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Author

Selwyn, Gary

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Gary Selwyn and Harold S. Johnston

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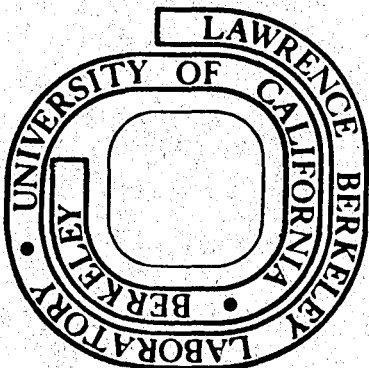
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Nitrous Oxide Ultraviolet Absorption
Spectrum at Stratospheric Temperatures

by

Gary Selwyn and Harold S. Johnston

Department of Chemistry

University of California

Berkeley, CA 94720

Abstract. The absorption spectrum of nitrous oxide (N_2O) has been determined at five temperatures from 194 to 302 K and over the wavelength range 173-240 nm. The variation of the absorption cross sections with temperature is large enough that it should be included in models of stratospheric photochemistry. The high-resolution structure between 173 and 190 nm has been observed more clearly than by previous studies.

Introduction

Previously we reported [Johnston and Selwyn, 1975] on the near ultraviolet absorption spectrum of nitrous oxide (N_2O) at room temperature, with references to previous literature and a discussion of the resulting lifetime of nitrous oxide in the atmosphere.

Holliday and Reuben [1967] found that the ultraviolet absorption cross section for nitrous oxide increased rapidly with increasing temperature from 293 K to 953 K over the wavelength range 200 to 270 nm, and Nicolle and Vodar [1940] obtained the ratio of absorption cross sections at 293 K to 183 K at wavelengths above 200 nm. Romand and Mayence [1949] reported on near ultraviolet absorption as well as the more intense absorption centered at 145 nm at 291 K. Apparently by combining and extrapolating these three studies, Hudson [1974] estimated N_2O absorption cross sections for 183, 293 and 373 K and from 176 to 202 nm.

Here we report the nitrous oxide spectrum at five temperatures spanning 194 to 302 K and at wavelengths from 173 to 240 nm. These experimental conditions cover the range of temperature and solar radiation encountered by N_2O in the stratosphere.

Previous studies have indicated that the spectrum of nitrous oxide may have some weak structure superimposed on the continuous absorption. Zelikoff et al. [1953] and Monahan and Walker [1975] have found evidence of diffuse bands by optical methods, and Lassetre et al. [1968] have observed diffuse bands by electron impact spectra. By pushing our instruments to maximum resolution, we have found a pronounced, relatively strong, structured spectra superimposed on the continuum in the wavelength range 173 to 190 nm.

Experimental

Spectra were obtained with a Cary 118C spectrophotometer, fitted with either one of two thermostated cells. A small quartz cell mounted in nitrogen purged Cary sample compartment was used in the wavelength range 173 to 210 nm. The optical pathlength was 6.5 cm and each end was closed with a pair of Suprasil windows with a vacuum between them for insulation. The cell was enclosed in an insulating jacket and was cooled by a stream of nitrogen boiled off from a liquid nitrogen dewar. Temperature was measured by a thermocouple. A large stainless steel cell, used over the wavelength range 200 to 240 nm, had a double-pass optical pathlength of 296 cm, and had a single optically flat, polished Suprasil window coated with MgF_2 to minimize reflective loss around 220 nm. A one-to-one focusing mirror inside the cell was also coated with MgF_2 to enhance reflection around 220 and to prevent oxidation. The cell was jacketed by an ethanol bath which was cooled by flowing cold methanol through submerged copper coils that encircled the cell. The entire cell was covered with one inch of insulating sponge rubber. The cell had an end-to-end temperature difference of 0.5 K at 243 K and 1 K at 225 K. At low temperatures, a stream of dry nitrogen gas was passed across the window to prevent frost formation.

The analog output of the spectrophotometer was collected and stored by a Fabritek 1074 data collector with a 12 Bit A/D converter and 4000 words of storage. The data were processed by a PDP 8/L minicomputer interfaced with the Fabritek. Data points were taken every 0.2 nm over the wavelength range studied with a resolution of 0.7 nm. For high

resolution studies, the slits were set at 0.15 nm. The resolution was 0.075 nm, the time constant was 5 seconds, the scan rate was 0.005 nm sec⁻¹, and signal averaging on the minicomputer was carried out for four runs. Data points were taken every 0.05 nm in this case.

