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COMPILED OF STRATOSPHERIC TRACE GAS
SPECTRAL PARAMETERS

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COMPILATION OF STRATOSPHERIC TRACE GAS SPECTRAL PARAMETERS

INTRODUCTION

About three years ago, AFCRL provided a set of data, for the infrared region of the spectrum, for most of the naturally occurring molecules of significance in the terrestrial atmosphere. The following set of molecules (and their identification code) which were included in this first data compilation was: (1) water vapor; (2) carbon dioxide; (3) ozone; (4) nitrous oxide; (5) carbon monoxide; (6) methane; (7) oxygen. The present data compilation extends the previous work, by computing the pure rotation spectrum for molecules (4) nitrous oxide and (5) carbon monoxide. It also provides data on some pollutant gases for their strongest lines in the infrared region. These gases (and their identification code) are: (8) nitric oxide; (9) sulfur dioxide; (10) nitrogen dioxide; (11) ammonia; (12) nitric acid; (13) the hydroxyl radical; (14) formaldehyde. Table 1 gives the typical concentration of these trace gases in the terrestrial atmosphere.

TABLE 1. TYPICAL CONCENTRATION OF STRATOSPHERIC TRACE GASES IN DRY AIR

Identification Number	Constituent	ppb by Volume	Reference
(4)	N ₂ O	280	Birkland and Shaw, 1959
(5)	CO	75	Shaw, 1968
(8)	NO	0.5	
(9)	SO ₂	1	
(10)	NO ₂	1	
(11)	NH ₃	4	
(12)	HNO ₃	3	
(13)	OH		
(14)	H ₂ CO		

DESCRIPTION OF THE COMPILATION

The present compilation follows the same description as that given for Part 1 (AFCRL-TR-73-0096). The four essential parameters for each line are the line frequency, ν_0 (cm^{-1}), the intensity per absorbing molecule, S ($\text{cm}^{-1}/\text{molecule cm}^{-2}$), the Lorentz line width parameter, α_0 ($\text{cm}^{-1}/\text{atm}$), and the energy of the lower vibration-rotational state, E'' (cm^{-1}). All of these quantities are given for a standard temperature, T_s , of 296°K . The Lorentz line-width is usually assumed to vary in the way predicted by kinetic theory:

$$\alpha_L = \alpha_s (p/p_s) (T_s/T)^{1/2}$$

At very low pressures the lines assume a Doppler line-shape. This occurs when the parameter $a = (\alpha_L/\alpha_D) < 1.0$. Here α_D is the width of a Doppler line at $1/e$ (where e is the base of Naperian logarithms) of the maximum absorption of the line. It is given by

$$\alpha_D = 4.298 \times 10^{-7} \nu_0 (T/M)^{1/2}$$

where M is the molecular weight of the absorbing gas. There is an intermediate regime when the line-shape is given by the Voigt line profile, which is simply the convolution of a Lorentz line profile and a Doppler line profile.

The line intensity, S , is independent of pressure but depends upon the temperature in the following way:

$$S(T) = S(T_s) \{Q_v(T_s) Q_r(T_s) / Q_r(T) Q_v(T)\} \exp [1.439 E'' (T - T_s)/T T_s]$$

where Q_v and Q_r are the vibrational and rotational partition functions for the molecule. The temperature dependence of the rotational partition function is given by $(T/T_s)^J$ where J is given in Table 2. The vibrational partition function is tabulated for some representative temperatures in Table 2.

In the past the line intensity has been defined in various units. We note that

$$1 (\text{cm atm})_{\text{stp}} = 2.69 \times 10^{19} \text{ molecules/cm}^2$$

and

$$1 (\text{cm atm})_{\text{room temperature (300}^{\circ}\text{K)}} = 2.45 \times 10^{19} \text{ molecules/cm}^2$$

TABLE 2. VIBRATIONAL PARTITION FUNCTION

Molecule J	Temperature (°K)						
	175	200	225	250	275	296	325
NO	1.0	1.000	1.000	1.000	1.000	1.000	1.000
NO ₂	1.5	1.005	1.010	1.016	1.025	1.036	1.047
SO ₂	1.5	1.014	1.025	1.038	1.055	1.074	1.093
NH ₃	1.5	1.001	1.002	1.005	1.009	1.014	1.021
HNO ₃	1.5	1.037	1.067	1.107	1.158	1.221	1.283
OH	1.0	1.000	1.000	1.000	1.000	1.000	1.000
H ₂ CO	1.5	1.000	1.000	1.001	1.002	1.004	1.007

