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Absorption Cross Sections and Lineshape for the NO_3 (0-0) Band

By

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Abstract

The absorption cross-section of the nitrate free radical has been scanned by a tunable dye laser with 0.05 nm resolution (FWHM) between 613 and 672 nm, and portions of the region were scanned at high resolution (200 Mhz) with the laser in single-frequency mode. These data, combined with other recent measurements, give a peak cross-section at 661.9 nm of $1.90 \times 10^{-17} \text{ cm}^2$; and the integrated cross-section over the 0-0 band from 14910 to 15290 cm^{-1} is $2.02 \times 10^{-15} \text{ cm}$. Two recent studies that were said to disagree because of different peak cross sections are shown to agree in terms of integrated absorption cross section over the 0-0 band. It is confirmed that the spectrum is diffuse even under very high resolution. The 0-0 band is well approximated by two closely spaced Lorentzian functions.

Introduction

The nitrate radical, NO_3 , exhibits a structured absorption spectrum¹⁻⁷ consisting of approximately 20 diffuse bands in the region 665-400 nm. Even though all of the bands are diffuse at high resolution,⁴ part of the spectrum is photochemically inactive,^{5,8} and the molecule shows no visible fluorescence,⁹ suggesting intramolecular energy transfer. There is some disagreement as to the shape and magnitude of this absorption spectrum.⁵⁻⁷ The present study was designed to characterize the shape of the strong absorption band around 662 nm, which has been interpreted as the 0-0 transition.⁴

Experimental

Apparatus — The experimental apparatus consisted of a 2 meter long, 3 cm diameter, single-pass, insulated and jacketed optical absorption cell through which the output of a tunable Spectra-Physics 581A dye laser was propagated. The dye laser was operated in two regimes. In a few experiments, it was operated as a single-frequency laser with line-width less than 200 Mhz (0.00029 nm), and the sweep width at a single setting was 15 Ghz (0.022 nm). Also, it was operated multimode using the birefringent filter as the sole tuning element; it had a line-width estimated to be 0.05 nm and a sweep range limited by the tuning range of the dye employed (R640), which was 675 to 613 nm in these experiments. The intensity of the transmitted beam was measured by a photodiode (UDT-PIN-8LC).

Most experiments were performed with the beam of 0.05 nm bandwidth. These data were recorded using a Nicolet Instruments (Fabritek) 1074

signal averager with external address advance. The laser wavelength was scanned using a stepping motor (200 steps per revolution at 2.5:1 gear reduction ratio) to drive the birefringent filter. A common pulse generator was used to drive both the stepping motor and the channel address of the signal averager. Typical scan conditions were 2.5 pulses per second covering approximately 0.023 nm per pulse. The signal averager was directly coupled to a PDP-8L minicomputer so that the data could be subtracted from background, converted to optical density, simply processed, and stored on punched paper tape.

The single-frequency 15 Ghz scans were recorded directly on an x-y recorder at scan times of approximately 120 seconds. These scans were made only at selected wavelengths, including regions where there was a neon line that could be used for wavelength calibration.

Laser wavelength calibration was accomplished both internally and externally. The external calibration involved deflecting a portion of the beam into an Interactive Technology one-meter monochromator with a PAR 1205D optical multichannel analyzer as detector, onto which was overlaid emission from a neon pilot lamp providing positioning accuracy to 0.08 nm. Internal wavelength calibration utilized the opto-galvanic effect¹⁰ by simultaneously recording in a second quadrant of the signal averager the impedance change produced in a neon-filled hollow-cathode lamp when a deflected portion of the laser beam comes into coincidence with a neon transition. The locations of these transitions are known within 10^{-3} nm, hence providing wavelength calibration. The width of these transitions is about 3 Ghz, much narrower than the bandwidth of the laser when operated multimode with the birefringent filter; and these lines were used to estimate the laser bandwidth,

which was found to be about 0.05 nm. The laser linewidth and the wavelength step width were found to be a non-linear function of the position on the dye lasing curve. The calibration points, based on neon lines, were fit to a three-term polynomial, and in this way the wavelength could be determined within a single channel width of the signal averager over the entire spectral range. The neon lines used for the calibration are at 650.65, 653.29, 659.89, 667.83, and 672.15 nm.

