

HADAMARD TRANSFORM SPECTROMETER

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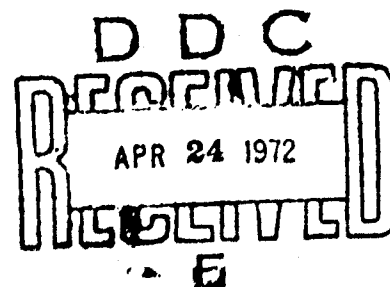
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ABSTRACT

A Hadamard Transform Spectrometer is described. This multiplexing spectrometer is based on a 127 square cyclic Hadamard matrix. A resolving power of 0.1 cm^{-1} is achieved with a multiplexing gain factor of over five-fold in signal-to-noise ratio over use of a conventional single exit slit.

A procedure for calibrating an infrared prism spectrometer plots drum numbers and wavelengths as ordinates against a trigonometric function of the index of the prism, as parameter and abscissae. The calibration data yields a straight line so only calibration data for two wavelengths is necessary.

TECHNICAL REPORT SUMMARY

The main thrust of our effort under Contract No. F19628-70-C-0296 was to develop Hadamard Transform Spectroscopy for improving our facilities to determine the molecular absorption parameters of the water and CO₂ molecules; and in preparation for studies of glow emission in our 92-meter path absorption cell. We have adapted the cell to serve for simulation of upper atmosphere conditions. It is suitable because of its large, 1-meter diameter and 31-meter length (it is provided with a 15-meter central electrode): the large dimensions minimize quenching at walls of metastable molecular species and states, and the long optical path maximizes detectability of absorption or emission by weak transitions.

The study of absorption by steam, a second aspect of the program under Contract No. F19628-70-C-0296, was not completely finished during the contract period because the spectrometer for it was involved in another program (the study of absorption by atmospheric pollutants [SO₂, N₂O, NO, and CO] in trace amounts). In preparation for the study of steam, we are using a Model 12-C Perkin-Elmer prism spectrometer to get preliminary spectra, and a Model 210-B Perkin-Elmer grating spectrometer for high resolution.

Mr. S.Y. Ho has published a practical and straightforward procedure for calibration of a prism spectrometer that requires only two datum points.¹

With respect to Hadamard Transform Spectroscopy, the lenses, echelle grating, and the cryogenic bolometer were provided outside Contract No. F19628-70-C-0296; but the constructions and "shake-down" were supported by that Contract--being largely the effort of Mr. P. Hansen.

The Hadamard Transform Spectrometer has fulfilled our expectations and it will be used with our upper atmosphere simulator--the 92-meter path absorption cell. A paper² describing our work under Contract No. F19628-70-C-0296 will appear in the March 1972 issue of *Applied Optics*.

We have acquired, separately, a set of lenses for the Hadamard Transform Spectrometer that are achromatic over the range λ 7 to 24μ so that, together with the first set, λ 5 to 14μ , we have the range λ 5 to 24μ available with a resolving power-- $\Delta\nu < 0.1 \text{ cm}^{-1}$.

PERSONNEL

Principal Investigator: Dr. John Strong

Project Engineer: Peter Hansen

Graduate Students: Harold Heaton) Research
Shau-Yau Ho)

Support Staff: William Dalton-Administrative
Linda Barron-Secretarial,
Reports, etc.
Ernest Provo-Machine Shop,
Assembly, etc.

FACILITIES ACQUIRED

This Contract provided for the acquisition, in January 1971, of a Princeton Applied Research Model HR-8 Lock-In Amplifier. This item of equipment is inventoried under Facilities Contract No. F19628-67-C-0421.

ACKNOWLEDGMENT

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2. P. Hansen and J. Strong, "A High Resolution Hadamard Transform Spectrometer," Appl. Opt. (in press-- March 1972 issue).

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New Calibration Method for Prism Infrared Spectrometers

Shau-Yau Ho

Based on the minimum deviation equation $N \sin \phi = \sin(\phi + \delta)$, a linear equation which relates drum screw scale to $\arcsin(N \sin \phi)$ for the prism spectrometer calibration has been developed. The use of this linear equation and the dispersion formula for prism material allows the preparation of a calibration table of numbers, rather than the usual less precise drum-wavelength calibration curve, for practical transfer of wavelength drum-scale values D to wavelengths λ . The method requires only two or three reference points, applicable to various prisms with high accuracy in their recommended wavelength range. The linearity suggests another advantage, because it permits linear transformation of the old drum setting for a prism that was first calibrated to the new drum setting.

Introduction

Precise calibration of an ir prism spectrometer requires determination of the prism angular positions or the wavelength drum scales, corresponding to reference wavelengths. And in addition some procedure of interpolation between cross points has been necessary since the number of good reference wavelengths is limited, especially for prisms working in the far ir range. The empirical equation developed by Friedel and McKinney¹ has been used for interpolation procedure. It is the purpose of this paper to describe another method that has been found precise for NaCl and KBr prisms, using convenient and reliable reference wavelengths available in modern literature.²⁻⁶

Theory

First, rewrite the equation for minimum deviation,⁷ 2δ , for a prism angle, 2ϕ , $N = [\sin(\phi + \delta)/\sin \phi]$ as follows:

$$D_0 + kD = \arcsin(tN). \quad (1)$$

Here $t = \sin \phi$, and D is the value of wavelength drum-scale of the spectrometer, presumed linearly proportional to prism angular position, with slope k and intercept D_0 .

We tested Eq. (1) with a Perkin-Elmer ir spectrometer. Its wavelength setting is controlled by a wavelength micrometer which rotates the Littrow mirror. The drum scale is arbitrary. Each small division, the D value in Eq. (1), corresponds to 16.1 sec of arc of Littrow motion. For the prisms tested, t was taken

as 0.5 for both NaCl and KBr. We used dispersion formulas, Eq. (2) for the sodium chloride prism,⁸ and Eq. (3) for the potassium bromide prism.⁹

$$N^2 = 2.330165 - 0.0009285837\lambda^2 - 0.000000286086\lambda^4 \\ + 0.01278685/(\lambda^2 - 0.0148500) \\ + 0.005343024/(\lambda^2 - 0.02547414) \quad (2)$$

$$N^2 = 2.361323 - 0.000311497\lambda^2 - 0.00000058613\lambda^4 \\ + 0.007676/\lambda^2 + 0.0156569/(\lambda^2 - 0.0324). \quad (3)$$

Equation (2) is valid to the fifth decimal place from 0.2μ to 23μ . The refractive index of KBr was measured at 22°C in the ir region from 1μ to 25μ , and it was found that the values predicted by Eq. (3) and the experimental values agree to the fifth decimal place.⁹ The use of these equations allows preparation of a calibration table of numbers, rather than the usual less precise drum-wavelength calibration curve, for practical transfer of drum scales to wavelengths. The validity of this procedure for all wavelength ranges, practically independent of resolving power, is demonstrated below.

