the coordination number of Ca2+ is indeed strongly concentration dependent in the solution and for  $l \sim 1$  is as low as six; alternatively, Ca<sup>2+</sup>-Ca<sup>2+</sup> interactions occur within the inner sphere, leading to a reduction in  $\bar{n}_{CaO}$  directly. We think this latter suggestion is implausible; it is, however, of interest that, of the five molten divalent metal chlorides so far studied, a short cation-cation bond length occurs only in molten CaCl<sub>2</sub>. Biggin and Enderby<sup>39</sup> found that  $\bar{r}_{CaCa}$  was 3.58 Å and, in spite of the double charge on the calcium ion, was some 4% less than  $\bar{r}_{ClCl}$  (3.73 Å).

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Once again, the importance of determining the cation-cation distribution function in the solution is clear, but the technology for doing this needs to be further developed and refined.

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# ARTICLES

### The Temperature Invariance of the NO<sub>3</sub> Absorption Cross Section in the 662-nm Region

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Several laboratory measurements of the absorption cross section of NO<sub>3</sub> in the visible region near 662 nm have been reported. Two recent studies have indicated a possible temperature dependence for this cross section. This paper describes the results of measurements of the peak absorption cross section  $(\sigma_{NO_3}^{SO_2})$  and the integrated area  $(\sigma_{NO_3}^I)$  of the 662-nm NO<sub>3</sub> band as a function of temperature from 215 to 348 K, using Fourier transform spectroscopy. Within the error limits of this study, no dependence of  $\sigma_{NO_3}^{662}$  or  $\sigma_{NO_3}^{I}$  on temperature could be seen. It is recommended that temperature-independent values of 2.08 (±0.38) × 10<sup>-17</sup> cm<sup>2</sup> molecule<sup>-1</sup> be used for the peak cross section of the 662-nm band (15106 cm<sup>-1</sup>) and 1.95 (±0.18)  $\times 10^{-15}$  cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup> be used for the integrated band intensity (14910–15290 cm<sup>-1</sup>). When possible, the integrated area of this band should be used to quantify NO<sub>3</sub> because there is less uncertainty in the integrated band strength as compared to the peak height.

#### Introduction

The NO<sub>3</sub> radical has been identified as a key reactant in the  $NO_x$  chemistry of the atmosphere and, as such, has been the subject of a number of laboratory and field studies. In many of these studies the concentration of NO3 has been determined through its absorption maximum near 662 nm. Since the accuracy of the NO<sub>3</sub> concentration determination is directly related to this absorption cross section maximum  $(\sigma_{NO_3}^{662})$ , it is crucial that it be accurately determined.

The visible absorption spectrum of NO<sub>3</sub> was first recorded by Jones and Wolf<sup>1</sup> and has subsequently been shown by Ramsey<sup>2</sup> and by Marinelli et al.<sup>3</sup> to be completely free of rotational structure even at very high resolution. The anomalously long lived fluorescence observed<sup>4-6</sup> and the photodissociation quantum yield of zero at wavelengths longer than about 630  $\rm nm^{7,8}$  rule out predissociation in explanation of the diffuse spectrum. Nelson et al.<sup>6</sup> have suggested that this diffuseness and the long lifetime of the excited state can be attributed to mixing of the excited-state electronic levels with high vibronic levels of the ground state. Schott and Davidson,<sup>9</sup> using thermal decomposition of  $N_2O_5$ 

as the NO3 source, were the first to determine an NO3 absorption cross section. Subsequent determinations have used a variety of

TABLE I: Results of Previous Determinations of the Cross Section for the Peak of the NO<sub>3</sub> Band near 662 nm ( $\sigma_{NO_3}^{662}$ ) and the Integrated Cross Section from 14910 and 15290 cm<sup>-1</sup> ( $\sigma_{NO}^{1/3}$ )

ref	source	temp, K	$\sigma_{\mathrm{NO}_3}^{662}$	$\sigma^{\rm I}_{\rm NO_3}{}^b$		
10	$NO_x + O_3$	298	1.48	1.83		
8	$NO_x + O_3$	298	1.71	1.99		
11	$NO_x + O_3$	298	1.21	2.06		
3	$NO_x + O_3$	298	1.90	2.02		
12	$F + HNO_3 (DF^c)$	298	1.78	1.88		
16	$Cl + ClONO_2 (P^d)$	298	1.63			
13	$F + HNO_3$ (DF),	298	1.85	1.82		
	$Cl + ClONO_2(P)$					
14	$F + HNO_3 (DF)$	298	1.90	1.94		
14	$F + HNO_3 (DF)$	240	2.31	2.22		
14	$F + HNO_3$ (DF)	220	2.71	2.42		
15	$Cl + ClONO_2 (FP^e)$	298	2.28			
15	$Cl + ClONO_2 (FP)$	250	2.62			
15	$Cl + ClONO_2$ (FP)	230	2.70			
15	$F + HNO_3 (DF)$	298	1.83			
this work	$NO_x + O_3$	215-348	2.06	2.02		

 $^a \rm cm^2$  molecule<sup>-1</sup>,  $\times 10^{17}$ .  $^b \rm cm^2$  molecule<sup>-1</sup> cm<sup>-1</sup>,  $\times 10^{15}$ .  $^c \rm Discharge flow. <math display="inline">^d$  Photolysis.  $^e \rm Flash$  photolysis.

