

## The Far-Infrared Spectrum of N<sub>2</sub>O<sub>5</sub> in the Gas Phase

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The far-infrared spectrum of N<sub>2</sub>O<sub>5</sub> at room temperature in the gas phase has been recorded. A broad, weak feature with its maximum near 50 cm<sup>-1</sup> was found and its intensity determined to be 1.20(10)% of that of the band at 350 cm<sup>-1</sup>. The latter band, in turn, has a band intensity approximately 0.33 that of the band at 1250 cm<sup>-1</sup>. © 1989 Academic Press, Inc.

### INTRODUCTION

The oxides of nitrogen are significant participants in the complex chemistry that leads to the destruction of atmospheric ozone. In particular, N<sub>2</sub>O<sub>5</sub> plays an important part in the photochemistry of odd nitrogen (NO<sub>x</sub>) (1). This is especially true in the polar night where it is believed to have a significant effect on the formation of the Antarctic ozone hole. As a result, there has been substantial recent interest in spectroscopically based methods for monitoring the global distribution of its concentration (2-8).

An observation of absorption due to dinitrogen pentoxide, N<sub>2</sub>O<sub>5</sub>, in the atmosphere was reported in 1986 by Toon *et al.* (9). ATMOS data from 1985 recorded at sunrise revealed the broad profile of a stretching band of N<sub>2</sub>O<sub>5</sub> between 1230 and 1260 cm<sup>-1</sup> with a peak concentration at an altitude of ca. 31 km. This observation stimulated the search for the far-infrared absorption of N<sub>2</sub>O<sub>5</sub>, since the possibility was suggested of monitoring N<sub>2</sub>O<sub>5</sub> in the submillimeter or far-infrared region. No far-infrared spectrum of N<sub>2</sub>O<sub>5</sub> had previously been reported.

The only attempt at a full vibrational assignment of N<sub>2</sub>O<sub>5</sub> was published in 1962 by Hisatsune *et al.* (10). Since then, two of the bands they observed have been shown by Lovejoy *et al.* (7) to overlap with absorptions of HNO<sub>3</sub>, although Hisatsune's

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original identification of the bands has been confirmed (2). There are thus five strong bands (associated with eight modes) and two weaker ones unambiguously attributable to  $\text{N}_2\text{O}_5$  fundamentals (2, 7, 10) and three modes that would be candidates for absorptions in the far infrared: the bending mode at the central oxygen and the symmetric and asymmetric twisting modes of the two  $\text{NO}_2$  groups. The symmetric twisting mode can only be infrared-active if the equilibrium configuration is nonplanar. A detailed analysis of electron diffraction data, based on a dynamical model, was carried out by McClelland *et al.* (11) and led to predictions of the antisymmetric twisting vibrational fundamental at  $45\text{--}55\text{ cm}^{-1}$  and the symmetric twisting mode at  $55\text{--}75\text{ cm}^{-1}$ . The NON bending mode was predicted by Hisatsune to lie at  $104\text{ cm}^{-1}$ , and from combination bands in the solid state spectrum he deduced a value of  $85\text{ cm}^{-1}$ . Values as high as  $160\text{ cm}^{-1}$  would be consistent with gas phase entropy measurements (10). Since the analysis of McClelland *et al.* (11) indicates the NON equilibrium angle to be  $111.8(16)^\circ$ , this is not likely to be a large amplitude bending motion. The twisting vibrations, on the other hand, most certainly are anharmonic and of large amplitude (11).

#### EXPERIMENTAL DETAILS

A sample of  $\text{N}_2\text{O}_5$  was prepared by ozonolysis of  $\text{NO}_2$  according to Ref. (12) and further purified by trap-to-trap distillation in a stream of  $\text{O}_2/\text{O}_3$ . With a Fourier transform infrared spectrometer we tried to measure, in the far-infrared region, a high-resolution spectrum of this sample of  $\text{N}_2\text{O}_5$ . Both a static sample and a flow system were tried, but the decomposition products  $\text{NO}_2$  and  $\text{HNO}_3$  developed rapidly and both have absorptions which are very strong relative to the far-infrared absorption of  $\text{N}_2\text{O}_5$ . It was not possible to obtain a spectrum which would reveal, between the dense, strong spectral features of the decomposition products, the presumably poorly defined structure that was all that we hoped to find in the  $\text{N}_2\text{O}_5$  spectrum at room temperature. Spectrum subtraction proved intractable at high resolution due to the low signal-to-noise ratio and due to the widely different time dependence of the various molecular components of the spectrum. We did not have spectra of pure  $\text{NO}_2$  or  $\text{HNO}_3$  to use for subtraction and could only subtract later spectra from earlier spectra. However, at low resolution we were able to obtain a spectrum showing the far-infrared absorption of  $\text{N}_2\text{O}_5$ .