All spectra were obtained in the double beam mode but were based on the ratio of I_0 through the evacuated cell and I through the same cell containing N_2O . The cross sections are defined as

$$\sigma = (\log_e I_0/I)(CL)^{-1}$$

where C is concentration in molecules cm^{-3} and L is the optical pathlength in cm.

Nitrous oxide from a Matheson cylinder was purified by passing through 3A molecular sieve to remove water and then by four successive vacuum distillations with retention of the middle third of each. By ultraviolet absorption studies, upper limits of certain possible impurities were set: $NO < 1$ ppm; $NO_2 < 1$ ppm. By high resolution mass spectrometry, the following upper limits were set: $N_2 < 0.1\%$; $CO_2 < 0.01\%$; $O_2 < 0.05\%$. Mass numbers from 12 to 800 were scanned, and no other impurities were detected with a sensitivity of about 0.05%.

Wavelength calibrations were made by filling a 10 cm cell with 7.5 torr NO and observing the rotational structure of the NO absorption doublet at 226 nm [Herzberg, 1950] and observing the rotational structuring of the Schumann-Runge oxygen bands below 195 nm [Knauss and Ballard, 1935]. The nominal Cary wavelengths were accurate to 0.08 nm with a reproducibility of better than 0.02 nm. The wavelengths reported here are believed to be accurate to ± 0.04 nm. The absence of photolysis of

N_2O by the Cary deuterium discharge lamp was established by the absence of any detectable NO produced during a special six hour run. The radiation is dispersed before passing through the sample cell, and thus the amount of radiation available for photolysis of N_2O is extremely low.

Results

The absorption cross sections for nitrous oxide for radiation between 173 and 240 nm and at five temperatures between 194 and 302 K are entered in Table 1. The portion of the data centered about the "stratospheric window" at about 210 nm, is shown in Figure 1. The ratio of the cross sections between the room temperature value and the value at 225 K is about 2.9 at 240 nm, about 1.6 at 210 nm, and about 1.15 at 190 nm. Careful modeling of the stratosphere should include the temperature dependence of the nitrous oxide cross sections. Otherwise the model overestimates the nitrous oxide flux into the stratosphere and underestimates the importance of nitric oxide production by chemical reaction relative to photolytic destruction.

The high resolution data at 302 K and 44 torr N_2O are given by Figure 2. A vibrational progression superimposed on a continuous spectrum is more clearly defined here than in previous studies. At low temperatures this spectral structure is less prominent than at room temperature. Explanations for the diffuse banding of nitrous oxide have been discussed by Chutjian and Segal [1972] and Monahan and Walker [1975].

Discussion

The basis for the temperature dependence of the nitrous oxide spectrum is concisely stated by Monahan and Walker: "The ${}^1\Delta[+X^1\Sigma]$ transition is orbitally forbidden but vibronically allowed by bending." The excited bending states of nitrous oxide have much larger Franck-Condon overlap with the upper state than does the (000) mode of the ground state molecule. The population of excited bending states (010, 020, ...) increases with temperature, as does the absorption cross section for ultraviolet radiation. With a fundamental bending frequency of 589 cm^{-1} , about 2.5 percent of the molecules are in the (010) bending mode at 194 K. At 296 K there are about 11 percent in the (010) mode, and 1.5 percent in the (020) vibrational state.

Acknowledgment

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Table 1. Ultraviolet absorption cross sections, $\sigma = (\lambda n \cdot I_0/I)(CL)^{-1} \text{ cm}^2$ for nitrous oxide as a function of temperature
 $3.83/24 = 3.83 \times 10^{-24}$