NO<sub>3</sub> sources including NO<sub>x</sub> + O<sub>3</sub>,  $^{3,8,10,11}$  F + HNO<sub>3</sub>,  $^{12-15}$  and Cl + ClONO<sub>2</sub>.<sup>13,15,16</sup> The most recent measurements of  $(\sigma_{NO_3}^{662})$  are

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Science Foundation



Figure 1. Schematic diagram of experimental apparatus used in measurement of the NO<sub>3</sub> absorption cross sections in the 662-nm region.

in good agreement although several different sources of NO3 were employed (Table I).

Since field measurements of atmospheric NO<sub>3</sub>,<sup>17-26</sup> laboratory measurements of the  $N_2O_5 = NO_2 + NO_3$  equilibrium constant, <sup>9,25,27,28</sup> NO<sub>3</sub><sup>7,8</sup> and N<sub>2</sub>O<sub>5</sub><sup>29,30</sup> photodissociation quantum yields, and NO<sub>3</sub> kinetic studies<sup>13,31,33</sup> depend on  $\sigma_{NO_3}^{662}$ , these too

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may be regarded as potentially well characterized. A question that remains is whether an absorption cross section determined near room temperature can be used without correction in measurements at other temperatures.

Two recent studies by Ravishankara and Mauldin<sup>14</sup> and Sander<sup>15</sup> have observed a strong temperature dependence with  $\sigma_{NO_3}^{662}$ increasing with decreasing temperature. If verified this dependence would have to be incorporated into field and laboratory measurements.

In this study, the NO<sub>3</sub> cross section was measured in the wavelength range from 600 to 700 nm and temperature range from 215 to 348 K. The NO<sub>3</sub> source used was O<sub>3</sub> oxidation of nitric oxide, and the  $NO_3$  concentration was modulated by passing a flow of  $NO_x$  in an excess of  $O_3$  alternatively through a heated or a cooled inlet. When the flow was through the heated inlet, the shift in the  $N_2O_5 = NO_2 + NO_3$  equilibrium drove nearly all the  $NO_x$  to  $NO_3$ . While the flow was through the cooled inlet, nearly all the  $NO_x$  existed as  $N_2O_5$ . By measurement of the change in the  $N_2O_5$  signal in the infrared and that of  $NO_3$  in the visible,  $\sigma_{\rm NO_3}^{662}$  was deduced.

#### **Experimental Section**

The apparatus used in this study is represented schematically in Figure 1. It consisted of a temperature-controlled flow tube with internal White-type cell optics, a BOMEM DA3.01 Fourier transform spectrometer capable of operation in either the infrared or visible region, and a prereactor in which  $O_3$  and NO were reacted to produce  $N_2O_5$  and  $NO_3$ .

The design of the temperature-controlled White cell will be described in detail elsewhere.<sup>34</sup> Briefly, it consisted of three concentric stainless steel tubes; the innermost with a volume of about 47 L housed the White-type cell mirrors. A temperature-regulating fluid (ethanol or ethylene glycol) was circulated through the annular space between the two inner tubes; the third tube provided an evacuable Dewar jacket. The long path cell had an optical base path of 2.000 ( $\pm 0.002$ ) m and employed mirrors in the Hanst configuration.<sup>35</sup> The mirrors themselves were gold plated for maximum infrared reflectivity and were adjusted for 48 passes, giving an optical path of 96 m. The reduced reflectivity of gold at shorter wavelengths limited these studies in the visible to wavelengths longer than 600 nm.

The mirrors were maintained at a fixed spacing and in alignment by means of three quartz rods against which the mirror mounts were held by stainless steel wires maintained under tension by springs. Once aligned, little degradation of the signal was observed when the cell was cooled to 215 K or heated to 348 K. At reduced temperatures, the temperature within the cell was found to be uniform (as measured by six thermocouples in the innermost tube) to 0.2 K, well within the stated accuracy of the thermocouple (1.7 K). At the highest temperatures employed, the uniformity was less but always within 0.5 K.