The same shorthand notation used in Part 1 has been adopted here to identify isotopic species. For example, ¹⁶O³²S¹⁶O = 626, etc. We have also used the same standard computer format for the data cards as was used in Part 1:

<u>v</u> ₀	<u>S</u>	<u>α</u> ₀	<u>E"</u>	<u>Rotation and Vibration ID</u>	<u>Date</u>	<u>Isotope</u>	<u>Molecule</u>
1-10	11-20	21-25	26-35	36-70	71-73	74-77	78-80
F10.3	E10.3	F5.3	F10.3	5A6, A5	I3	I4	I3

The numbers below each quantity refer to the columns on an IBM card, and the letter-number combinations represent the computer format. The first four quantities are v = frequency in wavenumbers (cm^{-1}), S = line intensity in $\text{cm}^{-1}/\text{molecules}\cdot\text{cm}^{-2}$ at 296 °K, α = halfwidth for Lorentz line shape, in cm^{-1} at a pressure of 1 atm and a temperature of 296 °K, and E'' = energy of the lower state expressed in wavenumbers (cm^{-1}). As in Part 1, the rotation and vibration identifications are difficult to put in a standard format, due to differences in the number of quantum numbers required to specify lines in a particular band. (For example HNO₃ has nine fundamental modes of vibration, while NO has one, but it is split into two bands - one for the ² $\Pi_{1/2}$ state and one for the ² $\Pi_{3/2}$ state.) We have followed the formats used in Part 1, whenever it was possible. The remaining three fields specified above include the date the data were computed to be put on the tape, the isotopic code described above, and the identification number for the molecule given in Table 1.

GENERAL REMARKS ON THE DERIVATION OF PARAMETERS

The four tabulated parameters, v_0 , E'' , S , and α_0 must, of course, be derived from experimental observations. These observations are generally reproduced by a set of spectroscopic parameters and the quantum numbers for the line. In some cases the published data are poorly represented by the spectroscopic constants derived by the authors of these publications. Because this data compilation is intended for users interested in detecting pollutant molecules, perhaps by use of a laser, we have attempted to give line positions (v_0) accurate to the Doppler (smallest) half-width of each line. The lower state energy levels have a similar accuracy. The line intensities should be accurate to ten percent and the line half-widths are of comparable accuracy. These details are discussed more fully in the following sections, where each of the molecules is described.

The parts of section 4 are numbered according to the identification number for each molecule and the missing parts have been described fully in Part 1 and this material will not be repeated here.

MOLECULAR SPECIES

Nitrous Oxide, Calculations by L.G. Young

The abundances of the isotopes used in computing the microwave (pure rotation) spectrum were taken from Part 1. The vibrational energy levels and the rotational constants associated with these levels were also taken from Part 1. Toth's measurements of nitrogen broadened half-widths were adopted, as in Part 1. A dipole moment of 0.166 Debye was adopted based on the microwave measurements of D.D. Coles, E.S. Elyash and J.G. Gorman (Phys. Rev. 72, 1265L), R.G. Shulman, B.P. Dailey and C.H. Townes (Phys. Rev. 75, 472A) and S.S. Tetenbaum (Phys. Rev. 88, 772, 1952). The computed line intensities are accurate to three significant figures; the half-widths are accurate to two significant figures.

Carbon Monoxide, Calculations by L.G. Young

The data in Part 1 were again used to compute the pure rotation spectrum of CO, and the dipole moment $\mu_e = 1.22$ Debye (J.S. Muenter "Electric Dipole Moment of Carbon Monoxide", J. Mol. Spectry. 55, 590-491, 1975) was used. As a check on our intensity calculations, they were compared with the calculations of S.A. Golden (J. Quant. Spectry. Radiat. Transfer, 2, 201-214, 1962), the agreement between the two sets of calculations was found to be quite good. The line frequencies were compared with those given by Krupenie for the pure rotational lines of $^{12}\text{C}^{16}\text{O}$ and its isotopes, and the agreement was again good. The same half-widths of the lines used for the fundamental band in Part 1, were used for the pure rotation spectrum. The computed line intensities are accurate to three significant figures; the half-widths are accurate to two significant figures.

