NATIONAL BUREAU OF STANDARDS REPORT

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THE SPECTRAL DISTRIBUTION OF RADIANT ENERGY OF A GAS–FIRED RADIANT HEAT PANEL AND SOME DIFFUSION FLAMES

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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THE SPECTRAL DISTRIBUTION OF RADIANT ENERGY OF A GAS-FIRED RADIANT HEAT PANEL AND SOME DIFFUSION FLAMES

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ABSTRACT

Measurements were made of the spectral distribution of energy from radiant sources employed in standard test methods of flammability. Radiant sources examined were a gas-fired radiant panel employed in ASTM Test E-162 and the electric heater employed in the Smoke Chamber Test. To afford a basis for comparison, the emission spectra of several diffusion flames in air were measured. The energy distribution of the flames occurred essentially in two narrow wavelength intervals corresponding to emission of carbon dioxide at 4.4 μm and water at 2.7 μm. Luminous diffusion flames containing large amounts of incandescent carbon, such as acetylene in air, show a blackbody background continuum with CO_2 and H_2O emission peaks superimposed on the continuum. The radiant test sources exhibited an energy distribution approximating that of a blackbody with atmospheric CO_2 and H_2O absorptions superimposed. The gas-fired radiant panel in addition showed a significant emission peak at 4.4 μm due to hot CO_2.

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INTRODUCTION

Interim Federal Standard No. 00136b (ASTM Standard Test E-162) for the measurement of flame-spread properties of materials employs a gas-fired porous refractory material as a radiant heat source. [1, 2] An important experimentally unverified assumption has been that the radiant panel has the same spectral energy distribution as a blackbody. Earlier approximate measurements on a similar type panel would suggest that its emission spectrum would show significant deviations from that of a blackbody emitter. In addition the radiant energy sources employed in the Smoke Chamber Test, ASTM STP 422, and the Pill Test for floor coverings were examined. These sources all have their energy maxima in the infrared region of the spectrum at wavelengths greater than 2 μm. The spectra of a number of diffusion flames were also recorded to provide a basis for comparison between radiant test sources and radiant energy distributions realizable in fire situations. In contrast with diffusion flames the wavelength distribution of energy of premixed flames has been studied extensively probably because of the ability to better specify the relevant parameters defining the flame. At least qualitative agreement would be expected between the emission spectra of diffusion and premixed flames.

EXPERIMENTAL PROCEDURE

Initial observations in the infrared (2-15 μm) were made using a Perkin-Elmer Model 21 double beam spectrophotometer modified for emission measurements using the technique of Steward and Richmond. [3] This system proved unsatisfactory due to limitations inherent in the spectrometer and transfer optical system, although some preliminary spectra were obtained measured relative to the Nernst glower of the spectrometer as an intermediate standard. The dual source mirror arrangement of the Model 21 was utilized by rotating the sample beam mirror to collect energy from the radiant panel. Unfortunately, this resulted in some uncompensated atmospheric absorption due to unequal path lengths as well as a poor object

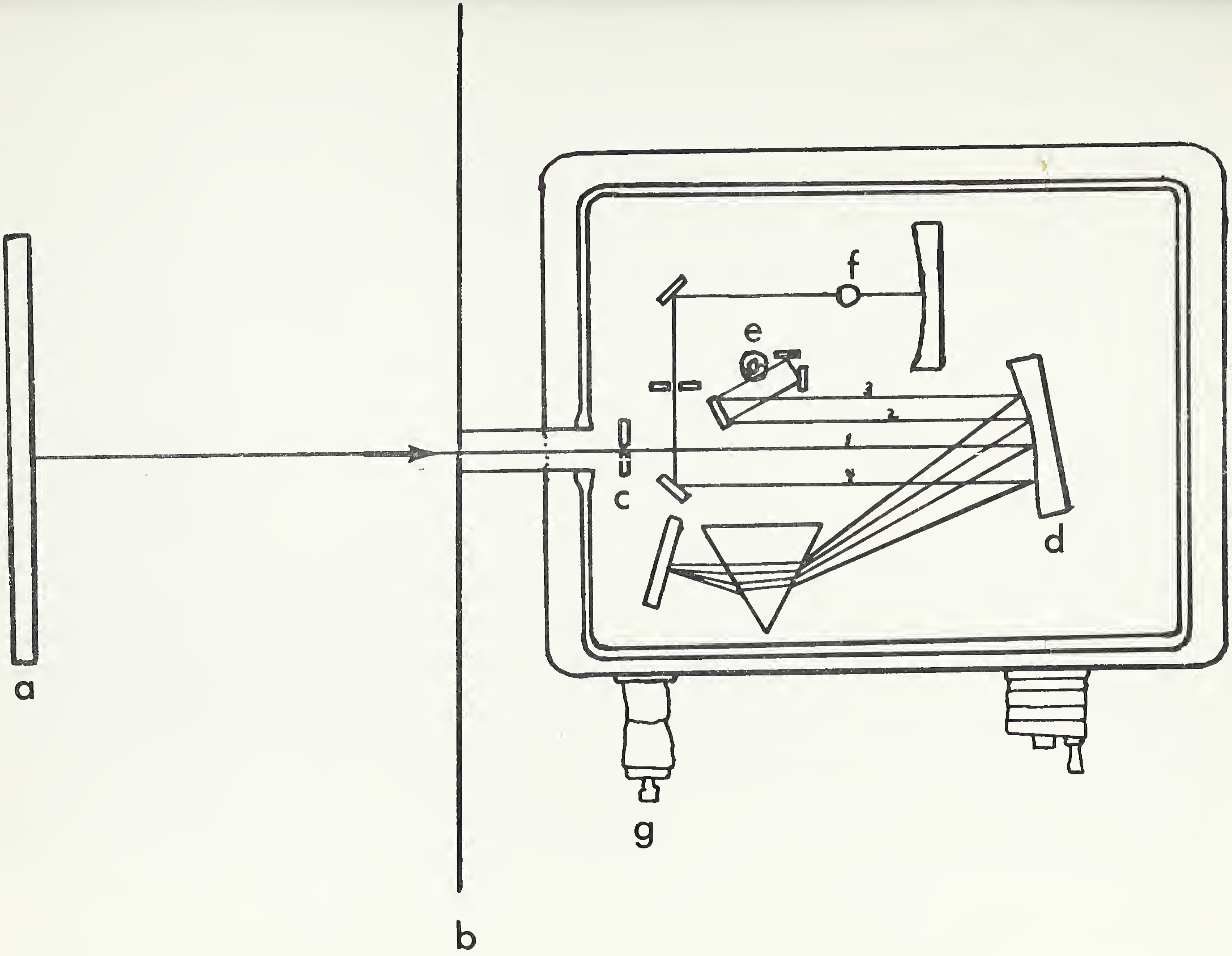

Figure 1. Optical Schematic of Spectrometer and Source: a - radiant test source; b - copper radiation shield; c - entrance slits; d - parabolic mirror; e - chopper; f - thermocouple detector; g - slit width control

image at the entrance slits of the instrument. More serious was the inability to make a direct comparison of the blackbody furnace with the radiant source due to the small aperature of the furnace and the relatively large panel to instrument distance. Also, the Nernst glower source of the Model 21 was required as an intermediate source to provide adequate energy in the reference beam. This system resulted in essentially the entrance slits being imaged on the source and hence a very narrow and inhomogenous section of the radiant test source was viewed. For these reasons the double beam spectrometer was not employed for further measurements.

A Perkin-Elmer Model 112 single beam double pass prism spectrophotometer was employed for the measurements reported here. (Figure 1) Calibration of the instrument was accomplished in the usual way using known frequencies of appropriate reference gases. [4] After calibration the prism was allowed to remain undisturbed during the measurements. A 2.3 mm thick 70 x 90 cm copper radiation shield was rigidly fixed relative to the spectrometer slits. The shield maintained at approximately 25 °C by means of water circulating through several meters of copper tubing soldered to the spectrometer side of the shield protected the instrument from the intense heat of the radiant source. A 1 cm diameter port in the shield the center of which was on the optic axis of the spectrometer opposite the entrance slit defined the aperature or field of view of the instrument. The shield to slit distance of 7 cm was selected so that with the 1 cm diameter shield opening the image of the blackbody reference furnace set at a maximum of 1-1/8 inch (6 cm^2 area) would fill the radiation shield port while at the same time filling approximately 80% of the parabolic mirror behind the entrance slits of the monochromator. The acceptance angle is determined by the size of the aperature in the radiation shield and its distance from the blackbody furnace. Because of the relatively small size of the reference furnace to provide adequate energy for the spectrometer, it is desirable to view the maximum area of the furnace without imaging of the cooler furnace walls on the entrance slits. For an image height (slit height) of 13 mm the minimum slit to furnace distance is 12.6 cm. This arrangement eliminated a transfer optical system and defined at the normal radiant panel to test sample or in this case radiation shield to panel distance of 50 cm a panel image of 10 cm diameter. In a typical experiment the spectrum would be scanned twice at two different speeds using a fixed slit width. The instrument and optical path between the radiation shield and instrument were purged with dry nitrogen to reduce atmospheric absorption to a negligible amount. The atmospheric absorption over the remaining optical path between shield and radiant panel was essentially that existing in the actual test arrangement. (Figure 2)

Figure 2. Experimental System

To provide a reference standard for intensity an ECI Thermal Radiation Standard Model 55 consisting of a large aperature (1-1/8 inch) isothermal cavity (blackbody) with a temperature control of ± 1 °C was employed. The blackbody furnace set at the desired temperature was positioned for maximum energy through the radiation shield as measured with the spectrometer set at the wavelength of the peak of the blackbody curve for the particular furnace temperature employed.

EXPERIMENTAL RESULTS

Gas-Fired Radiant Panel

A consideration of the energy distribution of a radiant test source is of interest because of the known deviations of radiant energy of premixed flames from that of a greybody. [5, 6] It seems probable that the spectral absorption characteristics of the material under test may also influence the ease of ignition of the material exposed to the heat source of the test unit. The radiant heat source for ASTM E-162 test for the flame-spread properties of materials is a gas-fired porous refractory material enclosed except for one face in a cast iron frame. The radiating surface of 18" x 12" is vertically mounted with a 6" x 18" test specimen facing the source but inclined at 30° angle with the top edge of the sample closest to the top of the radiant panel. Since we are interested in an effective spectral radiance of the panel, i.e., the radiation received by the exposed sample, the spectrometer and radiation shield were positioned approximately the same distance from the radiant heat source as the base of a typical sample. This resulted in a 50 cm panel to spectrometer slit distance. With this geometry a 10 cm vertical segment of the panel was viewed by the spectrometer through the same atmospheric path as a test sample; the remaining optical path from the radiation shield to the detector was purged with dry nitrogen. However, some residual atmospheric absorption due to 2.7 μm H_2O and 4.2 μm CO_2 remains, as may be seen in the reference furnace spectra, Figures 3 and 4. Spectra of the reference blackbody furnace were obtained at temperatures of 670 °C and 750 °C preceding measurements of the panel and at the end of the entire series of measurements. Agreement was good between both sets of data.