The BOMEM Fourier transform spectrometer, capable of 0.02-cm<sup>-1</sup> resolution, was operated with 5-cm<sup>-1</sup> resolution in this study. It and the transfer optics were evacuable, which eliminated interference due to water vapor in the 1600- and 3800-cm<sup>-1</sup> regions. The dynamic beam splitter alignment feature of this instrument permitted rapid changeover between the infrared and the visible regions. All absorbances reported here are base e.

The prereactor consisted of two tubes, one heated to about 410 K and the other cooled to about 260 K. The residence times in the inlets were about 12 and 5 s, respectively. The NO<sub>3</sub> and  $N_2O_5$ signals were modulated by changing the flow of a 2.57% mixture of NO in N<sub>2</sub> in an excess of ozonized oxygen from one tube to the other. The chemistry of the inlet reactors can be summarized in terms of the simplified mechanism:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{2}$$

<sup>(34)</sup> Shetter, R. E.; Davidson, J. A.; Cantrell, C. A.; Calvert, J. G., Rev. Sci. Instrum., in press. (35) Hanst, P. Adv. Environ. Sci. Technol. 1971, 2, 91.

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$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \tag{3}$$

$$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$$
 (4)

Of course there are other reactions that occur to a small degree in this system as part of the classical N2O5-catalyzed decomposition of  $O_3$  (see for example reference 36). Certainly the reactions of NO and NO<sub>2</sub> with NO<sub>3</sub> as well as the self-reaction of NO<sub>3</sub> are very important in the inlets; however, these are of minor importance in the cell. Using recommended rate constant and equilibrium constant parameters<sup>37</sup> and the fact that the inlets were maintained at 620 Torr, we can qualitatively investigate the mechanism of the modulation. As the flow is changed from the cold (260 K) to the hot (410 K) inlet, the most pronounced change occurs in the rate constant for reaction 4, which increases about  $10^7$  times. In effect, the heated reactor drives reactions 4 and 2 until much of the  $N_2O_5$  and nearly all of the  $NO_2$  are consumed. Upon entering the absorption cell, thermal equilibrium with the cell is readily established as evidenced by the consistent thermocouple readings at both ends and in the middle of the cell. Reaction rates that are characteristic of the cell temperature are also quickly established. In the cell small quantities of  $N_2O_5$  are formed by the combination of NO<sub>3</sub> with most of the remaining NO<sub>2</sub>. The concentrations of NO<sub>2</sub>, NO<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub> are within 1%of their equilibrium values soon after entering the cell as estimated by using computer simulations incorporating all the reactions pertinent to this system.

When the flow is through the cooled inlet, nearly all of the NO<sub>3</sub> formed in (2) combines with NO<sub>2</sub> with little subsequent dissociation. Upon entering the cell, thermal equilibrium is again quickly established, with the formation or dissociation of N<sub>2</sub>O<sub>5</sub> depending on the temperature of the cell relative to that of the inlet. In all experiments O<sub>3</sub> was present in excess over NO<sub>x</sub> by at least a factor of 20, and from 1–20% of the O<sub>3</sub> was consumed in the hot inlet.

Typically, a 5.0 slm (standard liter per minute) flow of ozonized  $O_2$  was mixed with from 2 to 20 sccm (standard cubic centimeters per minute) flow of a NO in N<sub>2</sub> mixture  $[2.57(\pm 0.12)\% v/v]$ . This concentration was determined by comparison of this mixture to pure nitric oxide using infrared spectroscopy as well as an instrument based on NO-O3 chemiluminescence. These two techniques gave very consistent results  $[2.54(\pm 0.12)\%$  and  $2.60(\pm 0.07)\%$ , respectively] and thus were averaged for the final concentration used in calculations for this study. The concentration of ozone in the cell with the flow through the cold inlet was in the range of  $(1.1-1.8 \times 10^{15} \text{ molecules cm}^{-3})$ . The residence time in the cell was about 12 s with a total pressure of 4-24 Torr. In one set of experiments (at 215 K) the residence time was increased by a factor of 4 and no significant difference in the value of  $\sigma_{NO_3}^{662}$ was found, thus indicating no problems with homogeneous or heterogeneous decay of  $NO_3$  or  $N_2O_5$  down the length of the cell. If decay did occur, it would not affect the cross-section determination as long as odd nitrogen (NO + NO<sub>2</sub> + NO<sub>3</sub> + N<sub>2</sub>O<sub>5</sub>) was conserved. However, if odd nitrogen was lost, a systematically low value for the NO<sub>3</sub> cross section would be obtained.