Experimental Results

The experiments were conducted at room temperature, which appears to be sufficiently close to those under which d for Eqs. (2) and (3) were determined and under which Eq. (1) is valid. Complete sample data using the sixteen points for the calibration of a Perkin-Elmer spectrometer with NaCl prism are given in Table I. The relationship between spectrometer drum-scale D and $\arcsin(tN)$ from 0.5461μ to 14.986μ is plotted in Fig. 1. Within the whole recommended wavelength range it is a straight line. In Fig. 2 we display the experimental results of the KBr prism for which the drum scale position varies linearly with $\arcsin(tN)$ for wavelengths from 14.29μ to 22.76μ .

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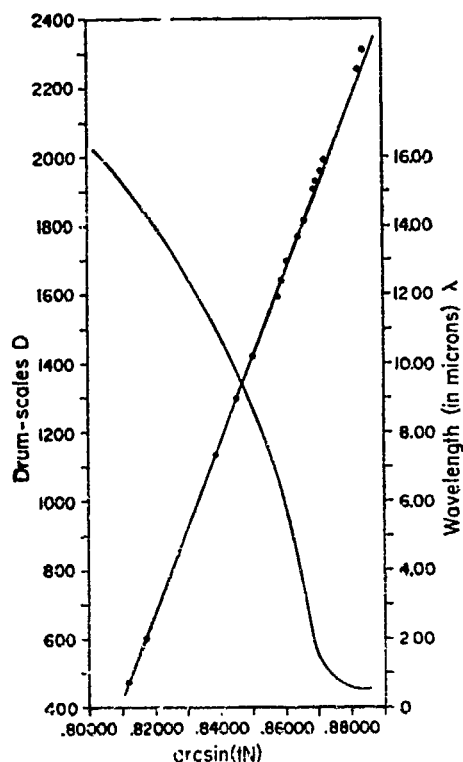


Fig. 1. Relationship between spectrometer drum-scale D and $\arcsin(tN)$ for NaCl prism, Perkin-Elmer spectrometer. Sixteen calibration points from 0.5461μ to 14.986μ (Table I). λ - $\arcsin(tN)$ curve for NaCl is also shown.

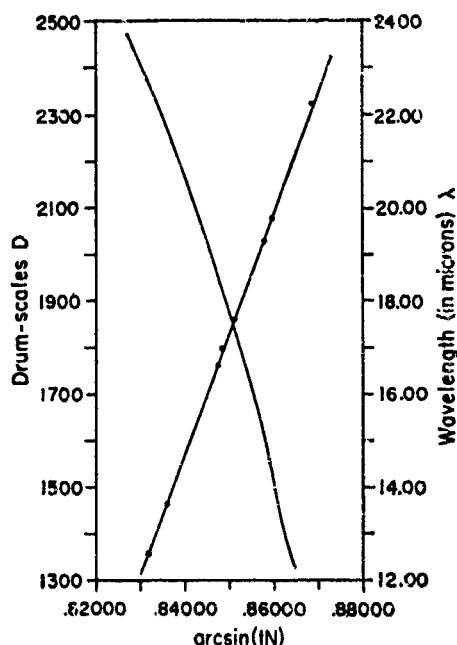


Fig. 2. Relationship between spectrometer drum-scale D and $\arcsin(tN)$ for KBr prism, Perkin-Elmer spectrometer. Eight calibration points from 9.724μ to 22.76μ (Table II). λ - $\arcsin(tN)$ curve for KBr is also shown.

Table I. Calibration Data for the NaCl Prism*

Drum-scale D	Wave-length (μ)	Sample used in calibration	Arcsin (tN)	Deviation $\Delta\lambda$ from the calibration straight line (μ)	Deviation $\Delta\lambda$ from $\lambda_S - \lambda_L$ line (μ)
1. 2301.8	0.5461	Hg	0.88470	0.01	0
2. 2252.7	0.5771	Hg	0.88287	0.01	0.005
3. 1989.0	1.01398	Hg	0.87263	0.03	0.037
4. 1962.6	1.12867	Hg	0.87168	0.07	0.093
5. 1929.3	1.3622	Hg	0.87038	0.05	0.121
6. 1905.0	1.5296	Hg	0.86975	0.09	0.226
7. 1820.8	3.267	Polystyrene	0.86622	0	0.333
8. 1771.5	4.258	CO ₂	0.86428	0	0.228
9. 1694.3	5.549	Polystyrene	0.86116	0.037	0.204
10. 1643.9	6.238	Polystyrene	0.85918	0	0.249
11. 1606.3	6.692	Polystyrene	0.85775	0.025	0.210
12. 1424.7	8.662	Polystyrene	0.85036	0	0.119
13. 1301.9	9.724	Polystyrene	0.84554	0	0.120
14. 1131.4	11.035	Polystyrene	0.83875	0	0.081
15. 604.7	14.29	Polystyrene	0.81760	0	0.014
16. 469.9	14.986	CO ₂	0.81223	0	0

* $\lambda_S = 0.5461\mu$; $\lambda_L = 14.986\mu$.

Table II. Calibration Data for the KBr Prism*

Drum-scale D	Wave-length (μ)	Sample used in calibration	Arcsin (tN)	Deviation $\Delta\lambda$ from the calibration straight line (μ)	Deviation $\Delta\lambda$ from $\lambda_S - \lambda_L$ line (μ)
1. 2322.9	9.724	Polystyrene	0.86868	0.186	0
2. 2078.2	14.29	Polystyrene	0.85952	0	0.123
3. 2033.8	14.986	CO ₂	0.85778	0	0.094
4. 1861.3	17.40	1,2,4-Trichlorobenzene	0.85102	0	0.062
5. 1800.0	18.16	1,2,4-Trichlorobenzene	0.84864	0.012	0.047
6. 1765.0	18.587	Polystyrene	0.84730	0	0.034
7. 1462.9	21.79	1,2,4-Trichlorobenzene	0.83555	0	0.013
8. 1359.9	22.76	1,2,4-Trichlorobenzene	0.83153	0	0

* $\lambda_S = 9.724\mu$; $\lambda_L = 22.76\mu$.

The sample data of KBr are collected in Table II. For each prism only wavelengths beyond its short wavelength end deviate from the calibration straight line. The λ - $\arcsin(tN)$ curves are also presented.

Discussion

This method provides an accurate way for prism in spectrometer calibration with only a few bands required. It is applicable to various prisms in their

recommended range and is practically independent of resolving power. It also exposes the doubtful wavelengths obtained from broad, weak, or unsymmetrical bands. Tabulation of $\arcsin(tN)$ in terms of wavelength can be done by computer at as small increments of wavelength as desired.

