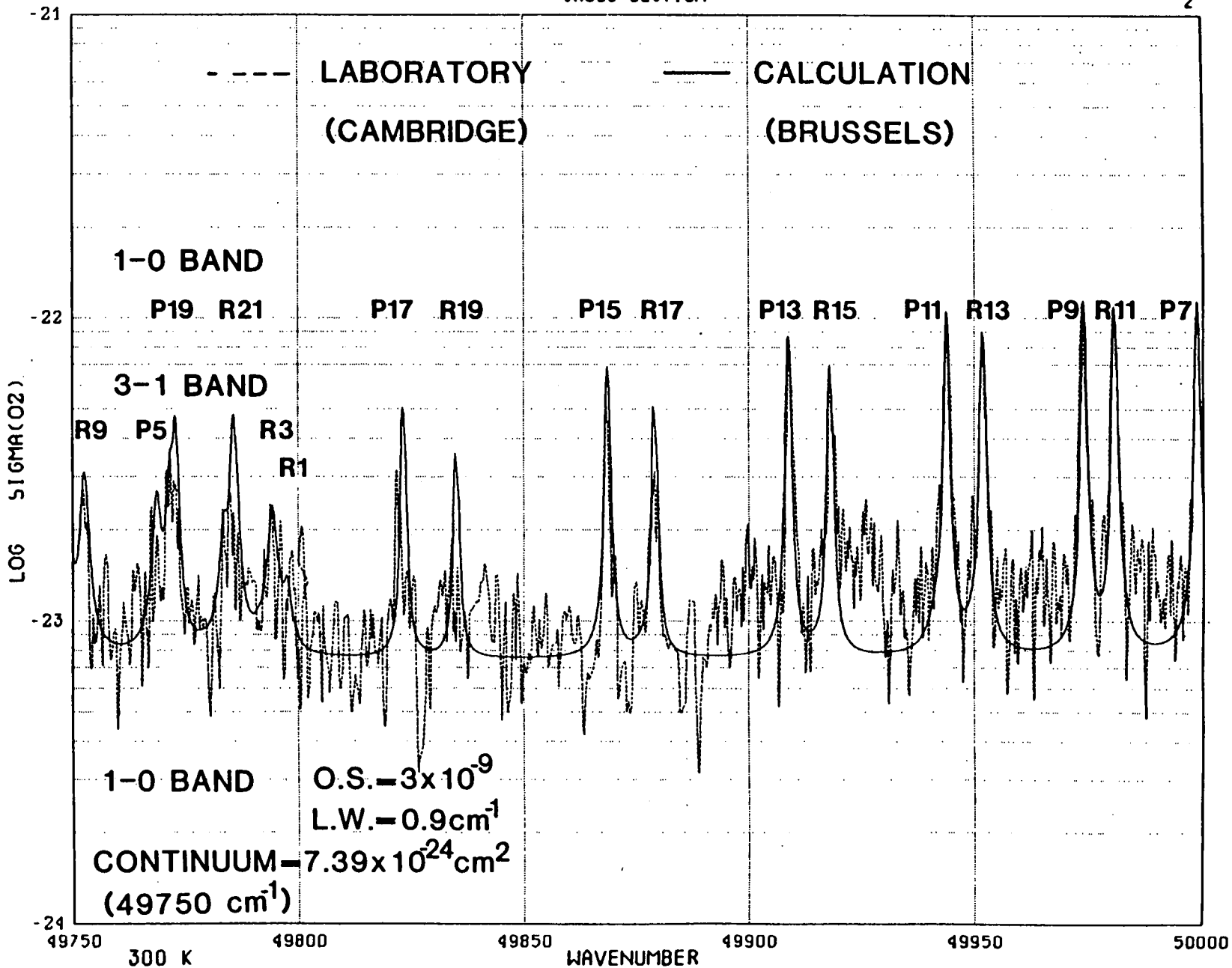
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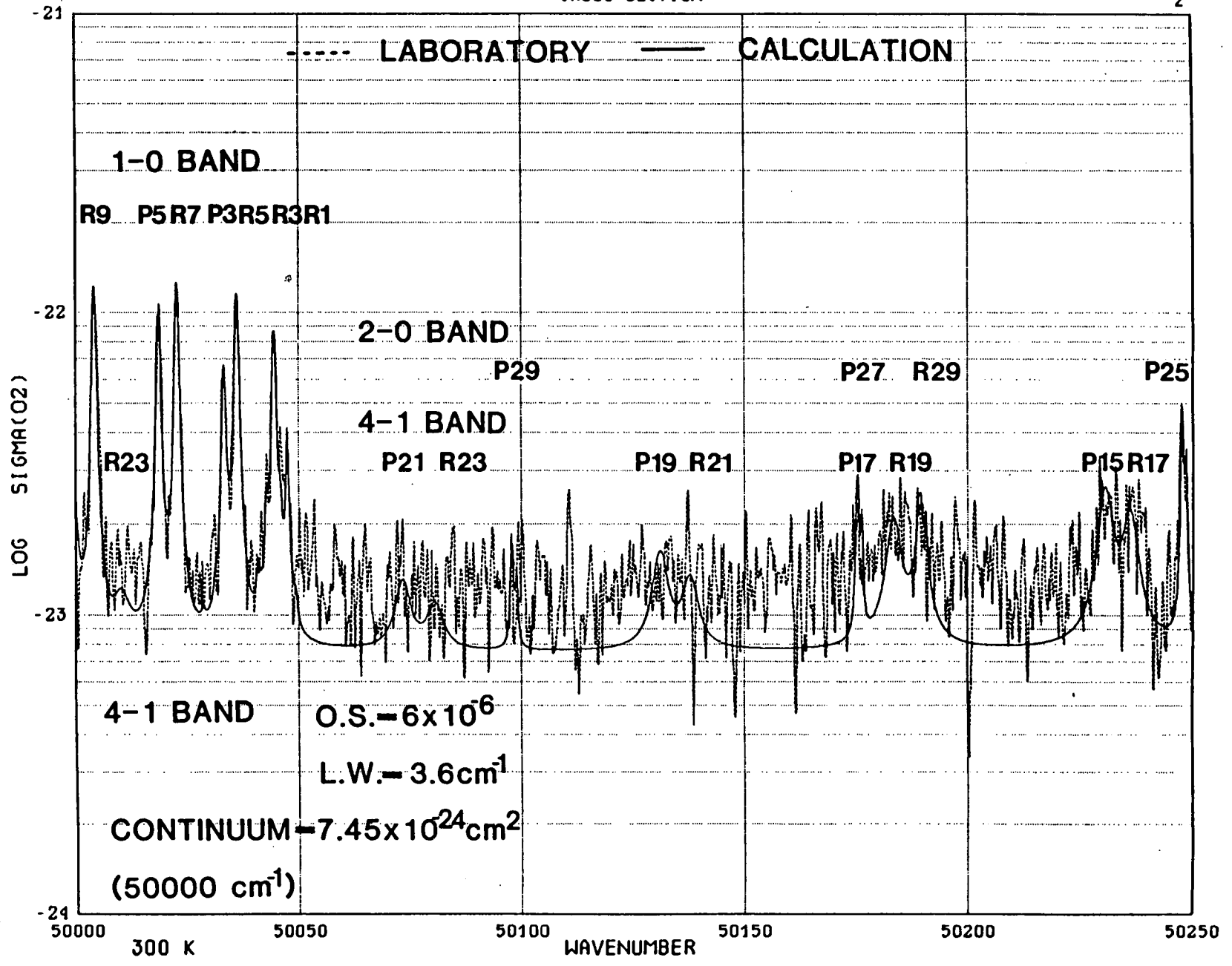
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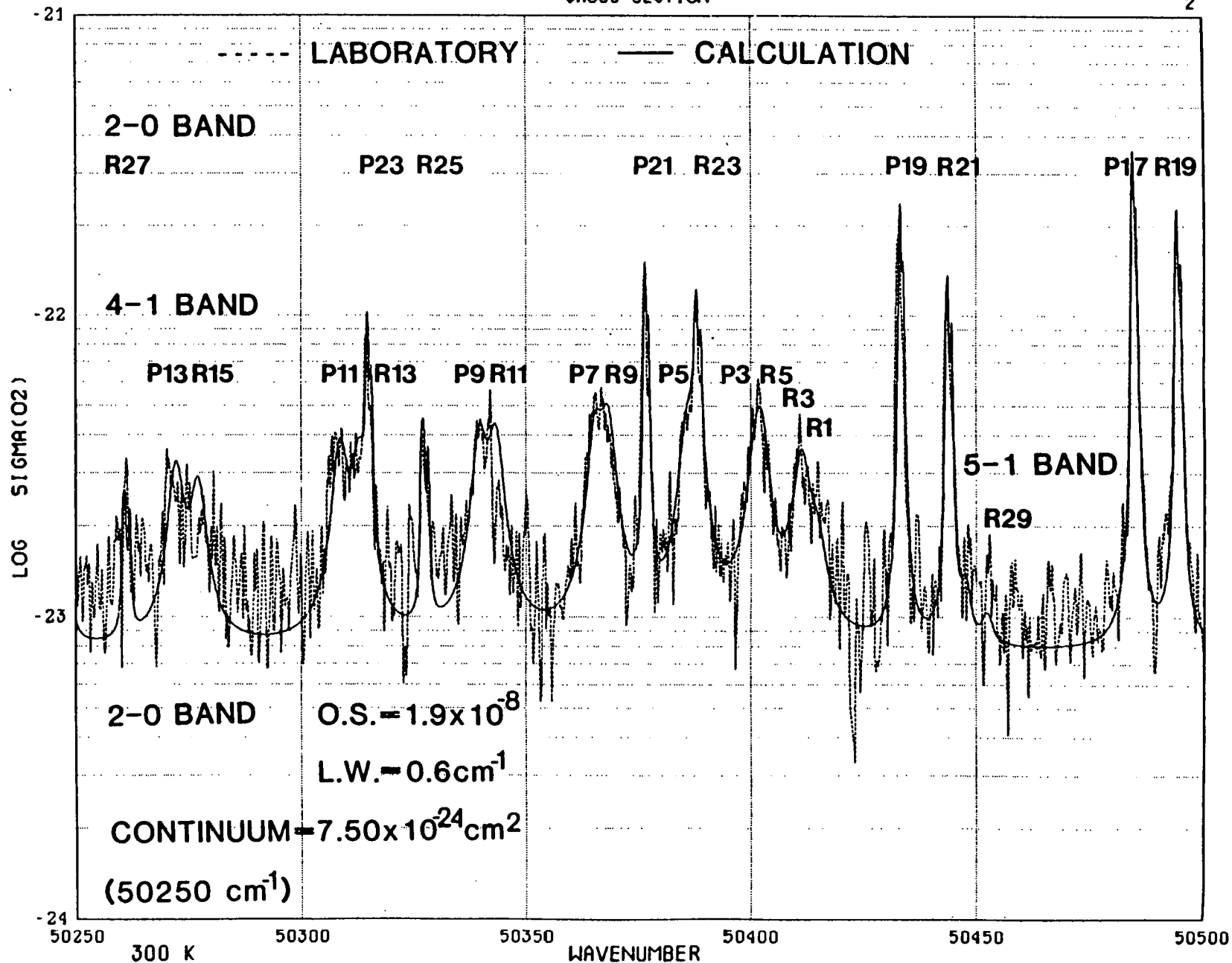
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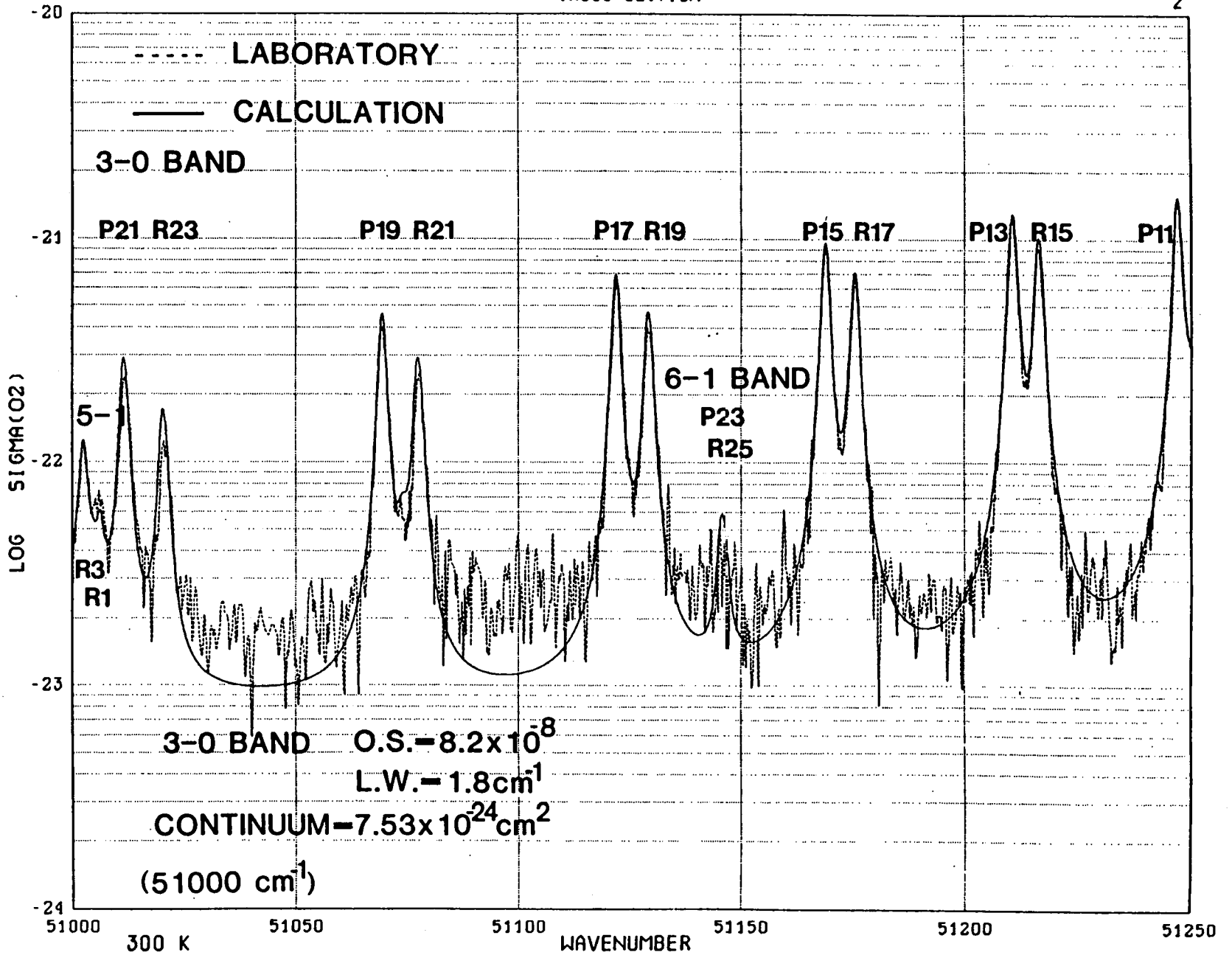