In a normal experiment the first data taken were in the infrared region with the gas flow through the heated inlet at low NO flows. The rationale was that under these conditions low levels of HNO<sub>3</sub> could be detected readily, if present. Any HNO<sub>3</sub> formed (presumably through the reaction  $N_2O_5$  with water on the cell walls) would interfere with our determinations by contributing to the  $N_2O_5$  signal as measured by the integrated band intensity from 1675 to 1775 and by reducing the total NO<sub>x</sub> available as NO<sub>3</sub> or  $N_2O_5$ . This reduction in total NO<sub>x</sub> would also give systematically low values for the NO<sub>3</sub> cross section; thus it was critical to check for this problem and eliminate the cause when necessary. In those few cases where HNO<sub>3</sub> was observed, the cell was conditioned with high NO and O<sub>3</sub> flows until no HNO<sub>3</sub> could be



Figure 2. Sample spectra of  $N_2O_5$  in the infrared spectral region at a cell temperature of 215 K, showing modulation of the signal through hot (lower) and cold (upper curve) inlets. Integrated areas of these bands were used in the NO<sub>3</sub> cross-section determinations.



Figure 3. Sample spectra of  $NO_3$  in the visible spectral region at a cell temperature of 215 K, showing modulation for flow through hot (upper) and cold (lower curve) inlets.

observed. Normally, when the system was not in use, it was maintained at a pressure above ambient and conditioning was not necessary. We estimate that, under all conditions where data were taken, HNO<sub>3</sub> accounted for less than 5% of the NO<sub>x</sub>. This is evidenced by the fact that there is no significant difference in the  $\sigma_{NO_3}^{662}$  determinations obtained with the 1250- or the 1700-cm<sup>-1</sup> band of  $N_2O_5$ , although HNO<sub>3</sub> absorption is significant only at the 1700-cm<sup>-1</sup> band. When the system was found to be free of HNO<sub>3</sub>, data were taken in the following way. With the flow through the heated inlet the infrared spectrum of the  $O_3/$  $N_2O_5/NO_2/NO_3$  mixture was recorded at several NO flows spanning a factor of nearly 10. The flow was then diverted to the cooled inlet, and the infrared spectra were recorded at the same set of flow conditions. Absorption due to NO<sub>3</sub> in the infrared spectral region was never observed as a result of its small infrared cross section, and at most cell temperatures the NO2 concentration was so low as to be undetectable. When the  $NO_2$  was present, its concentration was determined by the integrated area of the 1600-cm<sup>-1</sup> band compared to standard NO<sub>2</sub> spectra taken at the same conditions of temperature and pressure. Since O3 has a weak absorption underlying the 1725-cm<sup>-1</sup> band of N<sub>2</sub>O<sub>5</sub>, all features due to  $O_3$  were subtracted from the spectrum by using standard spectra of ozone recorded at the same temperature and pressure before the N<sub>2</sub>O<sub>5</sub> integration was performed. The pertinent information obtained from the infrared spectrum was the integrated band areas of the  $N_2O_5$  spectrum from 1220 to 1272.5 cm<sup>-1</sup> and from 1675 to 1775  $cm^{-1}$ , and the integrated band area of the O<sub>3</sub> spectrum from 990 to 1070 cm<sup>-1</sup>. Typically, the  $N_2O_5$  absorption increased by about a factor of 2 when the flow was changed from the heated to the cooled inlet (Figure 2).

The spectrometer was then converted for visible operation by changing the source, beam splitter and detector. The optical path followed by the spectroscopic probe was the same as that of the infrared source. NO<sub>3</sub> was modulated by switching from the cooled to the heated inlet at the same flows as used in taking the infrared

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Figure 4. Beer's law type plot for the peak height of  $NO_3$  at the maximum of the band in the 662 nm region. Plotted is S versus F or S from f1, f2, g1, or g2 for each of the temperatures (K) of this study. The line corresponds to the mean of the data at all temperatures, with the slope yielding the NO<sub>3</sub> cross section directly.

data. In general, the absorbance due to NO3 was weak when the flow was through the cooled inlet and increased by at least an order of magnitude when the heated inlet was used (Figure 3). When NO<sub>2</sub> was present (at elevated cell temperatures), the weak bands due to it were subtracted from the visible spectrum by using standard  $NO_2$  spectra obtained under the same conditions of temperature and pressure. Ozone also has a weak visible absorption spectrum that could interfere with absorption measurements of NO<sub>3</sub>. This was taken into account in large part by collecting the reference spectrum with the  $O_3/O_2$  mixture flowing through the cell at the same flow and pressure conditions used for the sample spectra. This procedure effectively corrects for ozone absorption as evidenced by very small absorbances near  $15\,400 \text{ cm}^{-1}$  where NO<sub>3</sub> has a very small cross section and O<sub>3</sub> has a cross section approximately half of that at its peak near 20000  $cm^{-1}$ . The modulation of the O<sub>3</sub> concentration between the hot and cold inlets was not accounted for through the use of the reference spectrum. The O<sub>3</sub> concentrations determined from the infrared spectra were used to correct the visible absorbances for this changing O3 absorbance. This resulted in an average decrease in the calculated  $NO_3$  cross section of 1.5%.

