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Strengths of absorption features in vibration-rotational band $v = 6 \leftarrow v = 0$ of ¹⁴N¹⁶O X ² Π_r in the near infrared region

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Abstract

The strengths or integrated absorption intensities of individual features in band $v = 6 \leftarrow v = 0$ of gaseous ${}^{14}N^{16}O$ X ${}^{2}\Pi_{r}$ are measured at (297.35 ± 0.4) K with spectral resolution 6 m⁻¹. For unresolved features near band heads in R branches, partition of total intensity enables estimates for each transition, apart from spin-rotation doubling and hyperfine effects. As a sum of these strengths of lines, the strength of the entire band centred near 1 083 606 m⁻¹, including sub-bands for both ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$, is $(5.63 \pm 0.28) \times 10^{-27}$ m. We compare measured strengths with those calculated from deduced values of transition moment for electric dipolar moment and Herman–Wallis coefficient. © 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

Nitrogen (II) oxide, NO, participates in important processes photophysical, chemical and even biochemical. In an atmospheric context NO is a significant product of fumes exhausted from engines involving combustion of hydrocarbon fuels with air as oxidant, and is also a primary product of photochemical decomposition of atmospheric nitrogen dioxide in relation to photochemical smog. Quantitative knowledge of radiative balance of our terrestrial atmosphere requires measurement of absorption of spectral lines of atmospheric consurement of a band that corresponds to the fifth overtone in the vibration-rotational spectrum of NO. Despite its small intrinsic intensity, befitting a fifth overtone, this band lies in the near infrared region, about wave number 1.08×10^6 m⁻¹ or wavelength 0.9 µm, at which there is great solar irradiance, such that activation of NO molecules with light in this near infrared region can produce energetic molecules that can transfer energy to other species, such as O₂ or O₃, to promote their chemical activity. For these reasons direct measurement of strengths of lines in this vibration-rotational band of NO is a worthy exercise in metrology.

stituents. There exists no previous report of mea-

2. Experiments

We recorded all spectra with an interferometric spectrometer (Bomem DA8, evacuated to

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 $\sim 4 \text{ Nm}^{-2}$) and a vessel to contain gaseous samples. The latter cylindrical cell (Infrared Analysis, model 100, of White type) has an optical path of length 1.375 m between mirrors that produce multiple internal reflections for an absorbing path of maximum length 107.25 m; spots in sequences on internal mirrors from the beam of a heliumneon laser enable a precise count of a number of passes of the beam through a gaseous sample, to define a total length from increments eight times the base path variable on adjusting the angle of a field mirror. Because the strength of this band is so small we employed the maximum practicable path for all measurements, but we managed to measure strengths of lines with pressures/ 10^5 N m⁻² in a range [0.4, 1.075] according to a limit of the apparatus. With a capacitance manometer (MKS model 221A, precision 0.5% of reading), we measured the pressure of a gaseous sample before and after each collection of interferograms. With a digital thermometer (Omega, two thermocouples of type K) that provides an indication of maximum and minimum temperatures (in °C) over a duration of spectral measurements, we monitored the temperature of the vessel; for all spectra subjected to analysis of line strengths, the mean temperature was 297.35 K, and a maximum acceptable variation of temperature was ± 0.4 K.

For all spectral measurements we employed a beam splitter made of fused silica, a tungsten filament as source and an avalanche Si photodiode at ambient temperature as detector. To limit the region of radiation reaching the detector we employed optical filters (CVI Corporation), with a pass band/ 10^6 m^{-1} [1.02, 1.14] at half maximum transmission. To attain a ratio of signal to noise sufficiently large, ~ 20 at best, for the weak lines being measured, we accepted a spectral resolution 6 m⁻¹, which was worse than the ultimate resolution 0.8 m⁻¹ of the interferometer in this region but still significantly greater than minimum widths of measured apparent lines in our spectra of NO, about 9 m^{-1} at the smallest pressure. About 600 interferograms accumulated over 13.5 h were co-added; a resulting interferogram was converted through Fourier transform into a spectrum with apparent energy as a function of wave number. A ratio of that spectrum with a reference spectrum yielded an absorbance spectrum, such as that appearing in Fig. 1. To process these data, and for further analysis of spectra, we employed software (Grams, Galactic Industries) designed to operate with the interferometric spectrometer, a commercial spreadsheet and a symbolic processor (Maple, Waterloo Maple Inc.) for regression procedures; we carried statistical information through the analysis.



