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BY

MICHAEL F. GOLDE, AIDAN E. ROCHE

AND FREDERICK KAUFMAN

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In the region 3.3 to 4.1μm, the previously-observed broad band, peaking at 3.7μm, shows a complex kinetic dependence on [O] and [M].

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Absolute Rate Constant for the O + NO Chemiluminescence in the Near Infrared*

Technical Report

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ABSTRACT

Infrared chemiluminescence from the process $O + NO\ (+M) \rightarrow NO_2 + h\nu\ (+M)$ has been studied between 1.3 and 4.1μm. The wavelength dependence of the continuum between 1.3 and 3.3μm is in fair agreement with previous studies and the measured radiative rate constant at 1.51μm, $I^{\circ}_{1.51} = I_{1.51}/[O][NO]$, of $(2.4 \pm 0.8) \times 10^{-17}\ cm^3\ sec^{-1}\ \mu m^{-1}$ establishes the NO-O glow in this spectral range as a secondary emission standard. Comparison with previous studies of the visible region of the glow implies that the overall radiative rate constant, I°, lies in the range $(9.4 \text{ to } 11.2) \times 10^{-17}\ cm^3\ sec^{-1}$.

In the region 3.3 to 4.1μm, the previously-observed broad band, peaking at 3.7μm, shows a complex kinetic dependence on [O] and [M].

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In recent years, there has been rapidly increasing interest in the study of infrared chemiluminescence, in particular from vibrationally excited molecules formed by chemical reaction. Often, such emissions are extremely weak and, although it is possible to increase greatly the light-gathering efficiency of the system with collecting and focusing optics or through the use of an integrating sphere, the measurement of the absolute volume emission rate then becomes more difficult. There is, therefore, a need to establish the absolute emission rate constant for an infrared chemiluminescent reaction, which can then be used as a standard for comparison with other processes.

This problem was solved, for the visible region of the spectrum, by use of the O-NO chemiluminescence, which is a pseudo-continuum, extending from 390nm to longer wavelengths and which arises from the radiative combination of O atoms with NO.[1-4] Although the spectral distribution of the glow is known to be pressure dependent, it is now accepted that the emission intensity at wavelength λ is given accurately by the equation:

$$I_\lambda = I^\circ_\lambda [O] [NO] \quad , \qquad (i)$$

where I°_λ is independent of pressure above about 0.3 Torr.[5,6]

Absolute values of I°_λ between 387.5 and 620nm were measured by Fontijn and Schiff[7] using an actinometric technique and this range was extended to 1.2μm by Fontijn, Meyer and Schiff.[8] The wavelength dependence of the glow in the visible was confirmed by Vanpee et al,[9] who studied the air afterglow up to 2μm in a free jet at 367°K. With calibration of their

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detectors by standard lamps, they found values of I°_{λ} about 30% greater than those of Fontijn et al.[8]

Stair and Kennealy,[10] using Fourier interferometer spectroscopy, found the air afterglow to extend well into the infrared, the continuum decreasing in intensity to 3.3μm, then peaking sharply, in an unidentified band, at 3.7μm. These workers did not report absolute intensities and their wavelength dependence differs significantly from that later reported by Vanpee et al over the common range 1.3 to 1.8μm.

The visible region of the air afterglow has been used extensively to calibrate detection systems for the study of other chemiluminescent reactions.[11-14] This technique is particularly useful and simple when it makes possible the use of the same apparatus for the standard air afterglow and the chemiluminescence under study, so that all geometric factors cancel. The method, its applicability and its limitations, have been thoroughly discussed by Fontijn et al.[8]

We have reinvestigated the infrared region of the air afterglow to clarify the wavelength dependence and to provide absolute values of I°_{λ} from 1.3 to 3.5μm, in order to establish the infrared glow, like its visible counterpart, as a standard emission source. In this experiment, which uses a conventional discharge-flow system, the infrared signal due to the glow from a known emitting volume is compared with that due to a black body, whose temperature is accurately known; the signal is corrected for the geometries of the chemiluminescent emission and of the black body radiation and the radiative rate constant is obtained by independent measurement of O and NO concentrations.

EXPERIMENTAL

The Flow System.

The experimental system is shown in Fig. 1. Oxygen atoms were generated by a microwave discharge (Raytheon Microtherm, 2450MHz) through oxygen flowing at rates of 1.7 to 13 atm·cm^3 sec^{-1} and at pressures between 0.3 and 3 Torr. The discharge tube led via a right-angle bend to the 4 cm i.d. pyrex flow-tube, which was coated internally with syrupy phosphoric acid to reduce wall removal of O atoms. Additions of NO or NO_2 to the flow were made through a loop injector pierced with many small holes, and the visible and infrared emissions from the afterglow were observed through CaF_2 windows (2.5 cm diameter, 2 mm thick), 10 cm downstream of this inlet. All experiments were carried out at 22 ± 1°C.

All gases were Matheson products, 'Extra-Dry' grade O_2 (>99.6% purity), NO (>99%) and NO_2 (>99.5%), and were used without further purification.