The calculation of  $\sigma_{NO}$ , depended on the reproducibility of the NO3 and N2O5 concentrations generated following changeover from the infrared. We anticipated that the reproducibility would be good since the identical gas mixtures and flow settings were employed in both parts of the experiment. Indeed, this was shown to be the case when checked by repeating the infrared measurements in a second cycle. Data taken in this way agreed with other determinations of  $\sigma_{NO_3}$  to within 10%. Another potential source of systematic error arises because of the possibility of NO<sub>3</sub> photolysis by the broad-band visible spectrometer source. While this effect would be reproducible, it would interfere with the determination of  $\sigma_{\rm NO_3}$  by reducing the NO\_3 concentration when data were taken in the visible while leaving the infrared data unperturbed. When visible spectra were taken with the spectroscopic source intensity reduced by factors of 2, 10, and 20 using neutral density filters, no increase in the NO3 absorbance was observed. Thus photolysis was not a problem, and all subsequent spectra were taken without optical filtering.

#### Results

The analysis of the data is based on Beer's law in the sense that the NO<sub>3</sub> absorbance near 662 nm and the N<sub>2</sub>O<sub>5</sub> infrared integrated absorbances must increase linearly with concentration. This expected linearity can be seen in Figure 4. As shown below, the analysis does not require an absolute concentration determination for any of the species (except for NO<sub>2</sub>, when present); rather, only the total added NO<sub>x</sub> is needed. This is determined by the NO concentration in the standard NO/N<sub>2</sub> mixture, the mass flow of this mixture and the flow of O<sub>2</sub>/O<sub>3</sub>, which are known to an accuracy of better than 5%, at the 95% confidence interval, and the cell temperature and pressure. Because of the modulation of  $N_2O_5$  and  $NO_3$  through the use of heated and cooled inlets, the measurement of four signals (for instance, the integrated  $N_2O_5$ band intensity—hot and cold—and the absorbance of  $NO_3$  at 662 nm—hot and cold) along with the nitrogen mass balance are sufficient to determine  $\sigma_{NO_3}$ .

The nitrogen mass balance is

$$[NO_x] = [NO_3] + 2[N_2O_5] + [NO_2]$$
 (a)

As mentioned above, in most experiments  $NO_2$  was below the detection limit; thus for those cases  $NO_2$  can be neglected. For each of the four signals measured, a Beer's law relationship can be written

$$[NO_3]_1 = S_1^{NO_3} / \sigma_{NO_3} \ell$$
 (b1)

$$[NO_3]_2 = S_2^{NO_3} / \sigma_{NO_3} \ell$$
 (b2)

$$[N_2O_5]_1 = S_{1_2O_5}^{N_2O_5} / \sigma_{N_2O_5} \ell$$
 (b3)

$$[N_2O_5]_2 = S_2^{N_2O_5} / \sigma_{N_2O_5} \ell$$
 (b4)

Where the subscripts 1 and 2 refer to the heated and cooled inlets, respectively, S refers to the measured absorbance (area or peak height, base e), and  $\ell$  refers to the optical path length.  $S_{NO_3}$  can be either the absorbance at 662 nm (about 15106 cm<sup>-1</sup>) or the integrated absorbance from 14910 to 15290 cm<sup>-1</sup>, and  $S_{N_2O_3}$  can be either the integrated absorbance from 1220 to 1272.5 cm<sup>-1</sup> or from 1675 to 1775 cm<sup>-1</sup>. Since the total NO<sub>x</sub> was determined by the NO flow and is not dependent on the inlet,  $[NO_x]_1 = [NO_x]_2$ . Utilizing mass balance (a), a sixth equality exists, namely

$$[NO_3]_1 - [NO_3]_2 = 2([N_2O_5]_2 - [N_2O_5]_1)$$
(c)

Substitution of the Beer's law relationships into (c) yields

$$\frac{S_1^{NO_3} - S_2^{NO_3}}{\sigma_{NO_3}\ell} = 2\left(\frac{S_2^{N_2O_5} - S_1^{N_2O_5}}{\sigma_{N_2O_5}\ell}\right)$$

or

$$\frac{\Delta S^{NO_3}}{\sigma_{NO_3}\ell} = \frac{2\Delta S^{N_2o_5}}{\sigma_{N_2O_5}\ell}$$
(d)

where  $\Delta S$  refers to the difference in the signal obtained with the hot and cold inlets, defined as to have a positive value in all cases. Substitution of (b1) and (b3) into (a) yields

$$[NO_x] = \frac{S_1^{NO_3}}{\sigma_{NO_3}\ell} + \frac{2S_1^{N_2O_5}}{\sigma_{N_2O_5}\ell}$$
(e)