Fig. 1. Vibration-rotational band 6–0 of gaseous ¹⁴N¹⁶O, at pressure 73 460 N m⁻², temperature (297.35 ± 0.4) K and length 107.25 m of optical path, in electronic ground state $X^2\Pi_r$; decadic absorbance plotted as a function of wave number recorded with spectral resolution 6 m⁻¹.

Passage of gaseous NO (AGA Specialty Gas, nominal chemical purity 99.0% in a cylinder as received) through a trap charged with silica gel and cooled to 195 K served to remove other oxides of nitrogen but not N_2 or O_2 . Because the gas cell had a large volume and large area of internal surface, its evacuation through a narrow valve presented a problem for removal of residual water vapour, notorious for its retention on polar or metallic surfaces. As the region of band 6-0 of NO, hence involving six vibrational quanta in the transition, corresponds to absorption by water molecules in transitions involving only three vibrational quanta, vestigial water vapour even at a much smaller pressure can absorb as intensely as NO. Although some lines due to water vapour remain visible in the figure near 1.075×10^6 m⁻¹, on heating the cell and protracted pumping we removed much water so that there was minimal interference with measurable features of NO.

3. Analysis of spectra

In its electronic ground state $X^2 \Pi_r$, NO has net electronic orbital angular momentum that couples with net spin angular momentum, reflecting electrons of odd number, to produce two substates ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ [1]. For NO this coupling of orbital and spin angular momenta is characterised according to a parameter $A_{\rm e} \sim 12325 \,{\rm m}^{-1}$; as implied by a symbol ${}^{2}\Pi_{r}$, substate ${}^{2}\Pi_{1/2}$ lies below substate ${}^{2}\Pi_{3/2}$. Because A_{e} has a value much smaller than harmonic vibrational parameter $Y_{1,0} \sim 190413$ m^{-1} , for small values of quantum number J for total angular momentum including a rotational contribution, NO tends towards Hund's limiting case a; for large values of J, spin uncoupling makes this limiting case tend towards case b. As A_e is less than mean thermal energy, corresponding to 20657 m^{-1} at the temperature of our measurements, both substates have comparable populations in states of the same value of J'' for the state v = 0. Apart from hyperfine effects resulting from finite nuclear spin on ¹⁴N, each rotational state in each electronic substate comprises two components, labeled e and f, corresponding to formal degeneracy implied by an electronic state of type Π , but an influence of molecular rotation eliminates this degeneracy. With rotational selection rules $\Delta J = -1$, 0 and +1, this condition yields 24 rotational branches associated with a given change of vibrational quantum number, $\Delta v > 0$. Of these branches, 12 correspond to a change also of total electronic angular momentum, implying transitions between two electronic substates; being much weaker than corresponding transitions within each separate substate, such transitions in two satellite bands are not detectable in our present experiments. Of 12 remaining branches, divided into two P, two Q and two R branches for a vibrational transition within each substate, the splitting/m⁻¹ originating from spin-rotational interaction in an expected range [0, 5], depending on substate, rotational branch and value of J'', is too small to be detected in our measurements because of both our spectral resolution and collisional broadening of spectral lines at pressures of sample that we employed. We likewise ignore hyperfine splitting of rotational transitions that has a maximum magnitude smaller than 5 m⁻¹. For this reason we observed features that appear to be single lines in, in total, two P, two O and two R branches, one of each branch within each substate. Because a line in either Q branch is much weaker than a line originating in the same lower state in P or R branches, only a few O lines are measurable, but for each P and R branch we measured about 20 lines.