Since the radiant panel is a fixed installation the spectrometer and radiation shield were mounted on a mobile rack facilitating movement with the associated electronic equipment from the laboratory to the test panel site. The height of the mobile assembly was such that the spectrometer initially viewed the second quadrant of the radiant panel. Allowing an hour for the radiant panel to reach thermal equilibrium, spectra of the lower portion of the panel were recorded (Figure 6). The entire spectrometer assembly was raised by means of a fork lift truck to obtain spectra of the center and upper portions of the panel (Figures 7 and 8). As a check on the reproducibility of the system the spectrometer was returned to the floor and spectra of the lower section again recorded.

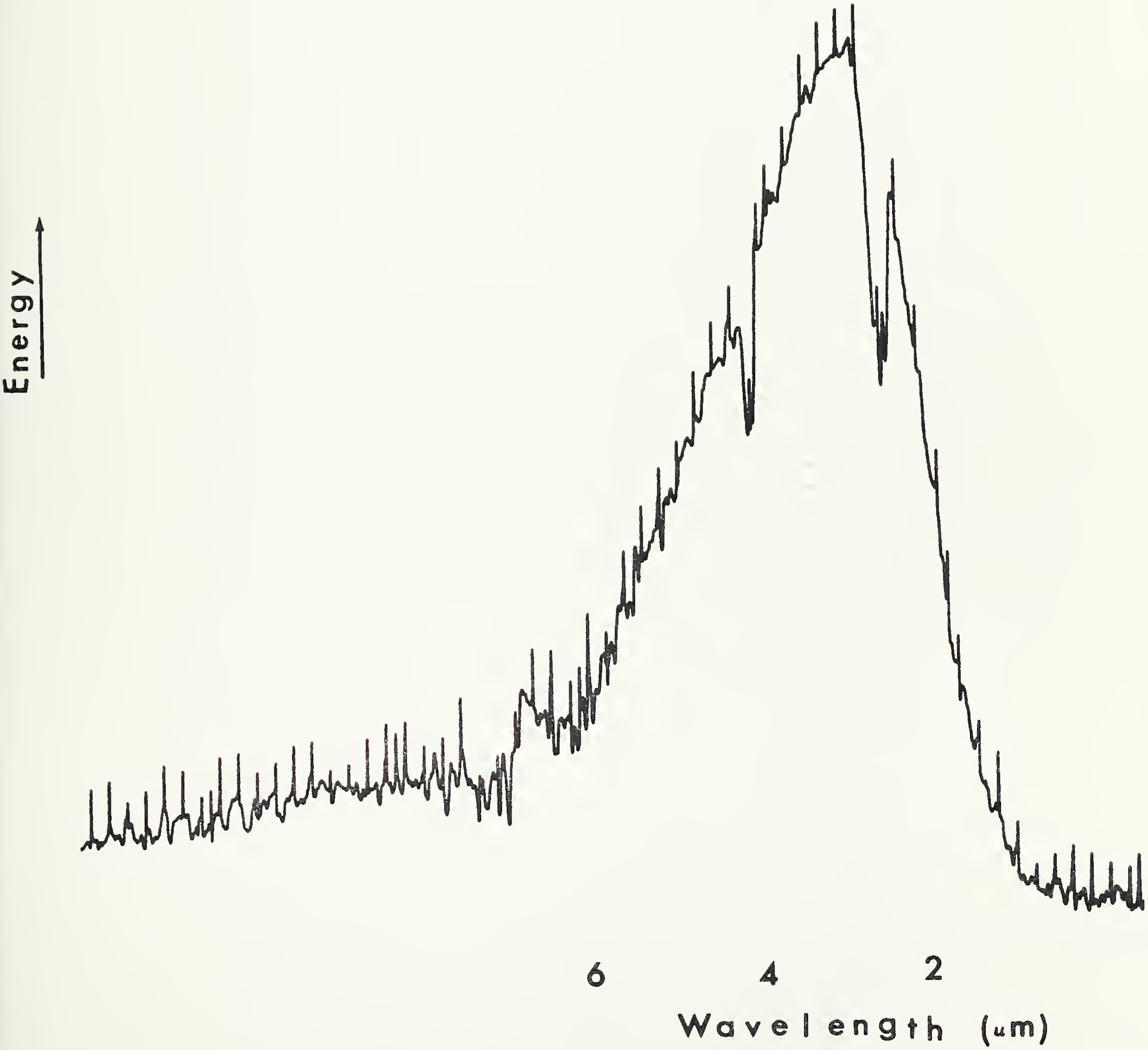

Figure 3. Spectrogram of Blackbody Furnace at 670 °C.
Slit Width of 65 µ

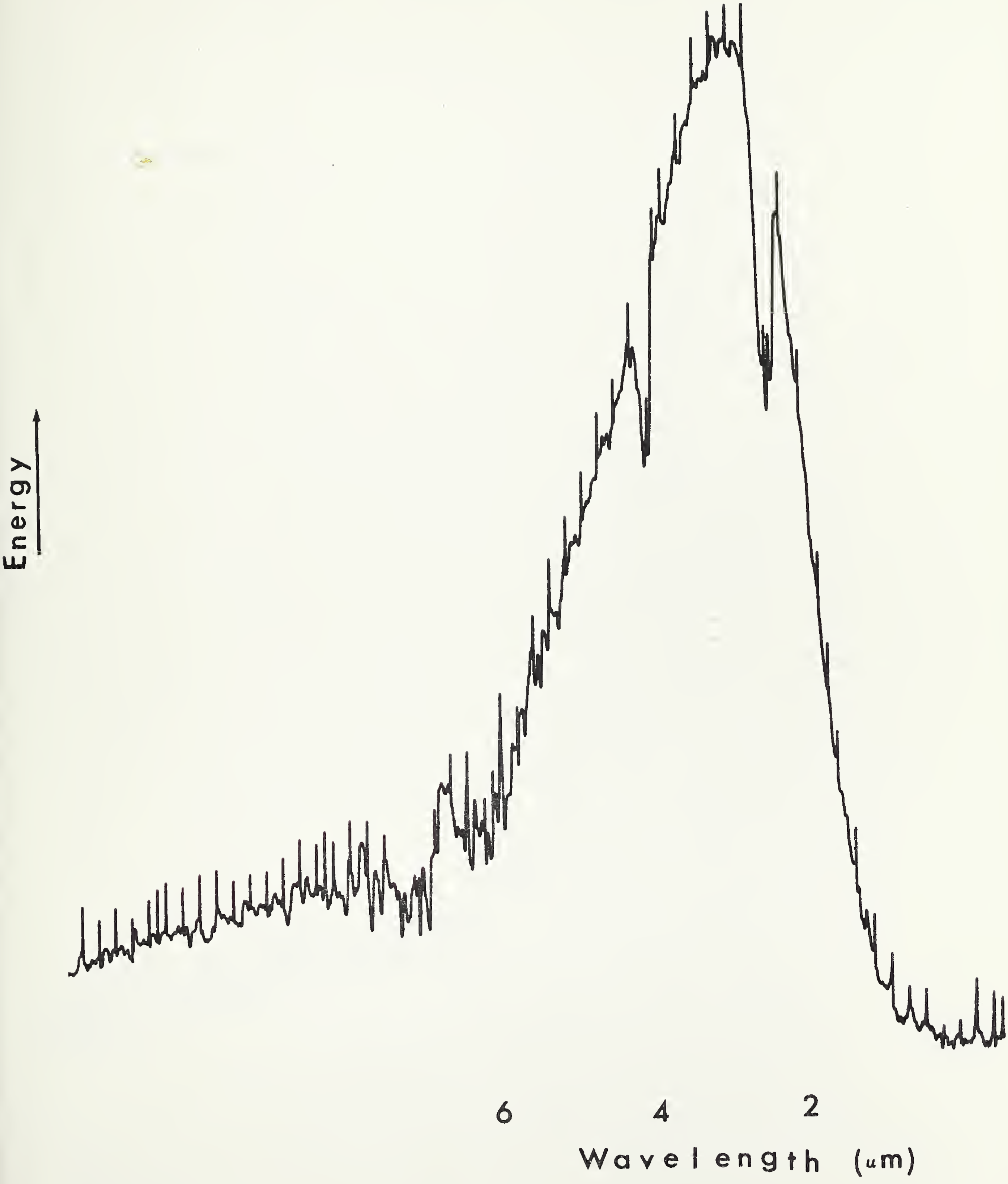

Figure 4. Blackbody Furnace at 670 °C, 75 μ Slit.