Combining (d) and (e) gives

$$\sigma_{NO_3} = \frac{S_1^{NO_3} + \frac{S_1^{N_2O_3}}{\Delta S^{N_2O_3}} \Delta S^{NO_3}}{[NO_x]\ell} = \frac{\vartheta_1}{\Im}$$
(f1)

A similar expression can be written for signals obtained when the flow was diverted through the cooled inlet:

$$\sigma_{NO_3} = \frac{S_2^{NO_3} + \frac{S_2^{N_2O_3}}{\Delta S^{N_2O_3}} \Delta S^{NO_3}}{[NO_x]\ell} = \frac{\vartheta_2}{\mathcal{F}}$$
(f2)

Note that the NO<sub>3</sub> cross section can be calculated from this expression knowing only the raw signal intensities and the total NO<sub>x</sub> added (and of course,  $\ell$ ).

When  $NO_2$  is present, its concentration is determined in separate calibrations and the relationship that must be used is

$$\sigma_{\rm NO_3} = \frac{S_1^{\rm NO_3} + \frac{S_1^{\rm NO_3}}{\Delta S^{\rm N_2O_3}} \Delta S^{\rm NO_3}}{\left\{ [\rm NO_x] - [\rm NO_2]_1 - \frac{S_1^{\rm N_2O_3}}{\Delta S^{\rm N_2O_3}} \Delta [\rm NO_2] \right\} \ell} = \frac{\mathscr{S}_1}{\mathscr{G}_1} \qquad (g1)$$

Of course, a similar relationship can be written for the cooled inlet

TABLE II: Summary of Determinations of the Peak Cross Section and Integrated Cross Section for the NO<sub>3</sub> Band Near 662 nm  $(14910-15290 \text{ cm}^{-1})$  from This Study

temp, K	$[NO_x]^a$	$\sigma^{662 b}$	$\sigma^{Ic}$
348	0.436	2.06	2.27
348	0.874	1.94	2.10
348	2.62	1.97	2.13
348	3.50	2.28	2.17
348		$2.06 \pm 0.27^{d}$	$2.17 \pm 0.13^{d}$
323	0.464	1.97	2.02
323	0.928	2.07	2.15
323	1.39	2.20	2.31
323	1.86	2.26	2.28
323	2.79	2.05	2.14
323	3.72	2.24	2.19
323		$2.13 \pm 0.22$	$2.18 \pm 0.19$
298	0.976	2.03	
298	4.07	2.11	
298	0.980	2.00	1.95
298	1.54	1.97	1.99
298	2.05	2.01	2.01
298	3.08	2.08	2.12
298	4.11	2.14	2.14
298	0.512	1.80	1.93
298		$2.02 \pm 0.20$	$2.02 \pm 0.16$
271	0.563	1.97	1.97
271	1.12	2.23	2.15
271	1.69	2.13	2.01
271	2.26	2.10	2.07
271	3.38	2.10	1.93
271	4.52	1.96	1.79
271		$2.08 \pm 0.18$	$1.99 \pm 0.22$
253	0.613	2.32	
253	1.23	2.05	2.12
253	1.84	1.79	1.88
253	2.46	1.70	1.79
253	3.69	1.90	1.89
253	4.92	1.74	1.78
253		$1.84 \pm 0.43$	1.89 ± 0.25
232	1.34	2.18	2.08
232	2.02	2.23	1.99
232	2.69	2.10	1.97
232	4.04	2.09	1.88
232	5.38	2.50	2.04
232		$2.22 \pm 0.33$	$1.99 \pm 0.15$
215	0.585	2.14	2.08
215	1.17	2.20	2.00
215	1.76	1.93	1.89
215	2.34	1.93	1.81
215	2.93	1.92	1.87
215		$2.02 \pm 0.24$	$1.93 \pm 0.19$
215-348		$2.06 \pm 0.32$	$2.02 \pm 0.28$

<sup>a</sup> Molecules cm<sup>-3</sup>, ×10<sup>-13</sup>. <sup>b</sup> cm<sup>2</sup> molecule<sup>-1</sup>, ×10<sup>17</sup>. <sup>c</sup> cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup>, ×10<sup>15</sup>. <sup>d</sup> The last entry for each temperature gives the mean and  $2\sigma$  value for that temperature, for the peak cross section and the integrated area. [Note: Complete data set available as supplementary material (see paragraph at end of paper regarding supplementary material).]