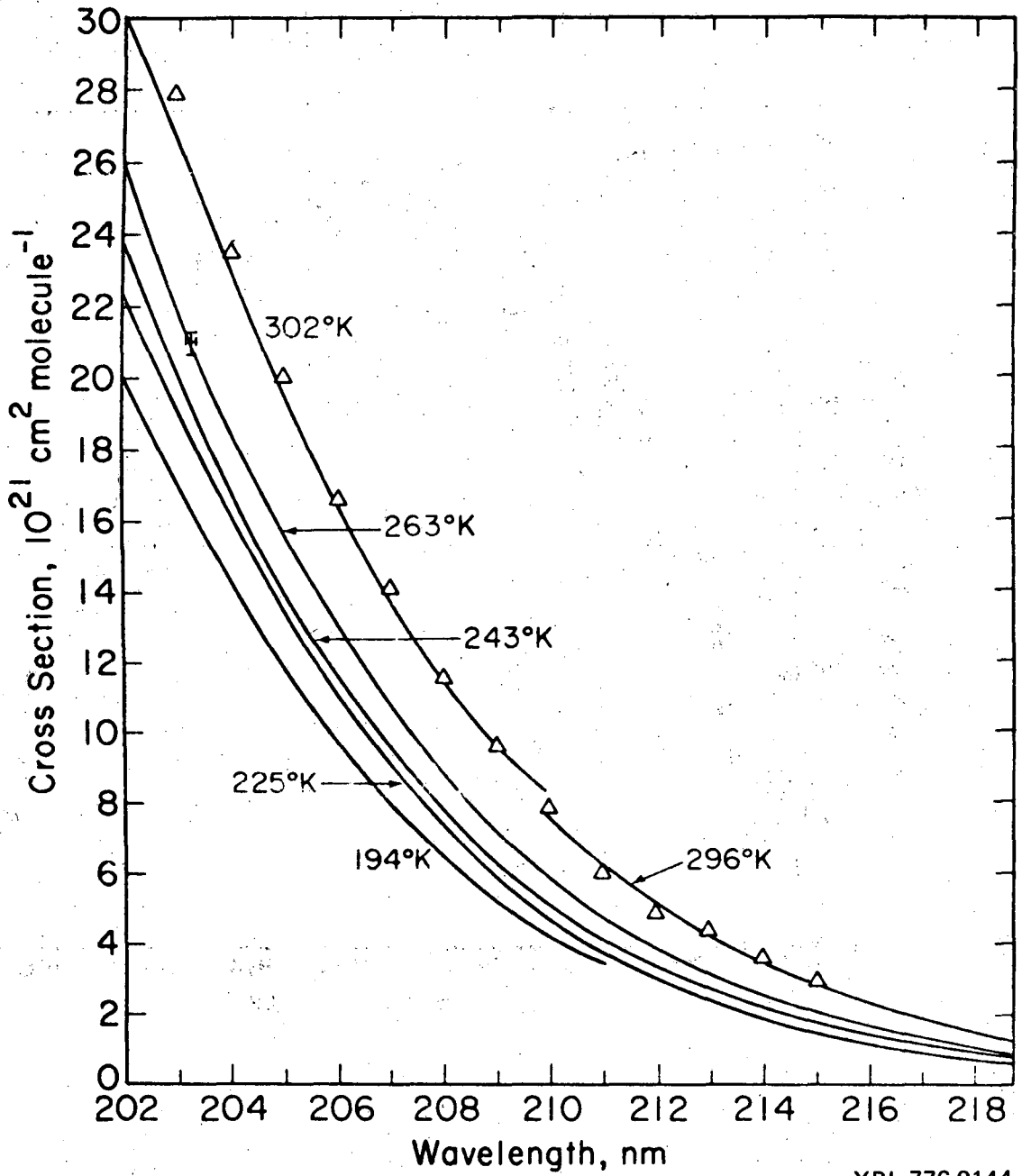
Wave-length nm	194 K	225 K	243 K	263 K	296 K	Wave-length nm	194 K	225 K	243 K	263 K	302 K
240		3.83/24	4.80/24	5.00/24	1.01/23	209	5.23/21	5.95/21	6.27/21	7.15/21	9.80/21
239		4.40/24	5.60/24	5.95/24	1.23/23	208	6.50/21	7.35/21	7.82/21	8.75/21	1.16/20
238		5.30/24	6.70/24	7.35/24	1.52/23	207	7.87/21	8.95/21	9.52/21	1.07/20	1.38/20
237		6.60/24	8.25/24	9.50/24	1.91/23	206	9.90/21	1.09/20	1.16/20	1.30/20	1.65/20
236		7.70/24	9.90/24	1.19/23	2.40/23	205	1.19/20	1.33/20	1.40/20	1.57/20	1.95/20
235		9.65/24	1.22/23	1.49/23	3.01/23	204	1.44/20	1.62/20	1.69/20	1.85/20	2.30/20
234		1.21/23	1.54/23	1.93/23	3.60/23	203	1.69/20	1.90/20	2.00/20	2.20/20	2.67/20
233		1.51/23	1.91/23	2.46/23	4.78/23	202	2.04/20	2.26/20	2.40/20	2.60/20	3.09/20
232		1.92/23	2.43/23	3.13/23	6.05/23	201	2.40/20	2.67/20	2.81/20	3.01/20	3.58/20
231		2.50/23	3.06/23	4.05/23	7.60/23	200	2.85/20	3.08/20	3.28/20	3.52/20	4.09/20
230		3.20/23	3.91/23	5.05/23	9.55/23	199	3.36/20	3.64/20	3.86/20	4.06/20	4.70/20
229		4.05/23	5.00/23	6.45/23	1.20/22	198	3.89/20	4.24/20	4.45/20	4.73/20	5.35/20
228		5.25/23	6.40/23	8.35/23	1.51/22	197	4.55/20	4.88/20	5.10/20	5.42/20	6.10/20
227		6.81/23	8.30/23	1.06/22	1.90/22	196	5.18/20	5.53/20	5.83/20	6.14/20	6.82/20
226		9.85/23	1.07/22	1.36/22	2.39/22	195	5.80/20	6.20/20	6.42/20	6.85/20	7.57/20
225		1.16/22	1.37/22	1.75/22	3.03/22	194	6.48/20	6.90/20	7.25/20	7.51/20	8.11/20
224		1.45/22	1.81/22	2.34/22	3.75/22	193	7.20/20	7.64/20	7.95/20	8.32/20	8.95/20