The spectra shown in Fig. 1 were recorded in a 270-cm Pyrex cell with polyethylene windows, containing initially 7.5 mbar of  $\text{N}_2\text{O}_5$  at room temperature. A Bruker IFS 120 HR interferometer was used with a  $12\text{-}\mu\text{m}$  Mylar beamsplitter and a liquid-He-cooled silicon bolometer as detector (13). Spectra were recorded alternately at 1.0 and  $0.1\text{ cm}^{-1}$  resolution at intervals of about 12 min (the time required for 100 scans at each resolution) over the next 24 hr. Spectrum (a) in Fig. 1 was recorded immediately after filling the cell; it is shown expanded to emphasize the low wavenumber band. The band at  $350\text{ cm}^{-1}$  is so strong that there was zero transmission above  $320\text{ cm}^{-1}$ . Spectrum (b) in Fig. 1 was recorded after 15.5 hr, by which time the strong band at  $350\text{ cm}^{-1}$  had decreased sufficiently to be no longer saturated.

The absorptions of the decomposition products dominated the far-infrared region at the end of the measurement period, as can be seen in spectrum (b) of Fig. 1. The

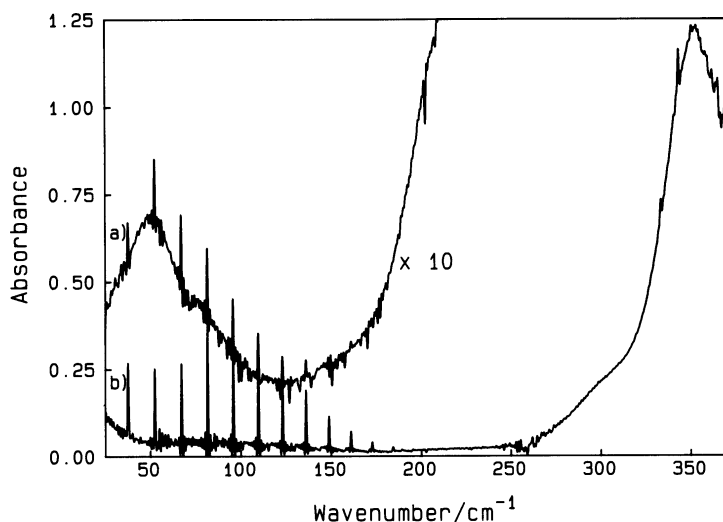


FIG. 1. Spectra of  $N_2O_5$  in (decadic) absorbance, as recorded at an initial pressure of 7.5 mbar, path length 270 cm, at room temperature, and  $1.0\text{ cm}^{-1}$  resolution. (a) Spectrum immediately after filling the cell, expanded relative to the absorbance scale by a factor of 10. (b) Spectrum of same sample after 15.5 hr in the cell.

prominent  $Q$  branches are due to  $NO_2$  and the rise at low wavenumber is due to  $HNO_3$ . The sharp features on the band at  $350\text{ cm}^{-1}$  are due to  $DNO_3$  (14) and reflect the efficiency of  $N_2O_5$  in pulling water off the walls, including  $D_2O$  from a previous experiment in the same cell.

#### EVALUATION OF THE SPECTRA

In order to obtain as clear a picture as possible of the  $N_2O_5$  band at  $50\text{ cm}^{-1}$ , the absorption due to the decomposition products was compensated by spectrum subtraction; the results are shown in Fig. 2. Since spectra of  $NO_2$  and  $HNO_3$  were not recorded independently under comparable conditions, the spectrum subtraction was done by subtracting a fraction of the absorbance of a later spectrum, in which all the decomposition products are strong while the  $N_2O_5$  absorbance has decreased, from the first spectrum. Accordingly, spectrum (a) of Fig. 2 was obtained by subtracting from spectrum (a) in Fig. 1 only 0.08 times a spectrum (not shown) recorded 5 hr after the first spectrum. Since after these 5 hr the  $NO_2$  absorbance had increased 12-fold, while the  $N_2O_5$  absorbance had decreased by about one-half, this subtraction eliminated all of the  $NO_2$  absorbance but only 0.04 of the  $N_2O_5$  absorbance. (The residual positive and negative  $NO_2$   $Q$  branches show the limitations of this subtraction procedure in the present experiment.) In order to present a version of spectrum (b) that is at least visually free of  $NO_2$  and  $HNO_3$  absorptions, a small fraction (0.15, determined from the region at  $220\text{ cm}^{-1}$  where the absorbance of the decomposition products is weak) of the "cleaned" spectrum of  $N_2O_5$  was then subtracted from spectrum (b) in Fig. 1. This gave a spectrum of the decomposition products alone after 15.5 hr. This in turn was subtracted from the original spectrum (b) in Fig. 1 to yield spectrum (b) in Fig.