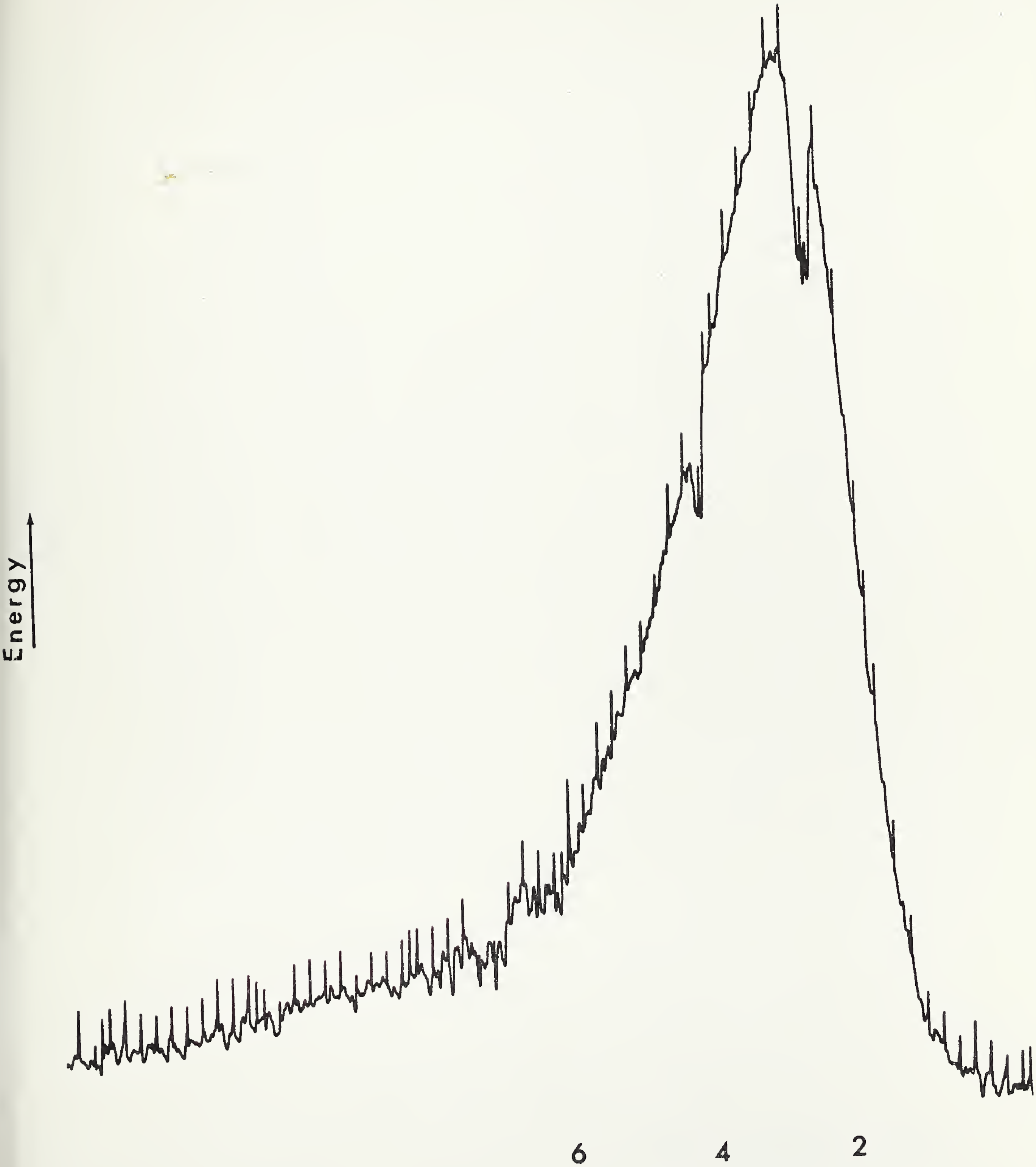

Figure 5. Blackbody Furnace at 750 °C, 65 μ Slit.

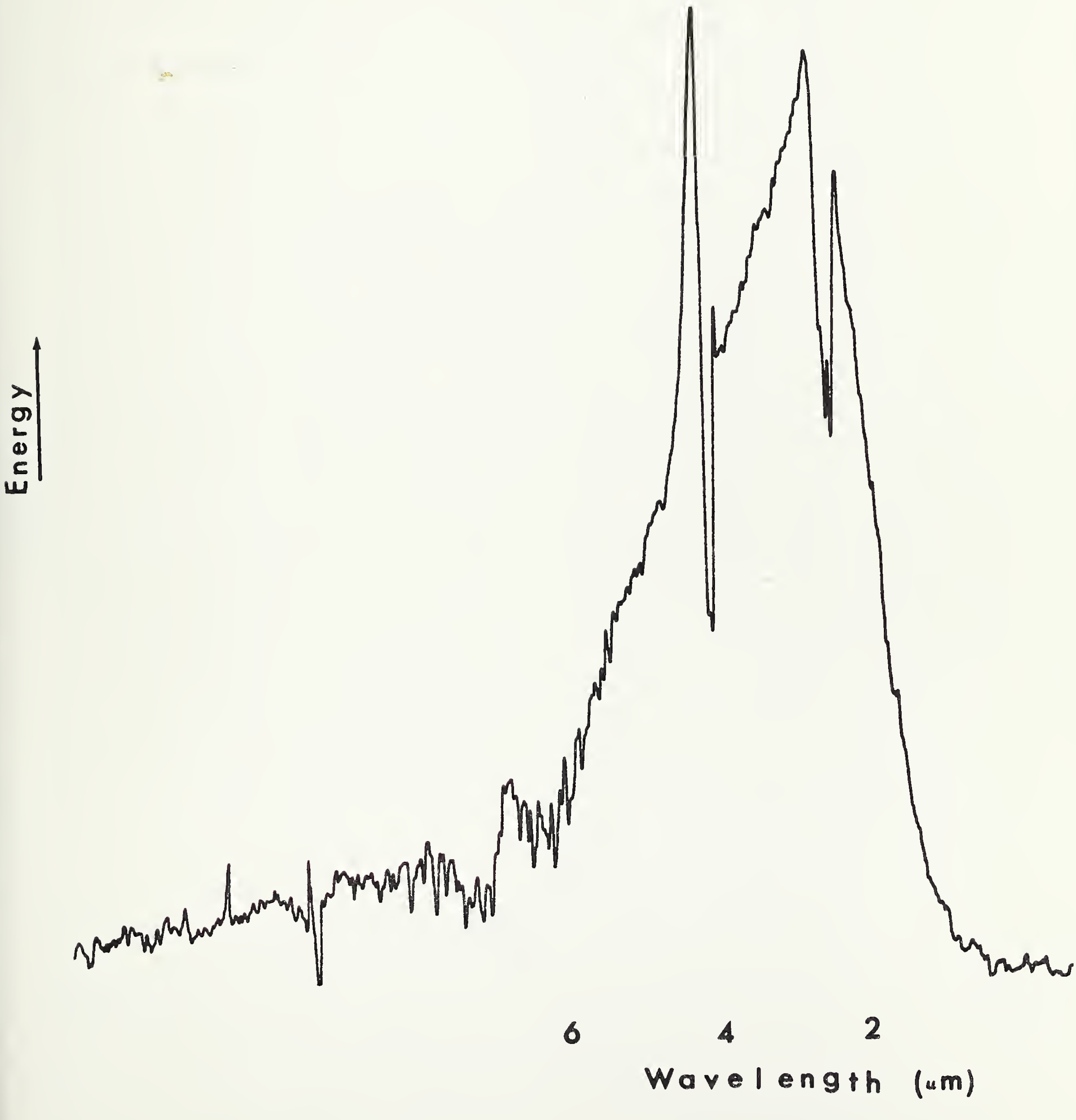

Figure 6. Spectrogram of Lower Center Portion of Gas-Fired Radiant Panel, 75 μ Slit.

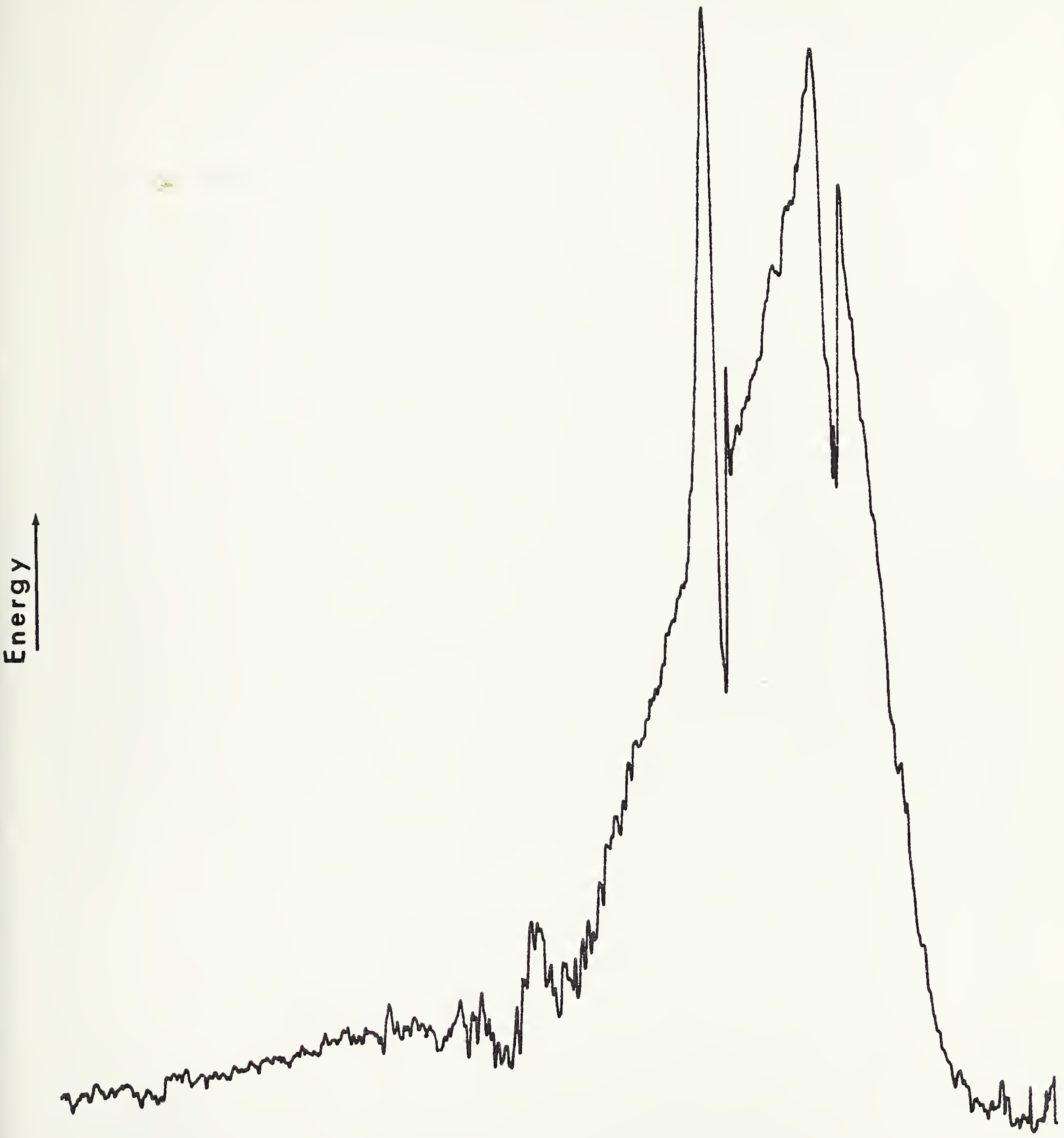

Figure 7. Center Portion of Radiant Panel, 75 μ Slit.