Each R branch has a head beyond which rotational transitions reverse direction, tending toward smaller wave number with increasing value of J''. These heads occur at J'' = 14.5, such that transitions for both smaller and larger values of J'' occur with significant intensity. For this reason, not only is there overlap of lines between R branches for each separate substate but also there is severe overlap and blending of lines near each head. In our attempt to assign a strength or integrated absorption intensity to each individual feature, during fitting of areas of lines we identified all likely significant transitions and specified both their wave numbers and their widths within narrow ranges, allowing the fitting programme to yield best estimates of individual contributions to a total intensity of several blended lines. Wave numbers are calculated as differences between terms of known vibrational states [2], and limits of widths are set according to widths of isolated features elsewhere in the band. For all lines we allowed a combination of gaussian and lorentzian shapes in the fitting; this procedure reflects an effort to obtain optimal estimates of areas under conditions of a moderate-at best-ratio of signal to noise and multiple underlying transitions, as described above. According to an expected wave number and quantum number J'' of a particular feature, we recorded in a spreadsheet the stature, full width at half maximum stature and area, as derived from the fitting procedure at convergence, for gaseous samples at three pressures. For lines in P branches, to ensure optimal precision of measurement of characteristics of each line, each region of fitting was so narrow as to contain, typically, only two discernible features; for lines in Q and R branches the regions were adjusted to comparable widths for isolated features, but were necessarily larger to encompass several overlapping lines near heads of R branches. According to these data, if all transitions were isolated single lines, we might extract a shift of wave number with pressure, a width of wave number with pressure and a wave number of a line extrapolated to zero pressure; under conditions of only multiplets and many blended lines and only moderate ratio of signal to noise at best, such data essentially lack meaning, and only the area of each double transition, due to spin-rotational splitting, we consider further.

Within experimental error, integrated areas of the same lines measured for samples at three varied pressures within the total specified range are proportional to the pressure of a sample; because the integrated absorbance is thus within a linear regime, we attribute the absorption to properties of individual NO molecules with minimal interference from intermolecular interactions, although an increasing width of a feature with increasing pressure in the same range clearly indicates the existence of such interactions; we hence neglect effects of presence of (NO)2. At such small net absorbances, <0.01, prospective distortion of line shape due to effects of saturation of absorption is negligible. An effective strength or integrated absorption intensity S_1 of an apparent line is defined according to an equation [1],

$$S_{\rm l} = \int \ln_{\rm e} \left[I_0(\tilde{\nu}) / I(\tilde{\nu}) \right] {\rm d}\tilde{\nu} / LN$$

in which an integral corresponds to a measured area of a spectral line, L denotes a length of optical path through an absorbing sample and N denotes the number of molecules per unit volume; $I_0(\tilde{v})$ denotes a signal at wave number \tilde{v} in absence of a sample, obtained from a reference spectrum, and $I(\tilde{v})$ denotes a corresponding signal in presence of a sample. The integral is formally evaluated over the entire range of wave number, but in practice the line is fitted to gaussian and lorentzian forms in optimal combination, from which an area is calculated within a fitting procedure. For a gaseous sample at pressure P and temperature T, we calculated the number density of molecules N according to a formula for an ideal gas,

 $N = PN_A/RT$

in which N_A is Avogadro's constant and R is the gas constant, with no correction for non-ideal behaviour within the range of pressure employed in our experiments. As vibrational states with $v \ge 1$ lie at least 187608 m⁻¹ above the ground state v = 0, thermal population of those states affects only 10^{-4} of the entire sample. Through a factor 0.99394 we account for a presence of isotopic variants other than ¹⁴N¹⁶O in supposed natural abundance. All such corrections are much smaller than experimental error in measuring strengths of individual features, 10% at best, or of the total as band strength, 5%.