Oxygen-atom concentrations at the observation region, typically 4 to 10% of the total flow, were measured by means of the NO_2 titration,[2]

$$O + NO_2 \rightarrow NO + O_2 \quad ; \qquad (1)$$

i.e. the extinction of the air afterglow corresponding to a flow of NO_2 equal to that of the O atoms. In all experiments, the visible glow intensity, I, was monitored as a function of NO_2 flow, F_{NO_2}, using an unfiltered 1P28 photomultiplier tube and the linear plot of I/F_{NO_2} against F_{NO_2} was extrapolated to the end point to obtain O-atom concentrations with an uncertainty of less than 5%. Under all conditions, corrections were applied

for the O-atom decay between the inlet loop and the observation region, principally due to reaction (2) followed by (1):

$$O + NO + M \rightarrow NO_2 + M \qquad \text{(Ref. 15).} \qquad (2)$$

This correction does not, in itself, affect the measured position of the titration endpoint, but insures that the above extrapolation is linear.

Infrared Detection System and Signal Processing

Infrared radiation from the flow tube was mechanically chopped at 250Hz, using a synchronous motor (Globe Industries, Model 75A121-2) driven by a variable frequency oscillator (Esterline Angus, Model F-1000). The modulated radiation was spectrally resolved using a circular variable filter (CVF). The CVF (Optical Coating Laboratories, Inc.), comprising two semi-circular disc filters glued together, had a spectral range of 1.2 to 4.4μm, a bandwidth (full width at half height) equal to 2% of the center wavelength and a transmittance of about 50% at the maximum. The CVF was calibrated as a function of the angle of rotation from one boundary of the two sectors, using a Cary 14 spectrometer for the wavelength region 1.2-2.5μm and a Beckmann IR-12 spectrometer for the region 2-4.5μm. The resulting uncertainty in the wavelength at a measured angle of rotation was less than 0.01μm.

The radiation was detected with liquid-nitrogen cooled PbS or InSb detectors (Santa Barbara Research Center), operated in their photoconductive or photovoltaic mode, respectively. Signals were preamplified using a low-noise impedance-matched wideband preamplifier (SBRC, Models 60L1K and 60L2K for the InSb and PbS detectors respectively) and synchronously detected with a lock-in amplifier (Keithley, Model 840).

The PbS detector was employed for the experiments described here. At 77°K, this detector has high sensitivity over the principal range of interest 1.3-4μm and, in our system, has three times greater collection efficiency than the InSb detector because of the greater size of the element, 5mm square compared to 2mm square for the InSb. With the InSb detector, however, studies can be extended to 6μm. At 3.4μm, the PbS detector had a D^* of 1.3×10^{11} $cm(Hz)^{1/2}$ $watt^{-1}$ or a noise equivalent power of 6.6×10^7 quanta sec^{-1}, and the InSb detector a D^*_λ of 9.9×10^{10} and NEP of 5.4×10^7 quanta sec^{-1}.

The chopper wheel, CVF, an optical shutter, the detector and preamplifier, and the lamp and diode photocell, which provided the modulated reference signal, were mounted in a metal box which, with dry-ice cooling, enabled all components in the field of view of the detector to be cooled to approximately -30°C. By flushing the box with dry N_2 gas, a CO_2- and H_2O-free light path could be provided.

In this mode of operation, the intensity of the air afterglow was measured as the difference between the infrared signals with and without a flow of NO added to the atomic oxygen stream. At wavelengths beyond 3μm, this technique could not be used, because variable background emission, principally from the flow-tube walls, became significant as the O + NO reaction caused slight warming of the flow tube.

Therefore, a double modulation technique was developed, in which the microwave discharge - and thereby the glow - were modulated at a low frequency, typically 1 Hz. A simple transistor - Zener diode switch, driven by a variable - frequency oscillator (Esterline Angus, Model F-1000), modulated the magnetron high-voltage supply in the square-wave mode by about 300V with respect to a mean level of about 1500V, which is sufficient to switch the discharge power between zero and the chosen operating level, up

to a maximum of 100 watts. A d.c. spark-gap discharge was run upstream of the microwave cavity between two W-wire electrodes 2mm apart, at a current of about 10μA, which assured initiation of the discharge at each cycle, but was too weak to cause appreciable dissociation of the gas by itself.

In this mode, the first lock-in amplifier was used to demodulate the 1Hz glow modulation signal from the 250Hz carrier frequency; the lock-in time constant (bandwidth) had to be reduced to about 30ms to accommodate the low-frequency sidebands. The 1Hz output was then fed to a second lock-in amplifier (Keithley, Model 840), whose reference was taken from the discharge modulation circuit, and integrated for up to 100 sec to provide the final output signal.

The glow could not be modulated faster than about 10Hz, due to severe degradation in wave shape as a result of diffusive mixing in the rather slowly-flowing gas stream.

In both single and double modulation modes, the final lock-in could be replaced with an Enhancetron wave-eductor (Nuclear Data) and actual wave shapes obtained.

Calibration of the Detection System.

The detection system was calibrated absolutely between 1.3 and 4.4μm by means of a black body constructed from a design by Hudson[16] consisting of a cylindrical cavity with a thermally-isolated limiting aperture. Over the operating temperature range 400 to 700K, the emissivity of the cavity was measured by comparison with a commercial black body (Barnes Engineering Co., Model 11-120T).

The black body source was placed directly behind the rear CaF_2

window of the observation region of the flow tube. Because of the extreme simplicity of the optical system, consisting of a single slit on either side of the CVF, and because the black-body aperture could be used as the effective emitting source,[16] the fraction of black-body radiation, C_B, reaching the detector element could be simply and accurately calculated.