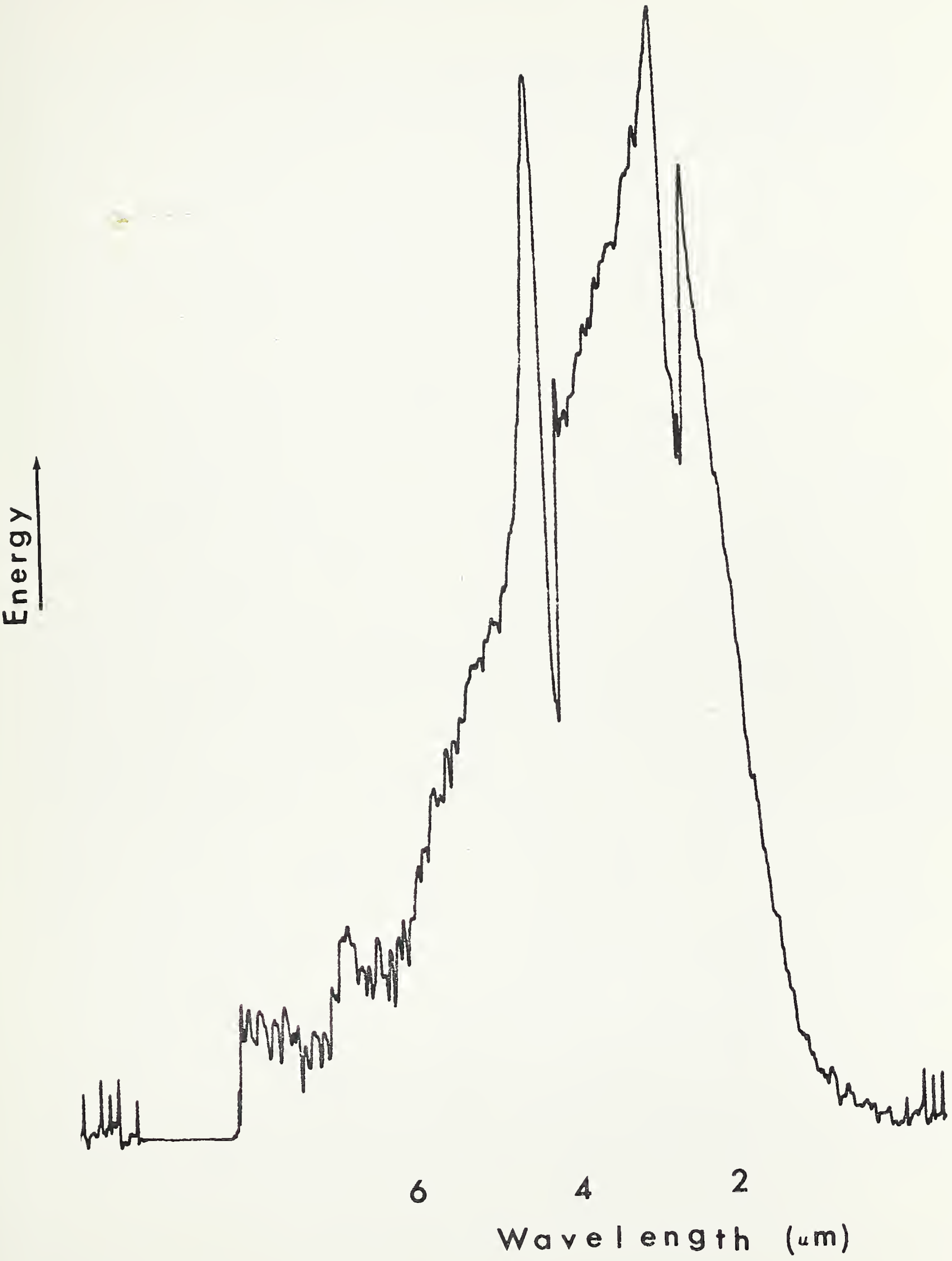

Figure 8. Upper Portion of Radiant Panel, 65 μ Slit.

The greybody curves for the panel show approximately the same skewness as the reference blackbody curves in figures 3 and 4. The spectrograms recorded with this instrument are neither linear in wavelength or wavenumber. The wavelength scale is considerably compressed at the shorter wavelengths due to the lower dispersion of the rock salt prism in this region. Using the Wien displacement law, $\lambda_{max}T = 2897.7$ μ·deg. K, obtained by differentiating the Plank radiation law, temperatures were calculated for the panel and furnace. Although it is difficult to obtain a precise measurement of λ_{max} primarily because of poor prism dispersion and a relatively flat maximum for the blackbody curve, the agreement of calculated and thermocouple measured furnace temperatures is within the wavelength uncertainty for this region [7] (Table 1).

Some additional uncertainty at higher temperatures is caused by the 2.7 μm atmospheric water absorption band which falls near the radiation maximum in the 750 °C temperature range. The furnace curves show atmospheric absorptions due to water and carbon dioxide over path lengths shorter than those employed with the radiant panel. The estimated overall uncertainty in the calculated temperature is ± 20 °C; an error of ± .05 μm at 3.10 μm represents an uncertainty of ± 15 °C. However, the calculated values are consistently low, with an average for the 670 °C ± 1° furnace spectra of 655 °C. In the case of the 750 °C furnace spectra the difference appears to be somewhat larger but an accurate assessment is not possible because of the smaller number of measurements made at this temperature. The radiant panel spectra approximate the furnace spectra with respect to energy distribution with wavelength. In the 4 μm region the CO_2 emission peak is sufficiently displaced to longer wavelengths that we observe about midway through the 4.2 μm absorption band the transition to the 4.5 μm emission band. The CO_2 emission is displaced to longer wavelengths because of population of "hot" vibrational bands other than the ν_3 fundamental we observe in absorption.[5] Assuming a Plankian distribution curve we note that if the peak (Wien) is shifted to shorter wavelengths, representing a higher temperature, until the CO_2 emission peak of the experimental curve falls under this curve we would have an unrealistically high temperature. Therefore, the temperature of the combustion gases is considerably higher than the blackbody temperature of the panel. This high intensity of the CO_2 peak relative to the blackbody portion of the radiant energy is due to the higher temperature of the CO_2 produced in the natural gas combustion. [8] The CO_2 appears to be in thermal equilibrium and not primarily chemically excited (chemiluminescent) CO_2 produced in the combustion process. [9] The radiating face of the panel has a layer of combustion gases, increasing in thickness from a few cm at the base to 35 or 50 cm at the top, which is at a temperature considerably higher than that of the panel itself. We may, however, neglect the radiative component of this hot gas mixture represented by the CO_2 emission in the transfer of energy to the test specimen. In the case of the panel a fortuitous

TABLE I

Source	Thermocouple Temp. °C	λ_{max} (μm)	Temp. °C (calculated)
Furnace - 1	670	3.14	650
Furnace - 3	670	3.10	662
Furnace - 5	670	3.10	662
Furnace - 6	670	3.15	647
Radiant Panel-Lower Center (P-1)		2.84	747
Radiant Panel-Left Center (P-2)			
Radiant Panel-Center (P-3a)		2.84	747
Radiant Panel-Top Center (P-4)		2.84	747
Radiant Panel-Lower Center (P-5A)		2.84	747
Smoke Chamber Source		2.84	747

choice of sample distance has resulted in about equal areas under the emission and absorption bands of CO_2 so they in effect cancel and may be disregarded in considering the total energy radiated. The effective temperature of the panel is estimated to be 747 °C (1020 K) calculated using the Wien displacement law. The E-162 test specifications call for a blackbody temperature of 923 K. The mean emissivity of the panel ε may be estimated from the ratio of blackbody to effective temperature:

$$\varepsilon = \left[\frac{923}{1020}\right]^4 = 0.67 \approx 0.7$$

The range in ε based on the estimated uncertainty in the temperature is 0.62 to 0.73.

Comparison of spectra of the lower center portion, Figure 6, and the lower left, obtained for the same vertical height revealed the same temperature and energy distribution. Increasing the height by 11.5 cm to an area near the center but slightly below the horizontal line bisecting the panel results in Figure 7. This section of the panel closely approximates the intensity and energy distribution of the furnace at 670 °C, Figure 4. However, the intensity of the CO_2 emission peak has increased significantly as well as the amount of radiation relative to the lower section. This trend became more manifest in the upper section of the panel requiring a reduction in the slit width from 75 to 65 μ to bring the spectrum on scale. Figure 5 represents the top center portion of the panel. Here the curve approximates the 750 °C curve thus representing a vertical temperature gradient of 100 °C over the face of the panel.

The Smoke Chamber Source

The electrically heated source employed in the smoke chamber yielded the anticipated spectrum approximating a blackbody energy distribution. The holder containing the ceramic backing plate and nichrome heating element were positioned 14.5 cm from the radiation shield and operated at 105 V. Several scans of the source were made using a 65 μ slit width with a typical spectrogram reproduced in Figure 9. This curve matches very closely, both in intensity and wavelength maximum, the 750 °C blackbody furnace curve.

Diffusion Flames

Premixed flames have been examined in considerable detail spectroscopically. [5, 6, 8, 9, 10, 11] Surprisingly little effort has been devoted to diffusion flames although at least qualitatively they should approximate premixed flames for a given type of fuel. Specification of the size of

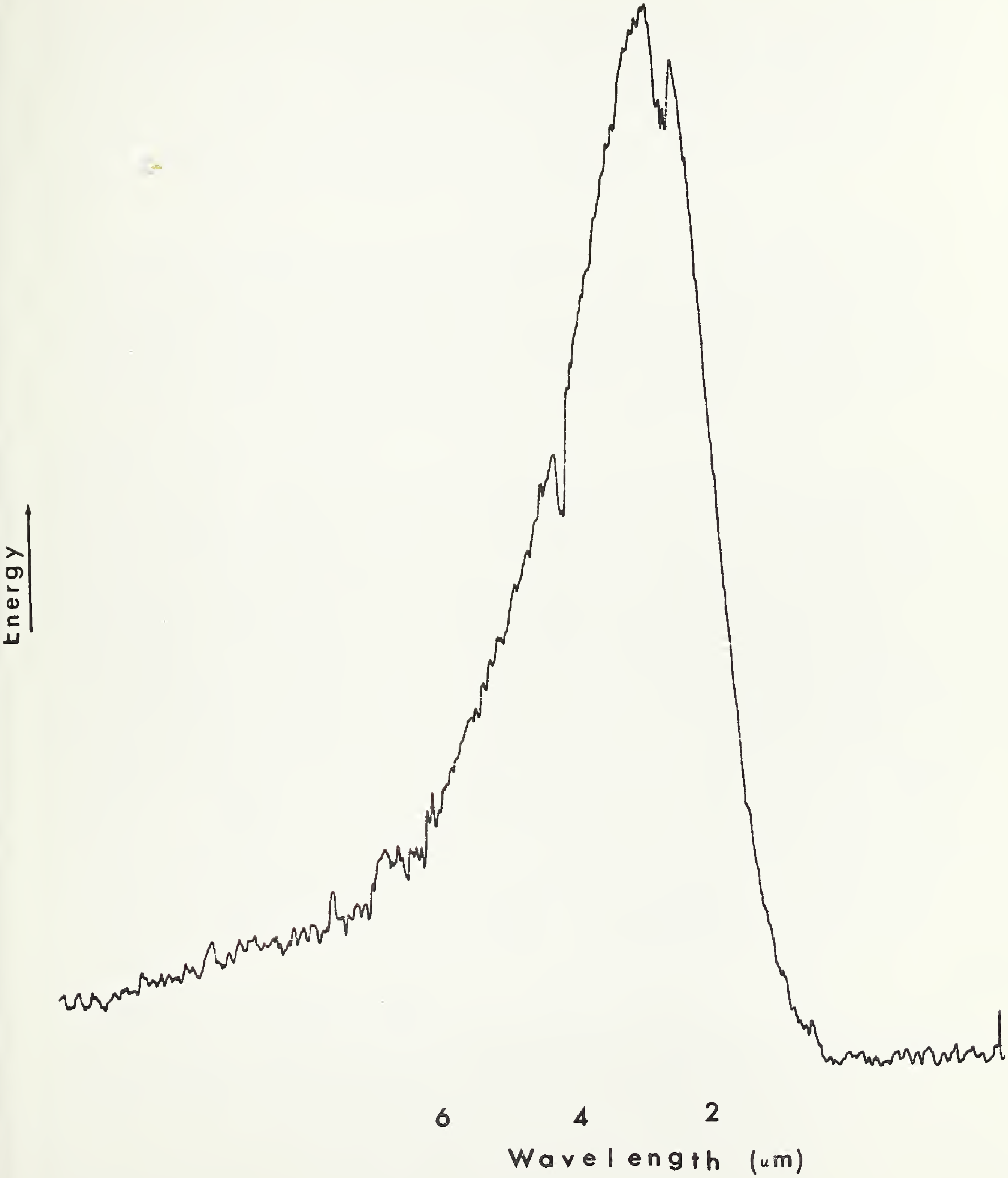

Figure 9. Spectrogram of electric Source for Smoke Test Chamber, 65 μ Slit.

flame, fuel rate, composition of the combustion mixture or stoichiometry is feasible for the premixed flame but not easily realized in the case of diffusion flames. The extent to which test sources approximate blackbody sources or resemble a diffusion flame, i.e., the spectral distribution of energy impinging on a test material, may effect the ease of ignition of the material. A number of diffusion flame spectra have been measured to provide a basis for comparison with the spectral energy distribution from the radiant test sources previously described.