In Table 1 we present the strength of each measurable apparent line, characterised by both a value of quantum number J'' for total angular momentum of the lower state of the transition in absorption and a wave number calculated as the difference of published spectral terms [2]. From a sum of all these strengths of spectral features denoting transitions within both substates,

$$S_{\rm b} = \sum S_{\rm l}$$

we derive a band strength $S_{\rm b} = (5.63 \pm 0.28) \times 10^{-27}$ m, in which an indicated uncertainty, here and elsewhere, denotes a single standard error associated with a weighted mean from multiple measurements on samples at three pressures. This

Table 1

Values of quantum number J" for total angular momentum of the lower state of a transition, wave number $\tilde{\nu}/m^{-1}$ of each apparent line in P, Q and R branches, and line strength $S_1/10^{-28}$ m observed and calculated, for vibration-rotational band 6–0 of ¹⁴N¹⁶O in electronic ground state X² Π_r at (297.35±0.4) K

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	J	P(J)	$S_{\rm l,ob}$	$S_{l,cal}$	Q(J)	$S_{\rm l,ob}$	$S_{l,cal}$	R(J)	$S_{\rm l,ob}$	$S_{l,cal}$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sub-band 6–0 for substate ${}^{2}\Pi_{1/2}$									
1.5 1083104.18 0.47 0.38 1083574.79 0.12 0.08 1084559.13 0.79 0.71 2.5 1082738.80 0.68 0.66 1083523.14 0.04 0.05 108462.21 1.17 0.98 3.5 1082352.77 0.96 0.88 1084862.63 1.38 1.20 4.5 1081946.07 1.15 1.06 1085083.34 1.38 1.38 5.5 1081070.67 1.27 1.25 1085462.63 1.53 1.57 7.5 1080601.95 1.24 1.27 1.25 1085758.94 1.53 1.56 9.5 1079602.38 1.29 1.19 1085875.91 1.47 1.49 10.5 1079071.52 1.04 1.10 1085972.06 1.32 1.38 11.5 1078519.92 1.08 0.99 1086047.35 1.29 1.26 12.5 1077947.57 0.94 0.88 1086107.6 1.16 1.11 13.5 107640.56 0.79 0.64 1086139.34 0.51 0.69	0.5				1083605.77	0.22	0.20	1084076.38	0.44	0.40
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1.5	1083104.18	0.47	0.38	1083574.79	0.12	0.08	1084359.13	0.79	0.71
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.5	1082738.80	0.68	0.66	1083523.14	0.04	0.05	1084621.21	1.17	0.98
4.51081946.071.151.061085083.341.381.385.51081518.711.141.181085283.351.521.506.51081070.671.271.251085462.631.531.577.51080601.951.241.271085621.171.551.598.51080112.521.351.25108575.941.531.569.5107902.381.291.191085875.911.471.4910.51079071.521.041.101085972.061.321.3811.51078519.921.080.991086047.351.291.2612.51077947.570.940.881086101.761.161.1113.51076740.560.790.641086132.251.300.9714.51076405.400.540.431086139.340.510.6916.51075450.400.540.431086109.880.770.5617.51074076.980.220.261085987.750.330.3519.51073359.020.240.201083430.420.340.391084236.160.250.2620.5108270.370.280.251083376.110.240.241084504.060.500.453.51082172.120.470.411083300.070.150.171084750.150.680.604.51081752.250.410.531083202.330.150.121084974.45	3.5	1082352.77	0.96	0.88				1084862.63	1.38	1.20
5.5 1081518.71 1.14 1.18 1085283.35 1.52 1.50 6.5 1081070.67 1.27 1.25 1085462.63 1.53 1.57 7.5 1080601.95 1.24 1.27 1.05 108575.94 1.53 1.56 9.5 1079602.38 1.29 1.19 1085875.91 1.47 1.49 10.5 1079071.52 1.04 1.10 1085972.06 1.32 1.38 11.5 1078519.92 1.08 0.99 1086047.35 1.29 1.26 12.5 1077947.57 0.94 0.88 1086101.76 1.16 1.11 13.5 107640.56 0.79 0.64 1086135.25 1.30 0.97 14.5 107640.56 0.79 0.64 1086139.34 0.51 0.69 15.5 107640.56 0.79 0.64 1086139.34 0.51 0.69 16.5 1075450.40 0.54 0.43 1086109.88 0.77 0.56 17.5 1074076.98 0.22 0.26 1085987.75 0.33	4.5	1081946.07	1.15	1.06				1085083.34	1.38	1.38