At a known black-body temperature, the rate of photon emission, Q_λ, was calculated and the rate of collection of photons by the detector, $Q_\lambda \cdot C_B$, compared with the observed signal output of the detection system, B_λ, to yield the absolute sensitivity of the detector as a function of wavelength.

The volume, V, of the flow tube from which O-NO chemiluminescence reached the detector and the fraction, C_S, of such emission detected were computer calculated, by summing over all possible volume elements in the field of view of the detector. In calculating C_S, no allowance was made for possible scattering of radiation from the rear wall of the flow tube to the detector. However, tests in which this effect was artificially increased by placing a mirror behind the rear CaF_2 window, indicated that such scattered light accounted for less than 10% of the total emission reaching the detector.

If the observed signal output of the detector when exposed to O-NO chemiluminescence at measured O-atom and NO concentrations is S_λ, the rate constant for radiative combination of O with NO, I°_λ, is given by:

$$I^\circ_\lambda = \frac{S_\lambda}{[O][NO]} \cdot \frac{Q_\lambda}{B_\lambda} \cdot \frac{C_B}{C_S . V} \quad . \qquad \text{(ii)}$$

RESULTS

Measurement of the Absolute Glow Intensity at 1.51μm.

The present investigation of the air afterglow comprised the determin-

ation of the relative infrared spectrum between 1.3 and 4.4μm, as well as an absolute measurement of I°_{λ} at a single wavelength, 1.51μm, in the high intensity region of the spectrum.

The ratio $S_{1.51}/[O][NO]$ (see equation (ii)) was measured at known O-atom concentration by monitoring $S_{1.51}$ as a function of NO added. Plots of S against [NO] showed slight negative curvature because, at high NO flows, reactions (2) and (1) removed up to 20% of the O atoms between the inlet port and the observation region. To eliminate the possibility of error in S/[O][NO] and to avoid the necessity of restricting measurements to low [NO], where the infrared signal was weak, use was made of the strong visible emission of the air afterglow. The ratio of visible emission intensity to [NO] was measured at low NO flows, where no dependence of the ratio on [NO] was found, and the ratio of visible to IR intensity was obtained at higher NO concentrations. The resulting uncertainty in $S_{1.51}/[NO]$ was always less than 5%.

Values of I°_{λ} at $\lambda = 1.51\mu m$, obtained by the use of equation (ii), are listed in Table 1 and show no significant variation over the pressure range 0.4 to 2 Torr and for $[O]/[O_2]$ ratios between 0.04 and 0.10.

Table 1 here

At higher pressures, apparent values of I°_{λ} at $\lambda = 1.51\mu m$ slowly decreased due to poor mixing of large injected flows of NO_2 and consequent overestimation of the O-atom concentration. This behavior was readily detected by the appearance of non-linear titration plots.

The data of Table 1 yield an average value of I°_{λ} at $\lambda = 1.51\mu m$ of $(2.4 \pm \sigma = 0.1) \times 10^{-17}$ cm^3 $sec^{-1}\mu m^{-1}$. The uncertainty in this value, comprising random errors associated with the glow measurements and systematic errors associated mainly with the black-body calibration measurements, is

estimated to be less than 30%.

There was no evidence for contributions by any emissions other than the air afterglow to the signal at 1.51μm; in particular, chemiluminescence from the process [11]

$$NO + O_3 \rightarrow NO_2^* + O_2 \qquad (3)$$

$$NO_2^* \rightarrow NO_2 + h\nu \quad , \qquad (4)$$

where O_3 is produced by:[17]

$$O + O_2 + M \rightarrow O_3 + M \quad , \qquad (5)$$

was shown to account for less than 1% of the total emission at this wavelength.

The present value of I°_λ at 1.51μm can be compared with that of Vanpee et al,[9] whose data in Fig. 7 of that paper yield a value of $(2.1 \pm 0.7) \times 10^{-17}$ cm^3 sec^{-1} μm^{-1} at 367K, which, with the known temperature dependence of the glow,[5] gives $(3.4 \pm 1.1) \times 10^{-17}$ cm^3 sec^{-1} μm^{-1} at 296K. This latter value represents the average of four experiments, three using oxygen and the fourth nitrogen as the carrier gas. Although I° is independent of pressure under these conditions, it is dependent on the nature of the carrier, because I° includes the ratio of the rate constant for three-body radiative combination of O with NO (or for the relaxation of vibrationally excited states of NO_2^*) to the rate constant for quenching of the emitting states of NO_2, both of which vary, in general, with M. There is good evidence[15,18] that $I^\circ_{N_2}$ is about 15% greater than $I^\circ_{O_2}$ and, in fact, the data of Vanpee et al, after correction for small temperature differences,

show N_2 to yield a value of I^o about 40% greater than that in O_2. It would appear more valid, therefore, to use their values obtained with O_2 for comparison with the present data; the relevant figure is calculated to be 2.9×10^{-17} cm^3 sec^{-1} μm^{-1}, in closer agreement with our value of 2.4×10^{-17} cm^3 sec^{-1} μm^{-1}. It should be noted further that Vanpee et al used high concentrations of NO, between 15 and 30% of the total flow; the relative efficiencies of NO and O_2 as third bodies in the radiative combination of O with NO are not known. In the present study, NO mole fractions were always less than 6%.