223		1.87/22	2.30/22	2.95/22	4.74/22	192	7.72/20	8.40/20	8.75/20	9.20/20	9.75/20
222		2.39/22	2.93/22	3.76/22	5.88/22	191	8.59/20	9.02/20	9.36/20	9.81/20	1.04/19
221		3.08/22	3.74/22	4.73/22	7.39/22	190	9.38/20	9.85/20	1.01/19	1.06/19	1.11/19
220		3.98/23	4.82/22	6.01/22	9.22/22	189	9.97/20	1.05/19	1.07/19	1.12/19	1.17/19
219		5.19/22	6.14/22	7.58/22	1.15/21	188	1.07/19	1.11/19	1.17/19	1.19/19	1.25/19
218		6.68/22	7.85/22	9.68/22	1.42/21	187	1.12/19	1.17/19	1.19/19	1.23/19	1.31/19
217		8.75/22	1.02/21	1.22/21	1.79/21	186	1.16/19	1.22/19	1.25/19	1.29/19	1.36/19
216		1.13/21	1.29/21	1.54/21	2.23/21	185	1.22/19	1.27/19	1.31/19	1.35/19	1.43/19
215		1.44/21	1.64/21	1.95/21	2.76/21	184	1.26/19	1.30/19	1.32/19	1.36/19	1.44/19
214		1.87/21	2.08/21	2.45/21	3.42/21	183	1.28/19	1.33/19	1.35/19	1.39/19	1.46/19
213		2.36/21	2.62/21	3.05/21	4.21/21	182	1.29/19	1.33/19	1.37/19	1.40/19	1.47/19
212		3.00/21	3.31/21	3.80/21	5.18/21	181	1.32/19	1.34/19	1.36/19	1.39/19	1.46/19
211		3.80/21	4.08/21	4.72/21	6.19/21	180	1.33/19	1.35/19	1.38/19	1.39/19	1.46/19
210	4.23/21	4.70/21	5.11/21	5.79/21	7.55/21	179	1.30/19	1.32/19	1.34/19	1.37/19	1.44/19
						178	1.28/19	1.28/19	1.29/19	1.31/19	1.39/19
						177	1.27/19	1.28/19	1.29/19	1.31/19	1.40/19
						176	1.24/19	1.23/19	1.25/19	1.27/19	1.34/19
						175	1.16/19	1.15/19	1.17/19	1.18/19	1.26/19
						174	1.14/19	1.14/19	1.15/19	1.17/19	1.19/19
						173	1.07/19	1.08/19	1.10/19	1.11/19	1.13/19