Materials — The nitrogen carrier gas used in this experiment was supplied by the Lawrence Berkeley Laboratory with impurity levels comparable to Matheson reagent grade, and it was used without further purification. A 1.0 percent mixture of reagent grade NO_2 in N_2 was supplied by the Matheson Company; about 5 percent of the NO_2 was dissociated to NO; this NO is rapidly converted to NO_2 by ozone in these experiments; and the NO impurity caused no problems. Ozone was prepared in the following manner. A stream of O_2 was purified by passing it through a silica tube with copper turnings at 900 K and through a column of 5 percent palladium on alumina at 620 K to convert hydrocarbon impurities to CO_2 and H_2O , which were removed by absorption on columns of ascarite and P_2O_5 -coated glass beads. The purified O_2 was passed through an Ozone Research and Equipment Company silent electric discharge ozonator, where about 7 percent of the oxygen was converted to ozone. After leaving the ozonator, the ozone-oxygen mixture was passed through a silica gel trap at 196 K where the O_3 was preferentially adsorbed and stored for subsequent use. Flow rates were controlled by Nupro stainless steel "S" needle valves and were measured by calibrated Hastings Model LF 300M mass flow meters. The absorption cell temperature was monitored

using two 0.1°C thermometers strapped to each end of the cell. The thermometers agreed within 0.4°C, and all experiments were conducted at ambient temperature, 295 to 297 K.

Procedure — The experiments were performed in a slowly flowing system at one atmosphere pressure such that the residence time in the absorption cell was approximately 1100 seconds. Ozone was picked up in a flow of N₂ through the silica gel trap held at 225 K by m-xylene slush. Its concentration was measured in the reaction cell by absorption at the NO₃ minimum at 650.0 nm, and it was redundantly measured beyond the cell in an external one-meter path absorption cell at 488.0 nm. This system consisted of a tuning-fork modulated deuterium lamp, a one-third meter McPherson 218 monochromator, photomultiplier tube, and associated phase-sensitive detection electronics. A separate stream of one percent NO₂ in N₂ was set up; and by switching flows the NO₂ plus the N₂ carrier stream later to be used for ozone went through the external light-absorption cell, where the NO₂ was measured by light absorption at 488.0 nm ($\sigma = 2.97 \times 10^{-19} \text{ cm}^2 \text{ molecules}^{-1}$ ¹¹). The monochromator was fitted with order-sorting filters, and it was set at a bandpass of 0.1 nm to correspond to that used for measuring the NO₂ cross-section. The flowing streams of O₃ and of NO₂, each carried by nitrogen at one atmosphere, were mixed in an external manifold with a volume such that the NO₃ concentration was calculated to attain at least 95 percent of its steady-state value before entering the absorption cell. The flowing system was monitored at the NO₃ absorption peak at 661.9 nm until the absorption there reached a stable, maximum value. The ozone cross-sections used at these wavelengths were those of Vigroux:¹²

$2.67 \times 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$ at 650.0 nm and $8.78 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$ at 488.0 nm. At each of these wavelengths there was an absorption by NO_3 of about 5 percent, but these small absorptions were corrected using the average cross sections found by Mitchell et al.⁷ and by Graham and Johnston.⁶

Results

The NO_3 cross sections were measured using the multimode laser of 0.05 nm linewidth and scanning from 672 to 648 nm. Twelve spectra at three different NO_2 input concentrations and six different ozone steady-state concentrations were recorded over this range. The chemistry of this system is characterized by the reactions⁶

To a good first approximation the steady-state concentration of NO_3 is given by

$$[\text{NO}_3] = \left(\left(K k_3 / 2k_4 \right) [\text{O}_3] [\text{N}_2\text{O}_5] \right)^{1/3} \quad (1)$$

where K is the equilibrium constant k_1/k_2 . Di-nitrogen pentoxide is able to extract water bonded to silica, and we have never been able to produce N_2O_5 completely free from HNO_3 . In these experiments the apparatus was conditioned by lengthy exposure to N_2O_5 before the spectra were taken, HNO_3 was not measured during these runs, but from previous

experience it is estimated that between 10 and 20 percent of the N_2O_5 was converted to HNO_3 . Because of the one-third power dependence of NO_3 on the concentration of N_2O_5 , these considerations indicate that the concentrations of NO_3 calculated here are 3 to 7 percent too high, because of the partial conversion of N_2O_5 to HNO_3 . The rate constants and equilibrium constants used are those of Graham and Johnston⁶

$$K = (8.4 \pm 1.8) \times 10^{26} e^{-11178/T} \text{ molecules cm}^{-3} \quad (2)$$

$$k_3 = (1.34 \pm 0.11) \times 10^{-13} e^{-2466/T} \text{ cm}^{-3} \text{ s}^{-1} \quad (3)$$

$$k_4 = (8.5 \pm 2.8) \times 10^{-13} e^{-2451/T} \text{ cm}^{-3} \text{ s}^{-1} \quad (4)$$