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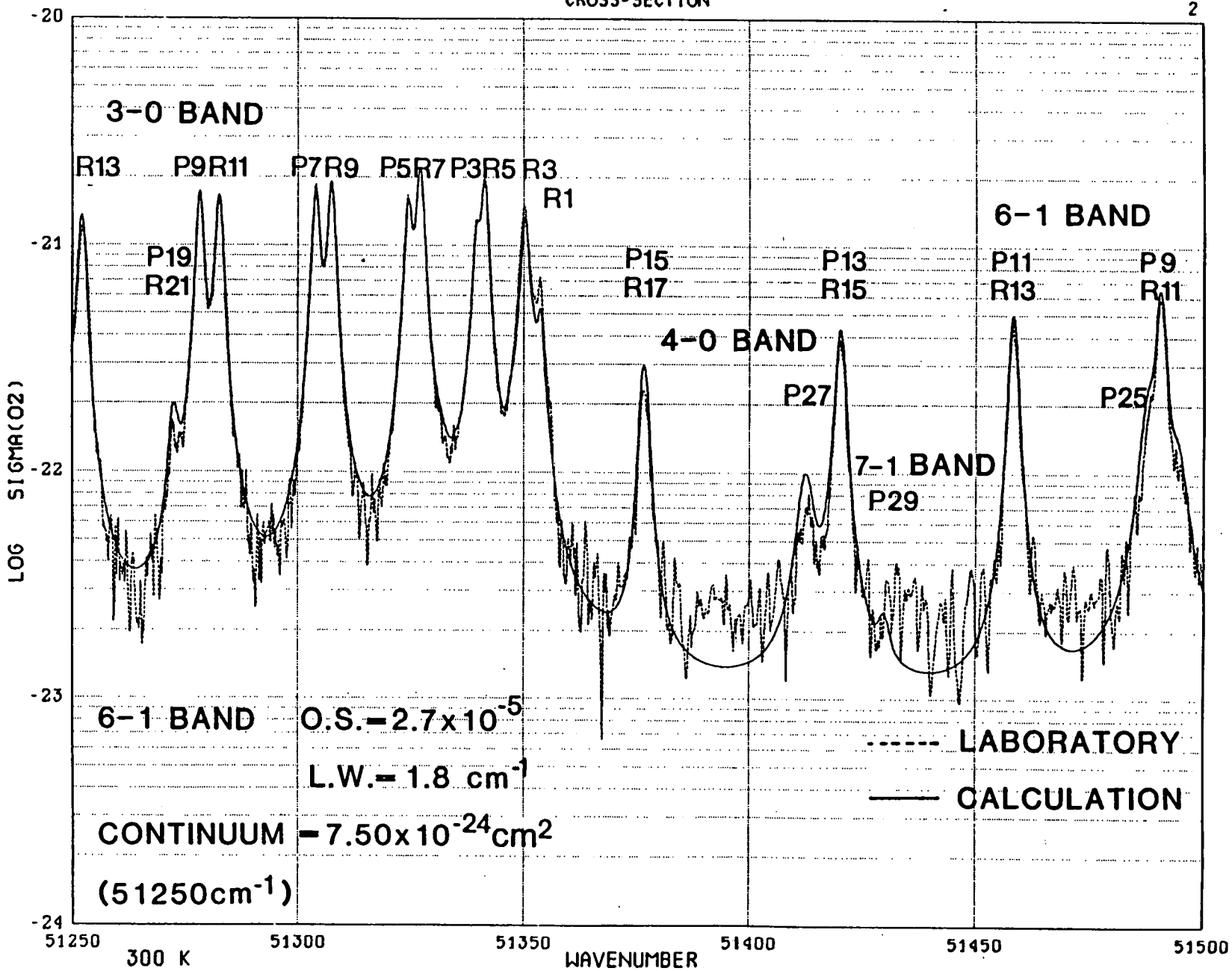
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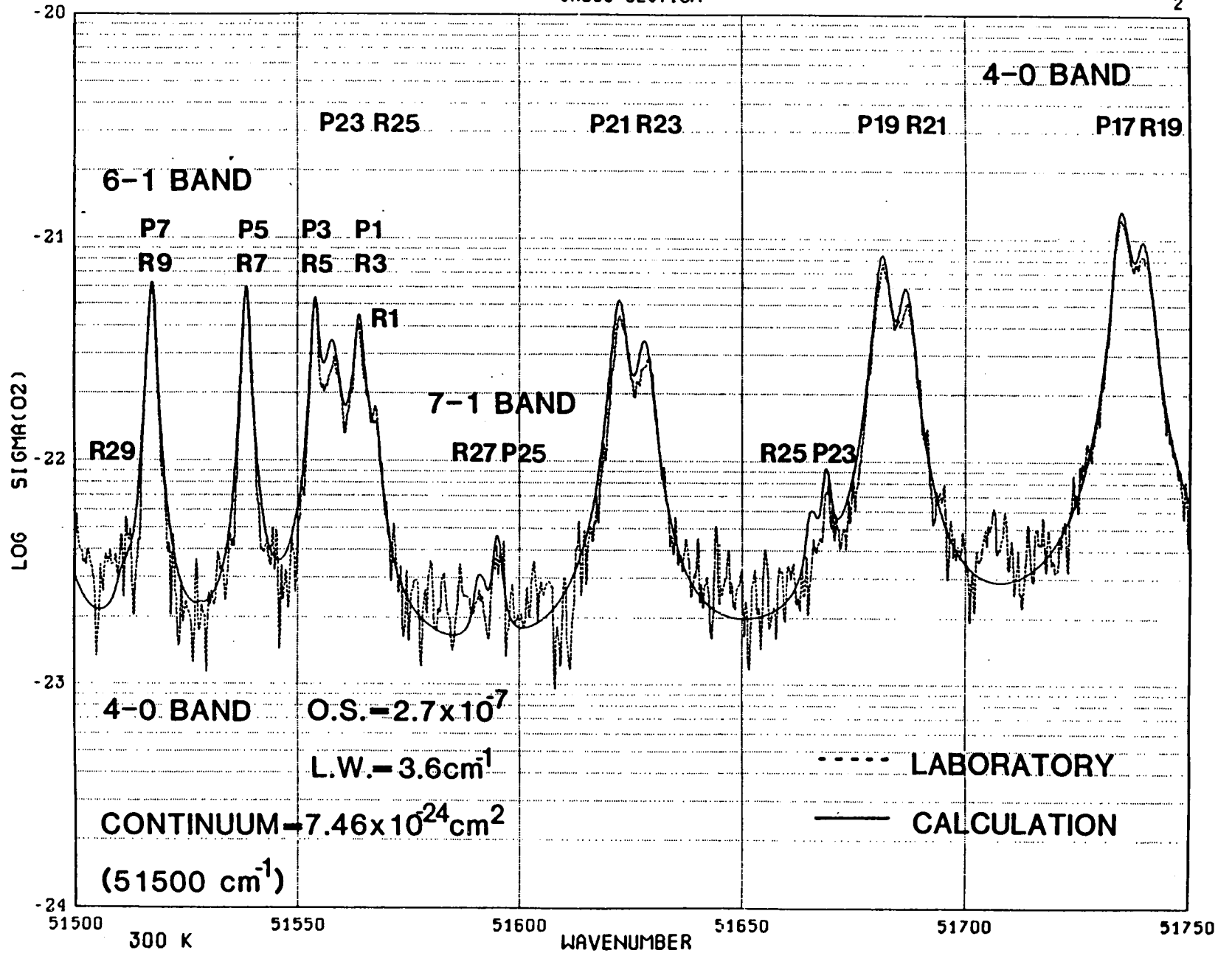