As is the case with premixed flames, water vapor and CO_2 bands account for nearly all the emitted energy. As mentioned earlier in the radiant panel spectra the high intensity of the CO_2 peak relative to the blackbody portion of the curve (radiant panel at 943 K) is probably due to the higher temperature of the CH_4--air flame (about 2000 K). In luminous diffusion flames such as acetylene in air we observe a significant fraction of the radiated energy appearing as a blackbody continuum with hot carbon acting as the source.

Methane Flames

The methane-air diffusion flame, Figure 10, is essentially the same as that reported by Bell, et al., for a premixed CH_4-air flame using a Meeker burner. Emission bands appear at 1.9 μm due to H_2O, 2.7 μm due to H_2O and CO_2, 4.4 μm due to CO_2 and H_2O in the 5 to 8 μm region. By far the strongest band is the 4.4 μm CO_2 with the 2.7 H_2O band an order of magnitude weaker. In one experiment employing the same burner and CH_4 flow, a diffusion and a premixed flame were compared (Figure 11). The methane flow was adjusted to provide a sufficiently large diffusion flame (yellow) to fill the entrance slits. The spectrum was recorded and compressed air admitted to the CH_4 stream to produce a premixed (blue) flame. The burner was positioned so that a vertical segment of the flame starting near the top edge of the burner was examined. Both flames exhibit CO_2 and water peaks in about the same intensity ratios with the amount of incandescent carbon in the yellow flame insufficient to appear in the spectrum under these conditions. Most striking, although more apparent in slower scans, are the abundance in the yellow flame of emission peaks falling between the 2.7 μm H_2O and the 4.4 μm CO_2. Although not readily assignable at this resolution the most prominant additional peak at 3.3 μm may be attributed to a carbon-hydrogen species, possibly CH radical.

Ethylene and Acetylene Flames

The ethylene spectrum, Figure 12, with the increased C to H ratio relative to CH_4 begins to show radiation from the incandescent carbon with the

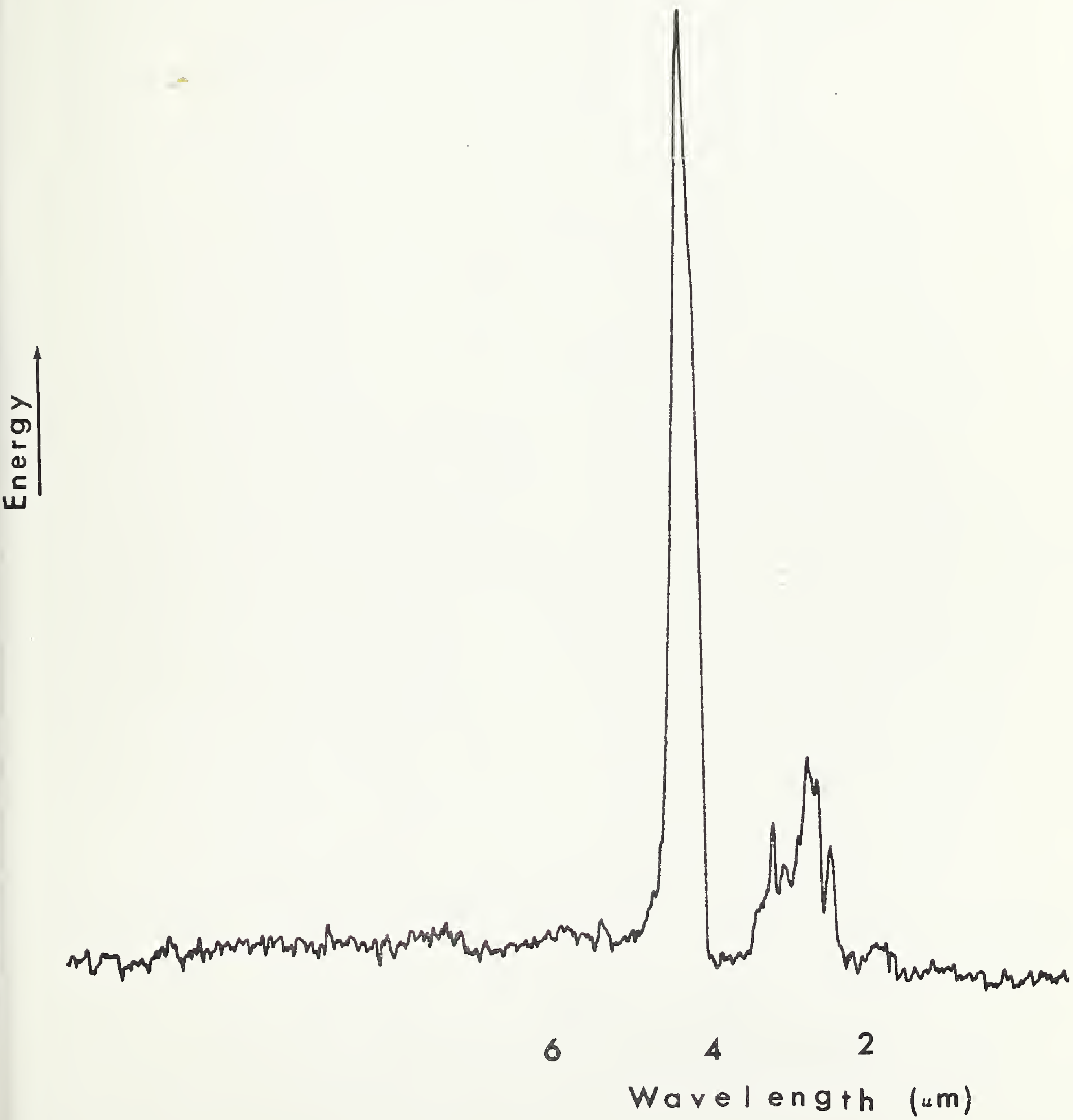

Figure 10. CH_4 Diffusion Flame (Yellow)

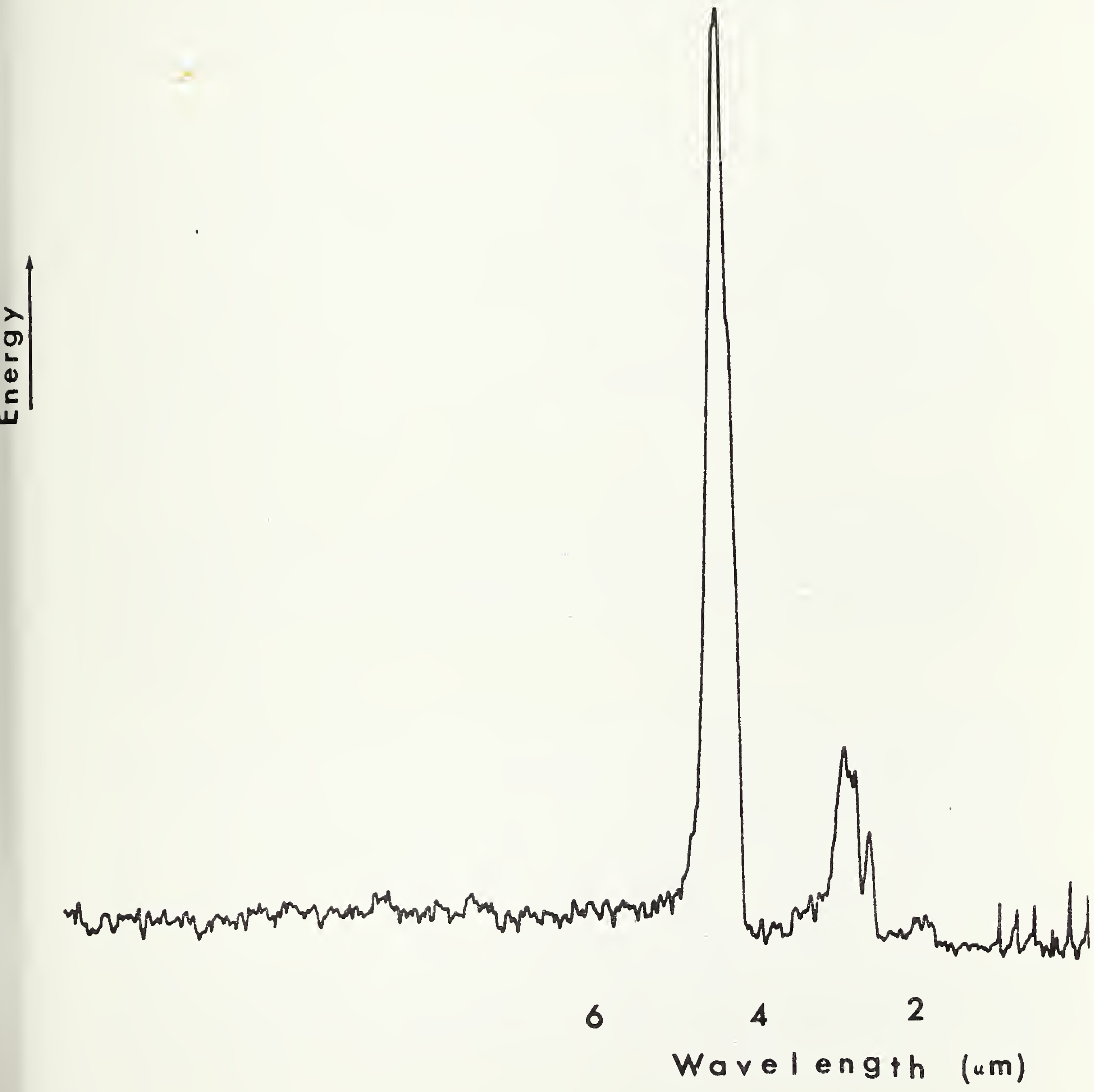

Figure 11. CH_4-Air Premixed Flame (Blue)

2.7 µm H_2O band superimposed. Only in the case of the acetylene diffusion flame (yellow), Figure 13, does the energy radiated by the incandescent carbon exceed the CO_2 emission. However, with the addition of air to form a premixed flame, Figure 14, we obtain an energy distribution approximating a CH_4 diffusion flame. The premixed acetylene flame showed a pale blue outer cone and an inner smaller aqua-colored cone. Figure 14 represents the pale blue outer cone.