data. Here,  $\Delta[NO_2]$  is defined to be  $[NO_2]_2 - [NO_2]_1$  so as to have a positive value.

$$\sigma_{NO_3} = \frac{S_2^{NO_3} + \frac{S_2^{NO_3}}{\Delta S^{N_2O_5}} \Delta S^{NO_3}}{\left\{ [NO_x] - [NO_2]_2 - \frac{S_2^{N_2O_5}}{\Delta S^{N_2O_5}} \Delta [NO_2] \right\} \ell} = \frac{\vartheta_2}{\vartheta_2} \qquad (g2)$$

Note that for (f1) or (f2) a plot of the appropriate  $\mathscr{S}$  versus the appropriate  $\mathscr{F}$  yields  $\sigma_{NO_2}$  as the slope, whereas, when NO<sub>2</sub> is present,  $\mathscr{S}$  must be plotted versus the appropriate  $\mathscr{G}$  values. Such a plot of the results for the NO<sub>3</sub> peak height at the maximum near 662 nm is shown in Figure 4. The fraction of the NO<sub>x</sub> present as NO<sub>2</sub> was a function of the total NO<sub>x</sub>, the cell temperature, and the inlet used. At the highest temperature studied (348 K), the fractions ranged from 0.18 to 0.33 for the cold inlet and from



Figure 5. Plot similar to Figure 4, for the integrated area of the  $NO_3$  band near 662 nm. The integration limits are from 14910 to 15290 cm<sup>-1</sup>.



Figure 6. Plot of mean NO<sub>3</sub> cross sections (cm<sup>2</sup> molecule<sup>-1</sup>) at the peak of the band near 662 nm versus temperature (K) ( $\bullet$ ). Error bars correspond to  $2\sigma$  (standard deviation), and the horizontal line is the mean cross section for all the data of this study. Also known are the data of Ravishankara and Mauldin ( $\Delta$ ) and Sander (O), along with linear regression lines for their data.

0.14 to 0.15 for the hot inlet. Similarly, at 323 K, the fractions ranged from 0.09 to 0.23 and from 0.02 to 0.04. Finally, at room temperature (298 K) the fractions ranged from 0.03 to 0.05 for the cold inlet and were less than 0.01 for the hot inlet. At all other temperatures the fraction of  $NO_x$  as  $NO_2$  was less than 0.01. This measurement does increase the overall uncertainty in the cross sections calculated for these temperature when  $NO_2$  is present; however, in the worst case this uncertainty is less than 3%, based on a 10% uncertainty in the  $NO_2$  measurement.

The results of this study are summarized in Table II. Four determinations of the NO3 cross section at 662 nm and the integrated cross section are made for each set of flow conditions at a given temperature. These are from the appropriate f or g equations for data from the two  $N_2O_5$  bands. The numbers in Table II are the average of these four determinations. Figure 4 shows a plot of S versus  $\mathcal{F}$  or  $\mathcal{G}$ , whichever is appropriate, for each temperature studied. For a given temperature the slope of the line gives the  $\sigma_{NO_3}^{662}$  at that temperature. Figure 5 is a similar plot for the integrated cross section of the 662-nm band. The constancies of the peak intensity and the integrated area are shown by the scatter of the data about the lines (which are the mean values for the determination at all temperatures). In Figure 6, the average of all determinations of  $\sigma_{NO_3}^{662}$  at each temperature is plotted versus temperature. The horizontal line is the average of all our determinations. Also shown are the data of Ravishankara and Mauldin, and Sander, along with linear regression lines of their results. The room temperature values are in excellent agreement. Except for the lowest temperatures employed, all determinations agree within the error limits given. The previous workers concluded that the  $\sigma_{NO_1}^{662}$  increases with decreasing temperature, whereas the results obtained in this study show no

apparent temperature effect within the uncertainty of the determinations. It should be pointed out that a slight systematic wavelength shift was observed in the location of the peak of 662-nm band. The band peak was shifted to higher energies by a few reciprocal centimeters at 215 K relative to 348 K. This effect will be discussed in more detail in another report.