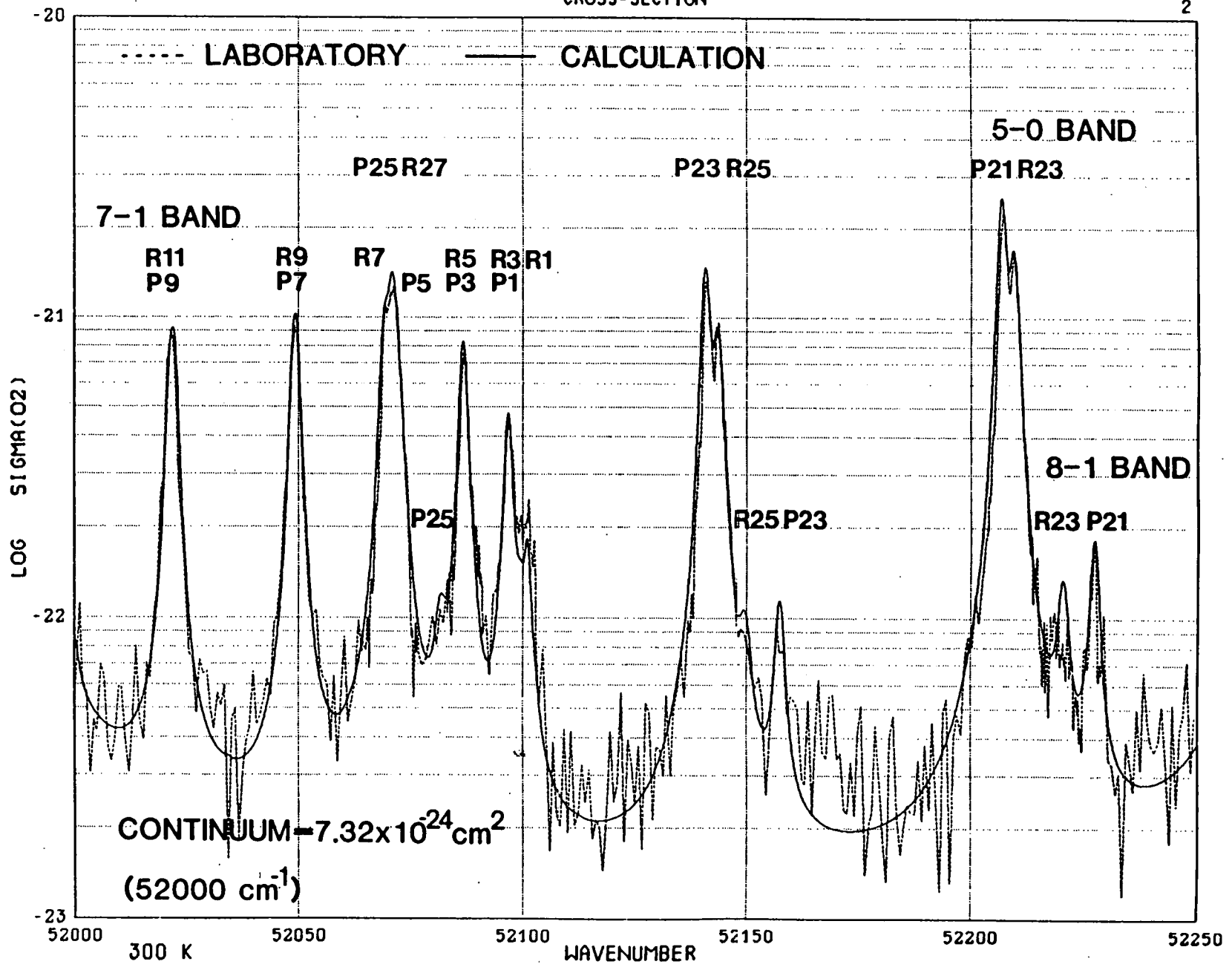


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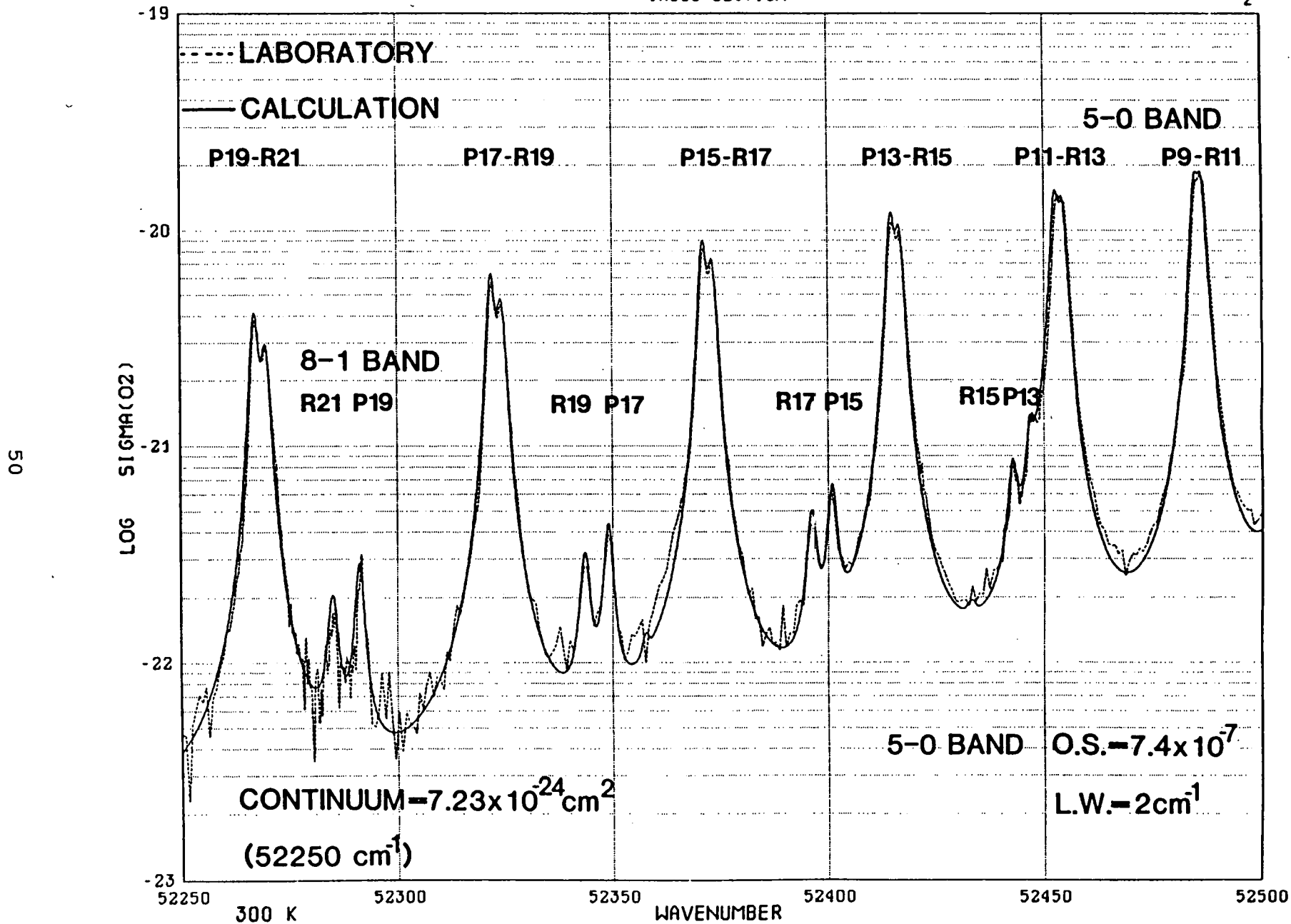
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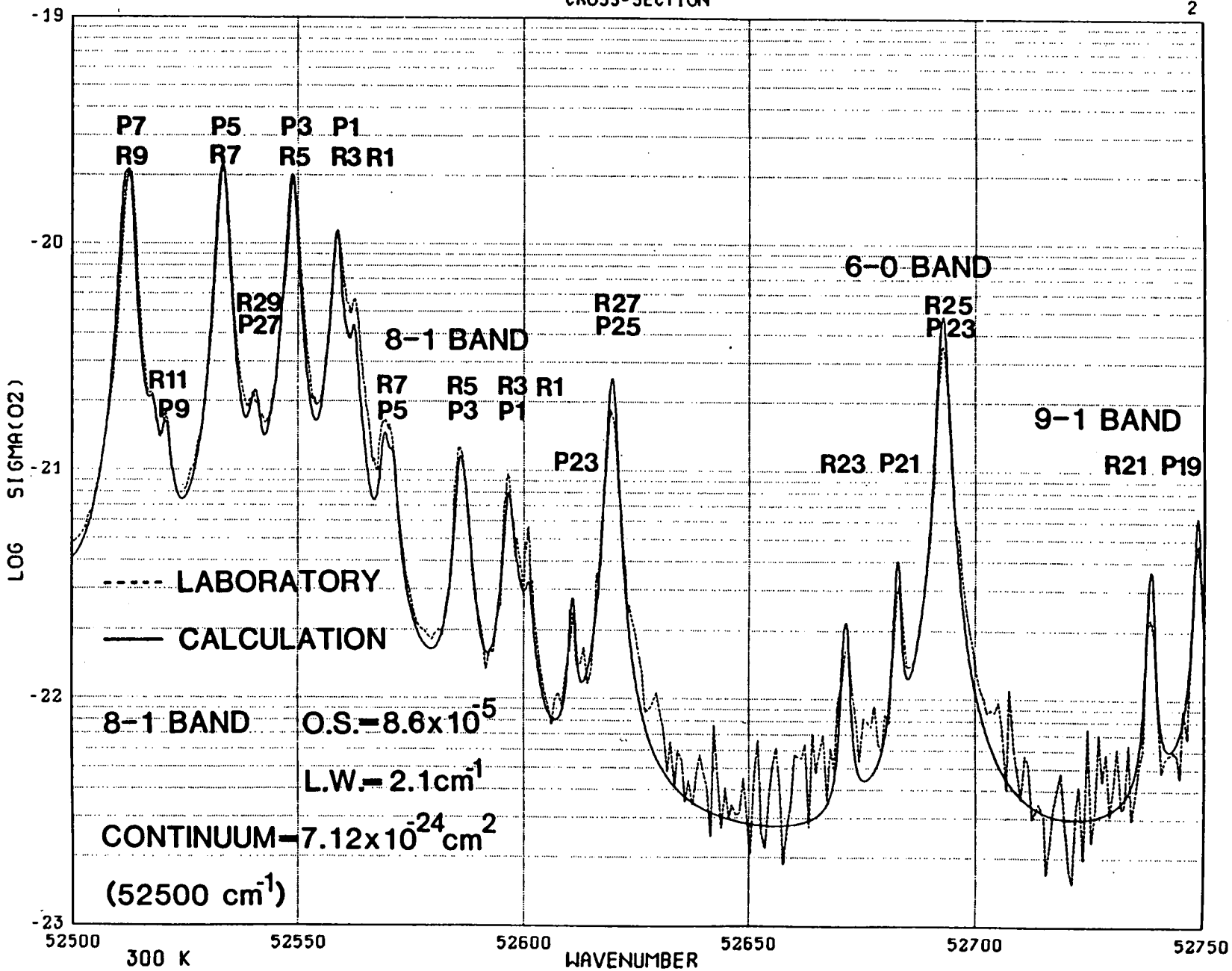


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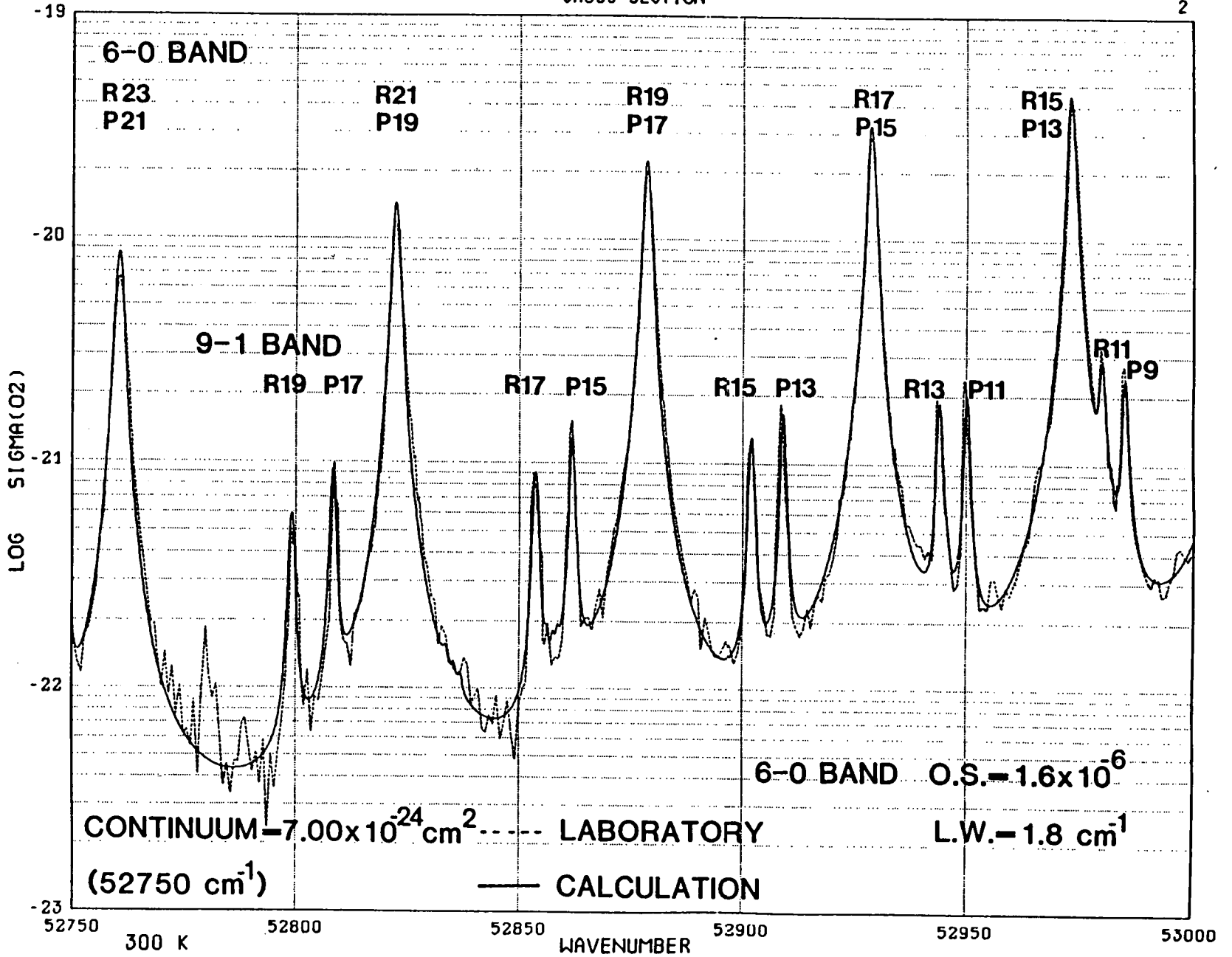
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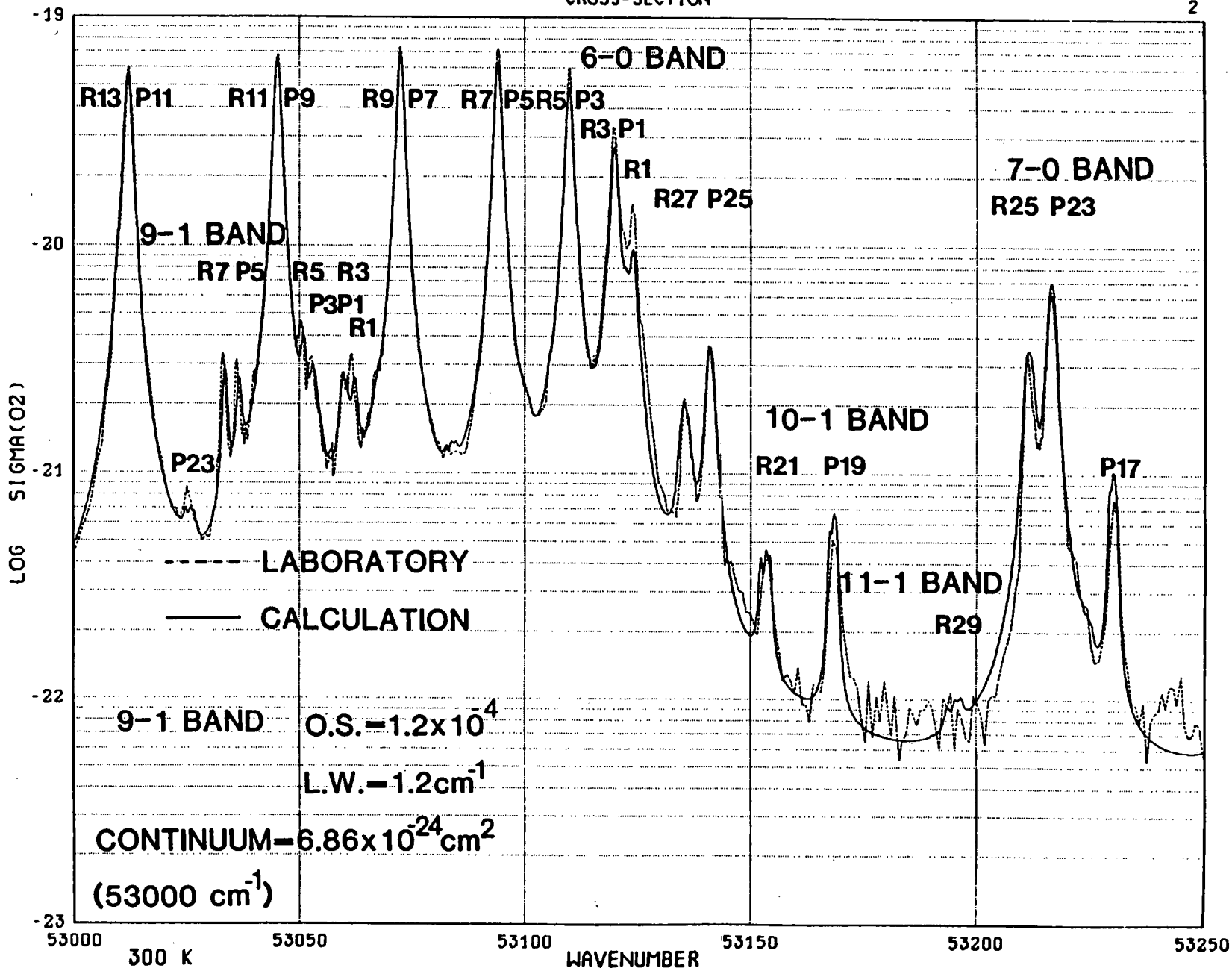