Nitric Oxide, Calculations by L.G. Young

Line Positions - Published spectroscopic data give a poor fit to measured line positions, so new constants had to be derived for this band. The effective rotational constants were obtained by fitting Keck's measurements of line positions in the P and R branches of the fundamental by a 6-th order polynomial in m :

$$\omega_i(m) = \omega_{0i} + a_i m + b_i m^2 + c_i m^3 + d_i m^4 + e_i m^5 + f_i m^6,$$

where the index $m = -J''$ for the P branch and $m = J'' + 1$ for the R branch. The coefficients in the polynomial are given by James and Thibault (eq.12) in terms of the effective rotational constants. Table 3 gives a comparison of the present rotational constants and previously published values.

The line positions and lower state energies of the fundamental band for the $^{14}\text{N}^{16}\text{O}$ isotope were calculated from the expression (eq.2 of James and Thibault)

$$\begin{aligned} \Sigma_{vi}(J) = & -3/4 B_v - 25/16 D_v (-)^i 1/2 \delta_v + B_{vi} J(J+1) - D_{vi} J^2(J+1)^2 \\ & + H_{vi} J^3(J+1)^3 \end{aligned}$$

where the subscript v refers to the vibrational state and the subscript $i = 1$ refers to the $^2\Pi_{1/2}$ state; $i = 2$ refers to the $^2\Pi_{3/2}$ state. The

TABLE 3. EFFECTIVE ROTATIONAL CONSTANTS FOR $^{14}\text{N}^{16}\text{O}$

present results	Keck	James and Thibault	Hall and Dowling	Palik and Rao	Meyer et al.	Olman et al.	Shaw
B_{01}	$1.672252 \pm .000030$	$1.672171 \pm .000074$	$1.67232 \pm .00029$	$1.671864 \pm .000081$	$1.671854 \pm .00004$	$1.67198 \pm .00004$	$1.67233 \pm .00019$
D_{01}	$x10^6 \quad 1.316 \pm .040$	$1.16 \pm .11$	$1.51 \pm .95$	$1.13 \pm .30$	$0.34 \pm .30$	1.8 ± 1.0	$1.2 \pm .3$
H_{01}	$x10^{10} \quad -6.54 \pm 0.16$	-7.26 ± 0.51	-3.98 ± 12.0	\dots	-14.2 ± 2.9	\dots	\dots
B_{02}	$1.719990 \pm .000025$	$1.720020 \pm .000086$	$1.72025 \pm .00025$	$1.7202435 \pm .000062$	$1.720138 \pm .000062$	$1.7198 \pm .00012$	$1.7200 \pm .00018$
$D_{02} \times 10^6$	$9.721 \pm .035$	$9.78 \pm .12$	$10.33 \pm .73$	$10.64 \pm .23$	$10.24 \pm .23$	10.0 ± 2.0	$9.7 \pm .3$
$H_{02} \times 10^{10}$	$7.02 \pm .15$	$7.26 \pm .51$	11.1 ± 6.9	\dots	24.2 ± 2.1	\dots	\dots
B_{11}	$1.655140 \pm .000030$	$1.655021 \pm .000084$	$1.65524 \pm .00029$	\dots	\dots	\dots	\dots
$D_{11} \times 10^6$	$1.496 \pm .040$	$1.27 \pm .13$	$1.71 \pm .95$	\dots	\dots	\dots	\dots
$H_{11} \times 10^{10}$	-6.12 ± 0.16	$-7.07 \pm .58$	-3.71 ± 12.0	\dots	\dots	\dots	\dots
B_{12}	$1.701946 \pm .000025$	$1.702053 \pm .000091$	$1.70223 \pm .00025$	\dots	\dots	\dots	\dots
$D_{12} \times 10^6$	9.556 ± 0.035	$9.71 \pm .13$	$10.15 \pm .73$	\dots	\dots	\dots	\dots
$H_{12} \times 10^{10}$	6.48 ± 0.15	$7.07 \pm .58$	10.1 ± 6.9	\dots	\dots	\dots	\dots

Table 3. (cont.)