Wavelength Dependence of the Glow.

Relative spectra of the air afterglow were obtained under conditions of constant [O] and [NO]. The visible glow intensity was monitored continuously and corrections applied for any small drift in the O-atom concentration.

For these experiments, the double-modulation technique was employed to eliminate the large background signal, principally from the flow-tube walls, at wavelengths beyond 2.5μm. With this technique, the possible importance of infrared emission from the flowing O/O_2 stream alone could be readily tested by observing the change in signal as the optical shutter was opened and closed under conditions of zero NO flow. No evidence was found for such interfering emission.

Spectra were obtained over the whole operating range of the CVF (1.2 to 4.4μm). Since the CVF had wavelength-dependent resolution and transmission functions, the relative spectra were calibrated using the black body.

In agreement with observations of Stair and Kennealy,[10] we find the intensity to decrease more than ten-fold between 1.3 and 3.3μm,

then to rise to a peak at 3.7μm, (See Fig. 2). We could detect no change in the wavelength dependence between 1.3 and 3.3μm as the pressure was increased from 0.7 to 3 Torr, which is consistent with previous studies of the visible region of the glow.[5] The uncertainty in the relative intensity increases from approximately 5% at 1.3μm to 12% at 3.3μm.

In Figure 3, the wavelength dependence of the afterglow is compared with relative data of Stair and Kennealy[10] and Vanpee et al,[9] which have been normalized to the present data at 1.5μm. The data of Vanpee et al do not agree well with the other two studies, which show excellent agreement up to 2μm. Beyond this wavelength, however, the curves diverge to an extent exceeding the uncertainty limit of this (12%) and of the earlier study (10%). It is possible that the discrepancy is associated with detectivity problems in this wavelength range; Stair and Kennealy employed a PbS detector, cooled to 196K, whose sensitivity falls off markedly beyond 3μm. whereas our liquid-N_2 cooled PbS detector retains high sensitivity to at least 4μm.

Published data on the absolute intensity of the air afterglow are compared in Fig. 4, which includes the results of Fontijn et al[8] and Vanpee et al[9] for the visible region of the glow. These curves were calculated from the published relative wavelength dependences and the quoted values of the overall rate constant for radiative combination, $I^o = \int_\lambda I^o_\lambda . d\lambda$

The relative wavelength dependences agree well up to 0.9μm, but it is clear that the early study of Fontijn et al seriously underestimated the infrared contribution to the glow.

In the visible, the values of I^o_λ of Fontijn et al lie about 30% below those of Vanpee et al. Our values in the infrared also lie about 30% below those of Vanpee et al. However, it is probably not valid to interpret this observation in terms of support for the data of Fontijn et al near 0.6μm,

because we find a steeper wavelength dependence in the infrared than did Vanpee et al.

Fontijn et al[8] obtained an overall value of I° of 6.4×10^{-17} cm^3 sec^{-1} for O + NO radiative combination. A minimum correction to this value for the sizable infrared contribution to the glow can be estimated by inclusion of our data between 1.3 and 3.3μm and a linear extrapolation of our spectral curve to that of Fontijn et al. The integrated area under this synthetic curve yields a value of I° of 9.4×10^{-17} cm^3 sec^{-1}.

Vanpee et al[9] obtained I° = 6.8×10^{-17} cm^3 sec^{-1} for the wavelength range 387.5-2000nm at a temperature of 367K. Including the small contribution of emission between 2 and 3.3μm, this yields I° = 11.2×10^{-17} cm^3 sec^{-1} at 296K.[5]

We deduce, therefore, a best value of I° from the available data of between (9.4 and 11.2) $\times 10^{-17}$ cm^3 sec^{-1} at 296K. Further refinement of this value requires a more precise knowledge of the wavelength dependence of the glow between 0.8 and 1.3μm.

The region from 3 to 4μm is dominated by the band peaking at 3.7μm, which was first observed by Stair and Kennealy.[10] They found the band intensity to show the same dependence on [O] and [NO] as the main continuum and proposed that the emission arises from an electronic transition from or to a low-lying electronic state of NO_2.

We have performed a preliminary study of the kinetics of this band, monitoring the ratio of the intensity at 3.7μm to that at 1.51μm as a function of experimental conditions and have found small but significant deviations of the kinetics from a simple [O] [NO] dependence. The ratio $I_{3.7}/I_{1.51}$ decreases by about 40% over a ten-fold increase in [O] (See Fig. [illegible]) and increases by about a factor of two as the total pressure is increased from 0.8 to 3 Torr.

Moreover, increases in $I_{3.7}/I_{1.51}$ are accompanied by small shifts of the peak of the band towards shorter wavelength.

On the basis of these preliminary results and the known absorption spectrum of NO_2, we propose that the band represents emission from several vibrational levels of the electronic ground state of NO_2, formed by three-body combination of O with NO, in part via intermediate electronically-excited states of NO_2. The emitting states are removed by vibrational relaxation and by chemical reaction with O atoms:

$$O + NO_2^{\dagger} \rightarrow NO + O_2 \quad ; \qquad (6)$$

competition between these two processes explains the dependence of the band shape and intensity on the ratio of oxygen-atom concentration to total pressure.