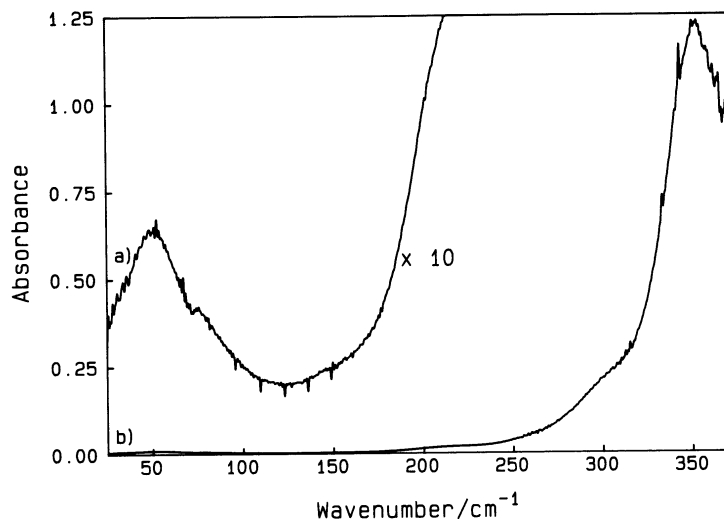


FIG. 2. Spectra of  $N_2O_5$  as in Fig. 1, but with spectra of decomposition products subtracted off up to  $320\text{ cm}^{-1}$ . (a) Spectrum immediately after filling the cell, expanded relative to the absorbance scale by a factor of 10. Residual sharp features are incompletely compensated  $NO_2$ . (b) Spectrum of same sample after 15.5 hr. Residual sharp features on band at  $350\text{ cm}^{-1}$  are due to  $DNO_3$ .

2. The subtraction could only be carried out up to  $320\text{ cm}^{-1}$ , since the band at  $350\text{ cm}^{-1}$  was saturated above that wavenumber in spectrum (a) which was the basis of the subtraction. Spectrum (b) is thus identical above  $320\text{ cm}^{-1}$  in Figs. 1 and 2.

The relative time dependence of the  $N_2O_5$ ,  $NO_2$ , and  $HNO_3$  absorbances was used to estimate the purity of the sample at the time of the first spectrum (Fig. 1a), immediately upon filling the cell. The spectrum recorded after 5 hr, which was used to subtract off the decomposition products, showed  $NO_2$  absorbance 12.5 times as intense as that in the first spectrum and  $N_2O_5$  absorbance 0.562 times as intense as that in the first spectrum. The  $HNO_3$  absorbance was twice as strong after 5 hr. Assuming that each molecule of  $N_2O_5$  decomposes to give two molecules of  $NO_2$  or two molecules of  $HNO_3$ , then for a given amount of  $HNO_3$  at the beginning we can calculate the concentrations of the components  $NO_2$  and  $N_2O_5$ . Thus, if there was no  $HNO_3$  in the sample at the time of the first spectrum we had 92.9%  $N_2O_5$ , or 83%  $N_2O_5$  if there was 10%  $HNO_3$ , or 75%  $N_2O_5$  if there was 20%  $HNO_3$ . Since the original sample had been carefully purified, and the cell and inlet system had been exposed to  $N_2O_5$  periodically over several days, we do not believe that there was more than 20%  $HNO_3$  in the cell, so that our initial sample in this set of spectra should have been at least 75% pure. However, since direct comparison spectra of pure  $NO_2$  and  $HNO_3$  were not made, we will not claim a higher sample purity than that claimed in, for example, Ref. (7), which was 70%.