	present results	Keck	James and Thibault Microwave	Hall and Dowling	Palik and Rao	Moyer <u>et al.</u>	Olman <u>et al.</u>	Shaw
"01	1876.0909 ± 0.0007	1876.082 .0073	1876.082 ...	1876.082 ...	1876.082 ...	1876.082 ...	1876.082 ...	1876.082 ...
"02	1875.8825 ± 0.0006	1875.874 .0062	1875.874 ...	1875.874 ...	1875.874 ...	1875.874 ...	1875.874 ...	1875.874 ...

molecular constants, B_v and D_v , are obtained from the effective rotational constants, B_{vi} and D_{vi} , by (eqs. 3 and 4 of Olman et al.)

$$D_v = 1/2 (D_{v1} + D_{v2}) \text{ and}$$

$$B_v = 1/2 (B_{v1} + B_{v2} - D_v)$$

The constant δ_v is related to the multiplet splitting parameter, A_v ; James and Thibault (eq.4) give that relation. The value of Brown et al., $A_0 = 123.158 \text{ cm}^{-1}$, was used for the ground state. Lambda doubling causes the rotational energy levels to be split such that

$$E_{\text{rot}} = E_{vi}(J) \pm E_{vi}^A(J)$$

where

$$E_{v1}^A(J) = - p(J + 1/2) + r_v(J - 1/2)(J + 1/2)(J + 3/2)$$

and

$$E_{v2}^A(J) = - r_v(J - 1/2)(J + 1/2)(J + 3/2)$$

Here

$$r_v = \frac{1}{\lambda_v - 2} [2q + \frac{p}{\lambda_v - 2}]$$

where p and q are the Λ -doubling constants (Favero et al. give $p = 5.875 \times 10^{-3}$ and $2q = 7.68 \times 10^{-5} \text{ cm}^{-1}$) and $\lambda_v = A_v/B_v$.

The line positions, including Λ -doubling, were computed from

$$\omega_i^P = \omega_i + \Delta^P + \delta_{i1}p$$

$$\omega_i^Q = \omega_i - \Delta^Q + \delta_{i1}2p(J + 1/2)$$

$$\omega_i^R = \omega_i + \Delta^R - \delta_{i1}p$$

where $\delta_{i1} = 0$ for $i \neq 1$ and $\delta_{i1} = 1$ for $i = 1$. The splitting common to both sub-bands is given by

$$\Delta^P = (J - 1/2)(J + 1/2) [3/2(r_0 + r_1) + J(r_0 - r_1)],$$

$$\Delta^Q = (J - 1/2)(J + 1/2)(J + 3/2)(r_0 + r_1),$$

$$\text{and } \Delta^R = (J + 1/2)(J + 3/2) [5/2 r_0 + 1/2 r_1 + J(r_0 - r_1)].$$

These calculated line positions differ slightly from those completed by Goldman et al., who fit Kecks data with a lower order polynomial in m .

Line Intensities - A value of $128 \text{ cm}^{-1}/\text{cm-atm}_{\text{stp}}$ has been adopted for the band intensity of the most abundant (99.3%) isotope. Table 4 lists all the published measurements of the total band intensity. The early measurements which have subsequently been re-evaluated by the same author, and other values known to be inaccurate are indicated in parentheses; an inaccurately drawn value of the continuum was generally the source of error. The average of the 11 most recent measurements of the band intensity is $126 \text{ cm}^{-1}/\text{cm atm}$, when the values in parentheses are disregarded. When the measurements are weighted inversely with the square of the experimental error, then a value of $131 \text{ cm}^{-1}/\text{cm atm}$ is obtained. The band intensity reported by Varanasi and Penner lies between these two average values and is probably accurate to ten percent; that is our estimate of the error in the value adopted for these calculations.

In computing the line strengths, a pure Hund's case (α) was assumed. For this case, the line strengths are given by

$$A^P(J) = \frac{J^2 - \Omega^2}{J}, \quad A^Q(J) = \frac{(2J+1)\Omega^2}{J(J+1)}, \quad A^R(J) = \frac{(J+1)^2 - \Omega^2}{J+1};$$

a comparison of line intensities computed in this approximation with the line intensities calculated by James for intermediate coupling gave good agreement (within 3 percent) for all three branches at low values of J . The discrepancies diminished with increasing J for the P and R branches, but increased in the Q branch (up to 10 percent by $J = 41/2$); for this data compilation the inaccuracies in the Q branch is not serious since the line intensities rapidly diminish with increasing J (at $J = 41/2$ a line in the Q branch is at least 2 orders of magnitude weaker than corresponding lines in the P or R branches) and lines in the Q branch are unlikely to be used to detect NO as a pollutant gas.