It is probable that the emission represents $\nu_1 + \nu_3$ combination bands of NO_2, corresponding to the absorption at 3.44um.[19] The shift in wavelength of the emission peak relative to the absorption band is consistent, on the basis of the known vibrational constants for NO_2,[20,21] with emission principally from molecules with 2 to 4 quanta in each of the ν_1 and ν_3 modes.

The absolute values of I^{o}_{λ} for the O + NO combination presented in this study enable the infrared region of the air afterglow, like the visible region, to be used as a secondary emission standard, allowing determination of the absolute intensities of many infrared chemiluminescent reactions, which involve emission in the wavelength region 1.3 to 3.3μm. Because the spectral distribution of the 3.7μm 'band' depends on experimental conditions, it is not possible, at present, to use the region beyond 3.3μm as a chemiluminescent standard. Further experiments are in progress to clarify the

behavior in this region.

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TABLE 1

The Radiative Rate Constant, I^{o}_{λ}, at $\lambda = 1.51\mu m$

Pressure Torr	$[O]/[O_2]$	$10^{17}\ I^{o}_{1.51}$ $cm^3\ molec^{-1}\ sec^{-1}\ \mu m^{-1}$
1.32	.049	2.59
1.41	.042	2.53
1.58	.053	2.56
0.81	.068	2.41
1.74	.058	2.53
1.10	.067	2.25
0.39	.094	2.12
1.48	.069	2.19
1.49	.073	2.15
0.86	.071	2.27
1.56	.059	2.49
2.06	.046	2.39

REFERENCES

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1. M. L. Spealman and W. H. Rodebush, J. Am. Chem. Soc. 57, 1474 (1935).
2. F. Kaufman, Proc. Roy. Soc. A247, 123 (1958).
3. H. P. Broida, H. I. Schiff and T. M. Sugden, Trans. Faraday Soc., 57, 259 (1961).
4. M. A. A. Clyne and B. A. Thrush, Proc. Roy. Soc. A269, 404 (1962).
5. F. Kaufman, International Conference on Chemiluminescence, Univ. of Georgia, 1972.
6. M. F. Golde and B. A. Thrush, Reports. Prog. Phys., 1973 in press.
7. A. Fontijn and H. I. Schiff, Chemical Reactions in the Lower and Upper Atmosphere (Interscience N.Y. 1961) p. 139.
8. A. Fontijn, C. B. Meyer and H. I. Schiff, J. Chem. Phys. 40, 64 (1964).
9. M. Vanpee, K. D. Hill and W. R. Kineyko, AIAA Journal 9, 135 (1971).
10. A. T. Stair and J. P. Kennealy, J. de Chim. Phys. 64, 124 (1967).
11. P. N. Clough and B. A. Thrush, Trans. Faraday Soc., 63, 915 (1967).
12. R. A. Young and R. L. Sharpless, J. Chem. Phys., 39, 1071 (1963).
13. I. M. Campbell and B. A. Thrush, Proc. Roy. Soc., A296, 201 (1967).
14. M. A. A. Clyne and B. A. Thrush, Disc. Faraday Soc., 33, 139 (1962).
15. F. Kaufman and J. R. Kelso, Symp. Chemiluminescence, Duke University, 1965.
16. R. D. Hudson, Infrared System Engineering (Wiley, New York 1969), pp 72-77.
17. F. Kaufman and J. R. Kelso, J. Chem. Phys., 46, 4541 (1967).
18. K. H. Becker, W. Groth and D. Thran, Chem. Phys. Lett., 15, 215 (1972).

19. G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules (Van Nostrand, New York 1945) p. 284.

20. E. T. Arakawa and A. H. Nielsen, J. Mol. Spectrosc. 2, 413 (1958).

21. R. E. Blank and C. D. Hause, J. Mol. Spectrosc. 34, 478 (1970).

FIGURE CAPTIONS

Figure 1. Experimental apparatus (schematic)

A: Observation region with two CaF_2 windows (2.5 cm diameter, 2mm thick); B: chopper motor; C: chopper wheel; D: reference lamp and diode photocell; E: shutter; F: slits; G: CVF; H: angle scale for CVF; J: detector element; K: liquid-N_2 dewar.

Figure 2. The Relative O + NO infrared spectrum including the [O]-dependent 3.7μm 'Band'.

1.3-3.3μm: Average of spectra at pressures between 0.7 and 3 Torr

3.3-4.1μm: pressure = 2.3 Torr. Lower curve corresponds to a higher O-atom concentration than the upper curve. The error bars represent the uncertainty in each reading.

Figure 3 Absolute intensity of O + NO infrared Chemiluminescence.

1.3-2μm: ——— This work; also relative data of Stair and Kennealy (ref. 10).

- - - - Data of Vanpee et al (ref. 9) fitted to present data at 1.5μm.

2-3.3μm: ——— This work.

—· —· Relative data of Stair and Kennealy fitted to present data at 2μm.

Figure 4. Absolute intensity of O + NO Chemiluminescence between 0.3 and 2μm.

- - - Fontijn et al (ref. 8).