The linearity depicted in Figs. 1 and 2 suggests another advantage of this procedure over the usual calibration method, because it permits linear transformation of the drum-scale readings from the old prism setting that was first calibrated to a new prism setting. For example, if the KBr prism is reinstalled for use in the second time, no alignment to a particular wavelength drum-scale is required. By using any one convenient, sharp, and readily identifiable reference wavelength, the calibration curve for the new prism setting can be accomplished by simply drawing another straight line passing through that point (D , $\arcsin(tN)$) and in parallel with the original calibration line in Fig. 2.

Mathematical manipulation of Eq. (1) shows that $\Delta D = \Delta N / [2k(1-N^2/4)^{1/2}]$, where t has been taken to be 0.5 for the two 60° prisms. The slope k of each calibration line is nearly constant with a variation of a few percent for the two prisms used on this slightly lower resolving power PE instrument in their recommended spectral range. For the NaCl prism, $1/k$ is found to be about 2.54×10^4 . Taking $N \simeq 1.5$, if $\Delta N \simeq 10^{-4}$, we get $\Delta D \simeq 0.019$; the error in wavelength drum-scale is too small to be measured. Therefore, Eq. (1) and the calibration lines can be used inversely to estimate $N(\lambda)$ from D values. To see the accuracy of the estimation we can draw a straight line $\lambda_s - \lambda_L$ through the plotted limiting points of the table. The deviation $\Delta\lambda$ in microns between this line and plotted points for median wavelengths is calculated and presented in the last column of each table. These data can be compared to those in the second to the

last column where the deviation $\Delta\lambda$ in microns for reference wavelengths from the calibration straight line is given.

D_0 represents $\arcsin(tN)$ for the wavelength corresponding to zero drum-scale when the system has been aligned and adjusted. A little shift in D_0 arising from temperature change simply shifts all the D values corresponding to their wavelengths. When more precise temperature coefficients are known we expect they may be accommodated in a working table by making D_0 a function of temperature.

The author would like to express his appreciation to John Strong for his suggestions and consultations. The work was supported in part by ARPA under Contract F19628-70-C-0296. The author also wishes to acknowledge the United States-China Cooperative Science Program.

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A HIGH RESOLUTION HADAMARD TRANSFORM SPECTROMETER

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The infrared spectrometer described employs alkaline halide lenses, an echelle grating, and a cryogenically cooled doped germanium bolometer as a detector. It is provided for two possible modes of operation: one is a single slit or conventional scan, the other is a multiplex or Hadamard scan. Signal strength, noise characteristics, scanning time and available computer facilities determine the mode of operation. Sample spectra are presented.

The Instrument

Fig. 1 illustrates the basic spectrometer. Radiation passes through the entrance slit which is located at the focus of a 16 cm NaCl-KBr lens.¹ After passing through the lens, the radiation is dispersed by the echelle grating and reflected back through the lens. The spectrum obtained is focused on the entrance slit. A 45-degree reflecting surface (Fig. 2) just in front of the entrance slit reflects the spectrum falling on either side of the entrance slit cutout (Fig. 2). Either a single slit or the multiplex slits are placed at the

downward focus--the exit focal plane. After passing through the slit, or slits, the spectrum is again reflected by the mirror m_2 (Fig. 1) and is returned to the lens. This reflection is at slightly less than 90 degrees so that the chief ray crosses the optic axis when it reaches the lens. Since the image is inverted by the two reflections, the spectrum is now de-dispersed² by the grating. In multiplex mode of operation, the final images of the multiplex slits are superimposed. They fall at a distance above the optic axis, at a focal plane approximately at the entrance slit focal plane. The mirror m_2 located 5 cm in front of this focal plane puts the de-dispersed spectrum on a 3:1 image slicer.¹ The entrance and exit slits are 0.38 mm wide and 12 mm long. The image slicer (Fig. 3) transforms the rectangular exit area from 0.38 x 12 mm to a circumscription rectangle of 1.2 x 4 mm dimensions. And the diverging spectrum ($f/16$) is focused onto the 1/2 x 1 mm detector chip at 4-fold reduction by a 2.5 cm NaCl-KBr achromat ($f/4$).¹ The Airy diffraction disks of the achromatic lenses at $\lambda \approx 6\mu$ are less than half the slit width (0.38 mm).

The echelle grating, due to its controlled groove shape and high angle of incidence (Fig. 4), directs substantially all of the incident energy into one or two

of the higher orders. The grating has a ruled area of 206 x 102 mm, a blaze angle of 63.7° and is ruled at 31.64 lines/mm. As an example, in the 6μ region, it is normally operated in the 9th order where the angle of incidence (and reflection) is close to the blaze angle. The projected grating area near the blaze angle is 10 x 10 cm (Fig. 4) which matches the stopped down area of the large NaCl-KBr lens. The theoretical resolving power is equal to the number of wavelengths contained in the path difference of the grooves at the outer edges of the grating. This from Fig. 4 is $\Delta v = \frac{1}{2D} = \frac{1}{37 \text{ cm}} = .027 \text{ cm}^{-1}$. A resolving power of .1 to .2 cm^{-1} is achieved.

Square wave chopping of the radiation is accomplished with a three-blade rotary chopper turning at 2000 rpm. This results in a satisfactory chopping frequency for the detector (100 Hz). The chopper is machined from a 38 cm diameter aluminum disk, and it is driven by a synchronous motor. Since an area of 1.2 x 4.8 cm (multiplex mask dimensions) is chopped, a large chopper diameter is necessary to assure that the spectral elements at the outer edges of the multiplex mask are chopped nearly in phase with those in the center, and that the edge of the chopper blade spends nearly equal time traversing each spectral element. The chopper also provides a reference signal to a lock-in amplifier (Fig. 5); and, since the

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amplifier makes use of only the 1st harmonic of the chopped signal, square wave modulation is desirable as the peak amplitude of the 1st harmonic exceeds the amplitude of the square wave by a factor of $4/\pi$. Also, chopping the second pass³ instead of the first, assures that unwanted scattered radiations reaching the detector are not detected, e.g., reflections of the much more intense first pass from the surfaces of the 6" lens.

The detector is a liquid helium cooled doped germanium bolometer (Infrared Laboratories, Tucson, Arizona). Pumping on the helium reduces the operating temperature to 1.9°K. At this temperature the noise equivalent power (NEP) has been measured and calculated to be less than $1 \times 10^{-13} \text{ W/Hz}^{1/2}$. A cold (1.9°K) bandpass filter is placed in front of the detector chip to suppress unwanted signals.