6.5 1081070.67 1.27 1.25 1085462.63 1.53 1.57 7.5 1080601.95 1.24 1.27 1085621.17 1.55 1.59 8.5 1080112.52 1.35 1.25 108575.91 1.47 1.49 10.5 1079071.52 1.04 1.10 1085875.91 1.47 1.49 10.5 1079071.52 1.04 1.10 1085072.06 1.32 1.38 11.5 1078519.92 1.08 0.99 1086047.35 1.29 1.26 12.5 107747.57 0.94 0.88 1086101.76 1.16 1.11 13.5 1076740.56 0.79 0.64 1086135.25 1.30 0.97 14.5 107640.56 0.79 0.64 1086139.34 0.51 0.69 16.5 1075450.40 0.54 0.43 108609.88 0.77 0.56 17.5 1074076.98 0.22 0.26 1085895.00 0.28 0.27 20.5 107359.02 0.24 0.20 1085895.00 0.28 0.21	5.5	1081518.71	1.14	1.18				1085283.35	1.52	1.50
7.51080601.951.241.271085621.171.551.598.51080112.521.351.251085758.941.531.569.51079602.381.291.191085875.911.471.4910.51079071.521.041.101085972.061.321.3811.51078519.921.080.991086047.351.291.2612.51077947.570.940.881086101.761.161.1113.51077354.450.640.761086135.251.300.9714.51076740.560.790.641086147.790.650.8215.51076105.880.600.531086139.340.510.6916.51075450.400.540.431086109.880.770.5617.51074774.100.300.341086059.360.370.4518.51074076.980.220.261085987.750.330.3519.51073359.020.240.201085985.000.280.2720.51082570.370.280.251083376.110.240.391084236.160.250.262.51082570.370.280.251083376.110.240.241084504.060.500.453.51082172.120.470.411083300.070.150.171084750.150.680.604.51081752.250.410.531083202.330.150.1210849	6.5	1081070.67	1.27	1.25				1085462.63	1.53	1.57
8.5 1080112.52 1.35 1.25 1085758.94 1.53 1.56 9.5 1079602.38 1.29 1.19 1085875.91 1.47 1.49 10.5 1079071.52 1.04 1.10 1085972.06 1.32 1.38 11.5 1078519.92 1.08 0.99 1086047.35 1.29 1.26 12.5 1077947.57 0.94 0.88 1086101.76 1.16 1.11 13.5 1076740.56 0.79 0.64 1086135.25 1.30 0.97 14.5 1076740.58 0.60 0.53 1086139.34 0.51 0.69 15.5 1076105.88 0.60 0.53 1086199.38 0.77 0.56 17.5 1074774.10 0.30 0.34 1086059.36 0.37 0.45 18.5 1074076.98 0.22 0.26 1085895.00 0.28 0.27 20.5 1083430.42 0.34 0.39 1084236.16 0.25 0.26 Sub-band 6-0 for substate ${}^2\Pi_{3/2}$ 1.5 1083430.42 0.34	7.5	1080601.95	1.24	1.27				1085621.17	1.55	1.59
9.5 1079602.38 1.29 1.19 1085875.91 1.47 1.49 10.5 1079071.52 1.04 1.10 1085972.06 1.32 1.38 11.5 1078519.92 1.08 0.99 1086047.35 1.29 1.26 12.5 1077947.57 0.94 0.88 1086101.76 1.16 1.11 13.5 1076740.56 0.79 0.64 1086135.25 1.30 0.97 14.5 1076740.56 0.79 0.64 1086147.79 0.65 0.82 15.5 1076105.88 0.60 0.53 1086109.88 0.51 0.69 16.5 1074774.10 0.30 0.34 1086109.88 0.77 0.56 17.5 1074076.98 0.22 0.26 1085987.75 0.33 0.35 19.5 1073359.02 0.24 0.20 1085430.42 0.34 0.39 1084236.16 0.25 0.26 Sub-band 6-0 for substate ${}^2\Pi_{3/2}$ 1.5 1083430.42 0.34 0.39 1084236.16 0.25 0.26	8.5	1080112.52	1.35	1.25				1085758.94	1.53	1.56
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	9.5	1079602.38	1.29	1.19				1085875.91	1.47	1.49
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10.5	1079071.52	1.04	1.10				1085972.06	1.32	1.38
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11.5	1078519.92	1.08	0.99				1086047.35	1.29	1.26