Optical temperature measurements are reviewed in detail for both luminous nonluminous flames by Mavrodineanu and Boiteux. [6] The carbon particles for the acetylene flame have an average diameter of 6 mµ and a temperature calculated to be at a blackbody temperature of 2070 K. For the C_2H_2 flame the blackbody portion of the spectrum was estimated to peak at approximately 1.6 µm (1800 K). Intercomparison of intensities for the various gaseous diffusion flames is not feasible because of the various sized flames. In each case the fuel rate was adjusted to bring the strongest peak (usually 4.4 µm CO_2) near full scale, except in the case of the wood fueled and candle flames. As anticipated the acetylene in air had a much higher fraction of total energy radiated in the blackbody portion of the spectrum measured relative to the CO_2 emission than did the other hydrocarbons.

Ethanol Flame

The ethanol flame was obtained using a glass alcohol lamp fitted with a cotton wick. The flame closely resembles the CH_4 in air flame (Figure 15). The spectrum contains other spectral features of molecules present in too low a concentration to appear under these conditions of resolution and energy.

Candle Flame

The candle flame is an interesting example of a diffusion flame which has been studied extensively. Again, Figure 14, the most prominent feature is the 4.4 µm CO_2 emission. The amount of 2.7 µm H_2O would appear to be less relative to the CO_2 although an accurate estimate is not possible due to obscuration by the blackbody background continuum from incandescent carbon exhibiting a maximum in the same wavelength region. A comparison of the spectrum of the candle flame (Figure 16) with the methane diffusion flame (Figure 10) and C_2H_2 in air (Figure 13) shows that the candle flame falls between the two flames in amount of blackbody radiation, or radiation originating from the incandescent carbon particles, when measured relative to the 4.4 µm CO_2 emission. The blackbody portion of the radiant energy shows a peak at approximately 2.2 µm. Using this value in the Wien displacement law a temperature of 1040 °C was obtained for the radiating

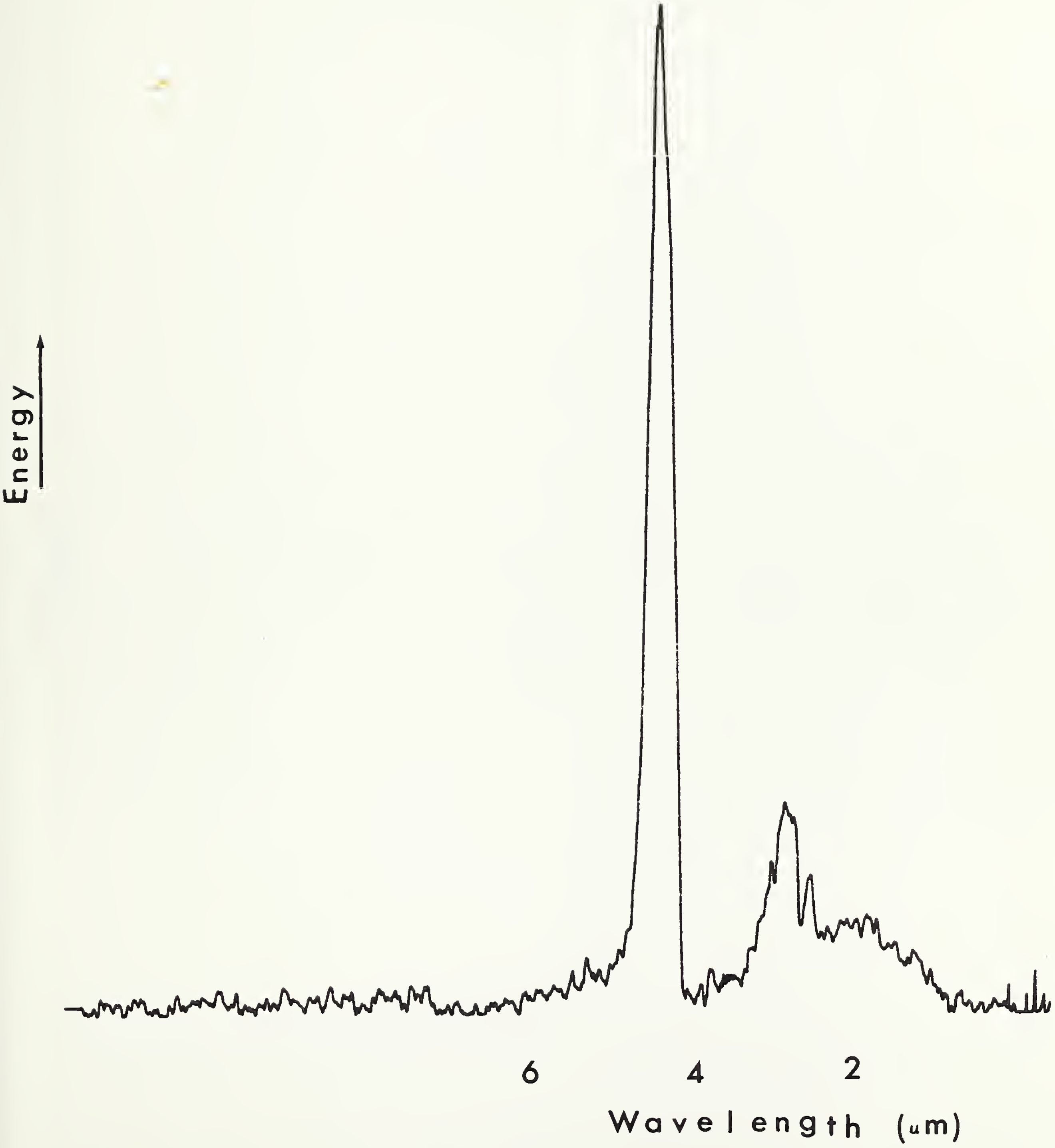

Figure 12. Ethylene Diffusion Flame (Yellow)

Figure 13. Acetylene Diffusion Flame (Yellow)

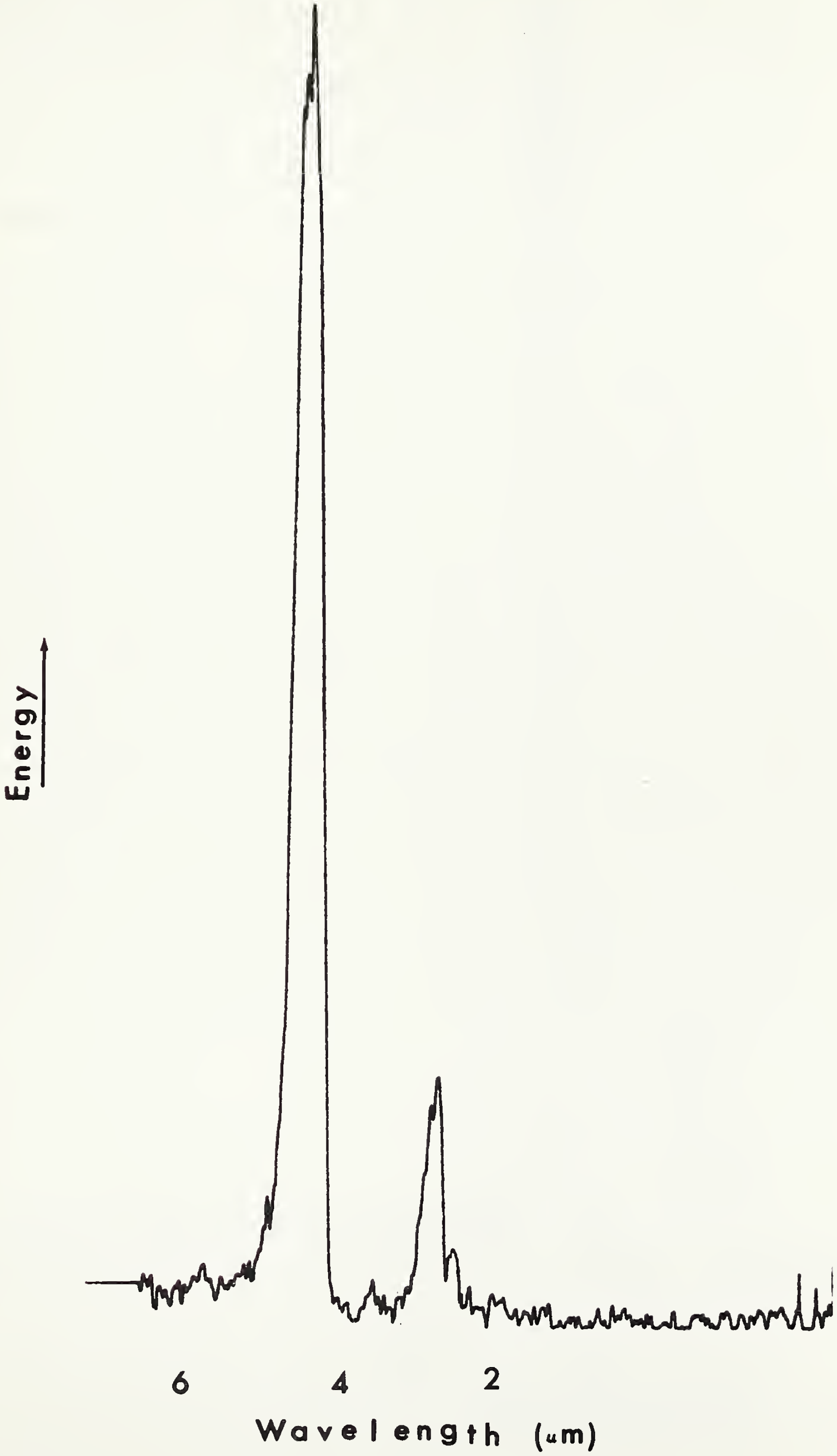

Figure 14. Acetylene-Air Premixed Flame (Blue)