—· —· Vanpee et al (ref. 9)

——— This work

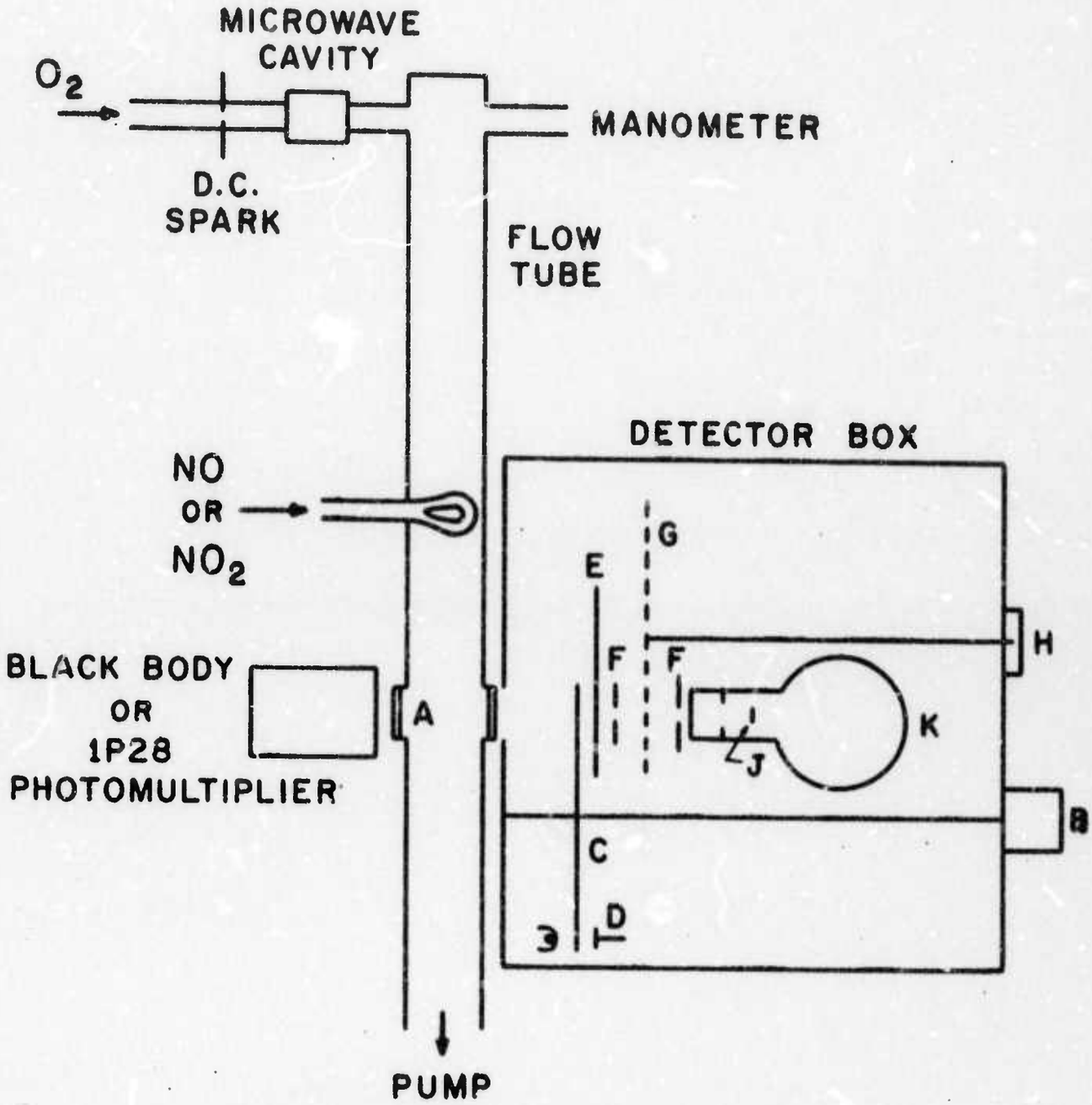
MICROWAVE
CAVITY
O_2
MANOMETER
D.C.
SPARK
FLOW
TUBE
DETECTOR BOX
NO
OR
NO_2
G
E
H
F
F
BLACK BODY
OR
1P28
PHOTOMULTIPLIER
A
K
J
B
C
D
PUMP

