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A Fourier-transform Infrared Investigation of the Gas-phase Photolysis of Nitrous Oxide at 184.9 nm

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The nitrous oxide actinometer at 184.9 nm has been investigated using Fourier-transform infrared spectroscopy as both a quantitative technique to determine $\Phi_{NO}^{184.9}$ and as a qualitative analytical method to observe secondary photoproducts in the system. The quantum-yield value of 1.0 ± 0.2 for $\Phi_{NO}^{184.9}$ obtained in this work must be regarded as a lower limit, because unquantifiable amounts of NO_2 and BrNO were formed in the photolysis cell over the data collection period. In view of these results, the reported value for $\Phi_{NO}^{184.9}$ of 1.2 using chemiluminescence methods is recommended in preference to values of *ca.* 0.82 obtained by mass spectrometry.

Nitrous oxide is one of the most commonly used actinometers in the vacuum-ultraviolet region,[1] with the quantum yield of its molecular nitrogen photoproduct at 184.9 nm, $\Phi_{N_2}^{184.9}$, measured as 1.44 ± 0.11.[2] However, literature reports for the nitric oxide quantum yield are in poor agreement and appear to depend on the method of analysis: mass-spectrometric determinations give $\Phi_{NO}^{184.9}$ as 0.82[3] and 0.81 ± 0.08,[4] while chemiluminescence methods have resulted in a value of 1.2.[5] The data from the latter experiments are supported by consideration of the mechanism for N_2O photochemistry and recent rate-constant calculations by the CODATA Task Group[6] on chemical kinetics, as outlined below.

Excitation of nitrous oxide at 184.9 nm into its first excited $^1B_2(^1\Delta)$ level produces $O(^1D_2)$ atoms with a quantum yield of unity[6] *via* the reaction

$$N_2O(^1\Delta) \rightarrow N_2(^1\Sigma_g^+) + O(^1D_2). \qquad (1)$$

The excited oxygen atoms go on to react with ground-state nitrous oxide *via* either reaction (2*a*) or (2*b*):

$$\begin{tikzcd} & N_2(^1\Sigma_g^+) + O_2(\text{singlet}) \qquad (2a) \\ O(^1D_2) + N_2O(^1\Sigma^+) \arrow[ur] \arrow[dr] & \\ & NO(^2\Pi) + NO(^2\Pi). \qquad (2b) \end{tikzcd}$$

The efficiency of reaction (2*b*) has recently been shown to depend upon the relative orientation of N_2O molecules in molecular-beam experiments[7] and in an argon matrix at 4.2 K.[8] In fact, the rate constant ratio, $k_{2b}/(k_{2a}+k_{2b})$, has a recommended value of 0.617 ± 0.015 based on the work of Marx *et al.*,[9] who used chromatographic and chemiluminescent detection methods to determine the N_2, O_2 and NO photoproducts. This corresponds to a yield of 1.23 ± 0.03 NO molecules for each N_2O molecule consumed by $O(^1D_2)$ in reaction (2*b*). Therefore a value of 1.23 ± 0.03 for $\Phi_{NO}^{184.9}$ can be obtained directly from the ratio $k_{2b}/(k_{2a}+k_{2b})$, as physical and chemical deactivation of $O(^1D_2)$ atoms to $O(^3P)$ atoms in the system is negligible:[10]

$$O(^1D_2) + N_2O \rightarrow O(^3P) + N_2O. \qquad (3)$$

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This evaluation is in good agreement with the value for $\Phi_{NO}^{184.9}$ of 1.2 given by Simonaitis and Heicklen,[5] but is much different from the mass-spectrometric determinations.[2,3] The aim of the present work was to investigate the N_2O actinometer using Fourier-transform infrared spectroscopy as both a quantitative technique to determine $\Phi_{NO}^{184.9}$ and as a qualitative analytical method to observe secondary photoproducts in the system, which might reduce the mass-spectrometry value from its theoretical prediction.

Experimental

Fourier-transform infrared spectra of the nitrous oxide actinometer system were obtained on a Digilab FTS 20V spectrometer using a mercury cadmium telluride detector cooled to 77 K. 1000 interferograms were collected and co-added at a spectral resolution of 0.2 cm^{-1} for each photolysis experiment. The resultant interferogram was zero-filled two-fold, boxcar-apodised and Fourier-transformed by the spectrometer mini-computer.