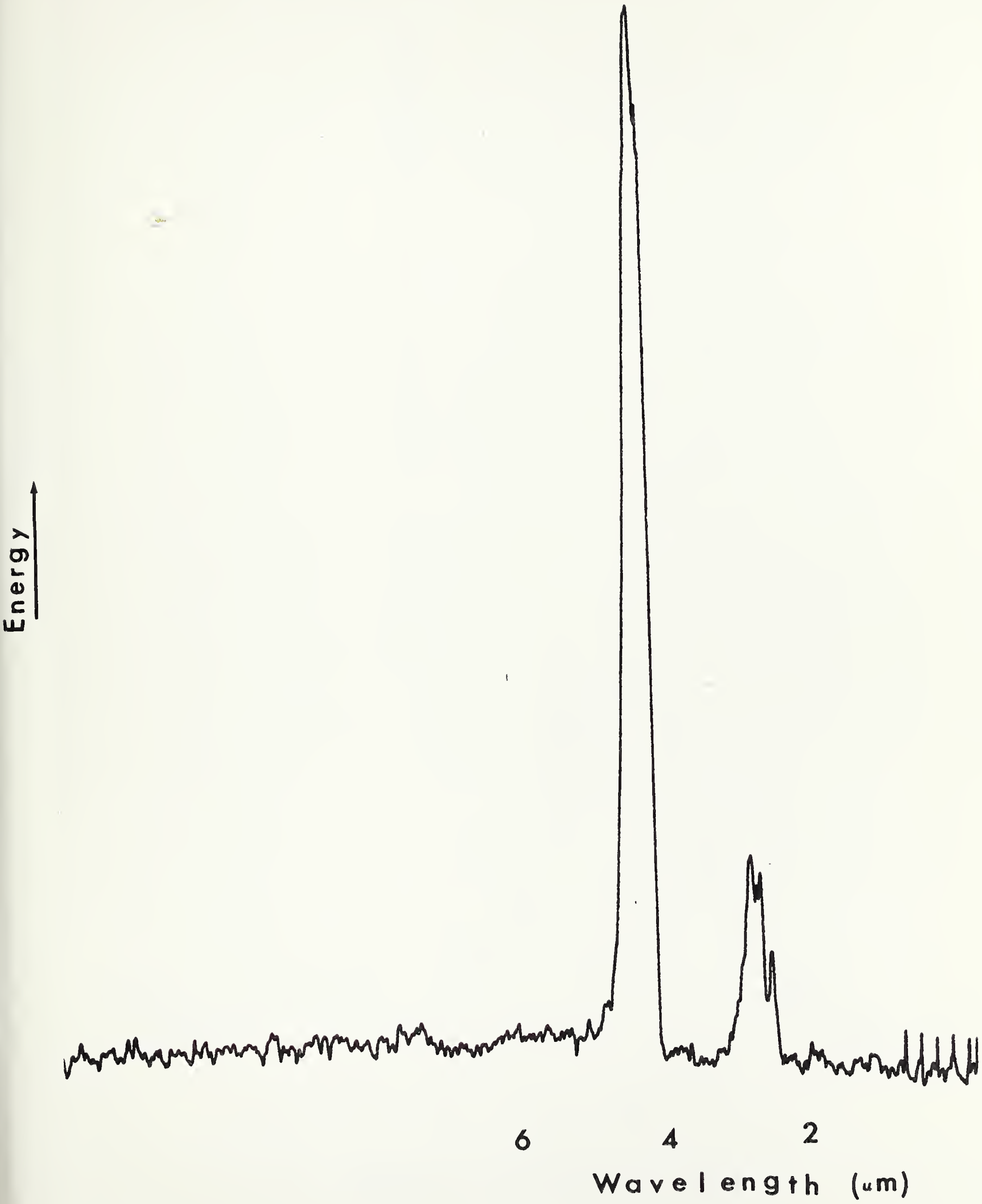

Figure 15. Ethanol Flame

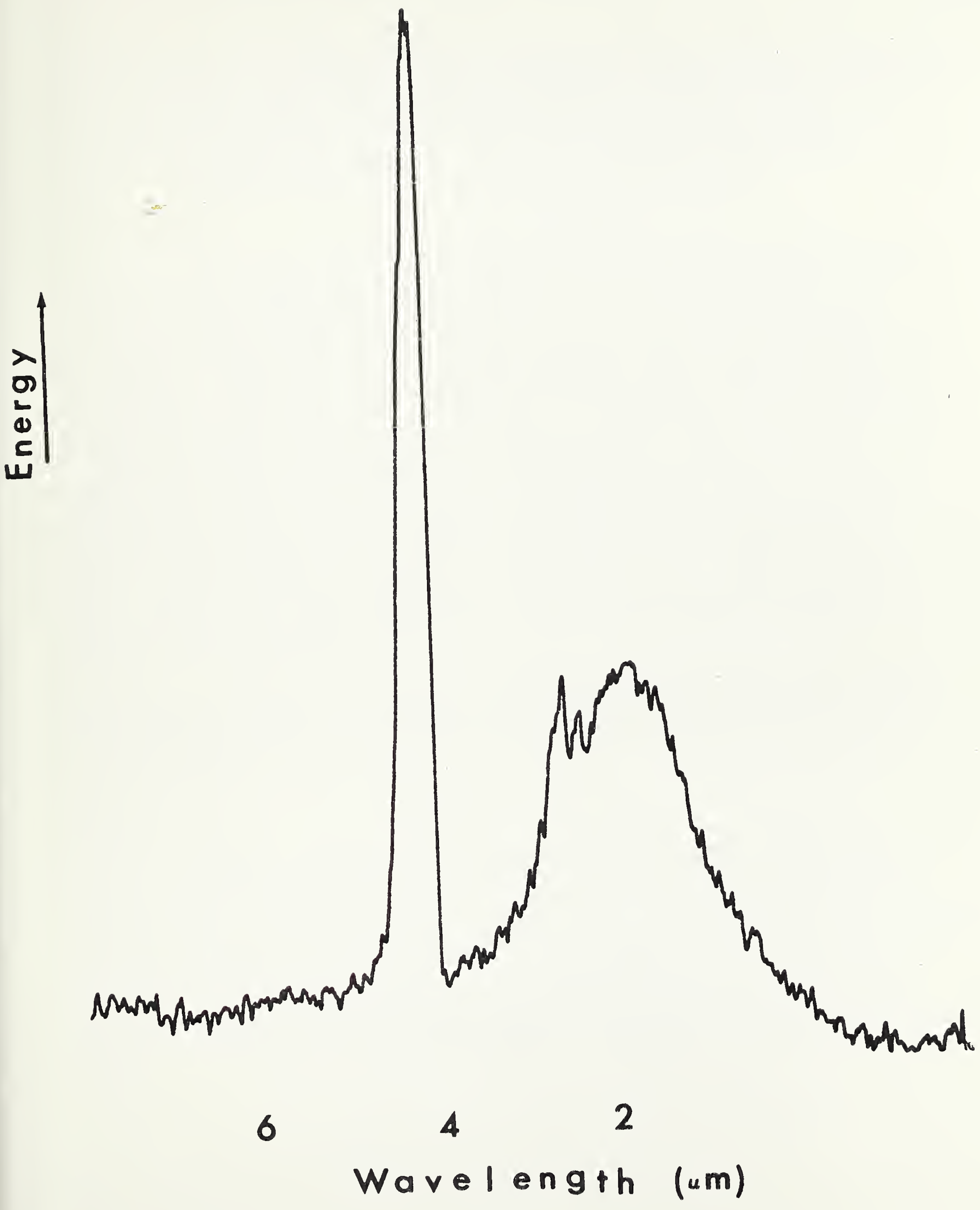

Figure 16. Candle Flame

carbon particles. Gaydon and Wolfhard [11] give a temperature field of a candle flame based on thermocouple measurements which shows the temperature of the luminous zone to fall in the 1000 to 1200 °C range. Since we are viewing predominantly radiation from the cooler surface region of the luminous zone we may expect the value to occur near the lower end of the range. The candle employed was a standard GSA 8 hour type.

Wood Flames

Figure 17 and 18 show spectra obtained for a wood-fueled diffusion flame in air. Well seasoned hard maple rods of 5 mm or 11 mm OD were ignited at one end and positioned about 1 cm from the copper radiation shield. The orientation of the burning rod was adjusted in both the horizontal and vertical planes so as to maintain as constant flame size and position as possible. However, considerable variability in the flame composition was evident from fluctuations in the flame color and differences in the recorded spectra. The dominant features as in the case of the hydrocarbon diffusion flames are the CO_2 and H_2O emission bands. In Figure 17 additional features which varied in intensity with the conditions of combustion are apparent. At 5.8 µm a peak assignable to carbonyl group most likely occurring in an aldehyde or ketone is readily apparent. The peak of about the same intensity at about 3.3 µm is assignable to CH group and the remaining bands to CO_2 and water or OH. [10] CO appears as an unresolved shoulder near 4.8 µm long wavelength edge of the 4.4 µm CO_2. A scan of the flame employing a LiF prism revealed an extremely rich and complex spectrum.

With the exception of the variable and relatively weak features discussed above the wood-fueled flame is seen to closely approximate the hydrocarbon diffusion flames (excluding C_2H_2) in the spectral distribution of the radiated energy.

Tablet Flame

A column of several hexamethyltetramine tablets employed as an ignition source in a floor covering flammability test (Pill Test) were positioned approximately 1 cm from the copper radiation shield. The column was supported before ignition with a hemicylinder of copper gauze. The resulting diffusion flame, Figure 19, unstable and difficult to maintain, resembles in its spectral energy distribution a methane diffusion flame with CO and possibly other lesser components accounting for the shoulder in the long wavelength side of the CO_2 emission band. However, in this test the radiative component in the energy transfer process is presumed to be minor.