FIGURE 1

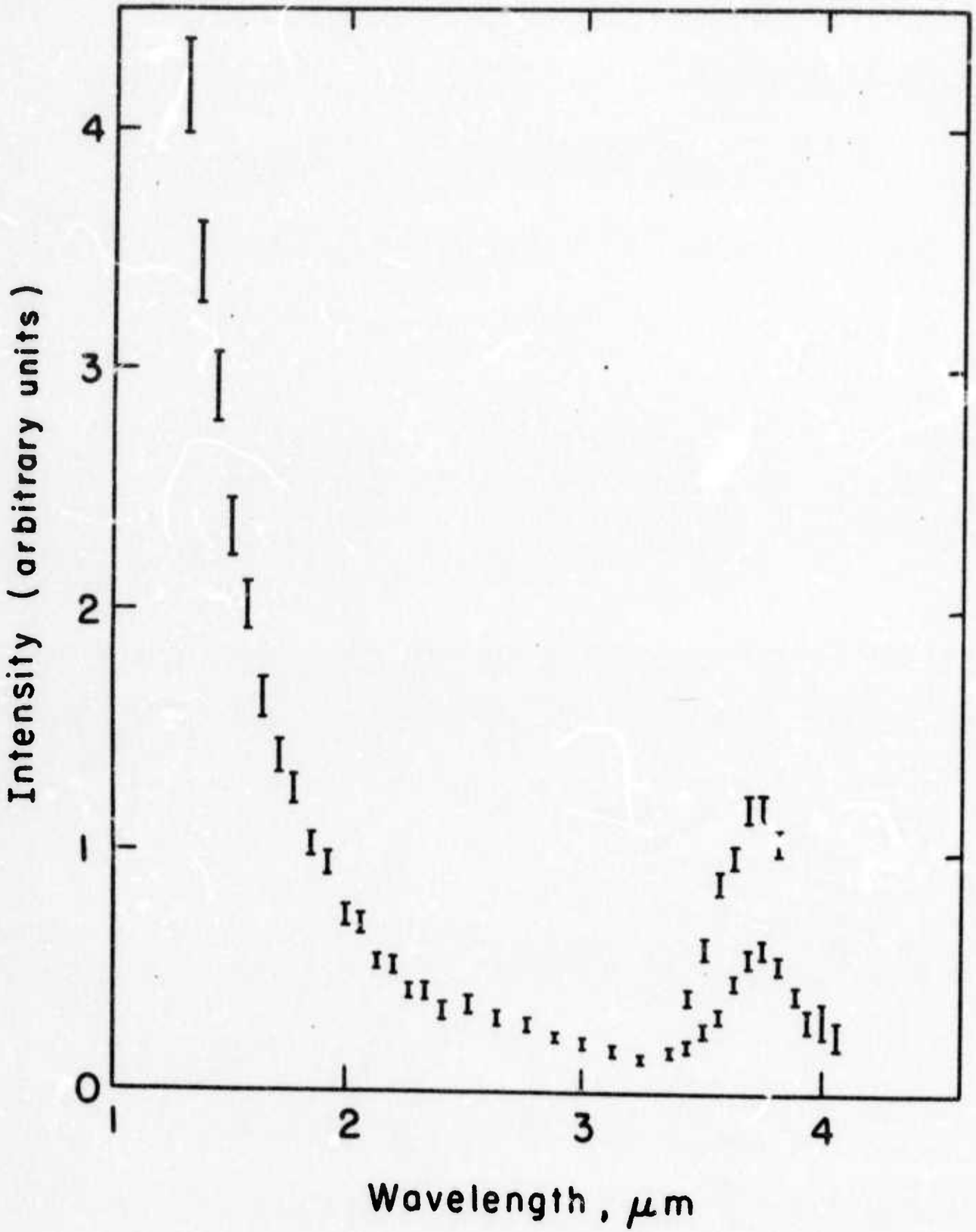

FIGURE 2

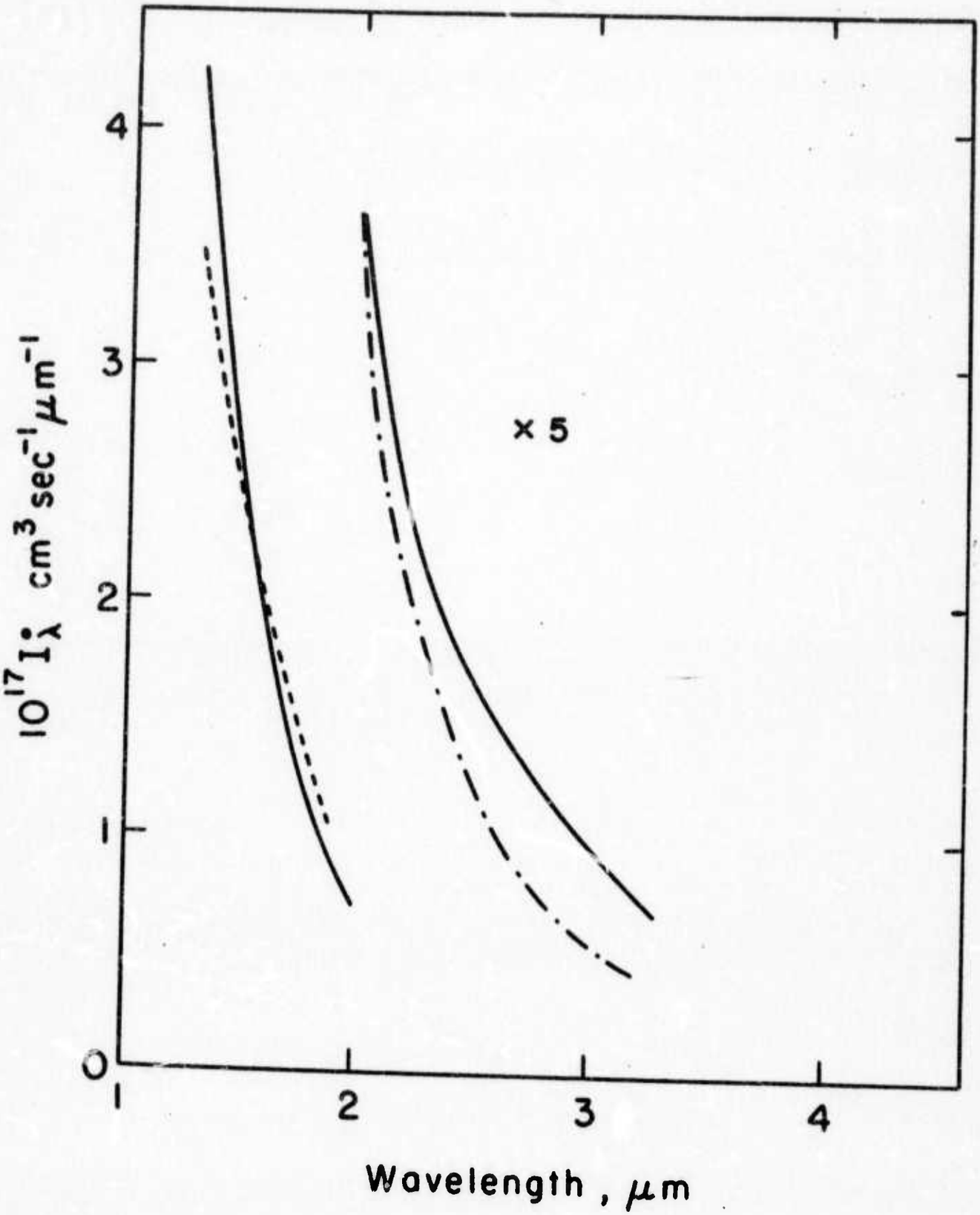
4
3
2
1
0
1
2
3
4
$10^{17} I_\lambda^\bullet$ cm^3 sec^{-1} μm^{-1}
× 5
Wavelength , μm