TABLE 4. BAND INTENSITY MEASUREMENTS FOR THE FUNDAMENTAL OF NO

Intensity $\text{cm}^{-1}/\text{cm atm}_{\text{stp}}$	Reference
121 \pm 6	Chandriah and Cho (1973)
135 \pm 5	King and Crawford (1972)
134 \pm 2	Michels (1971)
124 \pm 22	Feinberg and Carmac (1967)
125 \pm 8	Oppenheim, Aviv and Goldman (1967)
128 \pm 10	Varanasi and Penner (1967)
122 \pm 6	Abels and Shaw (1966)
132 \pm 13	Alamichel (1966)
(103)	Jouve (1966)
115 \pm 9	Ford and Shaw (1965)
(70)	Fukada (1965)
(76 \pm 7)	Breeze and Morriso (1964)
138 \pm 6	James (1964)
111 \pm 7	Schurin and Clough (1963)
(82)	Vincent-Geisse (1954)
(70 \pm 7)	Penner and Weber (1953)
(145 \pm 29)	Insmore and Crawford (1949)
121	Havens (1938)

As an intermediate step in computing rotational line intensities, the rotational partition function was obtained by direct summation over states. At 296°K, $Q_1^{\text{rot}} = 123.167062$ and $Q_2^{\text{rot}} = 121.668583$; these values are slightly (less than 2 percent) larger than the rigid-rotor partition functions.

Line Half-widths - Abels and Shaw have measured self-broadened half-widths of the lines in both the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ sub-bands and found "no significant difference either between the half-widths of lines with the same $|m|$ value in the R and P branches of the same sub-band or between corresponding lines of the two sub-bands." Their results agree within experimental error with the measurements of James, who also measured self-broadened linewidths. Ford reported that the self-broadening coefficient of NO, relative to N_2 , was 1.00 ± 0.05 and this result was confirmed by Nachson and Coleman. (The fact that self-broadening is no more effective than foreign gas broadening was also demonstrated by Oppenheim, Aviv and Goldman, who used helium as the broadening gas). As a result of these measurements, we have assumed that air-broadened half-widths of NO will be identical to the half-widths measured by Abels and Shaw. It should be noted that Abels and DeBall have found that the line shape becomes super-Lorentzian for wavelengths greater than 1 cm^{-1} from the line center.

Our tabulated half-widths were obtained from the linear fit to their data given by Abels and Shaw. Table 5 gives a comparison of half-widths measured for the fundamental with half-widths measured in the pure rotation spectrum and in overtone bands. The estimated error in the measurements for the fundamental band is 5 percent; the maximum spread in Abels and Shaw's data is 10 percent.

TABLE 5. COMPARISON OF HALF-WIDTHS MEASURED IN VARIOUS BANDS OF NO

Rotational Line		Half-width	Reference	Rotational Line		Half-width	Reference
1 - 0	3/2	0.061	James	0 - 0	3/2	0.071	French and Arnold
1 - 0	3/2	0.063	Abels and Shaw	3 - 0	3/2	0.090	Meyer et al.
1 - 0	15/2	0.055	James	3 - 0	15/2	0.077	Meyer et al.
1 - 0	17/2	0.059	Abels and Shaw	2 - 0	17/2	0.081	Nachshon and Coleman
1 - 0	19/2	0.059	Abels and Shaw	2 - 0	19/2	0.070	Meyer et al.
1 - 0	29/2	0.052	James	2 - 0	29/2	0.059	Meyer et al.
1 - 0	37/2	0.050	Abels and Shaw	3 - 0	37/2	0.047	Meyer et al.