Two T-configuration gas cells constructed from Pyrex glass were used. The first was fitted with a pair of KBr windows separated by a pathlength of 102 ± 1 mm. Vacuum-u.v. photolysis was performed through a third window made of Spectrosil B. The photolysis pathlength was 50 ± 1 mm and the volume of the cell determined as 180 ± 1 cm^3. The second cell was fitted with silicon windows for infrared transmission and separated by 110 ± 1 mm. A Spectrosil B window was also fitted, giving a photolysis pathlength of 50 ± 1 mm and a cell volume determined as 160 ± 1 cm^3.

A low-pressure mercury arc (Phillips Spectral LL, 93109) was used for photolysis. The lamp housing was flushed with oxygen-free nitrogen (B.O.C.) at a pressure of 10 p.s.i.† to prevent the photodissociation of atmospheric oxygen[11] leading to formation of an ozone u.v. filter at 184.9 nm.

A quadrupole mass spectrometer (VG Gas Analysis Ltd, model SX300) was used to assess the purity of gas samples and to determine the partial pressure of nitrogen resulting from photolysis of nitrous oxide. In all the actinometry experiments, 200.0 Torr‡ of N_2O, which absorbs over 99% of the incident radiation at 184.9 nm, was photolysed for measured intervals of time.[12] 1.00 Torr Ar was also added as an internal standard in the mass-spectrometry experiments. Argon was chosen for two main reasons: first it does not interfere with secondary chemical reactions involving $O(^1D_2)$ and N_2O; secondly it does not physically deactivate $O(^1D_2)$ to $O(^3P)$.[13] The amounts of nitrogen formed for set photolysis times were calculated by the measurement of the ratio of the peak intensities at $m/e = 28$ and $m/e = 40$ and comparison of the results with a calibration graph obtained for the relative mass-spectrometric sensitivities of N_2 and Ar at known partial pressures. Atmospheric leakage was negligible over the time taken for the experiment.

The vacuum line was constructed from Pyrex glass, pumped by a silicone oil diffusion pump (Edwards 704) and fitted with Young's greaseless Teflon stopcocks. Gas pressures were measured using a Wallace-Tiernan vacuum gauge (model FA 141) and an MKS baratron capacitance manometer (model 310).

Nitrous oxide (stated purity 99.997%) was supplied by B.D.H.; it was thoroughly degassed at 77 K and used without further purification. Nitrogen (stated purity 99.998%) and nitric oxide (stated purity 99.0%) were obtained from Matheson. Argon (stated purity 99.999%) was manufactured by Messer Griesheim GMBH. Mass spectra of the gases revealed no impurity leaks.

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† 1 p.s.i. ≈ 703.1 kg m^{-2}.

‡ 1 Torr = 101 325/760 Pa.