Although (1) is a good first approximation to the NO_3 concentration, there are additional corrections due to the finite rate of reaction (1) and to flow-in and flow-out of the cell. These corrections were carried out using the CHEMK¹³ computer program. Secondary reactions initiated by the reaction, $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{O}_2 + \text{NO}_2$, were found to have negligible effect in this system. From the measured O_3 concentration, a stored ozone spectrum was scaled and subtracted from the observed absorptions to give optical densities due to NO_3 . The cross sections were evaluated from

$$\sigma = (\ln I_0/I)/[\text{NO}_3]L \quad (5)$$

where the concentration of NO_3 (molecules cm^{-3}) was found as described above and L was the optical pathlength, 191.5 cm. The absorption spectra were evaluated between 672 and 648 nm for each of 12 experimental conditions, which are summarized in Table I. The peak absorption was found to occur at 661.9 nm, and the peak cross sections are listed in Table I. The average of the cross sections at the peak is 1.61 ± 0.34 (2σ) $\times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$.

The point-by-point average of the 12 spectra is plotted as a function of wave number (14910 to 15290 cm^{-1}) as curve A of Fig. 1. Experimental points are entered for every 2 cm^{-1} . The experimental curve appears to show some structure, for example near the peak. To see if this apparent structure is reproducible, four runs and their average are presented in Fig. 2 over a narrow range around the peak as identified by the horizontal bar in the upper center of Fig. 1. Over the 1.25 nm range between 661.45 and 662.70 nm, the four spectra and their average are entered from observations made at every 0.023 nm. The magnitude of experimental error is visible from the magnified spectra in Fig. 2, and it seems that the apparent structure near the peak of curve A in Fig. 1 is experimental noise.

By operating the dye laser in single frequency mode 0.00029 nm wide and with 0.022 nm sweep width, a sharp test was made concerning fine structure in the NO_3 spectrum. Curve A in Fig. 3 shows the opto-galvanic effect¹⁰ as the laser swept through a transition in a neon-filled hollow cathode lamp. Curve B shows the absorption spectrum through an $\text{O}_3\text{-N}_2\text{O}_5\text{-NO}_3$ mixture over the same wavelength range as curve A, which is located on Fig. 1 by the arrow at 15154 cm^{-1} . The flat curve shows no sign of rotational or other fine structure in the spectrum. Curve C shows a similar flat curve through the NO_3 peak, as located by the arrow at 15108 cm^{-1} in Fig. 1; and another sweep at 14974 cm^{-1} showed no structure in the spectrum.

The scanning multimode laser with 0.05 nm resolution was used to cover the range from 14900-16300 cm^{-1} , and some points obtained by Graham and Johnston between 14600 and 14900 are included in Fig. 4.

This spectrum includes the strong peak of Fig. 1 assigned as the 0-0 transition by Ramsay⁴ and the strong peak at 623.22 nm, which Ramsay identified as the 1-0 transition of the symmetric stretching vibration.

Comparison With Other Studies

Ramsay⁴ photographed the NO_3 spectrum between 665 and 500 nm using a Hilger E 1 spectrograph with glass optics. The NO_3 was prepared by mixing NO_2 and O_3 , and the optical path length was several meters. Quantitative results were presented as the reproduction of a photographic plate with calibration lines from an iron hollow-cathode lamp superimposed on about 20 absorption bands. The location of absorption bands are marked along the photographic plate, and the vacuum wavenumbers are printed with these marks. The resolution of this spectrograph appeared to be a few cm^{-1} . Also, Ramsay examined the NO_3 absorption bands at much higher resolution with a 21 foot concave grating instrument. These results were not presented, but it was stated that all the NO_3 bands were diffuse at this high resolution. By comparison with results that Ramsay has obtained using the 21 foot grating instrument on other molecules,¹⁴ its resolution appears to be about 0.001 nm.