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12.5	1077947.57	0.94	0.88				1086101.76	1.16	1.11
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	13.5	1077354.45	0.64	0.76				1086135.25	1.30	0.97
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	14.5	1076740.56	0.79	0.64				1086147.79	0.65	0.82
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	15.5	1076105.88	0.60	0.53				1086139.34	0.51	0.69
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	16.5	1075450.40	0.54	0.43				1086109.88	0.77	0.56
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	17.5	1074774.10	0.30	0.34				1086059.36	0.37	0.45
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	18.5	1074076.98	0.22	0.26				1085987.75	0.33	0.35
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	19.5	1073359.02	0.24	0.20				1085895.00	0.28	0.27
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	20.5							1085781.08	0.18	0.21
1.5 1083430.42 0.34 0.39 1084236.16 0.25 0.26 2.5 1082570.37 0.28 0.25 1083376.11 0.24 0.24 1084504.06 0.50 0.45 3.5 1082172.12 0.47 0.41 1083300.07 0.15 0.17 1084750.15 0.68 0.60 4.5 1081752.25 0.41 0.53 1083202.33 0.15 0.12 1084974.45 0.73 0.72	Sub-band 6–0 for substate ${}^{2}\Pi_{3/2}$									
2.5 1082570.37 0.28 0.25 1083376.11 0.24 0.24 1084504.06 0.50 0.45 3.5 1082172.12 0.47 0.41 1083300.07 0.15 0.17 1084750.15 0.68 0.60 4.5 1081752.25 0.41 0.53 1083202.33 0.15 0.12 1084974.45 0.73 0.72	1.5		5/2		1083430.42	0.34	0.39	1084236.16	0.25	0.26
3.5 1082172.12 0.47 0.41 1083300.07 0.15 0.17 1084750.15 0.68 0.60 4.5 1081752.25 0.41 0.53 1083202.33 0.15 0.12 1084974.45 0.73 0.72	2.5	1082570.37	0.28	0.25	1083376.11	0.24	0.24	1084504.06	0.50	0.45
4.5 1081752.25 0.41 0.53 1083202.33 0.15 0.12 1084974.45 0.73 0.72	3.5	1082172.12	0.47	0.41	1083300.07	0.15	0.17	1084750.15	0.68	0.60
	4.5	1081752.25	0.41	0.53	1083202.33	0.15	0.12	1084974.45	0.73	0.72
5.5 1081310.77 0.66 0.61 1085176.90 0.68 0.80	5.5	1081310.77	0.66	0.61				1085176.90	0.68	0.80
6.5 1080847.74 0.74 0.66 1085357.52 0.72 0.84	6.5	1080847.74	0.74	0.66				1085357.52	0.72	0.84
7.5 1080363.17 0.79 0.68 1085516.29 0.69 0.85	7.5	1080363.17	0.79	0.68				1085516.29	0.69	0.85
8.5 1079857.10 0.66 0.67 1085653.20 0.93 0.84	8.5	1079857.10	0.66	0.67				1085653.20	0.93	0.84
9.5 1079329.57 0.59 0.64 1085768.26 0.86 0.80	9.5	1079329.57	0.59	0.64				1085768.26	0.86	0.80
10.5 1078780.60 0.64 0.59 1085861.44 0.68 0.74	10.5	1078780.60	0.64	0.59				1085861.44	0.68	0.74
11.5 1078210.25 0.65 0.53 1085932.76 0.66 0.67	11.5	1078210.25	0.65	0.53				1085932.76	0.66	0.67
12.5 1077618.54 0.41 0.47 1085982.21 0.49 0.59	12.5	1077618.54	0.41	0.47				1085982.21	0.49	0.59
13.5 1077005.49 0.35 0.40 1086009.78 0.52 0.51	13.5	1077005.49	0.35	0.40				1086009.78	0.52	0.51
14.5 1076371.16 0.38 0.34 1086015.50 0.45 0.43	14.5	1076371.16	0.38	0.34				1086015.50	0.45	0.43
15.5 1075715.56 0.25 0.28 1085999.33 0.43 0.36	15.5	1075715.56	0.25	0.28				1085999.33	0.43	0.36
16.5 1075038.73 0.23 0.22 1085961.29 0.29 0.29	16.5	1075038.73	0.23	0.22				1085961.29	0.29	0.29
17.5 1074340.70 0.25 0.18 1085901.39 0.28 0.23	17.5	1074340.70	0.25	0.18				1085901.39	0.28	0.23
18.5 1073621.49 0.14 0.14 1085819.61 0.13 0.18	18.5	1073621.49	0.14	0.14				1085819.61	0.13	0.18
19.5 1085715.97 0.08 0.14	19.5							1085715.97	0.08	0.14