Ravishankara and Mauldin used the F + HNO<sub>3</sub> reaction as the NO<sub>3</sub> source and measured the NO<sub>3</sub> absorbance with a tunable dye laser. The  $NO_3$  concentration was determined by titration with NO. Sander generated NO<sub>3</sub> by the  $F + HNO_3$  and Cl +ClONO<sub>2</sub> reactions in a flow system or by the flash photolysis of  $Cl_2$ -ClONO<sub>2</sub> mixtures. In the flow system Sander titrated the NO<sub>3</sub> with 2,3-dimethyl-2-butene or NO, with the former being preferred. In the flash photolysis system the initial [NO<sub>3</sub>] was equated to the [ClONO<sub>2</sub>] loss by using published ClONO<sub>2</sub> absorption cross sections. As noted by Sander, all of these systems have the possibility for systematic error. In the flow systems this arises because of the possibility of F or Cl atom regeneration through secondary chemistry. The flash photolysis system suffers from the reliance on ultraviolet ClONO<sub>2</sub> cross sections, the possibility of interfering absorption in the ultraviolet, and the possibility of interfering secondary chemistry. Indeed, the cross sections obtained by the two techniques differed significantly with a room temperature value of  $1.83 \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> obtained in the flow system compared with  $2.28 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ for flash photolysis. For reasons discussed in his paper, Sander preferred the higher of these determinations. In both of these studies it was observed that the absorption cross section increased with decreasing temperature although Mauldin and Ravishankara found a somewhat larger fractional increase than Sander.

The apparatus and approach used in the present study has several advantages: (1) The chemistry involved in the  $N_2O_5$ catalyzed decomposition of O<sub>3</sub> has been well characterized in many studies made over a 50-year period.<sup>36</sup> (2) No complications were introduced in this experiment by the addition of titrants, and thus the possibility of secondary unknown chemistry was minimized. (3) Measurements in both the visible and infrared regions allowed detection of all  $NO_x$  species as well as interfering species (for example, HNO<sub>3</sub>). (4) The  $N_2O_5$ -NO<sub>3</sub> modulation permits the determination of  $\sigma_{NO_3}$  without recourse to absolute concentration determinations for NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, although flow and pressure calibrations are required. The only possible source of systematic error that we could identify was the loss of NO<sub>3</sub> (and/or  $N_2O_5$ ) through formation of HNO<sub>3</sub> or other unidentified adsorbed species, and as noted above, efforts were taken to minimize this error. If irreversible adsorption losses were significant, one would expect these to increase with temperature decrease and lead to an underestimate of the cross section of NO<sub>3</sub>. While irreversible adsorption at the walls could account for the lack of temperature dependence, we feel that it is unlikely.

Due to the fact that the room temperature determinations of several recent studies all overlap, we recommend that a temperature-independent value for  $\sigma_{NO}^{662}$ , of  $(2.08 \pm 0.38) \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> (base e) be employed in field and laboratory absorption measurements of  $NO_3$ . This value is the average of the present study and the results at 298 K of the two most recent studies<sup>14,15</sup> and is consistent with most other recent determinations within their stated error limits. Although one might perceive a small decrease in  $\sigma_{NO_3}^I$  from the highest to the lowest temperature studied, it is not statistically significant, given the uncertainty associated with the mean at each temperature. Therefore, we also recommend a temperature-independent value for  $\sigma_{NO_3}^i$  of (1.95  $\pm 0.18$ )  $\times 10^{-15}$  cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup> be used. This value is the average of all values derived from the room temperature measurements of the integrated area (14910-15290 cm<sup>-1</sup>) shown in Table I.

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Supplementary Material Available: Table containing complete data set for determinations of the peak cross section and integrated cross section for the NO<sub>3</sub> band near 662 nm (1 page). Ordering information is given on any current masthead page.

## Hydrogen-Bond Theories and Models Based on Nuclear Quadrupole Resonance Spectroscopy Studies

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An analysis is presented of the results of the <sup>35</sup>Cl NQR investigation (frequencies at 77 K) of 63 hydrogen-bonded complexes of trichloroacetic acid (TCA) with various organic bases (B) from very weak to very strong ones. A characteristic sigmoidal curve  $\Delta \bar{\nu}_0 = f(\Delta p K_a)$  was obtained by determining the <sup>35</sup>Cl NQR frequencies for two boundary hydrogen-bond forms: the covalent and fully ionic ones. The NQR results were interpreted on the basis of the models with one or two minima in the proton potential energy curve as well as in terms of the charge-transfer theory of hydrogen bonding. The process of proton transfer in the hydrogen bond was analyzed. Some important parameters determining the hydrogen-bond nature in TCA-B complexes were obtained. A general applicability of NQR spectroscopy in investigations of hydrogen-bond nature was discussed.

#### 1. Introduction

Hydrogen bonding (A-H...B) is an interaction between a covalently bound H atom (A-H), with some tendency to be donated, and a region of high electron density on an electronegative atom or group of atoms (B), which can accept the proton.<sup>1-8</sup> The hydrogen bond is said to be intramolecular or intermolecular; that is whether the atoms (or groups of atoms) A and B belong to the

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