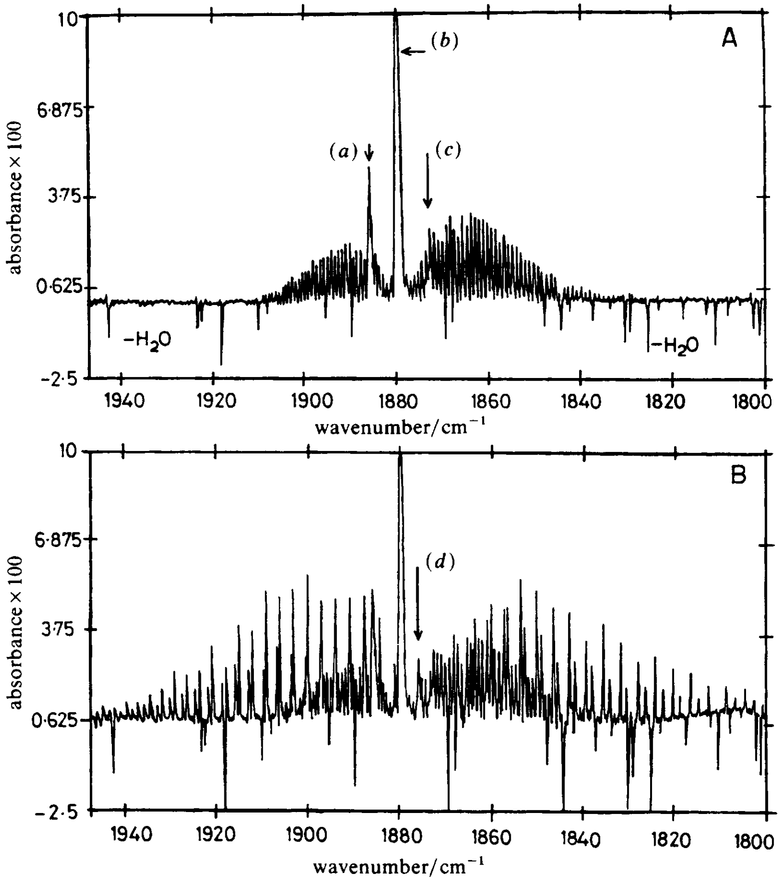

Fig. 1. Absorbance plot of the infrared spectrum of 200.0 Torr N_2O over the 1950-1800 cm^{-1} region at a spectral resolution of 0.2 cm^{-1}: (A) before photolysis; (B) immediately after 1.50 h of photolysis at 184.9 nm. (*a*) Q branch of $\nu_1+2\nu_2^2-\nu_2^1$, (*b*) Q branch of $\nu_1+\nu_2^1$, (*c*) Q branch of $\nu_1+2\nu_2^0-\nu_2^1$ and (*d*) Q branches of the main sub-band of the 1-0 band of NO.

Results

An absorbance plot of the F.t.i.r. spectrum of 200.0 Torr N_2O over the region 1950-1800 cm^{-1} at a spectral resolution of 0.2 cm^{-1} is shown in fig. 1(A). Negative peaks are due to the ν_2 band of H_2O and the assignments of the N_2O absorptions[14] are as follows: (*a*) 1886.0 cm^{-1}, Q branch of the $\nu_1+2\nu_2^2-\nu_2^1$ band; (*b*) 1880.3 cm^{-1}, Q branch of the $\nu_1+\nu_2^1$ band; (*c*) 1873.2 cm^{-1}, Q branch of the $\nu_1+2\nu_2^0-\nu_2^1$ band. An absorbance plot of the F.t.i.r. spectrum taken immediately after 1.50 h of photolysis at 184.9 nm of 200.0 Torr nitrous oxide is shown in fig. 1(B). The Q branches of the $^2\Pi_{1/2}$-$^2\Pi_{1/2}$ and $^2\Pi_{3/2}$-$^2\Pi_{3/2}$ sub-bands of the 1-0 band of nitric oxide are clearly observed (*d*).[15] Additional absorptions are seen in the 1575-1650 cm^{-1} region and are assigned to the ν_3 antisymmetric stretch of nitrogen dioxide[16] (fig. 2). The contour of the R branch of the ν_3 band of NO_2 has a discontinuity at 1634.8 cm^{-1} where it is superimposed on the Q branch of the ν_3-ν_1^1 'hot' band of N_2O. No additional absorptions were seen in the infrared spectrum taken immediately after photolysis in the KBr cell, apart from those mentioned above. After 12.00 h storage of the photolysis mixture an absorption at