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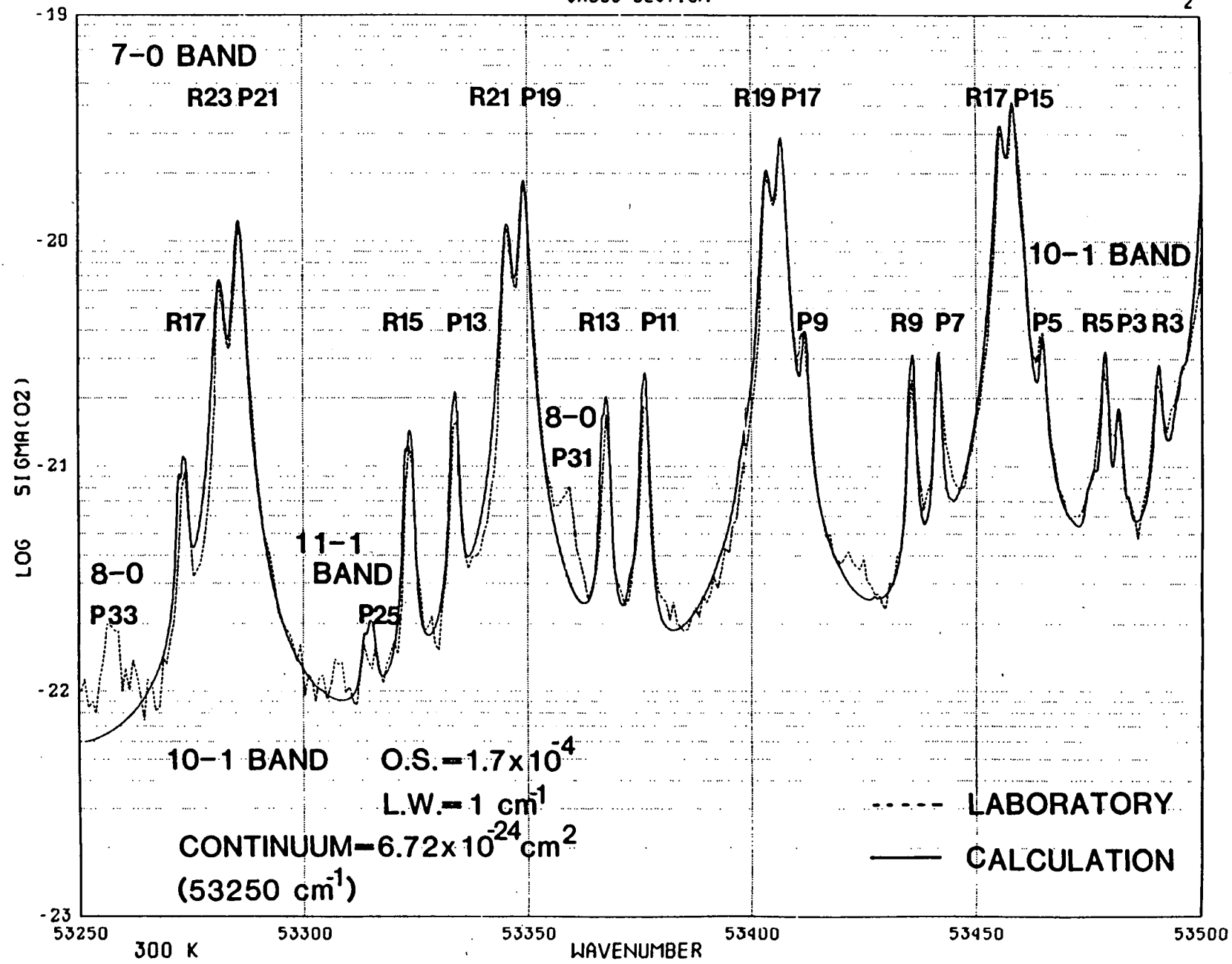
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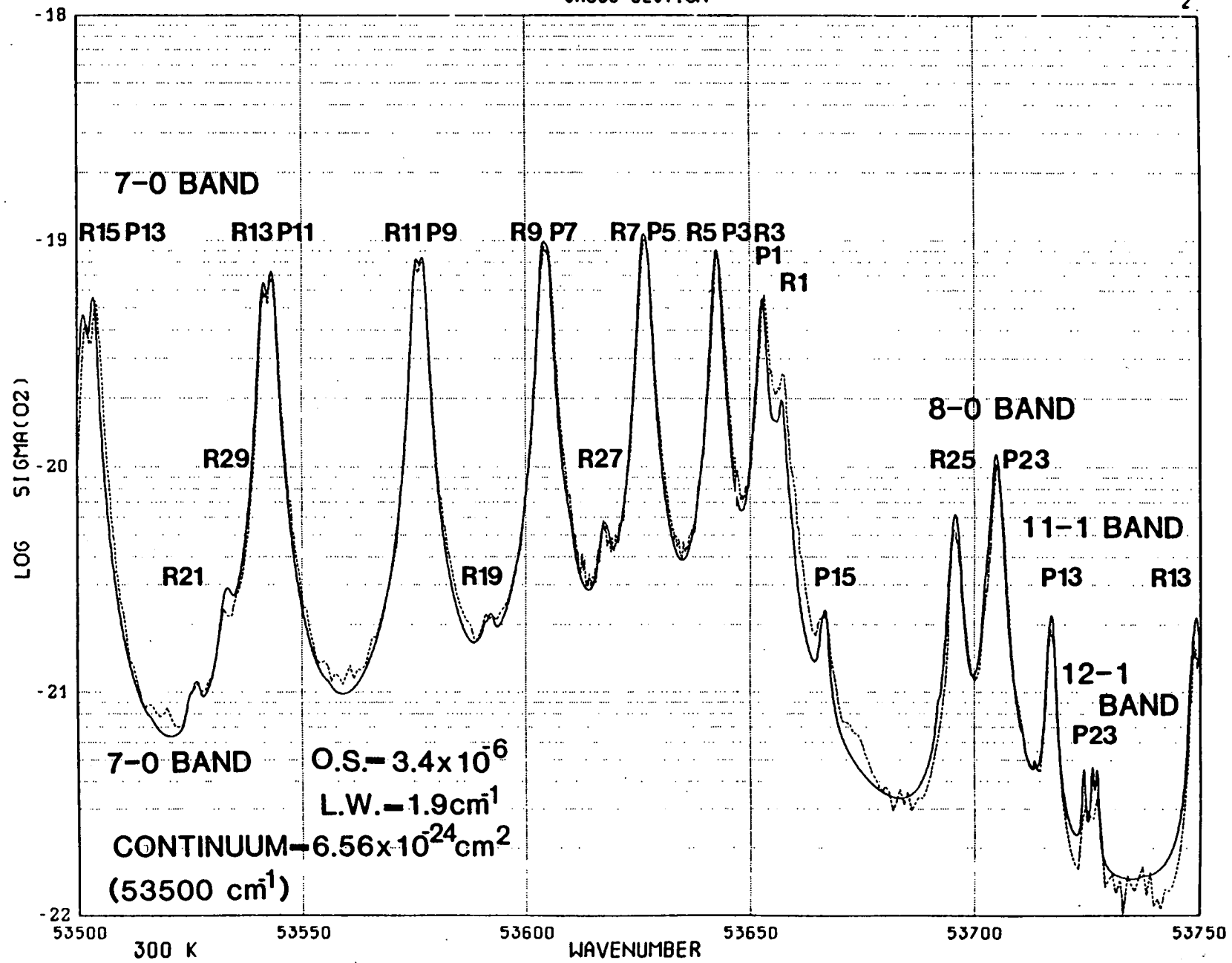