When signal levels are low, and non-signal-dependent noise predominates, i.e., statistical noise, use of the multiplex slits increases the signal-to-noise ratio,⁴ as they allow for the simultaneous observation of half of all spectra elements. Multiplex or Hadamard Transform Spectroscopy (HTS) has the advantage over other indirect methods such as Fourier Transform Spectroscopy (FTS) in that (1) there is no instrumental dynamic range problem;

(2) micrometric instead of interferometric tolerances are involved; and (3) special masks may be constructed which discriminate against unwanted wavelengths anywhere in the measured spectrum. In addition, the Hadamard transform computations are straightforward and HTS makes good use of the well developed technology of grating spectrometers.

Since, for random noise, the signal-to-noise ratio increases with the square root of the observation time, a 253 element multiplex mask is employed (Fig. 6). 127 elements are exposed to the spectrum at all times. Since half of the elements represent opaque slits, the multiplex slits increase the integrated observation time by a factor of 64; and the signal-to-noise ratio is increased by a factor of ≈ 5.6 , as compared to an equivalent single slit scan using an equal total observation time.

The multiplex mask is stepped 126 times during a measurement and its transparent and opaque slits generate a 127 square cyclic⁴ Hadamard matrix having zeros (transparent) and ones (opaque) as elements. This is a suitable form for digital computation. If

$$[H^{127}] [S] = [I]$$

where $[H^{127}]$ is the square Hadamard matrix generated

by the multiplex slits, $[S]$ is the one-dimensional matrix containing the 127 unknown spectral elements, and $[I]$ is the one-dimensional matrix containing the 127 observed intensities; then

$$[S] = \left[H^{127} \right]^{-1} [I]$$

This equation is solved by computer. To minimize computing time, the $[H^{127}]$ matrix is inverted only once and then stored, thus allowing use of computing facilities having less than 8K memories. The present computer program provides for both a numerical listing of the multiplex spectrum and for a graphic plot. Total computing time is 3 seconds and the spectrum plot is completed within 7 minutes.

In spectral regions where source and/or background noise predominate, a single slit is used. Under these conditions the multiplex advantage does not come into play. The optical path for single and multiplex spectra is identical and single slit spectra may be obtained by either stepping the slit or grating rotation.

Performance and Measurements

The six micron water vapor bands were chosen for the initial alignment, calibration and performance checks. The echelle grating was used in its ninth order

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with some overlapping of the eighth order. A cold filter used with the detector passed a wavelength band 1.25μ wide ($5.85 - 7.1\mu$) with additional long wavelength suppression provided by a LiF detector window. Wavelength calibration was accomplished by proper identification of water vapor absorption lines.^{5,6} The spectrometer was purged with dry air to eliminate all but the strongest lines and its entire path length (8m) was used as an absorption cell. A Nernst glower was the source and all the measurements were made at atmospheric pressure. Fig. 7 illustrates a typical water vapor spectrum obtained with a single slit. The 16 cm KBr-NaCl collimator-telescope lens was bolometrically focused on the slits for maximum signal and highest resolution. Identified ninth-order lines are indicated and listed in Table I.

The cold bandpass filter was changed ($12.1 - 15.4\mu$) and the LiF detector window was replaced with NaCl to observe performance at longer wavelengths. The grating is used here in the fourth order. The resulting increase in the free spectral range allows the use of a wider bandpass filter. As spectral reference features, the 14μ carbon dioxide bands⁷ were observed. CO_2 (along with dry air) was admitted to the spectrometer and the

resulting single slit spectrum is shown in Fig. 8. This figure also shows the CO_2 lines in a sky emission spectrum. This spectrum was taken with the spectrometer purged with dry air. The emission spectrum of this low temperature source has required use of lower resolution: both entrance and exit slits were widened to three times (1.2 mm) their previous width. The focus of the alkaline halide lenses remained the same at 14μ as at 6μ , an indication of their good achromatism in the infrared.

The multiplex advantage is best realized at very low signal levels. A stepped single slit scan was made at the exit focal plane with the grating in a fixed position and the slits again narrow (0.4 mm), the spectrometer purged with dry air, and with very little energy incident on the entrance slit. The slit was then replaced with the multiplex slits and another spectrum was obtained. The total observation time was the same for both single slit and multiplex measurements. The two results are shown in Fig. 9. The single slit spectrum is simply the detector output. The multiplex spectrum is obtained by connecting the 127 consecutive computer output points by straight lines. It is apparent that the signal-to-noise ratio

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is significantly improved in the multiplex spectrum. The strong "absorption line" in the center is caused by the entrance slit cutout. Its equivalent spectral width is less than 0.2 cm^{-1} . The entrance slit cutout is also an example of a property of HTS mentioned earlier: wavelength discrimination. At 700 cm^{-1} (14.3μ) a multiplex spectrum covers six wavenumbers--the position of the grating determines the spectral location of this frequency interval. For example, to cover the spectrum in Fig. 8, twelve multiplex scans are necessary with a grating rotation of approximately fifty arc minutes between each successive scan.

We presently have bandpass filters covering the range from 5.8μ to 15.4μ . A new set of alkaline halide achromats is under construction for wavelengths longer than 15μ , to 23μ . The overlapping order problem at short wavelengths can be overcome with a more densely ruled echelle grating, e.g., 70 lines per millimeter. The spectrometer is being interfaced with several absorption cells with various absorption path lengths, including one with a 100-meter optical path.

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the detector and grating were provided by ESSA under Contract No. E-174-69(N). Sprague Electric Company photo-etched the multiplex slits.

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Table I

Indicated Water Vapor Lines From Fig. 7

<u>Line #</u>	<u>Frequency (cm⁻¹)</u>
1	1576.2
2	1616.7
3	1623.6
4	1635.6
5	1646.0
6	1652.4
7	1653.3
8	1684.8
9	1695.9

Figure Captions

- Fig. 1 (a) Basic HTS spectrometer, and (b) equivalent optical path.
- Fig. 2 View of exit focal plane with multiplex slits, corner reflector and chopper.
- Fig. 3 Image slicer.
- Fig. 4 Echelle grating and 16 cm focusing lens indicating grating dimensions and groove shape (grooves not to scale).
- Fig. 5 Block diagram of synchronous detection system.
- Fig. 6 253 slot multiplex mask.
- Fig. 7 Water vapor spectrum at atmospheric pressure.
- Fig. 8 Laboratory CO₂ absorption spectrum and sky emission spectrum.
- Fig. 9 Comparison of single slit and multiplex scans.