For comparison with these results, Ramsay's vacuum frequencies are converted to those for one atmosphere air by adding 4 cm^{-1} to his values. Ramsay interpreted one progression as the symmetric stretching vibration in the excited electronic state. The 0-0 transition is the high intensity absorption presented in Fig. 1. Ramsay tentatively made the following assignments

Transition	ν/cm^{-1}	$\Delta\nu$
0-0	15093	
1-0	16043	950
2-0	16969	926
3-0	17890	921

This study observed the first two transitions, Fig. 4, and the results were

Transition	ν	$\Delta\nu$
0-0	15109	
1-0	16044	935

Using a 21 foot grating spectrograph, Ramsay found all the NO_3 bands to be diffuse, which he interpreted as pre-dissociation. In this study, the width of the single mode laser appears to be about three-fold more narrow than the resolution of Ramsay's 21 foot grating. At this higher resolution, there is still no evidence of fine structure in the NO_3 spectrum, Fig. 3, and this study confirms and extends Ramsay's finding that the NO_3 spectrum is diffuse.

Ramsay did not determine absorption cross sections in his study. However, there are three other quantitative studies of the absorption cross section spectra of NO_3 . One of these⁵ depends on use of rate constants and equilibrium constant (K , k_3 , k_4) to evaluate the concentration of NO_3 , and two of these studies were direct, absolute methods.^{6,7}

(1) Johnston and Graham⁵ determined the absorption spectrum in a flowing system of N_2O_5 and O_3 , measured the spectrum with a one-third

meter (McPherson Model 218) monochromator, and calculated the concentration of NO_3 from K , k_3 , and k_4 on the basis of kinetic data obtained in the 1930's and 1950's. The article gives the experimental conditions used so that the NO_3 concentration can be recalculated using recent⁶ values of K , k_3 , and k_4 . The calculated concentration of NO_3 is lowered by a factor of 3.68, and the published cross sections should be increased by the same factor. The concentration of nitric acid was not measured during the experiments, but it was noted that about 15 percent of the N_2O_5 was converted to HNO_3 . This experiment is very similar in method to the present study except for the use of a 1/3 meter monochromator then and use of a tunable laser here.

(2) Graham and Johnston⁶ measured the NO_3 spectrum by a direct absolute method, and the results are negligibly dependent on values of rate constants. In a steady flowing system of N_2O_5 and O_3 , NO_3 was photolyzed by on-off fluorescent light bulbs of green or gold color. The change in visible NO_3 absorption was measured at the flat topped peak at 627.0 nm. The associated change of N_2O_5 was measured by infrared absorption at 8.028 μm , using an easily converted VIS/IR molecular modulation apparatus.¹¹ As the photolysis lamp flashed on-and-off, the molecular modulations of NO_3 and N_2O_5 were repeatedly, alternately measured. In this system N_2O_5 and NO_3 are strongly coupled by reactions k_1 , k_2 , k_3 , and k_4 , and the situation may be abbreviated as

To a first approximation the stoichiometric factor between N_2O_5 and NO_3 is 2.00. However, as NO_3 is photolyzed to yield $\text{NO} + \text{O}_2$ or $\text{NO}_2 + \text{O}$, there are some secondary reactions involving NO and O . The system was computer modeled by a complete set of reactions, and these secondary reactions were found to have only a minor effect on the stoichiometric factor of two. The absolute cross section of NO_3 at 627.00 nm was measured at 24 different conditions: with varied O_2 (0.5 to 99%), O_3 (3.5 to 10.5×10^{16} molecules cm^{-3}), N_2O_5 (3.1 to 13.9×10^{14} molecules cm^{-3}), two reaction cells of different surface to volume ratios and two photolysis lamps (green or gold). The average stoichiometric factor was 2.07, the maximum value was 2.16. These data were reported⁶ as the average cross section over 1 nm band width; for a nominal wavelength of 627, for example, the average reported is between 626 and 627 nm. This spectrum is presented as a bar graph, curve B, in Fig. 1. Graham¹¹ reported the maximum σ at 662.2 nm, and this point is indicated by the triangle in Fig. 1.