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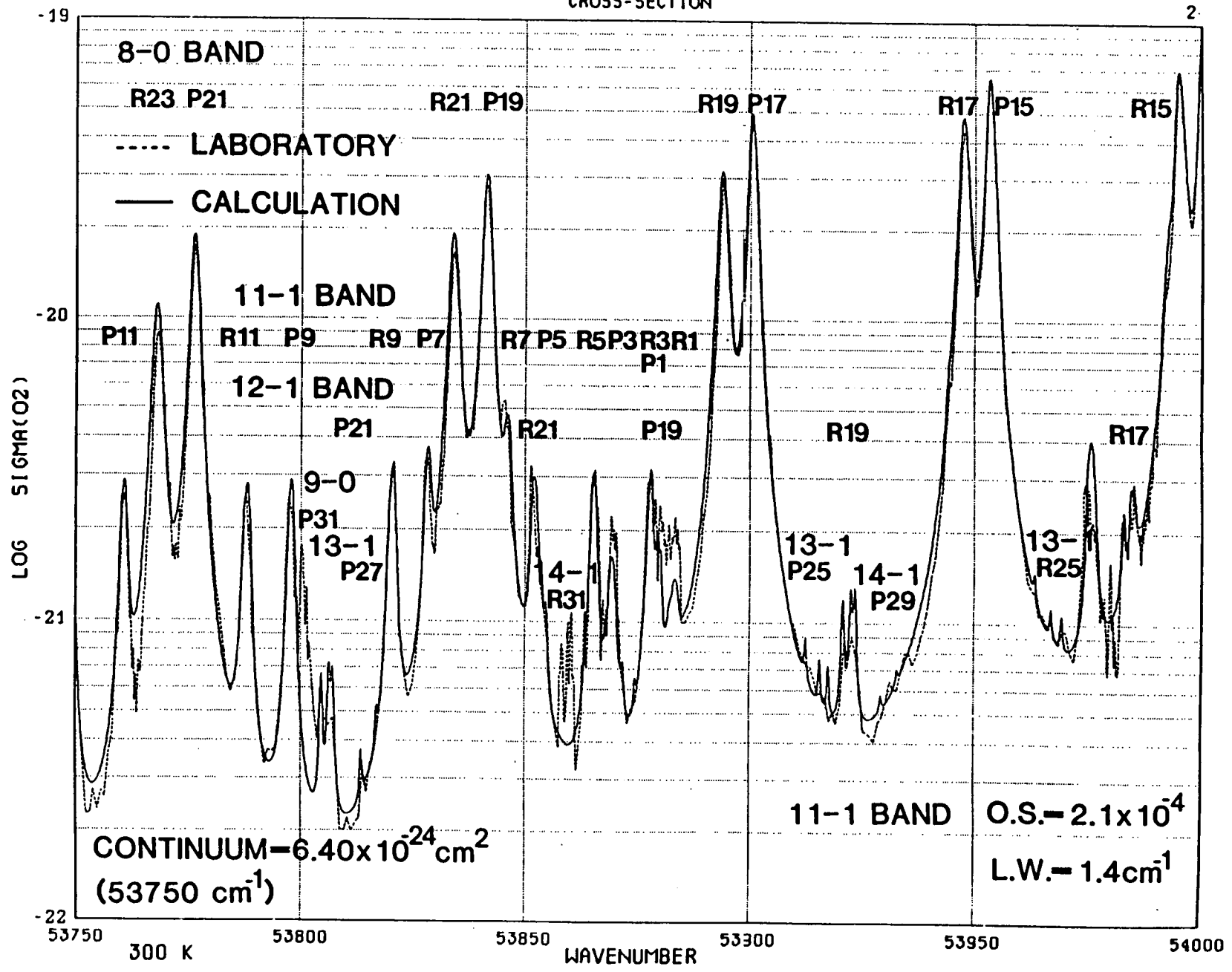
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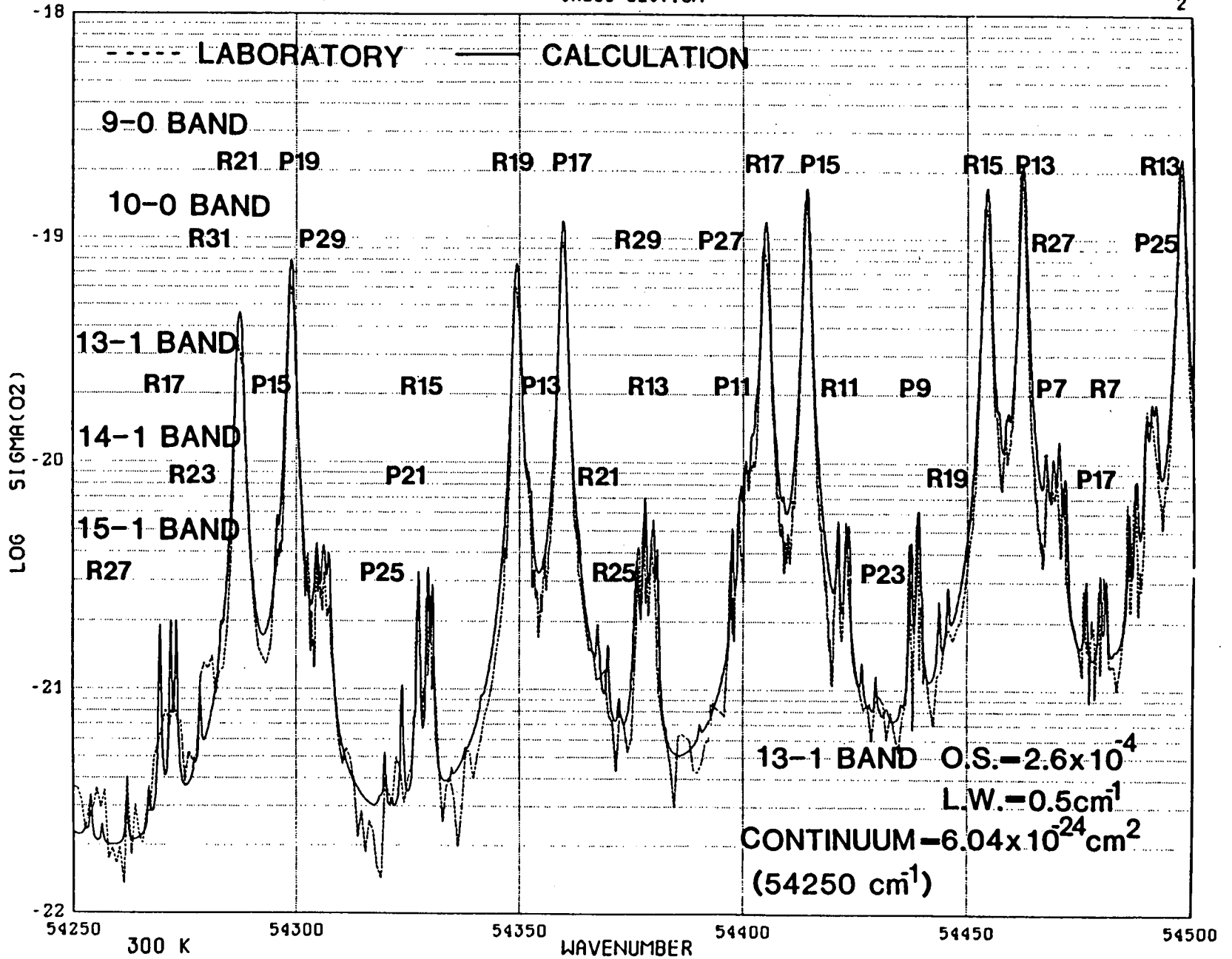