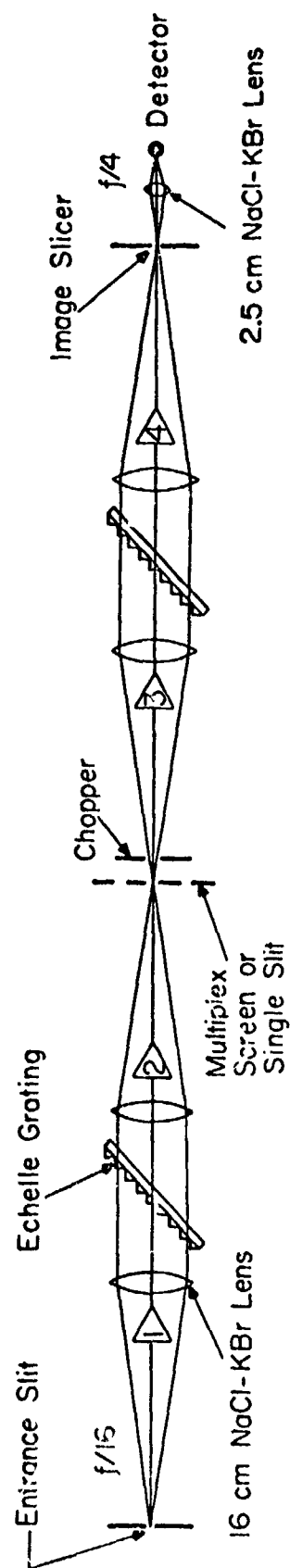
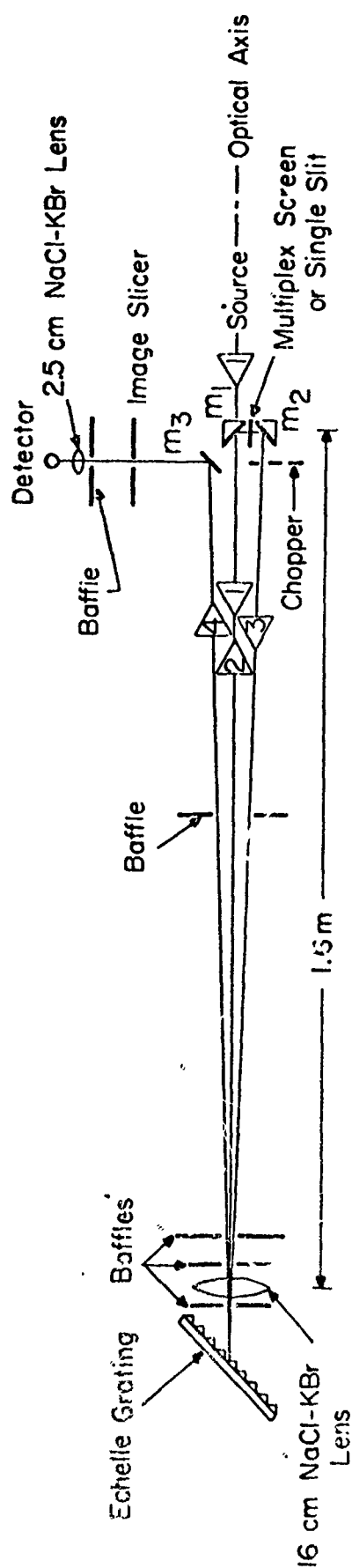


Fig. 1 (a) Basic HTS spectrometer, and (b) equivalent optical path.

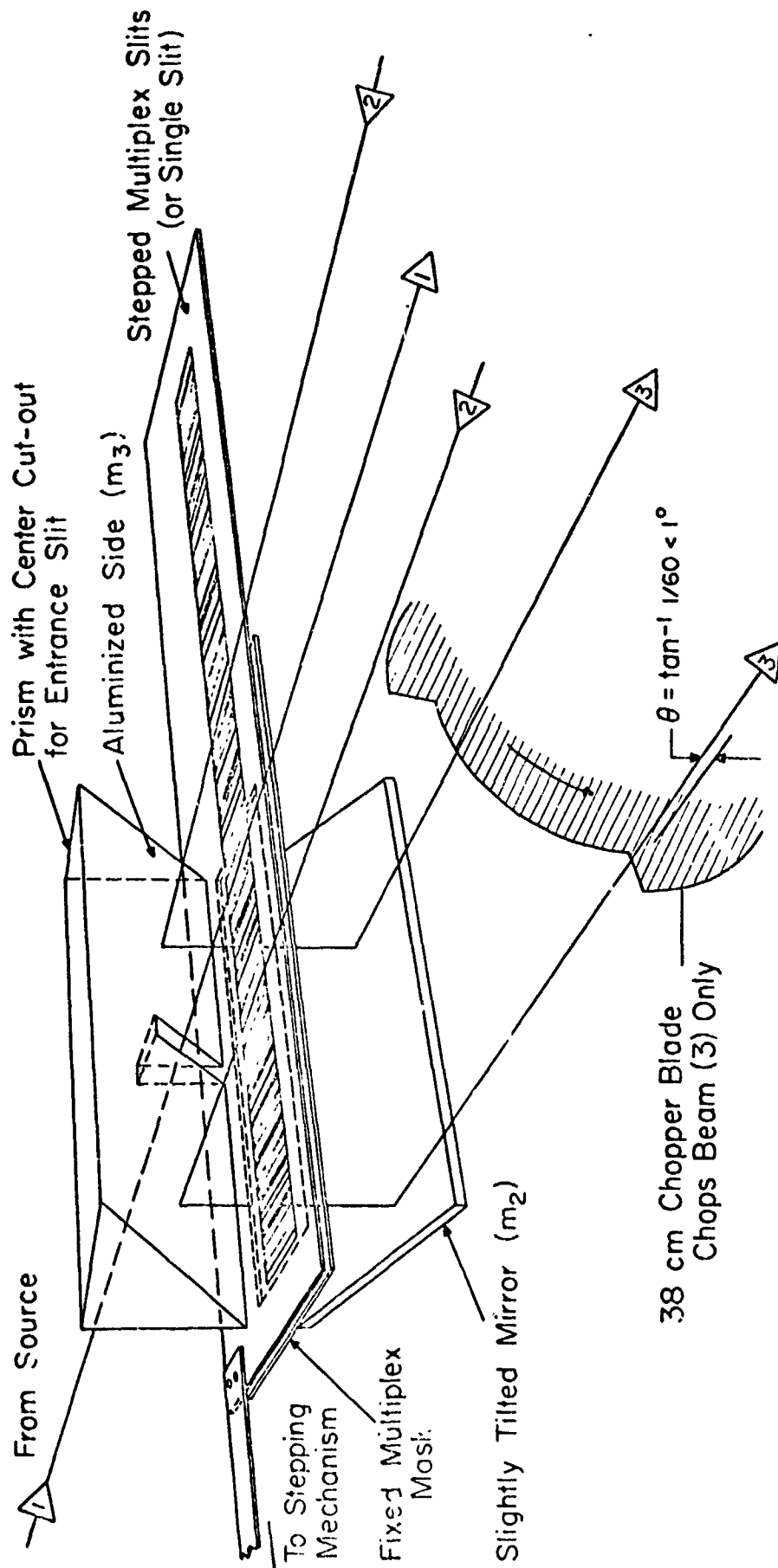


Fig. 2 View of exit focal plane with multiplex slits, corner reflector and chopper.