(3) Mitchell et al.⁷ also determined the NO_3 absorption spectrum by a direct absolute method. By considering the rates of reactions, k_1 , k_2 , k_3 , k_4 , and others, they found experimental conditions where essentially all NO_x (NO , NO_2 , NO_3 , N_2O_5) in the system would be in the form of NO_3 . Thus the measured NO_2 input was equal to NO_3 in the system. The required experimental conditions were that NO_x should be less than 10^{12} molecules cm^{-3} and ozone should be 5×10^{17} molecules cm^{-3} or more. These conditions yield an optical density ($\ln I_0/I$) for NO_3 of 3×10^{-4} in the 25 cm cell, and the superimposed optical density of O_3 at 662 nm is 2.5×10^{-2} or about 80-fold greater than that for NO_3 . By a carefully designed double

detector, they were able to overcome much of the difficulty posed by the weak NO_3 signal and the large overlapping O_3 signal. Their relative cross sections as a function of wavelength were tabulated in a laboratory publication,¹⁵ these values were scaled by us to the published⁷ value of $121 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ at the maximum, and their absorption spectrum of the strong peak around 662 nm is plotted as curve C in Fig. 1.

The four determinations of the NO_3 absorption spectrum are compared in Table II in terms of 3 quantities: the value of the cross section at the peak at 662 nm, the ratio of peak cross section of 662 nm to that at 627 nm, and the integrated absorption spectrum over the range of Fig. 1.

$$I = \int_{14910}^{15290} \sigma d(1/\lambda) \quad (6)$$

The four studies differ significantly in terms of maximum σ , from Mitchell et al.'s value of $121 \times 10^{-19} \text{ cm}^2$ to Graham's¹¹ value of $186 \times 10^{-19} \text{ cm}^2$. It is apparent from Fig. 1 that curve C (Mitchell et al.) has less resolution than the other two curves, and the comparison should be made in terms of integrated absorption coefficient, not peak height. The integrated absorption coefficient for Mitchell et al. is $2.06 \times 10^{-15} \text{ cm}$ and that for Graham and Johnston over the same range is $1.99 \times 10^{-15} \text{ cm}$. Thus the two direct, absolute determinations agree within 3 percent so far as integrated absorption is concerned. For the two studies that depend on values of K , k_3 , and k_4 , the integrated cross sections are $1.83 \times 10^{-15} \text{ cm}$ for Johnston and Graham⁵ and $1.73 \times 10^{-15} \text{ cm}$ for this study. These values are about 10 percent lower than

the values based on an absolute method of measuring NO_3 . The loss of about 15 percent N_2O_5 to HNO_3 in these two systems would cause about a 5 percent underestimate of the cross section (note $1/3$ power law in Eq. 1). By difference this indicates an error of about $15 \pm 15\%$ error in the product $\text{K}k_3/k_4$, that is, $\text{K}k_3/k_4$ may be too large by this factor. Graham and Johnston⁶ assigned an error of ± 20 percent to K , ± 8 percent to k_3 , and ± 33 percent error to k_4 .

The ratio of σ_{max} near 662 nm to σ at 627 nm is a good test for spectral resolution, since the peak at 662 nm is tall and sharp and the peak at 627 nm is broad and almost flat-topped (compare Fig. 4 at 15109 cm^{-1} and 15922 cm^{-1}). From the data of Mitchell et al., this ratio is 1.6. The other three studies agree with each other, 2.61, 2.65, and 2.61, but disagree with Mitchell et al. From the shape of the three spectra in Fig. 1 and from these ratios, it appears that Mitchell et al. were correct in judging "that the breadth of our peaks is a result of the actual monochromator resolution being appreciably greater than that calculated." (Our experience with that model monochromator, Bausch and Lomb 33-86-79, shows that it has a large amount of scattered light that tends to degrade its resolution.)

It appears that the present study gives the best determination yet reported of the shape of the strong NO_3 absorption spectrum around 662 nm, but the absolute absorption is best obtained from the integrated absorption spectra of Graham and Johnston⁶ or Mitchell et al.⁷ Their two results are averaged to give an integrated absorption of $202 \times 10^{-19} \text{ cm}$ between 14910 cm^{-1} and 15290 cm^{-1} , and the average of the 12 curves observed here was scaled to give the same integrated absorption curve.