FIGURE 3

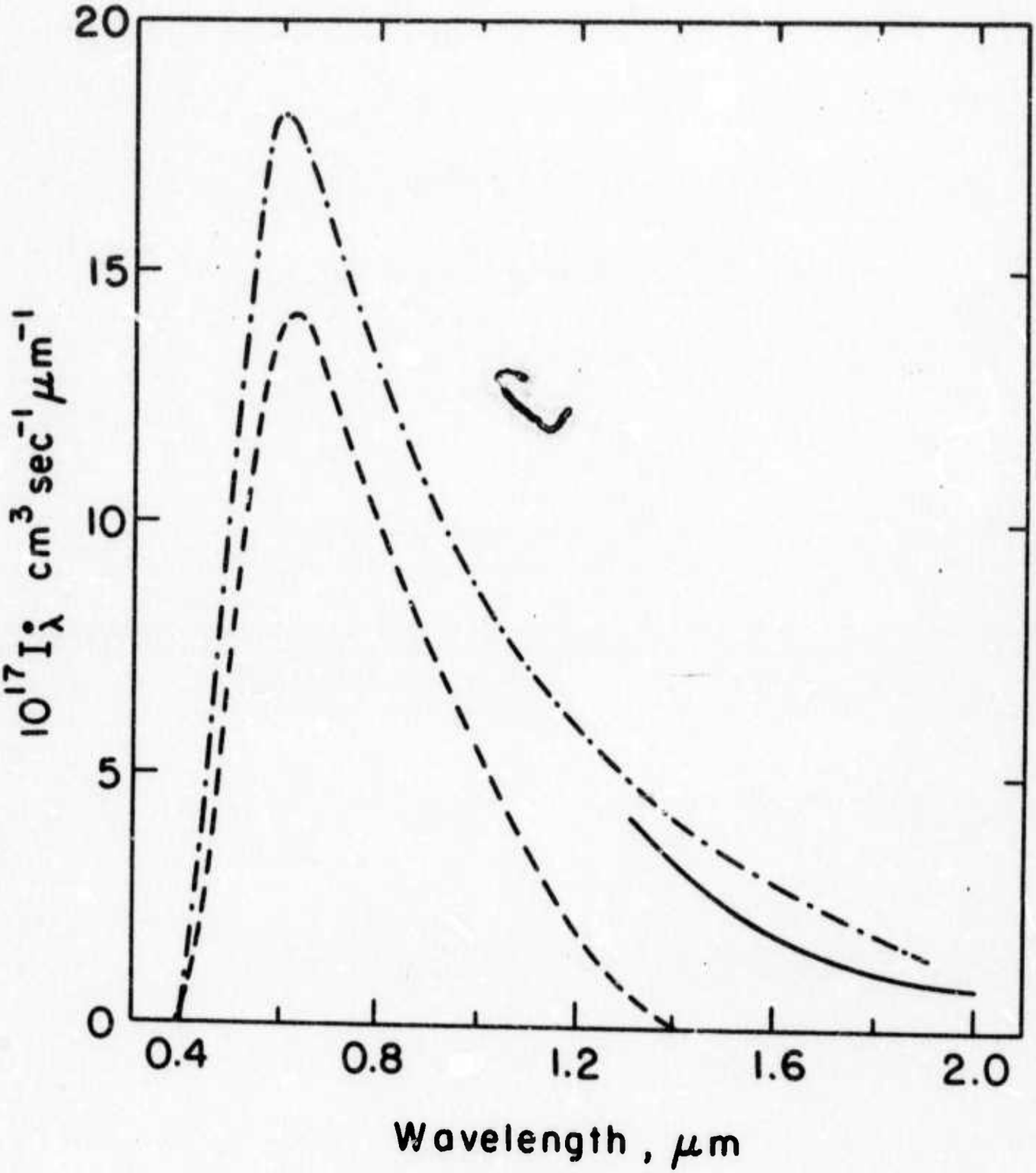
20
15
10
5
0
0.4
0.8
1.2
1.6
2.0
$10^{17} I_\lambda^\circ$ cm^3 sec^{-1} μm^{-1}
Wavelength, μm

FIGURE 4