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Figure Captions

Figure 1. Cross section, $\text{cm}^2 \times 10^{21}$ vs wavelength, nm for five temperatures -- this work, Δ data points of Zelikoff, Watanabe and Inn [1953]. Note the discontinuity at 210 nm due to two different "room temperatures." The estimated standard deviation of wavelength (± 0.04 nm) and cross sections ($\pm 2\%$) is indicated by the cross on the 263 K curve. Resolution 0.7 nm.

Figure 2. High resolution spectrum in the structured region. Cross section, $\text{cm}^2 \times 10^{19}$, vs wavelength, nm. Temperature = 302 K. Pressure is 44 torr N_2O . Resolution 0.075 nm.



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Fig. 1

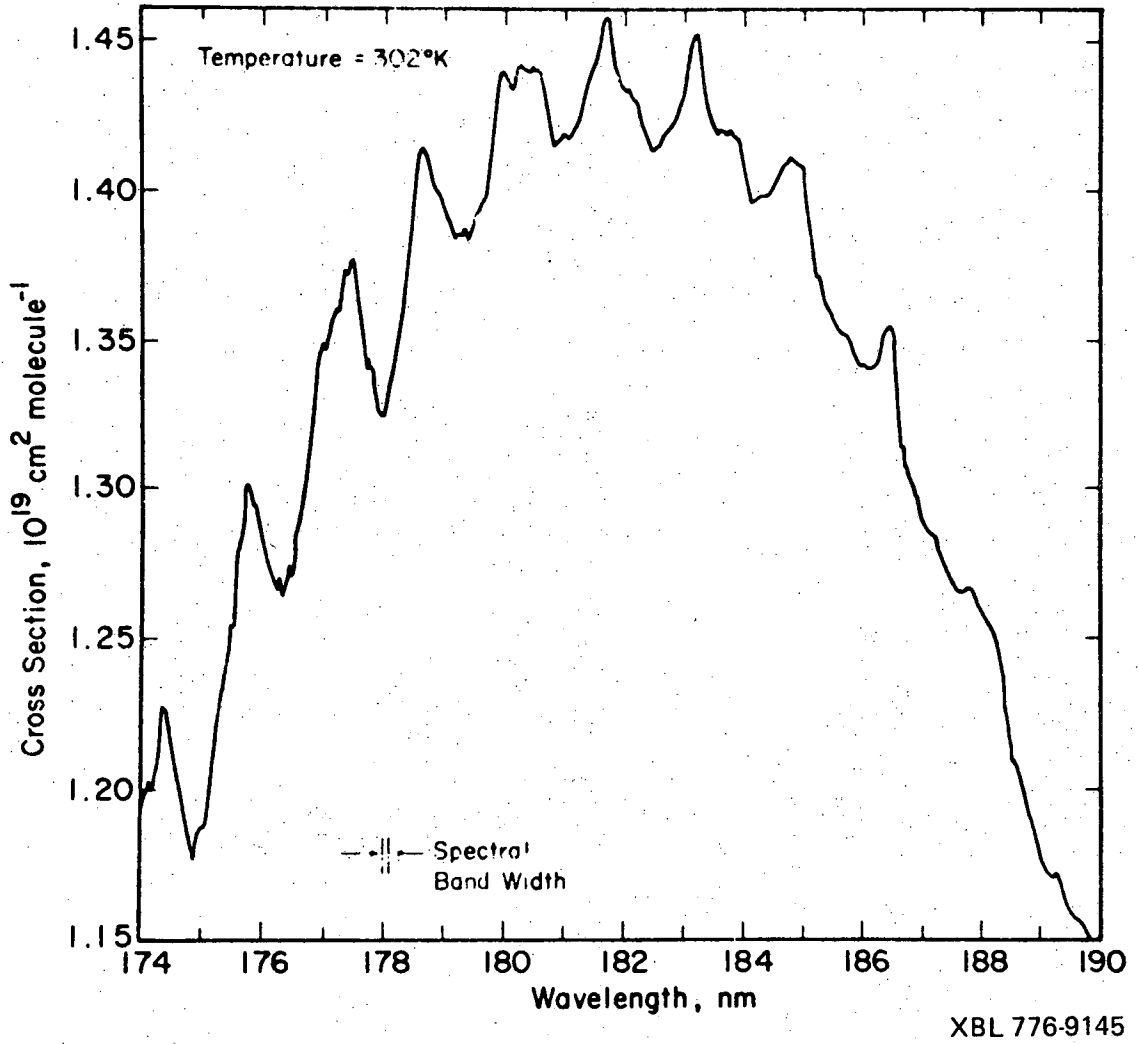


Fig. 2

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