Nitrogen Dioxide, computed by D. Snider

Goldman *et al.* (1975) have computed the rigid rotor line intensities for the v_3 fundamental of $^{14}\text{N}^{16}\text{O}_2$. Their data compilation uses the spectroscopic constants derived by Hurlock, Lafferty and Rao (1974; see Table 6a) to fit their measurements of line positions for the v_3 fundamental. This is the strongest band of nitrogen dioxide; while it falls in the same spectral region (6.2 micron) as water vapor, it should be readily detectable at high resolution, particularly in the stratosphere. Goldman *et al.* have also computed data for the combination band $v_1 + v_3$ which is located at 3.4 microns, an atmospheric window region. For this weaker band, Goldman *et al.* used the spectroscopic constants derived by Olman and Hause (1968; see Table 6b). For both bands they used the integrated band intensity measured by Guttman: $S(v_3) = 2250 \text{ cm}^{-1}/\text{cm atm}_{\text{stp}}$ and $S(v_1 + v_3) = 69 \text{ cm}^{-1}/\text{cm atm}_{\text{stp}}$. Goldman *et al.* had measured the intensity of v_3 and found a somewhat lower value: $1640 \text{ cm}^{-1}/\text{cm atm}_{\text{stp}}$. The estimated accuracy of Guttman's value is ten percent, while the estimated accuracy of Goldman's value was twenty percent. Snider has recently revised the data for the v_3 band; he is currently revising the $v_1 + v_3$ band and is also doing v_2 .

Tejwani computed half-widths for NO_2 broadened by nitrogen, $\gamma_{\text{NO}_2 - \text{N}_2}$ of $0.045 \text{ cm}^{-1}/\text{atm}$ and for NO_2 broadened by oxygen, $\gamma_{\text{NO}_2 - \text{O}_2}$ of $0.033 \text{ cm}^{-1}/\text{atm}$. He suggested that these values should be multiplied by factors

of 1.4 and 1.2, respectively, to approximate the contribution of higher order terms which he neglected in his calculations. When this is done, we obtain a half-width for NO₂ broadened by air, $\gamma_{\text{NO}_2 - \text{air}}$ of 0.058 cm⁻¹/atm. On the other hand, Goldman *et al.* assumed a half-width of 0.10 for their computed synthetic spectrum of the ν_3 band. This suggests that the real value of the half-width is larger than the value obtained from Varanasi, so we have assumed a constant value for the half-width of 0.08 cm⁻¹/atm for this data compilation.

TABLE 6a. GROUND STATE AND UPPER STATE CONSTANTS (IN UNITS OF cm⁻¹)
FOR THE ν_3 BAND OF $^{14}\text{N}^{16}\text{O}_2$ CENTERED AT 1616.846 ± 0.0024 cm⁻¹

Constant	Vibrational State	
	000	001
A	8.002366 ± 0.000016	7.777200 ± 0.000742
B	0.4337050 ± 0.0000046	0.4309593 ± 0.0000123
C	0.4104482 ± 0.0000046	0.4078448 ± 0.0000115
Δ_N	$(3.238 \pm 0.066) \times 10^{-7}$	$(3.263 \pm 0.030) \times 10^{-7}$
Δ_{NK}	$(-1.943 \pm 0.016) \times 10^{-5}$	$(-2.254 \pm 0.010) \times 10^{-5}$
Δ_K	$(2.684 \pm 0.011) \times 10^{-3}$	$(2.744 \pm 0.062) \times 10^{-3}$
δ_N	$(2.950 \pm 0.088) \times 10^{-8}$	$(3.556 \pm 0.268) \times 10^{-8}$
δ_K	$(1.832 \pm 2.4) \times 10^{-6}$	$(-5.252 \pm 2.610) \times 10^{-6}$
H_K	$(2.04 \pm 0.532) \times 10^{-6}$	$(5.46 \pm 1.21) \times 10^{-6}$

TABLE 6b. CONSTANTS FOR THE $\nu_1 + \nu_3$ BAND OF $^{14}\text{N}^{16}\text{O}_2$ (IN UNITS OF cm^{-1})
WHICH IS CENTERED AT $2906.073_7 \pm \text{cm}^{-1}$

A	$7.8540_4 \pm 0.0010$
B	$0.428597_5 \pm 0.000017$
C	$0.405007_0 \pm 0.000015$
τ_{aaaa}	$(-1.155_8 \pm 0.016) \times 10^{-2}$
τ_{bbbb}	$(-1.430_9 \pm 0.030) \times 10^{-6}$
τ_{aabbb}	$(7.46_9 \pm 0.17) \times 10^{-5}$
τ_{abab}	-8.214×10^{-3}
H_{KN}	$(-1.12_9 \pm 0.19) \times 10^{-7}$
H_K	$(2.89_3 \pm 0.04) \times 10^{-5}$