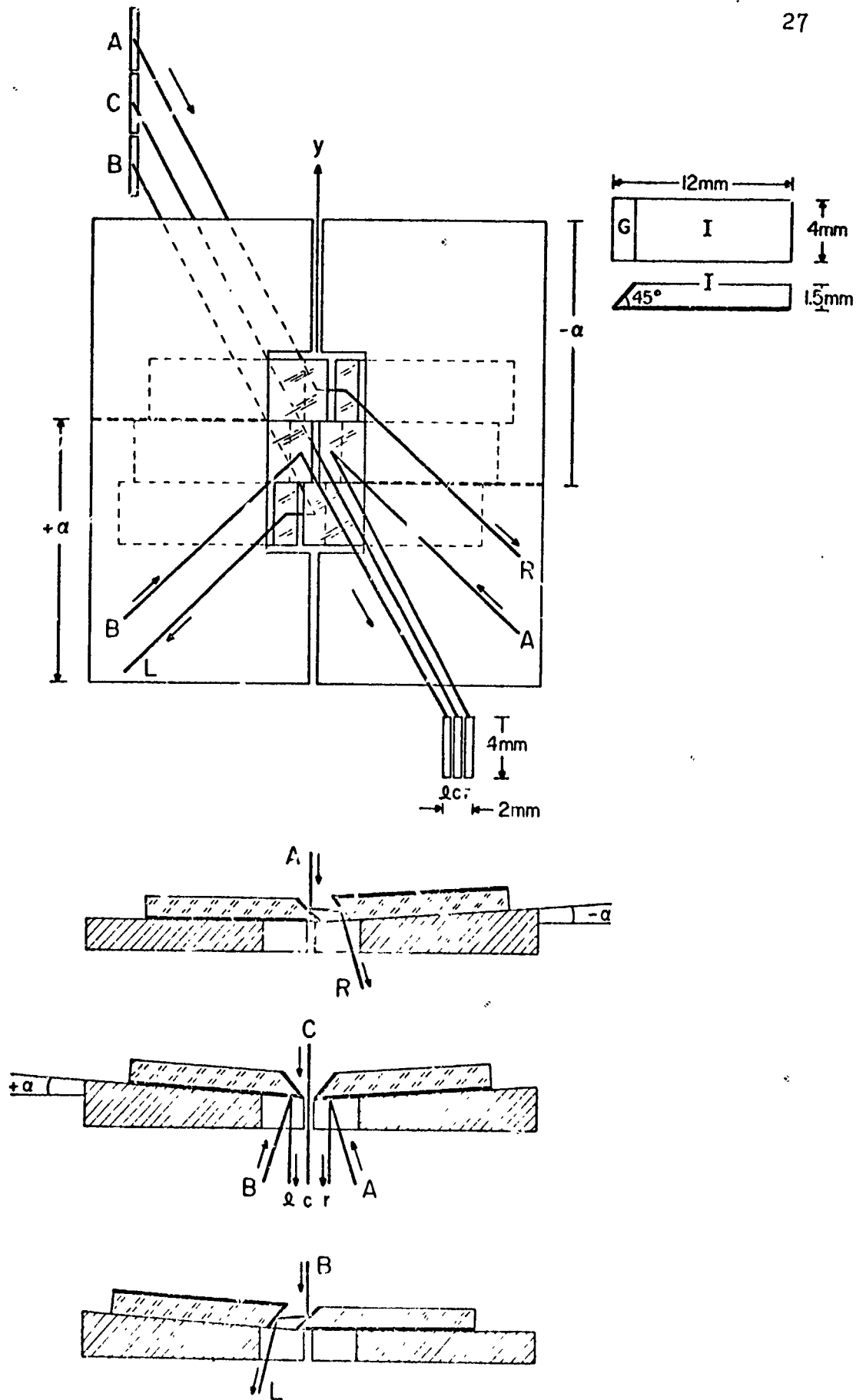


Fig. 3

Image Slicer

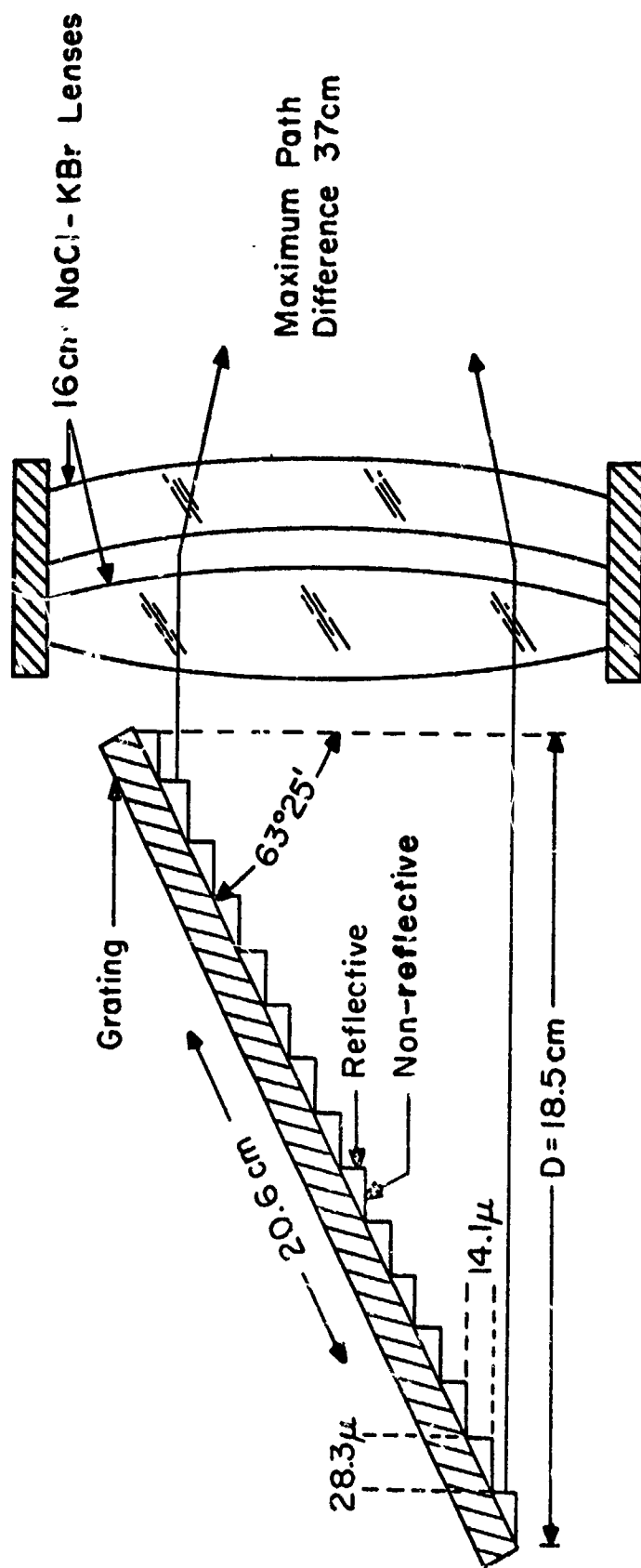


Fig. 4 Echelle grating and 16 cm focusing lens indicating grating dimensions and groove shape (grooves not to scale).