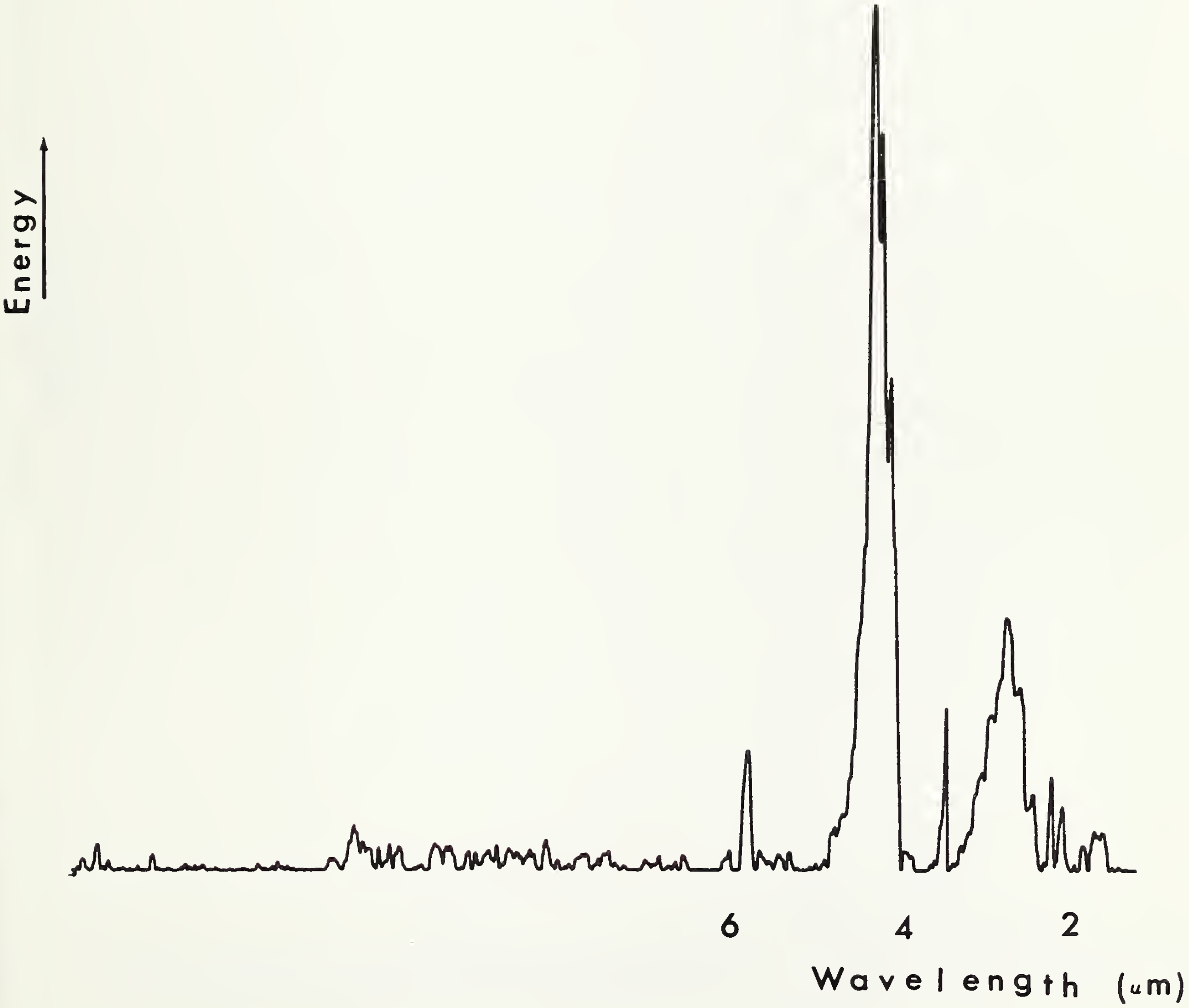

Figure 17. Wood-Fueled Diffusion Flame

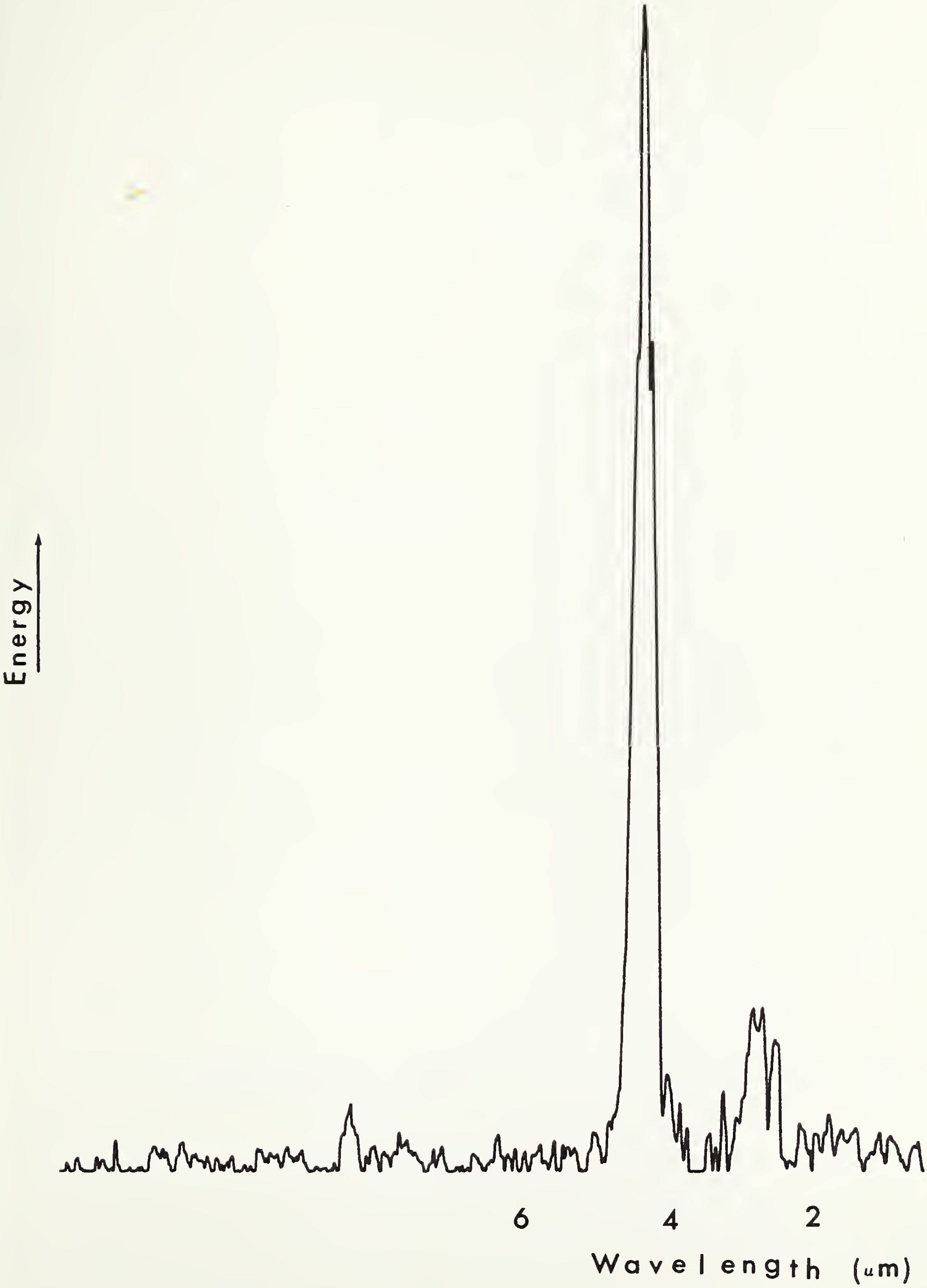

Figure 18. Wood-Fueled Diffusion Flame

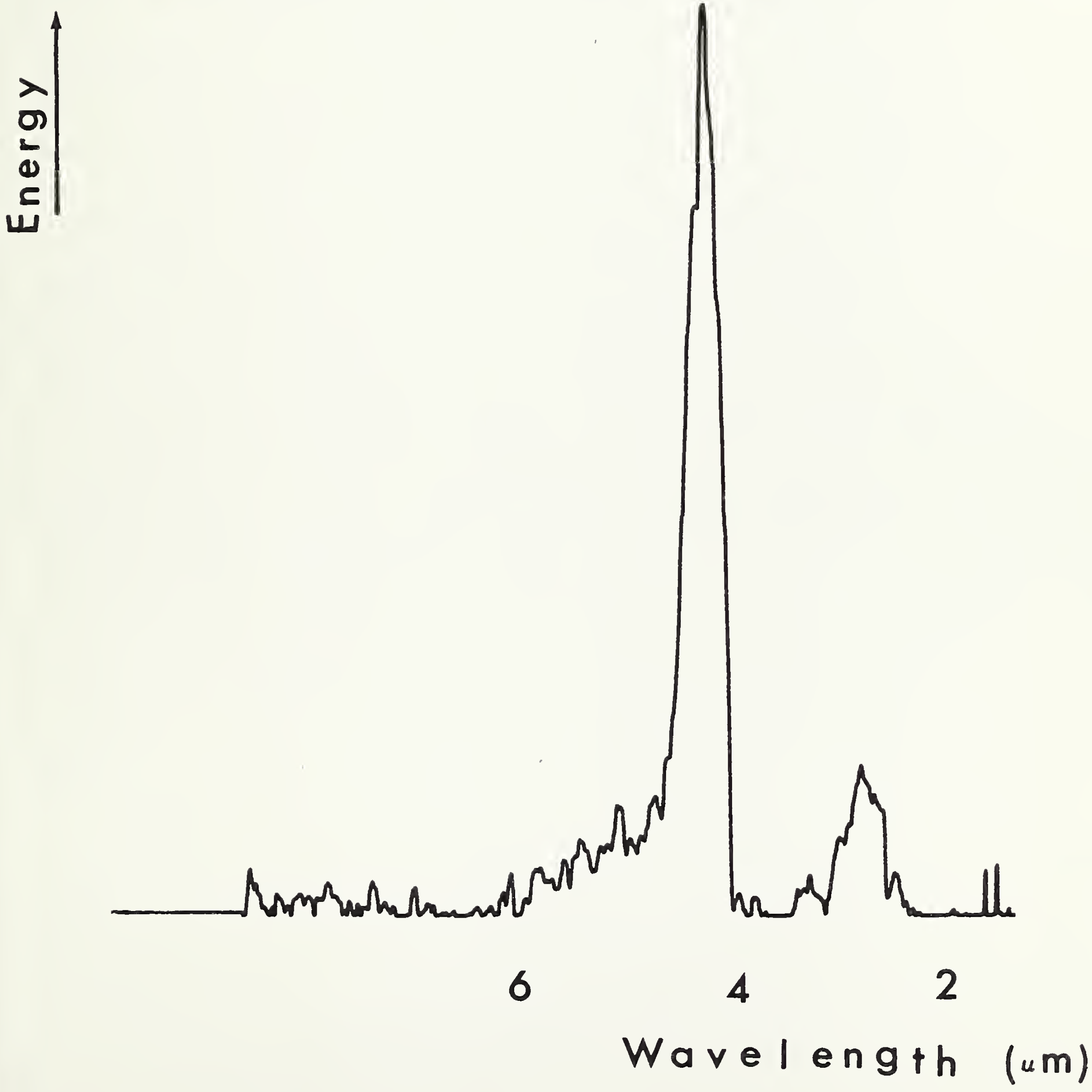

Figure 19. Hexamethyltetramine Flame

CONCLUSIONS

The center portion of the radiant test panel is found to approximate a blackbody source at 670 °C. A variety of diffusion flames, except for those involving fuels such as acetylene containing high C/H ratios, radiate in discreet narrow wavelength intervals determined by CO_2 and water emission bands. The flame portion of the maple wood-fueled fire approximated the methane diffusion flame in its energy distribution.

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