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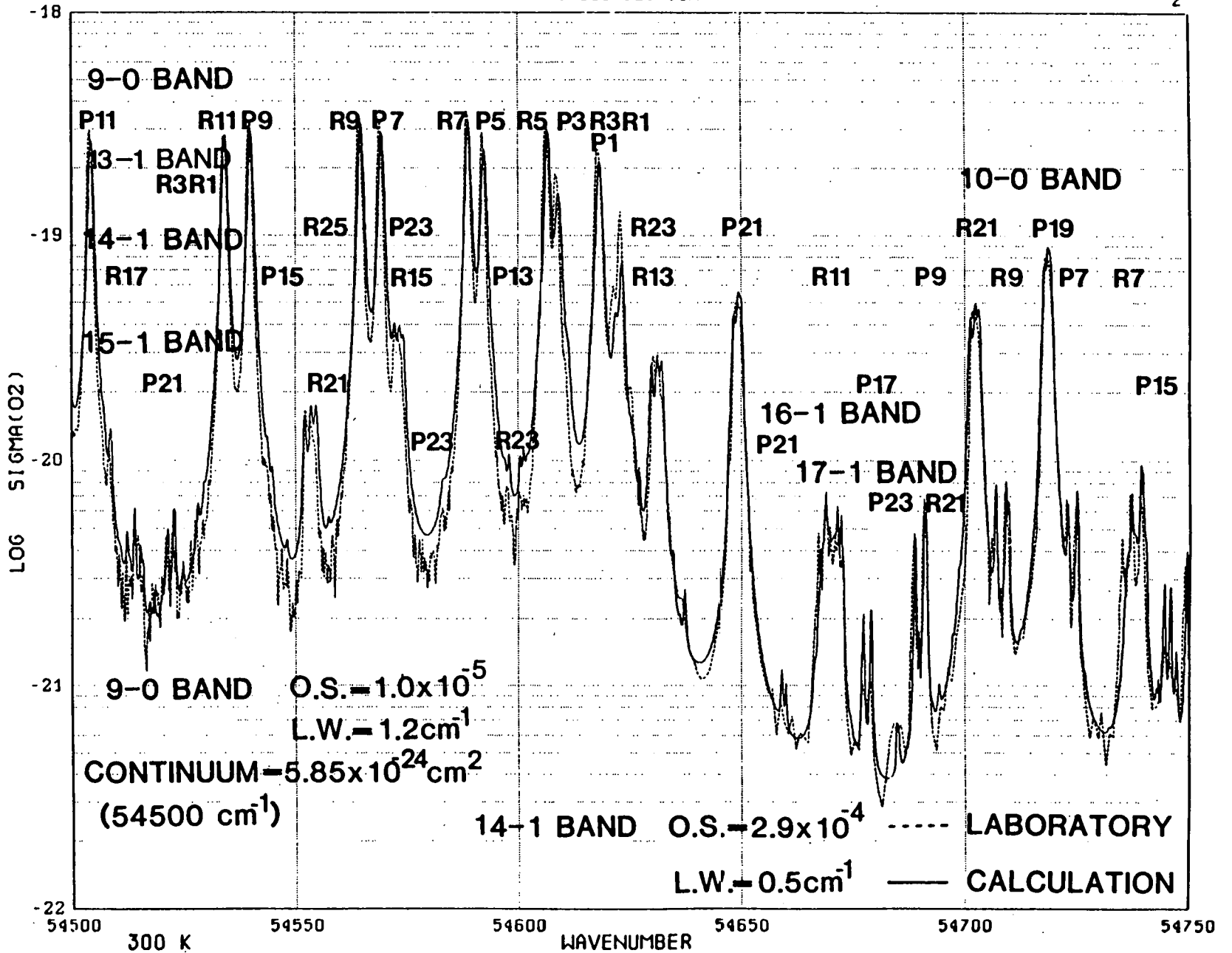
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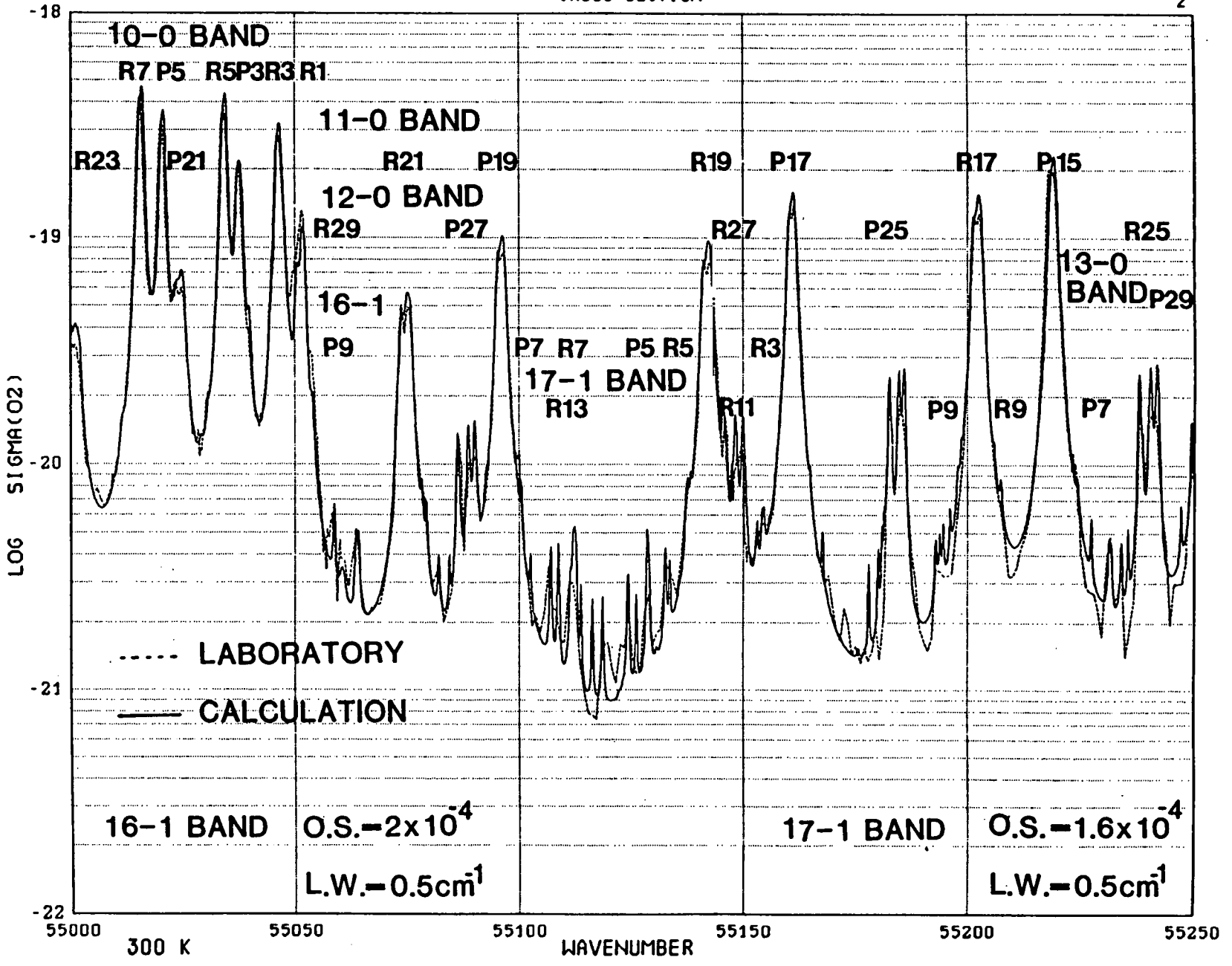
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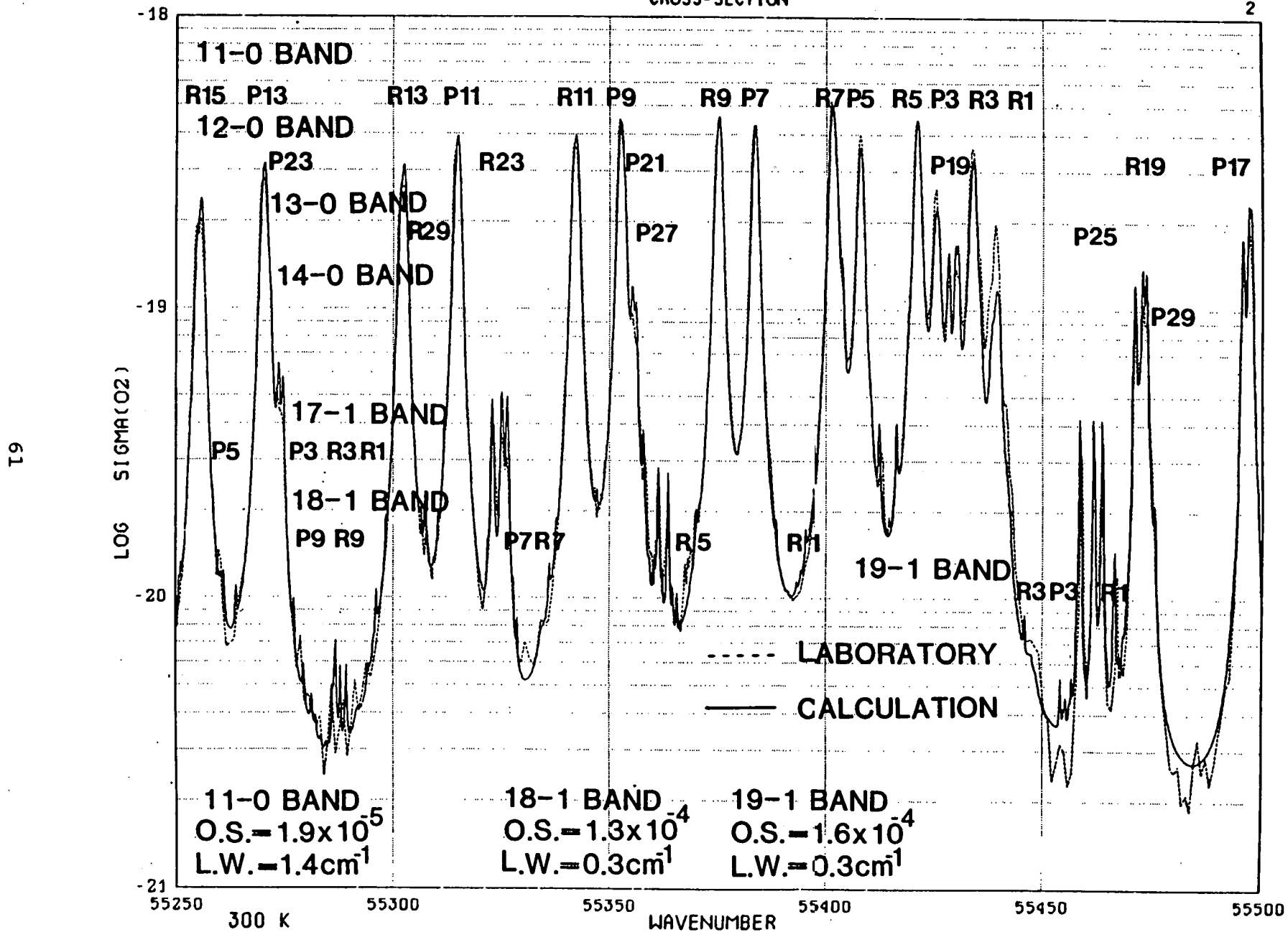
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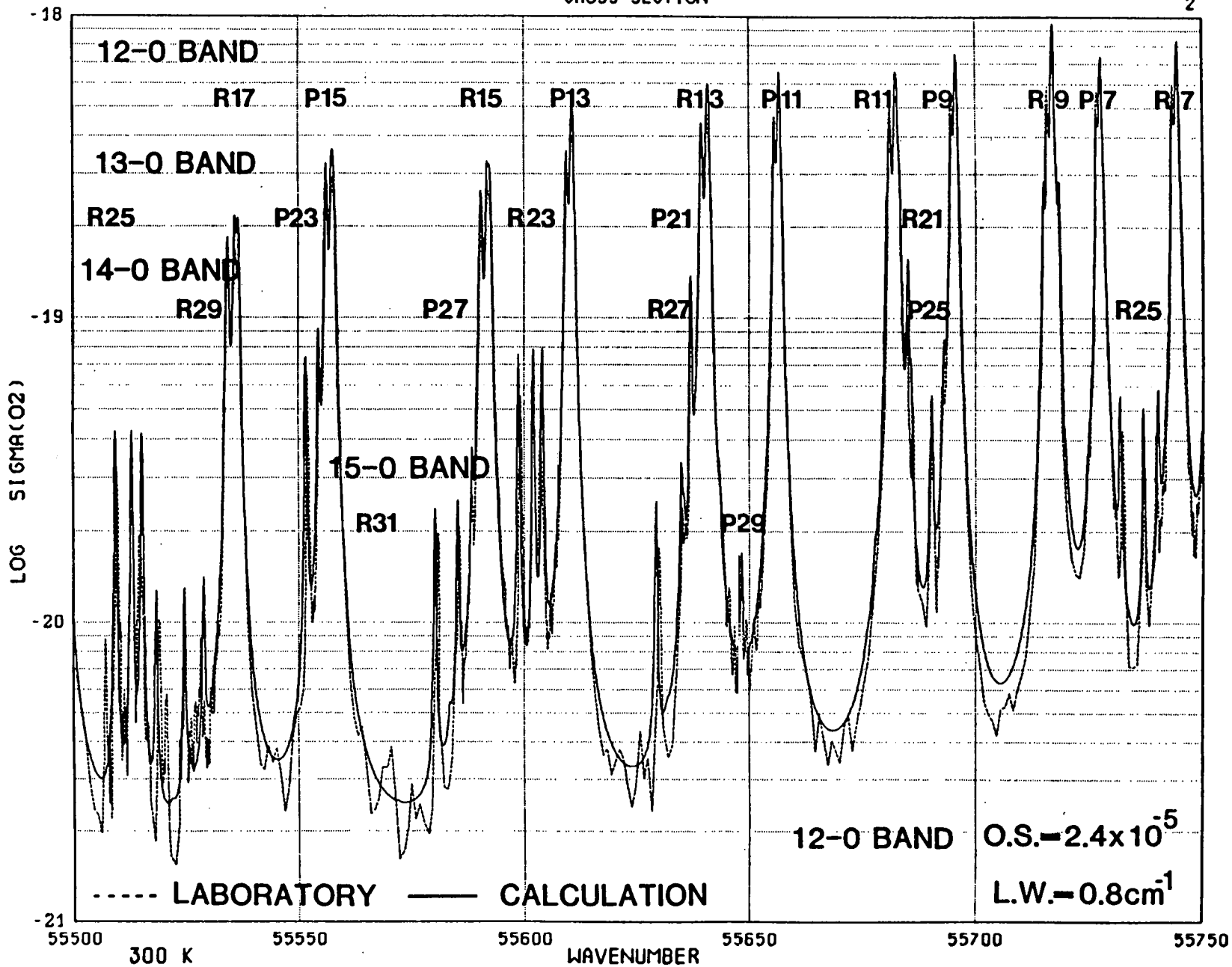
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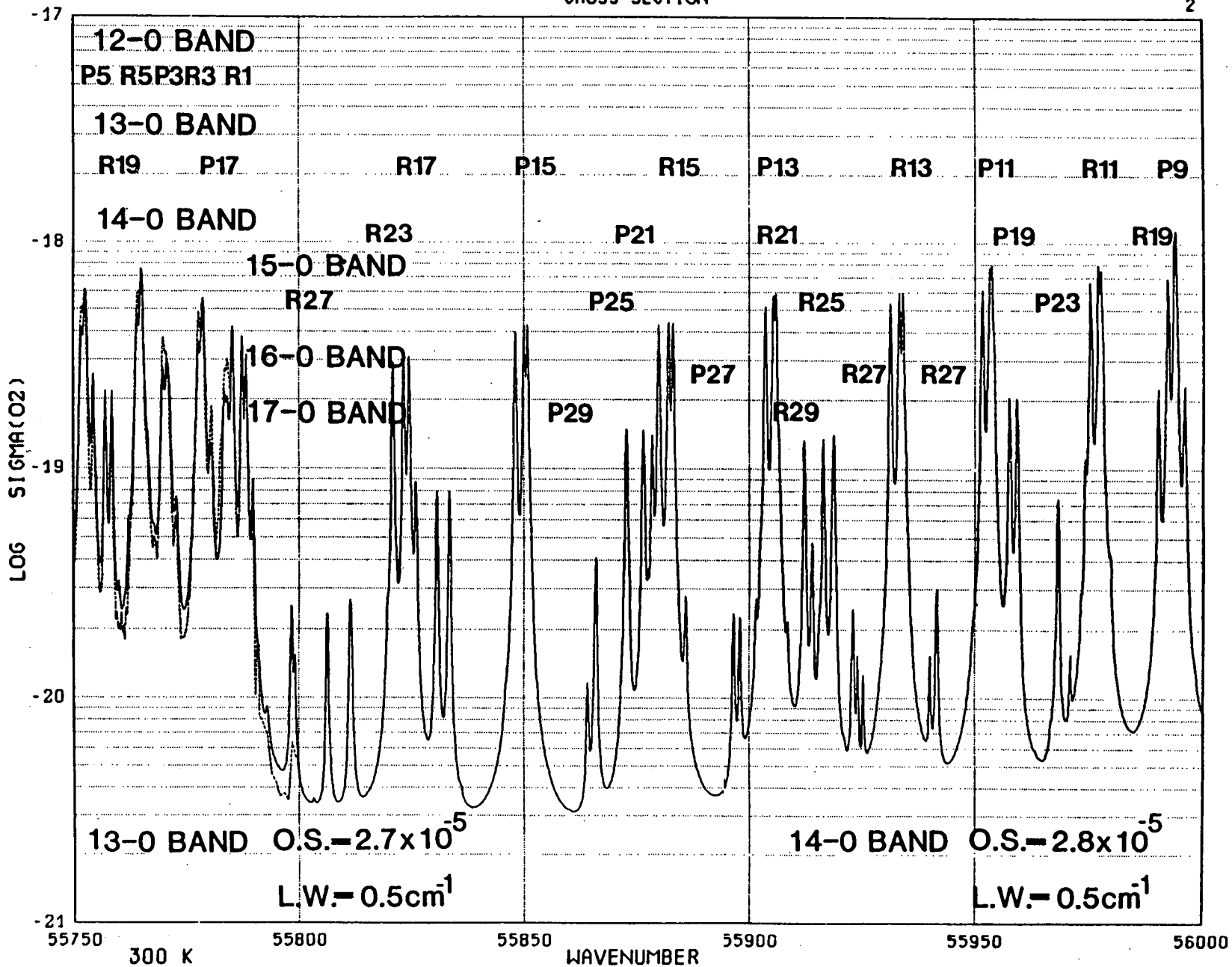