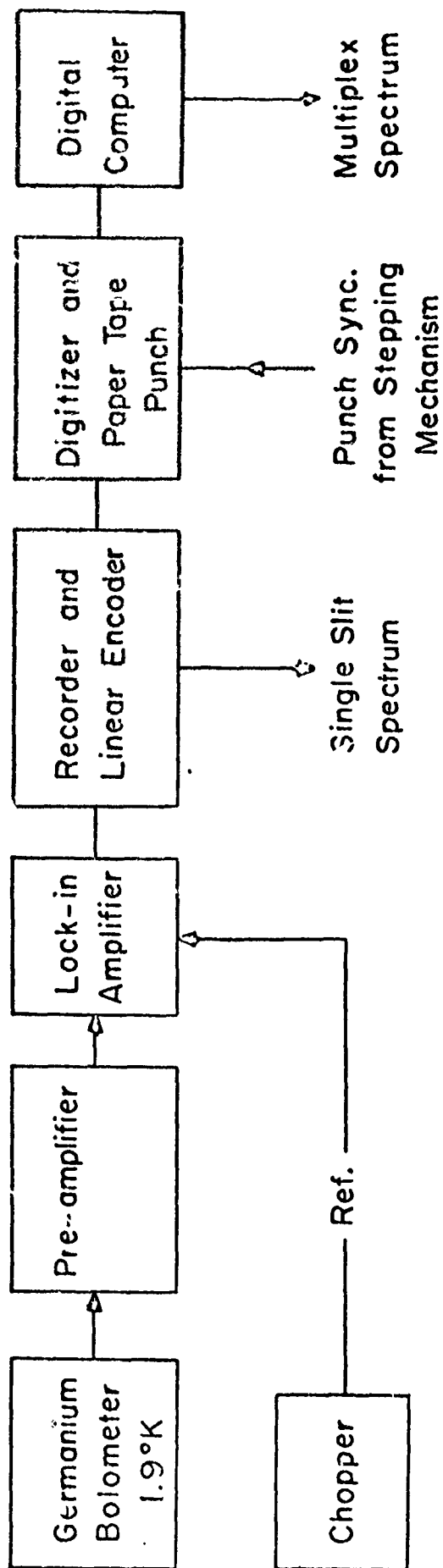


Fig. 5 Block diagram of synchronous detection system.

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Fig. 6 253-Slot Multiplex Mask

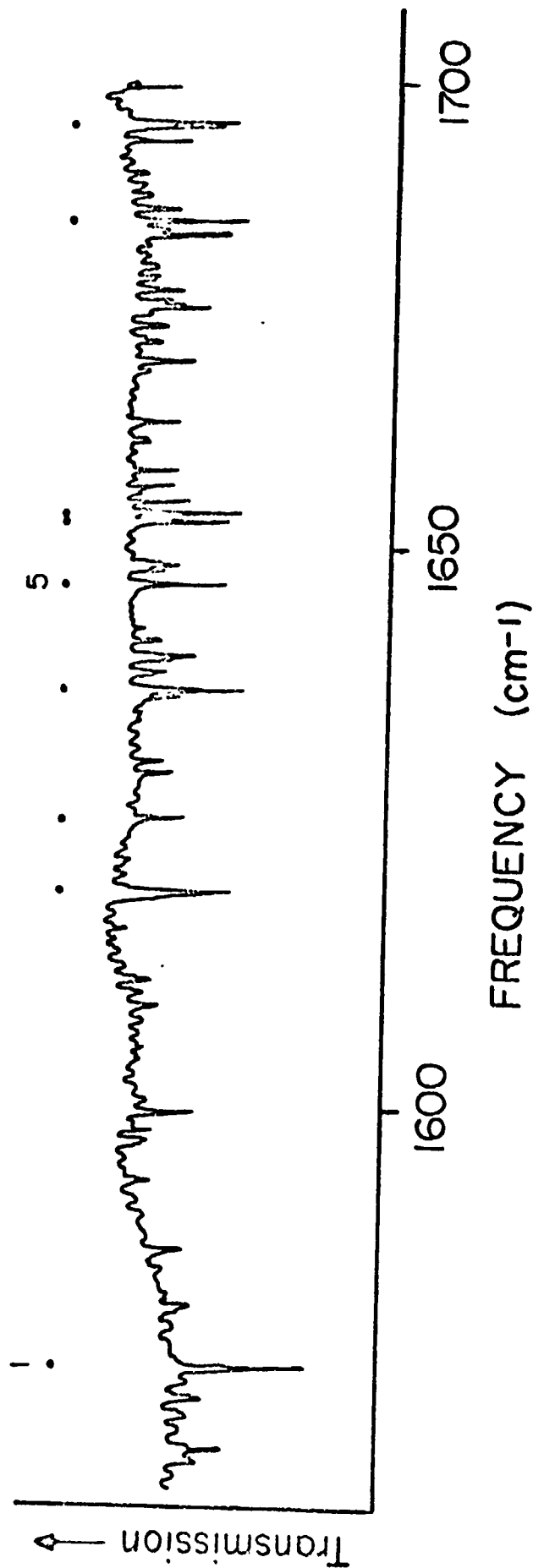


Fig. 7 Water vapor spectrum at atmospheric pressure.