band strength corresponds to a magnitude of electric dipolar moment $|p_0^6| = (5.27 \pm 0.13) \times 10^{-35}$ C m for the pure vibrational transition. For comparison, the corresponding magnitude of electric dipolar moment p_0^6 for this transition 6–0 from strengths of individual features [1,3] in the

sub-band for ${}^{2}\Pi_{1/2}$ is $|p_{0}^{6}| = (5.263 \pm 0.019) \times 10^{-35}$ Cm and Herman–Wallis coefficient $C_{0}^{6} = 0.00596 \pm 0.00089$; for features in the weaker subband for substate ${}^{2}\Pi_{3/2}$, $|p_{0}^{6}| = (5.378 \pm 0.028) \times 10^{-35}$ Cm and $C_{0}^{6} = 0.00590 \pm 0.00097$. The best estimate of this transition moment from all data is thus $|p_0^6| = (5.31 \pm 0.13) \times 10^{-35}$ Cm. For each observed line the table includes a corresponding strength calculated on that basis.

4. Discussion

Despite the importance of NO in atmospheric processes, this work marks the first direct observation of a vibration-rotational band of NO in electronic ground state $X^2\Pi_r$ for which $\Delta v = 6$, from the vibrational ground state in absorption. For reasons already mentioned, no useful information is derived from measurements of wave numbers of features that are actually at least doublets due to spin-rotational splitting—apart from additional hyperfine splitting, of widths or of shifts of features caused by collisional effects in our samples at finite pressures.