Sulfur Dioxide, Computed by D. Snider and S.A. Clough

The ν_3 band, the strongest band of SO_2 , is located near 7.3 microns and is overlapped strongly by the water vapor band at 6.3 microns. This fundamental band can only be used as a pollutant detector in the stratosphere. The ν_1 band, which is only about ten percent as strong as the ν_3 band, is much more suitably located, at 8.7 microns, for ground based measurements. It has also been suggested (Corrice *et al.*) that the combination band $\nu_1 + \nu_3$, located at 4 microns, might be suitable for detecting sulfur dioxide in the telluric atmosphere. However the combination band is nearly an order of magnitude weaker than the ν_1 fundamental and its strength, as measured in the laboratory, is not well known (see Table 7). As a result, we have not included it in this data compilation. We have used Clough's calculations for the ν_1 band and a band intensity of $104 \text{ cm}^{-1}/\text{cm atm stp}$. For the ν_3 band we have used Snider's calculations of line positions and intensities but have adjusted the band origin by 0.029 cm^{-1} to agree with the recent measurements of Dana and Fontinella of this band. Mayhood's band intensity was used for ν_3 .

TABLE 7. MEASURED BAND INTENSITIES FOR SULFUR DIOXIDE

Band Identification	Band Origin	Band Intensity $\text{cm}^{-1}/\text{cm atm}_{\text{scp}}$	Band Intensity $\times 10^{20} \text{ cm}^{-1}/\text{molecule cm}^{-2}$	Reference
v_1	1151.71 <u>+0.01</u>			Hinkley <u>et al.</u>
		93 \pm 9	345 \pm 35	Eggers and Schmid
		106 \pm 3	393 \pm 10	Mayhood
		117 \pm 6	434 \pm 25	Morcillo and Herranz
		96 \pm 5	357 \pm 20	Hinkley <u>et al.</u>
		100 \pm 5	371 \pm 20	Burch <u>et al.</u>
		107 \pm 6	397 \pm 24	Tejwani <u>et al.</u>
average		103		
σ_{int}		3		
σ_{ext}		4		
weighted average		104		
v_2	517.75 <u>+0.10</u>			Fox <u>et al.</u>
		116 \pm 9	432 \pm 43	Eggers and Schmid
		125 \pm 7	466 \pm 25	Mayhood
		120 \pm 10	466 \pm 37	Morcillo and Herranz
		125 \pm 8	465 \pm 29	Tejwani <u>et al.</u>
average		122		
σ_{int}		5		
σ_{ext}		2		
weighted average		123		
v_3	1362.0295 <u>+0.0011</u>			Dana and Fontenella
		841 \pm 84	3120 \pm 300	Eggers and Schmid
		845 \pm 23	3170 \pm 90	Mayhood
		880 \pm 27	3270 \pm 100	Morcillo and Herranz
		815 \pm 54	3020 \pm 200	Burch <u>et al.</u>
average		848		
σ_{int}		31		
σ_{ext}		14		
weighted average		864		

Table 7. (Continued)

Band Identification	Band Origin	Band Intensity $\text{cm}^{-1}/\text{cm atm}_{\text{stp}}$	$\times 10^{20} \text{cm}^{-1}/\text{molecule cm}^{-2}$	Reference
$\nu_1 + \nu_3$	2499.872 <u>+0.003</u>			Barbe <u>et al.</u>
		4.3 \pm 0.3	16 \pm 1	Secrun and Jouve
		10 \pm 2	37 \pm 7	Chan and Tien
		17.3 \pm 3.5	64 \pm 13	Burch <u>et al.</u>
		36.3 \pm 0.3	104 \pm 10	Tejwani <u>et al.</u>
average		17		
σ_{int}		1.2		
σ_{ext}		7		
weighted average		20		

Table 8 gives the Lorentz half-widths for SO_2 which were computed by Tejwani and measured by other investigators. There is quite a spread in the average values for the half-width, and we have arbitrarily chosen a value of $\gamma(296^{\circ}\text{K})_{\text{SO}_2 - \text{air}} = 0.135 \text{ cm}^{-1}$.