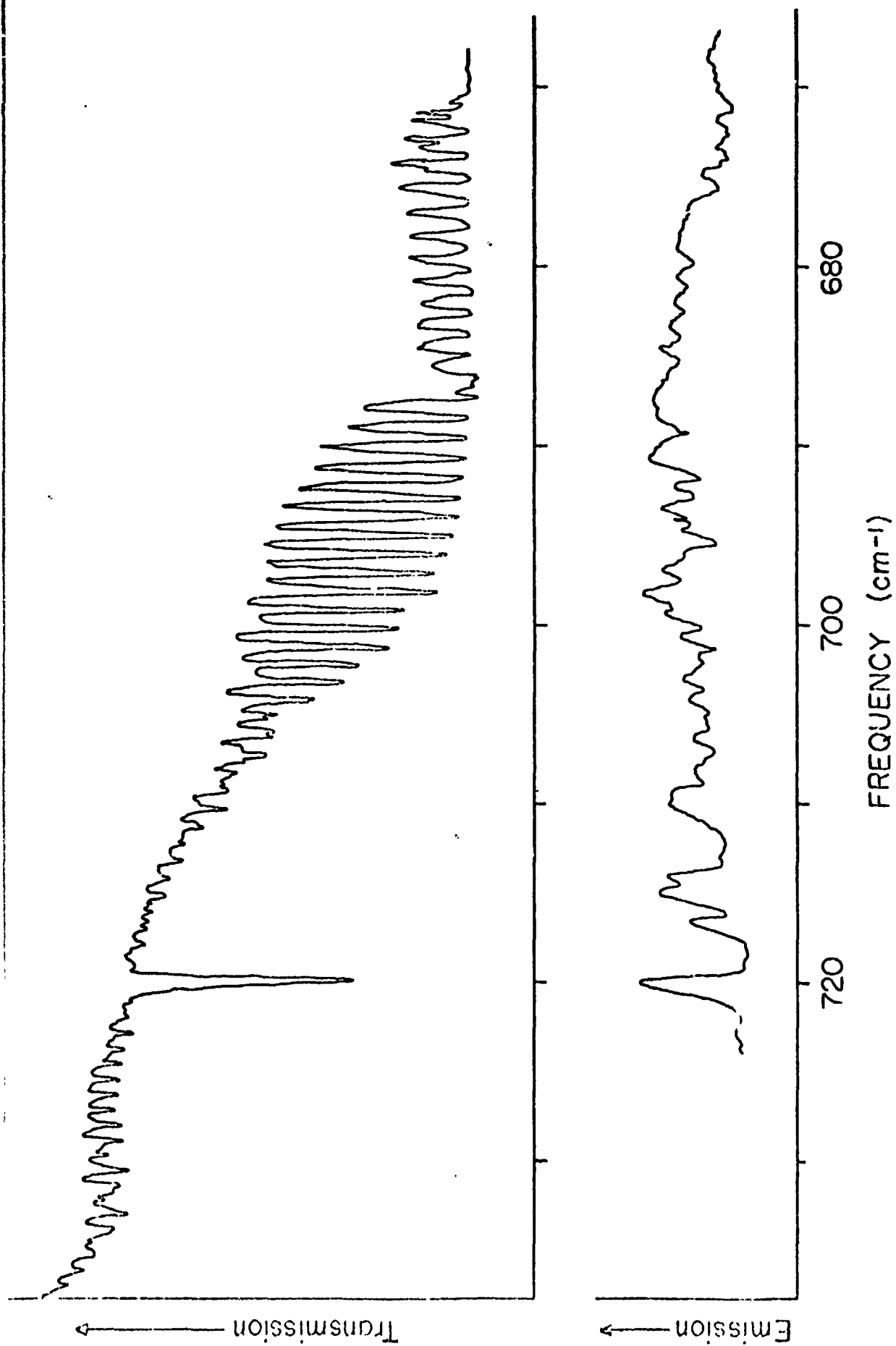


Fig. 8 Laboratory CO₂ absorption spectrum and sky emission spectrum.

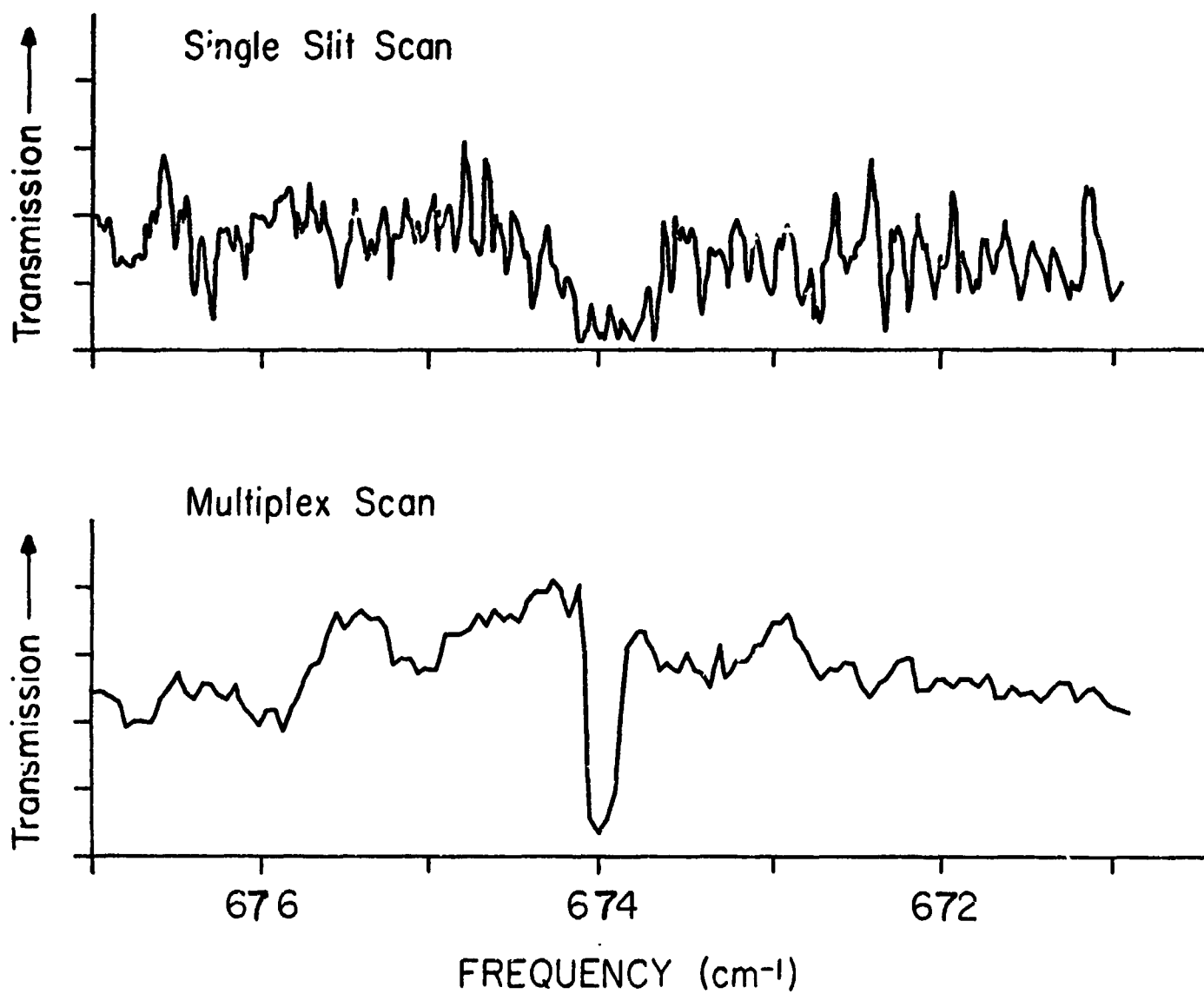


Fig. 9 Comparison of single slit and multiplex scans.

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