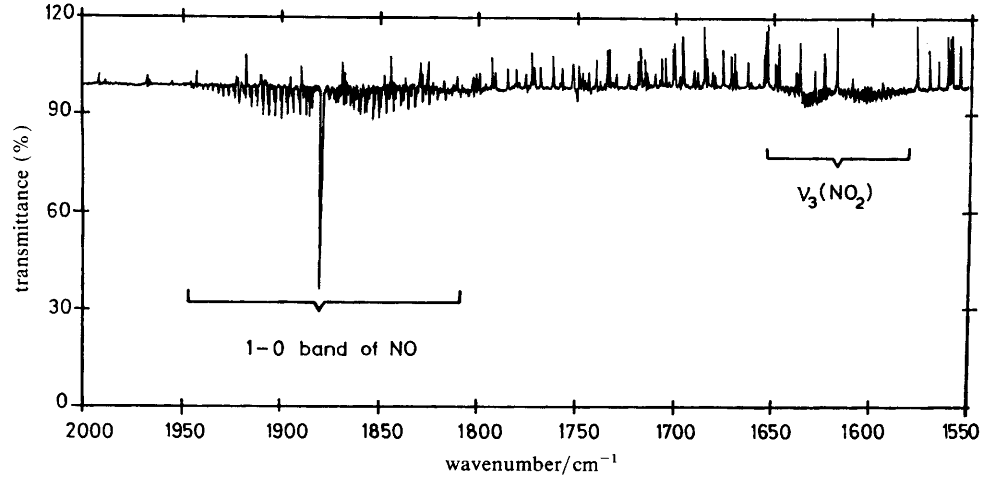

Fig. 2. Transmittance plot of the infrared spectrum of 200.0 Torr N_2O over the 2000-1550 cm^{-1} region at a spectral resolution of 0.2 cm^{-1} taken immediately after 1.50 h photolysis at 184.9 nm.

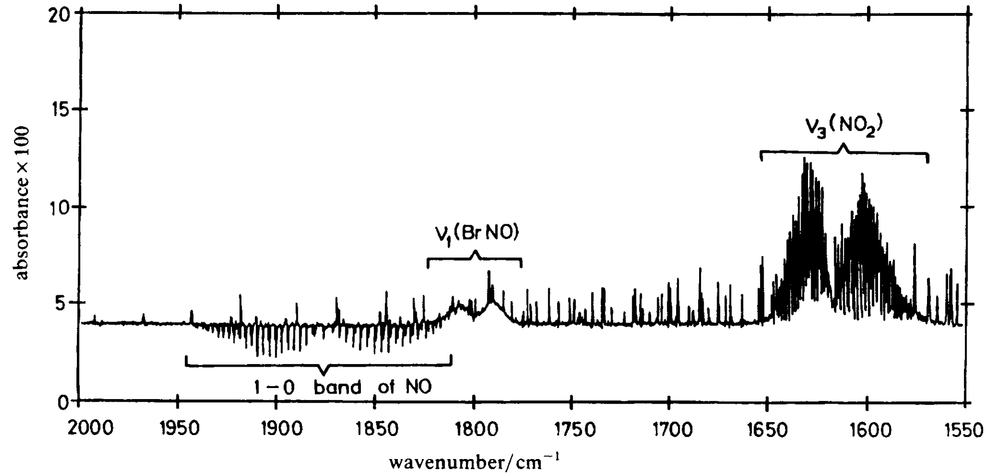

Fig. 3. Absorbance subtraction plot of the absorbance spectrum taken immediately after photolysis from the absorbance spectrum taken after 12.00 h storage of the mixture.

1360 cm^{-1} was observed which was assigned to the antisymmetric stretch of nitrate anion[17] impurity that was produced on the potassium bromide infrared windows. Furthermore, the 1-0 band of NO decreased in intensity, the ν_3 band of NO_2 increased in intensity and a broad feature centred on 1799.0 cm^{-1} was observed and is assigned to nitrosyl bromide.[18] These results are summarised in fig. 3. An absorbance plot of NO_2 monitored at 1623 cm^{-1} *vs.* storage time, *t*, showed that the nitrogen dioxide concentration extrapolated to $t = 0$ is very small (*ca.* 1×10^{-2} absorbance units). These observations show that the NO_2 originates from the oxidation of NO, presumably by reaction with the O_2 photoproduct, which is not observable in the infrared spectra. The production of BrNO was eliminated in the silicon-windowed cell, but interference fringes were observed in the spectra, making quantitative measurement of NO difficult.

At a spectral resolution of 0.2 cm^{-1} the determination of the NO concentration from the infrared spectrum must be based either on the intensity of individual vibration–