According to entries in the table, measured strengths of individual lines vary fairly regularly within each branch, although we performed no further manual smoothing after averaging for our multiple samples at three pressures. Overlapping and blended lines in the region of heads in R branches are a further complication, but a strategy of limiting both wave number and width of each component contributing to a measured profile of absorption seems to have proved reasonably effective. In P branches measurement of further lines of NO is hampered by a presence of lines of water vapour; the total contribution of all further lines of NO to a total band strength is estimated to be less than 10^{-29} m, which is much smaller than the estimated error of our total band strength. As all features have small maximum net absorbance in our spectra and as lines overlap and blend in a region of heads of R branches, observed and calculated strengths of lines generally agree satisfactorily in relation to rough values of measured strength; agreement is typically superior for features in a sub-band belonging to substate ${}^{2}\Pi_{1/2}$ than for those of substate ${}^{2}\Pi_{3/2}$ because of smaller absorbances of the latter. For practical use in other contexts, values of line strengths calculated, rather than measured, are recommended because calculated values result from application of two parameters deduced from 80 separate absorption features through well established theoretical relations [1,3]; with two parameters, namely $|p_0^6|$ and C_0^6 , according to their derived values, we not only reproduce strengths of 80 apparent lines up to J'' = 20.5 within error of measurement at (297.35 ± 0.4) K, but also can estimate strengths of lines within that range of J'' at arbitrary other temperature.

With the same samples we remeasured strengths of lines in band 5–0 of NO near 9.1×10^5 m⁻¹, yielding a band strength $S_{\rm b} = (5.058 \pm 0.055) \times$ 10^{-26} m at (297.35 ± 0.4) K. Apart from a factor $\ln_{e}(10)$ that was inadvertently omitted in calculating line strengths from integrated areas in our previous work [4], such that all strengths of lines and the total band strength there reported should be multiplied by 2.3026, the present results are consistent with the former results, which we made on samples in an optical path of length only 20.25 m. A ratio of strengths of these two bands is thus about 9, implying a much smaller decrease of ratio for successive overtones than for CO [5] for which the ratio is about 150. This condition reflects a fact that with our present apparatus we can measure strengths of individual lines in the fifth overtone band of NO but only the third overtone of CO [5].

We are aware of significant problems in deriving intensities of lines under conditions of our experiments and analysis, not only a small net absorbance of a line and severe overlap and blending of apparent features near each head of an R branch, but particularly the nature of unresolvable doublets due to spin-rotational interaction [3], apart from further complication from hyperfine effects. We tested selected isolated apparent lines in two P branches by fitting with either one or two lorentzian components, and with either one or two components of mixed lorentzian and gaussian character; within an uncertainty indicated by fitting a selected feature in varied ranges, the total area is independent of such variation of fitting conditions. As we can detect, within experimental error, no deviation of profiles of isolated absorption features from what might be expected for a line due to a single transition, we expect that error from such sources is smaller than other error present in our measurement of these weak lines.

5. Conclusion

From measurement of strengths of individual features in vibration-rotational band 6–0 of $^{14}N^{16}O$ in its electronic ground state $X^2\Pi_r$, we estimate, as a sum of contributions from lines in both sub-bands consistent with fitting to lines in each sub-band, a total band strength $S_b = (5.63 \pm 0.28) \times 10^{-27}$ m at (297.35 ± 0.4) K, which is about one ninth the strength of band 5–0.

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References

- J.F. Ogilvie, The Vibrational and Rotational Spectrometry of Diatomic Molecules, Academic Press, London, UK, 1998.
- [2] C. Amiot, The infrared emission spectrum of NO; analysis of the sequence with $\Delta v = 3$ up to v = 22, J. Mol. Spectrosc. 94 (1982) 150–172.
- [3] V. Dana, J.-Y. Mandin, L.H. Coudert, M. Badaqui, F. LeRoy, G. Guelachvili, L.S. Rothman, Λ-splittings and line intensities in the hot band 2 ← 1 of nitrogen oxide, J. Mol. Spectrosc. 165 (1994) 525–540.
- [4] Y.-P. Lee, J.F. Ogilvie, Strengths of absorption lines in the vibration-rotational band $v = 5 \leftarrow v = 0$ of NO $X^2 \Pi_r$, Infrared Phys. 28 (1988) 321–324.
- [5] J.F. Ogilvie, S.-L. Cheah, Y.-P. Lee, S.P.A. Sauer, Infrared spectra of CO in absorption and evaluation of radial functions for potential energy and electric dipolar moment, Theor. Chem. Acc. 108 (2002) 85–97.