Although measurements of the spectral positions rather than band intensities were the main thrust of this work, estimates of their intensities are useful for the purpose of evaluating the suitability of the features around 50 and  $350\text{ cm}^{-1}$  for remote sensing applications. Similar requirements have led to a number of laboratory measurements of the near- and midinfrared bands of  $N_2O_5$  (2-8).

First a rough measurement of the absolute band intensity of the 350-cm<sup>-1</sup> band was carried out. Because of its strong absorbance, this band was first observed in a 19-cm-long cell fitted with polyethylene windows and filled to a total pressure of 2.08 Torr (2.78 mbar). Under these conditions an absorbance of ca. 0.27 was measured. As in all N<sub>2</sub>O<sub>5</sub> experiments, the largest uncertainty is sample purity and decomposition. Although this measurement was made in a different cell than the main series of spectra, the gas handling was similar to that described above, and we can take the fractional concentration of N<sub>2</sub>O<sub>5</sub> for this measurement to be similar to that derived above, at least 0.70. From this we calculate that the integrated band intensity of the 350-cm<sup>-1</sup> band is ca. 0.33 that of the 1250-cm<sup>-1</sup> band, although if one defined more of the absorption below 350 cm<sup>-1</sup> (and presumably above, where we did not record spectra) a somewhat larger value would be obtained. If the value of  $4.01 \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup> of Cantrell *et al.* (2) for the integrated band intensity of the 1250-cm<sup>-1</sup> band is adopted, the integrated band intensity of the 350-cm<sup>-1</sup> band is about  $1.32 \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup>.

The spectrum which shows the 50-cm<sup>-1</sup> band clearly, Fig. 2a, only extends to 320 cm<sup>-1</sup> and does not show the band at 350 cm<sup>-1</sup>. In Fig. 2b, the band at 50 cm<sup>-1</sup> can be measured when the scale is expanded, but the actual subtracted spectrum file only extends up to 320 cm<sup>-1</sup>. In order to compare the intensities of the two bands, we compared the maxima of both to a point in the N<sub>2</sub>O<sub>5</sub> spectrum which appears in both spectra (a) and (b). At 188.5 cm<sup>-1</sup> the absorbance is the same as that at 50 cm<sup>-1</sup>. At this position, there is no distortion of the spectrum due to the decomposition products. This was confirmed from inspection of the spectra recorded at 0.1 cm<sup>-1</sup> resolution. The intensities at 188.5 and at 350 cm<sup>-1</sup> were then compared in the spectrum shown in Fig. 1b from which the decomposition products had not been subtracted, so that no distortion could have been introduced. We obtained the intensity of the maximum at 50 cm<sup>-1</sup> as 1.20(10)% of the absorbance at 350 cm<sup>-1</sup>. Assuming a similar band width for the two bands, this corresponds to an integrated band intensity of  $1.59 \times 10^{-19}$  cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup>.

From the point of view of molecular dynamics, the question remains as to the identity of the observed feature. None of the three low-lying modes of N<sub>2</sub>O<sub>5</sub> is expected to exhibit a large change in dipole moment, so that none of them is expected to have a strong fundamental band. For a planar equilibrium configuration, only two of them would be infrared-active. The position and extent of the observed far-infrared absorption of N<sub>2</sub>O<sub>5</sub> coincide very well with the predictions of McClelland *et al.* (11) for the antisymmetric twisting mode. The broad, shapeless profile is consistent with an anharmonic mode. The dip at 70 cm<sup>-1</sup> correlates unfortunately with a difference between our two background spectra (before and after the measurements) at the position of a polyethylene absorption in the windows. The dip is clearly visible in the N<sub>2</sub>O<sub>5</sub> spectrum no matter which of the two backgrounds we use, but it is at most twice the amplitude (0.5%) of the background variation. If we consider the dip to be an artifact, and not an indication of *P*, *Q*, *R* structure or two bands, then the only indication of more than one band in this region would be the high wavenumber tail of the band at 50 cm<sup>-1</sup>. The higher wavenumber component might be the symmetric twisting mode or the NON bending mode, although this latter transition is expected to be somewhat higher. The shoulders below the 350-cm<sup>-1</sup> band, at 300, 260, and 220 cm<sup>-1</sup>, are most easily explained as difference bands with the anharmonic mode at 50 cm<sup>-1</sup>.

## ACKNOWLEDGMENTS

The work in Giessen was supported in part by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. This work was also supported by NASA. The authors thank Klaus Lattner for his expertise and assistance in obtaining the spectra.

RECEIVED: February 27, 1989

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