TABLE 8. LORENTZ LINE HALF-WIDTHS FOR SULFUR DIOXIDE (cm^{-1})

$\gamma_{\text{SO}_2-\text{SO}_2}$ at 300°K	$\gamma_{\text{SO}_2-\text{air}}$ at 300°K	$\gamma_{\text{SO}_2-\text{air}}$ at 250°K	Reference
0.27 - 0.58		0.079 - 0.129	Tejwani
0.13 - 0.45		0.083 - 0.125	Tejwani
0.304 - 0.431			Yang et al.
	0.15		Gebbie et al.
	0.076 - 0.129		Krishnaji et al.
0.500 ± 0.075	0.152 ± 0.015		Hinkley et al

Ammonia, Computed By L.G. Young

The strongest band of NH_3 is the ν_2 fundamental, located near 10.5 microns. The experimental results of Garing et al. and Mould et al. are poorly fit by the spectroscopic constants they obtained. The errors which result from using their constants to fit the line frequencies they measured are greater than 1 cm^{-1} for large values of the quantum numbers J and K (eg. $J = K = 12$). Taylor's (1973) calculations have this same fault: see Table 9. We have done a least squares fit to both sets of measurements and have obtained new constants for this band, which give better agreement with the observed line positions. We have used the band intensity measured by France and Williams, in computing the line intensity. Table 10 gives the published data for NH_3 . We have assumed a value of 0.09 cm^{-1} for the half-width.

TABLE 9. COMPARISON OF OBSERVED LINE POSITIONS FOR THE ν_2 BAND OF AMMONIA
AND THOSE PREDICTED USING THE ROTATIONAL CONSTANTS OF RAO et al.

Line	Measured Line Position		Computed Taylor (1973)	Observed Minus Computed (cm^{-1})
	Mould et al. (1959)	Garing et al. (1959)		
a(14,11)	-	648.20	648.328	-.128
a(14,10)	-	654.31	654.502	-.192
s(13,12)	-	655.46	655.525	-.065
s(15,14)	-	656.57	658.079	-1.491
s(14,12)	-	680.86	680.925	-.065
s(14,11)	-	682.24	682.389	-.149
a(8,8)	1104.33	1104.33	1104.24	+.09
a(10,10)	1139.46	1139.45	1139.28	+.175
a(12,12)	1173.44	1173.46	1173.01	+.44
a(15,15)	1221.68	-	1220.94	+.74
a(15,10)	1245.81	-	1245.61	+.20
s(14,K)	1247.48	1247.50	1247.79	-.30
s(15,K)	1264.53	1264.51	1264.99	-.47
s(16,K)	1281.37	-	1281.98	-.61

TABLE 10. INTENSITY AND HALF-WIDTH MEASUREMENTS FOR AMMONIA

Band Center	Band Identification	Band Intensity ($\text{cm}^{-1}/\text{cm atm}_{\text{stp}}$)	Reference
950 cm^{-1}	v_2	790 ± 3	France and Williams
		553 ± 110	McKean and Schatz
1628 cm^{-1}	v_4	150 ± 5	France and Williams
		67 ± 13	McKean and Schatz
3300 cm^{-1}	$v_1, v_3, \text{ and } 2v_4$	47 ± 3	France and Williams
3336 cm^{-1}	v_1	20 ± 4	McKean and Schatz
3414 cm^{-1}	v_3	13 ± 3	McKean and Schatz

Half-width cm^{-1}	$\gamma_{\text{NH}_3 - \text{O}_2}$	$\gamma_{\text{NH}_3 - \text{N}_2}$	$\gamma_{\text{NH}_3 - \text{air}}$	Reference
0.0524	0.0925	0.0845	Legan et al.	
0.0583	0.0963	0.0887	Smith and Howard	
0.0470	0.0966	0.0867	Howard and Smith	
0.0741	0.130	0.118	Bleany and Penrose	
0.0510	--	--	Potter et al.	

Nitric Acid Vapor

Snider and Goldman have made preliminary calculations for HNO_3 , but they do not feel that these are sufficiently accurate for our data tabulation.

Hydroxyl Radical

Benedict and Hall are making calculations for the strengths, energy levels and line positions based on Hall's solar spectrum. These calculations are not yet available, but they should be ready in a comparatively short span of time. They are using the Einstein A coefficients computed by Mies to calculate their line intensities.

Formaldehyde

The most extensive measurements of this vapor were made by Blau (1955). The two strong bands best suited for detecting H₂CO are ν_4 at 2843 cm⁻¹ and ν_2 at 1746 cm⁻¹. Unfortunately, I have been unable to find any measurements of band strengths for these fundamentals; as a result it is impossible to calculate absolute line intensities for this molecule in the infrared region of the spectrum.

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