These data are given for every 0.2 nm between 649 and 672 nm in Table III. For spectroscopic studies of NO_3 in the atmosphere, these data are probably the best currently available. For photochemical models, the NO_3 cross sections integrated over 1 nm bands as given by Graham and Johnston are probably the most convenient form of the data.

Magnotta and Johnston⁸ studied the wavelength-dependent quantum yields for two channels of NO_3 photolysis, $\text{NO}_2 + \text{O}$ or $\text{NO} + \text{O}_2$. Using literature values for K and Graham and Johnston's values for σ , their results indicated a primary quantum yield of about 1.5 at 580 nm, which, of course, is impossible. They gave four, different, possible explanations for this apparent high quantum yield. One of these was that the cross section for NO_3 should be increased by about 50 percent. In view of the excellent agreement for the two absolute determinations of the integrated absorption spectrum,^{6,7} it appears unlikely that their anomalous quantum yield is due to incorrect NO_3 cross sections. Some of their discrepancy could be explained by K being larger than the literature value, which is consistent with the low integrated absorptions observed here and in Ref. 5.

Discussion of Band Head Lineshape

Our inability to observe fluorescence following excitation of any portion of the photochemically inactive region of the spectrum would suggest some fast internal conversion process to non-radiative or easily quenched states. Olsen and Burnelle¹⁶ have estimated an oscillator strength for the transition ($f = 0.013$) from which a radiative lifetime

of approximately 500 ns may be calculated. If this estimate of the lifetime is accurate, then strong visible fluorescence is expected under the experimental conditions employed.

A close examination of the band head shows that it appears to be a slightly distorted Lorentzian function, perhaps composed of two overlapping envelopes. We have been able to fit it (Fig. 5) to a pair of Lorentzian functions centered at 15066 cm^{-1} and 15109 cm^{-1} with linewidths (FWHM) of approximately 96 cm^{-1} and 60 cm^{-1} , respectively. This finding is somewhat similar to that of Reddy, Bray, and Berry¹⁷ who studied high vibrational overtone spectra in benzene. They found that many of the overtone bands assume Lorentzian lineshapes on the order of 80 cm^{-1} to 120 cm^{-1} linewidth. They attributed this to a coupling of the excited discrete states with the quasi-continuum of background states available to produce an embedded state with a Lorentzian lineshape. Jones, Zewail, and Diestler¹⁸ have treated this effect theoretically and showed that, for molecules where the width of the absorption lines is narrow compared to the separations between them and in the absence of collisions, a Lorentzian lineshape is expected with the inverse of the linewidth giving the lifetime of the discrete state. If the density of states is high or intermolecular processes are important, the line is inhomogeneously broadened and the interpretation of the linewidth becomes less straightforward.

A similar scheme can be constructed for NO_3 involving curve crossing from the excited electronic state to high vibrational levels of the ground state. The complications of curve crossing, collisions, and possibly a high density of states may explain why a Lorentzian function is not

observed. The linewidth observed here would indicate a lifetime of approximately 2 picoseconds for relaxation to the quasi-continuum in contrast to a lifetime of 500 ns for radiation of the excitation energy. The ratio of relaxation to radiation rates is approximately 2.5×10^5 , and in this case little visible emission is expected. The relative density of states would favor maintaining the excitation energy in the quasi-continuum from which energy is lost primarily through quenching and infrared emission. Little or no fluorescence would be expected in the visible region, and the apparent radiative lifetime is much longer than that calculated on the basis of the oscillator strength. Effects of this type have been observed for NO_2 , SO_2 and CS_2 . They have been explained in a similar manner by Douglas¹⁹ as coupling to either a metastable or to the ground state. An investigation is currently underway in our laboratory attempting to detect infrared emission following excitation of the band head. This may provide information about the ground state vibrational frequencies in addition to the mechanism of energy transfer.

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Table I. Experimental conditions and maximum cross sections.

$[\text{NO}_2]_0$ $\text{cm}^{-3}/10^{16}$	$[\text{O}_3]_{ss}$ $\text{cm}^{-3}/10^{17}$	$[\text{NO}_3]_{calc}$ $\text{cm}^{-3}/10^{14}$	T K	σ_{max} $\text{cm}^2/10^{-17}$
7.65	10.0	3.95	297.3	1.66
7.65	10.0	3.95	297.3	1.64
7.65	4.74	2.79	295.8	1.83
7.65	4.95	2.85	295.8	1.79
4.75	6.33	2.76	295.5	1.58
4.75	7.48	2.98	295.5	1.53
4.75	5.48	2.62	295.7	1.77
4.75	5.47	2.65	295.9	1.81
2.02	21.7	3.69	296.5	1.31
2.02	20.4	3.61	296.5	1.38
2.02	10.4	2.93	295.8	1.46
2.02	10.1	2.89	295.8	1.52

Table II. Comparison of features of NO_3 absorption spectrum as found by different investigators.