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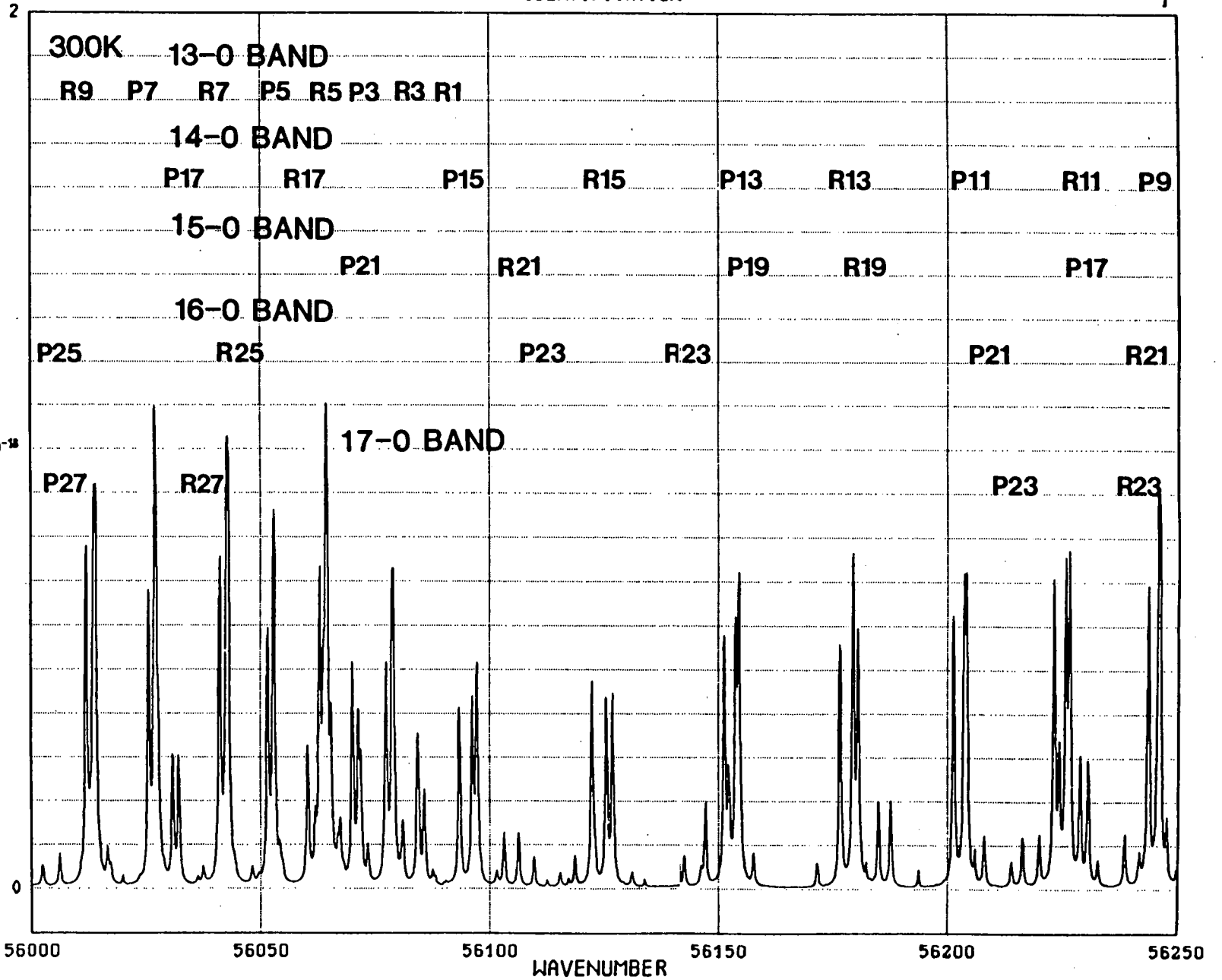


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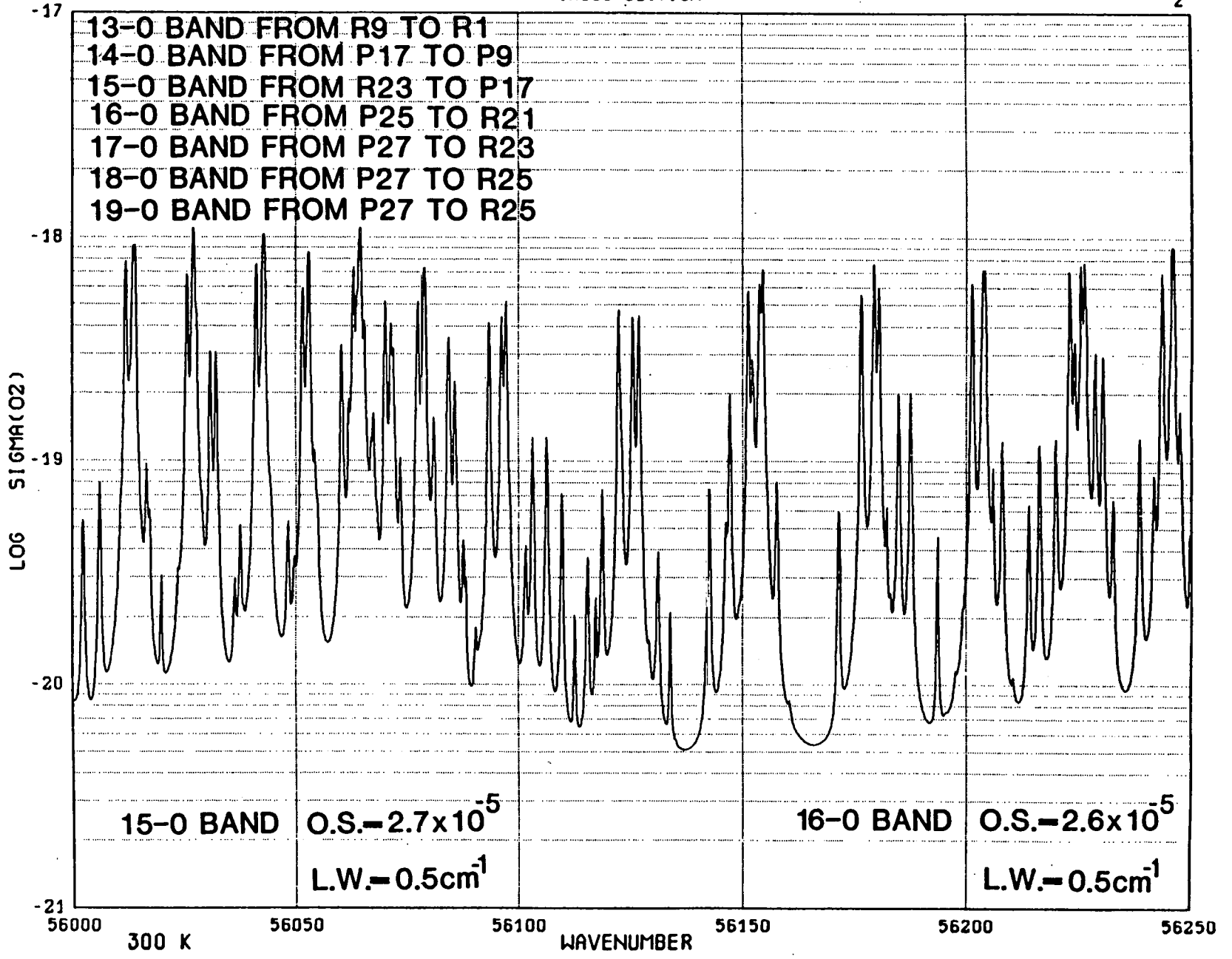


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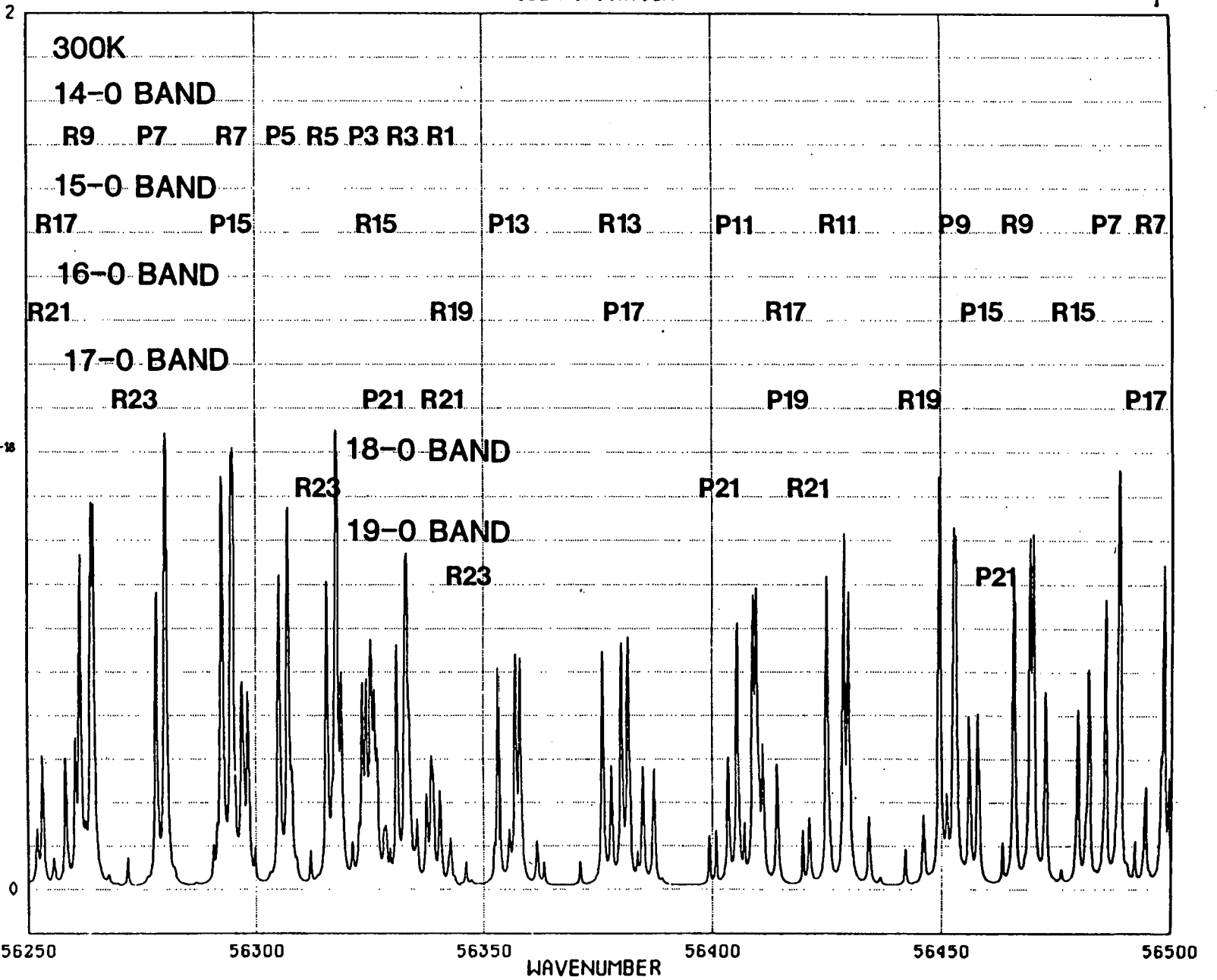