Table 1. Maximum observed absorbances of some vibration-rotation lines[a] of the $^2\Pi_{1/2}$-$^2\Pi_{1/2}$ sub-band of the 1-0 band of NO in the infrared spectra of NO-N_2O gas mixtures

line	frequency of peak maximum[b] /cm^{-1}	maximum observed absorbance (×10^2)			200.0 Torr N_2O sampled immediately after 1.50 h
		0.70 Torr NO+ 200.0 Torr N_2O[c]	0.80 Torr NO+ 200.0 Torr N_2O[c]	0.90 Torr NO+ 200.0 Torr N_2O[c]	
P (6.5)	1853.7424	6.09 (0.92)	6.39 (0.96)	7.29 (1.10)	6.63
P (7.5)	1850.1762	5.67 (0.89)	6.31 (0.98)	7.09 (1.11)	6.41
P (8.5)	1846.5752	5.23 (0.92)	5.98 (1.05)	6.63 (1.16)	5.70
P (9.5)	1842.9408	4.65 (0.86)	5.20 (0.96)	6.14 (1.13)	5.42
R (6.5)	1900.0764	6.19 (0.90)	6.82 (0.99)	7.92 (1.15)	6.90
		(0.90 ± 0.05)	(0.99 ± 0.07)	(1.13 ± 0.05)	

[a] All lines are unresolved doublets on account of Λ-type doubling. The separation is less than the linewidths. [b] Taken from ref. (15). [c] The value in parentheses is the maximum observed absorbance of NO in this calibration mixture divided by the maximum observed absorbance of NO photoproduct which is given in column 6. The mean value of these ratios is given to two standard deviations at the bottom of the column, for each calibration mixture.

rotation lines, many of which are resolved, or on the intensity of the unresolved Q branches of the 1-0 band of NO. In general terms, at this moderate resolution the monitoring of individual vibration-rotation lines is not as straightforward as the monitoring of an unresolved band because the pressure-broadened linewidth is of the same order of magnitude as the best resolution which was attainable (*ca.* 0.1 cm^{-1}). On account of this the true line contour is not observed, as it would be for infinite resolving power, but the observed absorption is modified by the instrument lineshape. This so-called convolution of the spectral absorption by the instrument lineshape distorts the linewidth and the maximum intensity of the line, although the position of the line at its maximum intensity is not affected. For small distortion of the line profile, the inverse of the maximum optical retardation, Δ^{-1}, must be very much smaller than the linewidth.[19]

In principle it is possible to determine the NO concentration from the NO absorbance of the unresolved Q sub-bands: in this case the observed bandshape is close to the true bandshape because the bandwith (*ca.* 1.25 cm^{-1}) is considerably larger than the spectral resolution.[20] Indeed, this method has been used by Chan *et al.*[21] in their F.t.i.r. spectroscopic study of the reactions in a gaseous system of HONO, NO, NO_2 and H_2O. Unfortunately in the present study it was found that the N_2O, $\nu_1 + \nu_2^1$ combination band absorbs in the same region as the NO Q branches, making quantitation difficult at the low levels of conversion essential in accurate photochemical quantum-yield determination.[1]

Hence an estimate for the partial pressure of NO formed on photolysis of N_2O at 184.9 nm was obtained simply by comparison of the absorbances for the instrumentally distorted absorption profiles of the NO photoproduct with those of NO in calibration mixtures of NO and N_2O. It can be seen from table 1 that the maximum observed absorbances of NO photoproduct are nearest in magnitude to those of NO in the 0.80 Torr NO-200.0 Torr N_2O calibration mixture. This is because the mean values of the ratios, which are in parentheses, are closer to unity for this calibration mixture than they are for the other two mixtures. Therefore an estimate for the partial pressure of NO, P_{NO}, in the mixture immediately after 1.50 h photolysis is 0.80 ± 0.10 Torr. The maximum observed absorbance corresponds to a frequency on the shoulder of the $^2\Pi_{1/2}$-$^2\Pi_{1/2}$ sub-band of the 1-0 band as a linear interpolation of the data points at fixed frequency intervals in the Fourier domain was carried out. As long as the laser wavenumber alignment is not adjusted, the data points are sampled at the same frequency (to the nearest 0.005 cm^{-1}) in each spectrum.