Investigator	$\frac{\sigma_{\text{max}}}{10^{-19} \text{ cm}^2 \text{ 662 nm}}$	$\frac{\sigma(662)}{\sigma(627)}$	$\frac{I}{10^{-15} \text{ cm Eq. (6)}}$	Ref.
Johnston and Graham ^a (1974)	148	2.61	1.83	5
Graham and Johnston (1978)	186	2.65	1.99	6,11
Mitchell <u>et al.</u> (1980)	121	1.59	2.06	7
This work (ave. obs.)	161	2.61	1.73	
This work (scaled) ^b	190		2.02	

^aCorrected using current (Ref. 6) values of K , k_3 , and k_4 .

^bThe scaling factor is $2.02/1.73$ based on integrated cross sections, I .

Table III. Average NO_3 cross sections in units of 10^{-19} cm^2 as measured here and scaled to give same integrated absorption between 14910 and 15290 cm^{-1} as those obtained from curves B and C in Fig. 1.

	0.0	0.2	0.4	0.6	0.8
648.					5.7
649.	3.7	5.7	4.3	4.8	3.4
650.	3.5	4.7	4.1	3.9	4.5
651.	5.1	4.9	5.1	5.3	6.7
652.	5.8	5.4	5.9	5.5	6.9
653.	5.5	7.7	7.3	5.9	8.5
654.	7.1	7.5	8.4	7.9	8.3
655.	8.7	9.6	9.6	11.3	12.5
656.	11.4	12.2	11.8	12.4	12.7
657.	14.0	14.6	16.4	17.9	19.3
658.	19.4	20.6	23.7	25.7	27.9
659.	32.9	39.1	43.9	48.0	56.4
660.	65.4	75.6	86.2	106.7	119.6
661.	136.8	150.0	164.0	181.5	189.6
662.	185.5	178.7	171.9	166.8	154.0
663.	144.1	132.5	121.5	113.8	99.8
664.	93.2	86.0	78.2	70.9	66.5
665.	61.3	60.1	53.8	49.4	44.6
666.	42.2	39.6	35.0	31.7	27.9
667.	23.8	23.2	22.0	19.9	17.1
668.	16.2	16.7	14.5	14.4	12.7
669.	12.3	12.3	11.8	11.7	11.1
670.	10.4	11.6	11.1	9.1	9.1
671.	9.6	8.6	11.7	10.5	9.6
672.	8.9	8.6	11.4	8.0	8.0

Figure Captions

Fig. 1. Absorption spectra of the 0-0 band of NO_3 . A. The average of 12 determinations in this study. B. The average over each nm as reported by Graham and Johnston.⁶ C. The reported points, 0, connected by a smooth curve as reported by Mitchell *et al.*⁷ $\triangle$ The height and location of the peak of Ref. 6. $|—|$ The wavenumber range of Fig. 2. The arrows are the wavenumber regions for Fig. 3.

Fig. 2. Expanded spectra near the peak of the 0-0 band of NO_3 , compare $|—|$ in Fig. 1. In terms of the entries in Table I the curves are: A, 4; B, 3; C, 6; D, 5; and E is the average of the four.

Fig. 3. Very high resolution spectral scans with single-frequency dye laser. A. Opto-galvanic effect through neon line at 659.895 nm. B. NO_3 spectral scan through same wavelength region. C. NO_3 spectral scan near the peak at 661.9 nm.

Fig. 4. Relative absorption spectrum of NO_3 from 14900 cm^{-1} to 16200 cm^{-1} as observed here; + weak, presumably, hot band from Ref. 6. Table II compares value of cross section at sharp peak at 15108 cm^{-1} with the relatively broad peak between 15850 and 15975 cm^{-1} .

Fig. 5. Average observed spectrum of the NO_3 0-0 spectrum, dots, and a fitted line based on two superimposed Lorentzian functions.

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