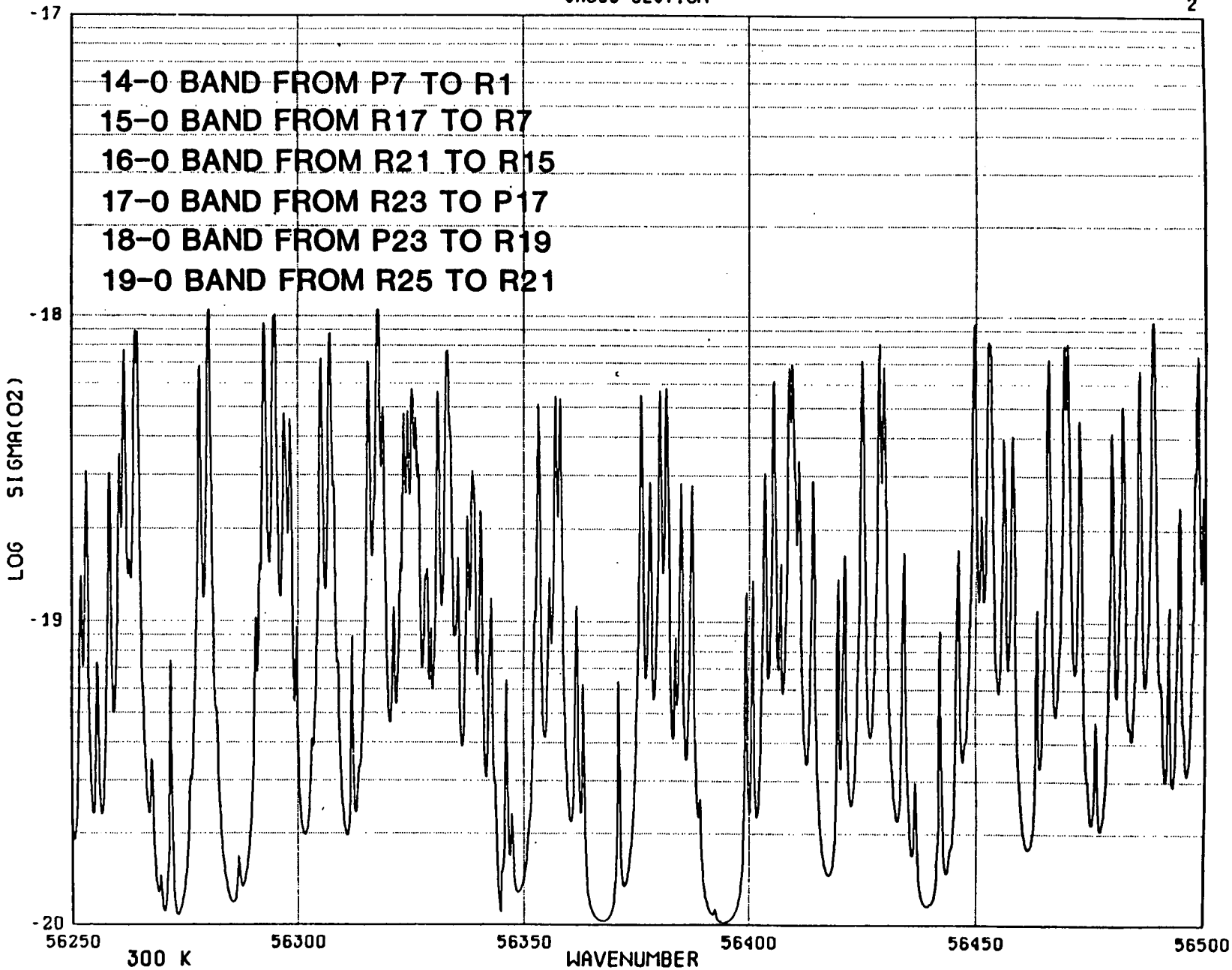
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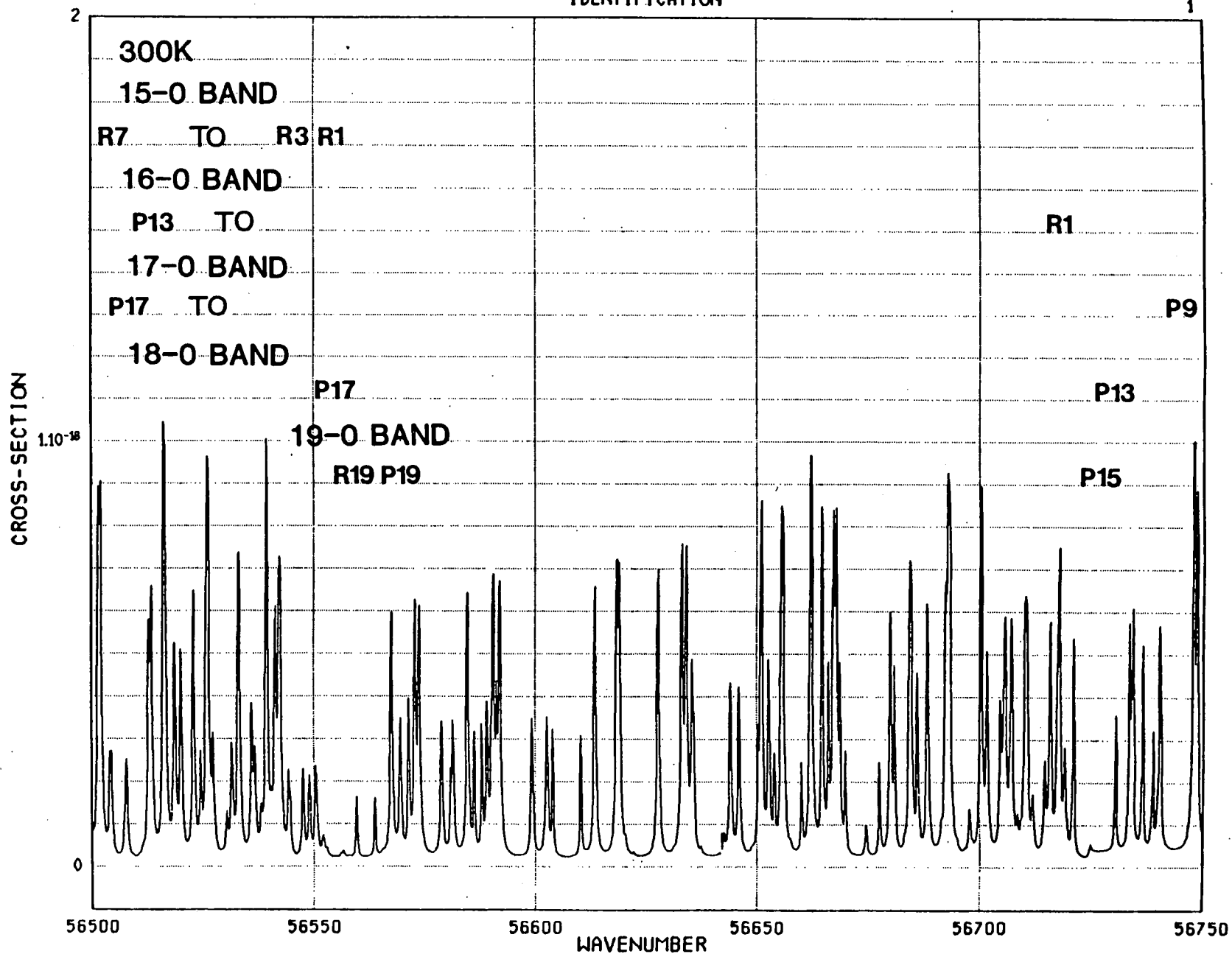
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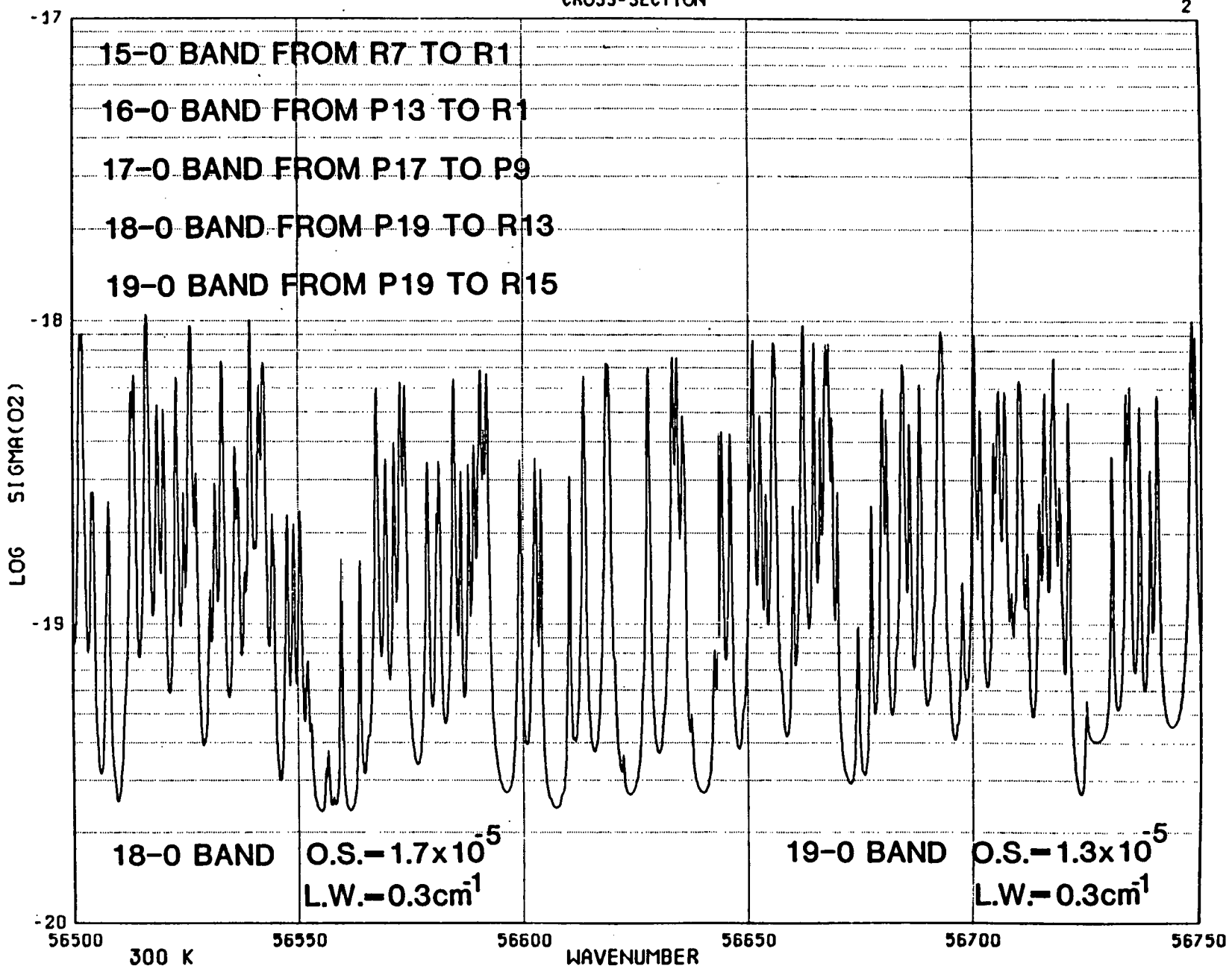
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CROSS-SECTION

69



IDENTIFICATION

1

2

300K

17-0 BAND

R9 P7 R7 P5 R5 P3 R3 R1

18-0 BAND

R13 P11 R11 P9 R9 P7R7P7R7 P5R5 R5 R3 P3R3R1

19-0 BAND

R15 P13 R13 R13 P11 R11P11R11 P9R9 R7P7R7 P5R5 R5P3

CROSS-SECTION

10^{-18}

56750

56800

56850

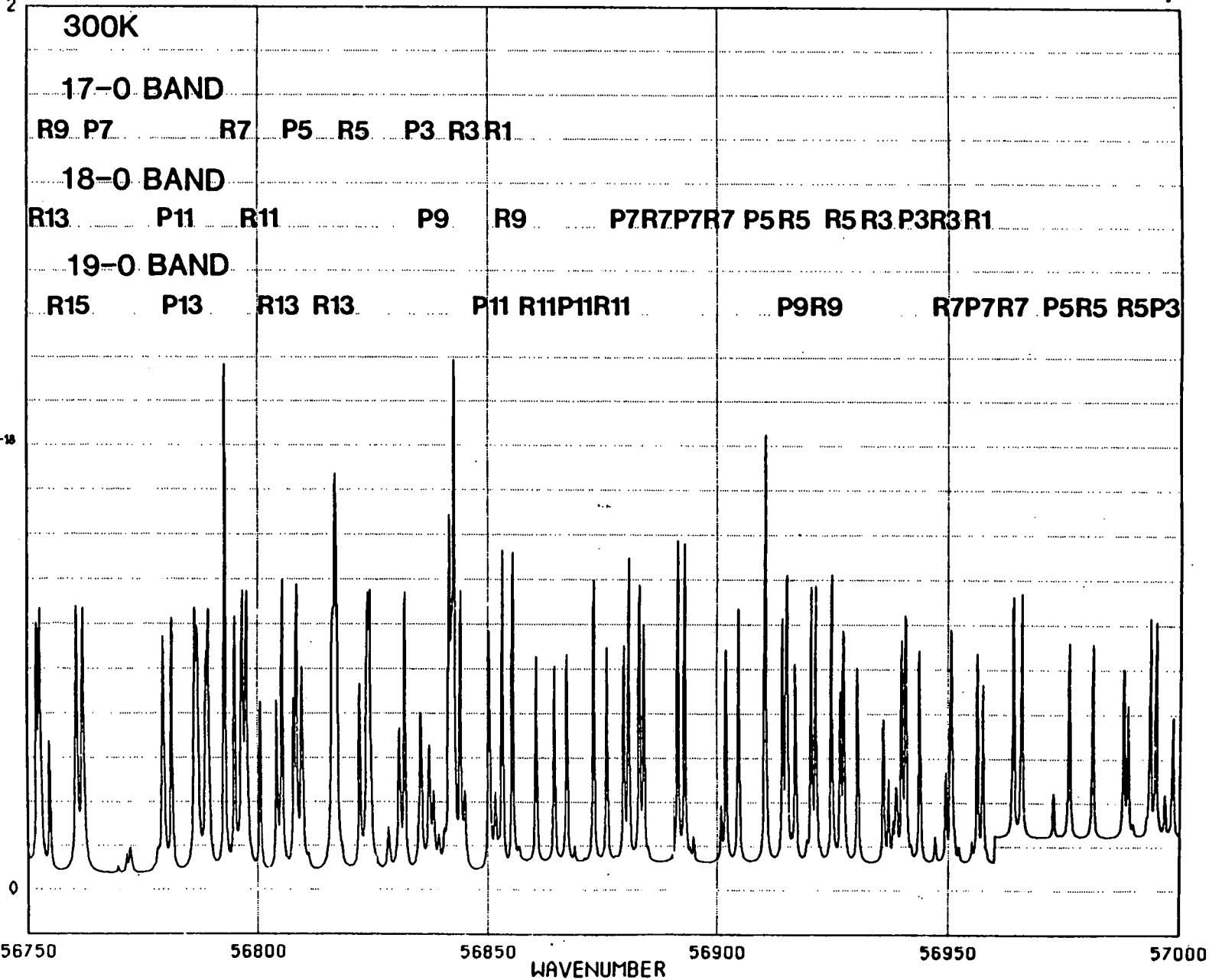
56900

56950

57000

WAVENUMBER

70



CROSS-SECTION

-17

17-0 BAND FROM R9 TO R1

18-0 BAND FROM R13 TO R1

19-0 BAND FROM R15 TO P3

-18

LOG SIGMA(O2)

-19

-20

56750

300 K

56800

56850

WAVENUMBER

56900

56950

57000

71