The incident light intensity, I_0, at 184.9 nm was calculated from a mass-spectrometric determination of N_2 from the N_2O actinometer using Ar as an internal standard. The known quantum yield of the actinometer,[2] $\Phi_{N_2}^{184.9} = 1.44 \pm 0.11$, is related to the absorbed intensity, I_a, by the following expression:

$$\Phi_{N_2}^{184.9} = N_{N_2}/I_a t$$

where N_{N_2} is the number of N_2 molecules that were generated in the reaction cell by photolysis for a known time, t. This immediately measures the incident intensity of light entering the cell, I_0, which is related to I_a as follows:

$$I_a = I_0[1 - \exp(\sigma c l)]$$

where σ is the absorption cross-section of N_2O at 184.9 nm and 298 K (1.40×10^{-19} cm^2),[22] c is the concentration of N_2O and l is the optical path length. The relative mass-spectrometer sensitivity of N_2 to Ar was measured from calibration mixtures of nitrogen and argon. This factor was calculated to be 1.09 from least-squares analysis, with a correlation coefficient of 0.999. Appropriate substitution of the above factors gives a value for I_0 of $(0.954 \pm 0.08) \times 10^{15}$ quanta s^{-1} over a series of five runs.[12]

The quantum yield of nitric oxide production at 184.9, $\Phi_{NO}^{184.9}$ is given by the equation

$$\Phi_{NO}^{184.9} = \frac{d[NO]/dt}{I_0[1 - \exp(-\sigma c l)]}$$

and is calculated from the above data to be 1.0 ± 0.2.

Discussion

The results obtained in this study indicate that the value for $\Phi_{NO}^{184.9}$ of 1.2 obtained by chemiluminescence analysis is to be preferred over the values obtained by mass spectrometry.[3,4] F.t.i.r. measurement of the nitrous oxide actinometer shows that in static systems a slow, termolecular reaction between nitric oxide and oxygen photoproducts occurs:

$$NO + NO + O_2 \rightarrow NO_2 + NO_2. \qquad (4)$$

The rate constant for this reaction has been previously determined[23] to be $(1.54 \pm 0.09) \times 10^4$ dm^6 mol^{-2} s^{-1} at 296 K. Such a process can occur within the mass-spectrometer chamber during analysis, leading to an underestimate for $\Phi_{NO}^{184.9}$. In contrast, the low concentrations of NO and O_2 used in the flow apparatus of the chemiluminescence experiments prevent reaction (4) from occurring. An alternative spin-restricted process to account for the production of NO_2 in the system, namely

$$O(^1D_2) + N_2O(^1\Sigma^+) \rightarrow N(^4S) + NO_2(^2A_1) \qquad (5)$$

has been shown to be insignificant.[10]

The quantum yield obtained in this work, 1.0 ± 0.2, must be regarded as a lower limit since the infrared data acquisition time for the collection of 1000 interferograms at 0.2 cm^{-1} resolution was not sufficiently short in order to be able to neglect the termolecular process. Furthermore, the KBr infrared windows were attacked by the nitrogen dioxide secondary product. Although unreactive silicon windows were tried, it was found that interference fringes were observed at 0.2 cm^{-1} spectral resolution, leading to large inaccuracies in the quantitative determination of nitric oxide. In fact, calculation of the NO photoproduct concentration from the F.t.i.r. spectra was not straightforward because: (a) the main Q sub-band of the NO fundamental absorbs in the same spectral region as the P branch of the N_2O $\nu_1 + \nu_2^1$ combination and (b) the moderate resolution obtainable with the FTS.20V instrument ($\Delta\tilde{\nu}_{max} = 0.1$ cm^{-1}) is of the same order of magnitude as the linewidths of the NO vibration-rotation lines.

In view of the errors involved in determining the NO concentration, the use of F.t.i.r. to determine $\Phi_{NO}^{184.9}$ in the presence of N_2O is not recommended. However, the method may find greater utility in other gas-phase actinometric systems, *e.g.* the determination of $\Phi_{CO}^{253.7}$ in the trifluoroacetic anhydride actinometer, which has been discussed by Whittle.[24]

In conclusion, one of the major advantages of F.t.i.r. spectroscopy over conventional (dispersive) infrared spectroscopy is the multiplex advantage, which allows observation of all the wavelength components simultaneously. Although this is useful when monitoring multicomponent systems, when a single species is the object of study a smaller spectral range (*ca.* 10 cm^{-1}) is sufficient. Hence an i.r.-laser-based spectrometer would have been more suited to monitoring the NO photoproduct in the N_2O mixtures, as spectra are obtainable with greater resolution, higher sensitivity and with a faster acquisition time.

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