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Precise Measurement of Wavelengths in Infrared Spectra

Earle K. Plyler, Lamdin R. Blaine, and Eugene D. Tidwell

The precise measurement of infrared absorption spectra has been accomplished by using the white-light fringes of a Fabry-Perot interferometer in conjunction with atomic spectral lines. Wavelengths from the first spectra of neon, argon, krypton, and xenon were used for calibrating the fringes. The absorption spectra and the fringe system are recorded simultaneously by a two-pen recorder. One pen records the higher orders of the fringe system of visible light as detected by a 1P28 photomultiplier. The other pen records the infrared absorption spectrum, which is detected by a PbTe cell. A measurement of the distance from the center of the absorption line to the neighboring maxima of the fringe system determines the line position to a high precision. Wavelengths of infrared lines can be measured with an error of one part in 500,000. Eight infrared lines of mercury, seventeen lines of krypton, and five lines of xenon have been measured by this method. Tables are given of visible and infrared lines of the noble gases, which are useful for calibration.

1. Introduction

While infrared spectra have been measured for the last 150 years, the precision of wavelength determination has been very low. The values given, up to 1900, for the wavelengths of absorption bands were in error by about one part in a hundred. This low precision resulted from the small amounts of energy available for thermopiles, which made it necessary to use wide slits. Another contributing factor was the error introduced by the use of the indices of refraction, which were not known to a high precision for most prism materials. There was also the feeling that high precision optics was not necessary for infrared measurements. In 1917 Professor Randall [1][1] made measurements with gratings, and high resolution was obtained. In order to measure the rotational structure of bands, graduated circles were placed on the grating assembly, so that angles could be read to a few seconds of arc. This method of measurement, which was in use until about 4 years ago, greatly increased the accuracy and made it possible to measure sharp lines with an error of about one part in 10,000. More recently standard atomic lines have been used as a comparison spectrum. In the measurement of the CO band at 2.4 μ [2] with a grating, higher orders of well known atomic lines of mercury, krypton, and xenon were superimposed on the absorption spectrum, and it found that the rotational lines could be measured with an error of one part in 100,000. The main drawback to this method of measurement is the fact that many lines are of low intensity, and they cannot be observed with narrow slits in the higher orders.

The next advance in the precise measurement of infrared spectra was the introduction of the Fabry-Perot interferometer. Douglas and Sharma [3] showed that, when illuminated with white light, the interferometer gave a series of fringes which were equally spaced, and these, therefore, offered an excellent comparison spectrum when calibrated with Hg^{198} standards. Channeled spectra of white light fringe systems have been used by several observers in earlier investigations. Observed as early as 1850 by Fizeau and Foucault [4], the channeled spectrum was first used for measuring ultraviolet wavelengths by Esselback a century ago [5], and in 1879 Mouton [6] applied it to the measurement of invisible heat waves. However, no precise measurements could be made by this method until accurate standards of wavelength and improvements in spectrographs and radiation detectors became available. The use of the channeled spectrum provides very high precision in the relative measurements, but may be in error for the absolute values. The errors in the absolute measurements arise primarily from the condition that the fringe system is not transmitted along the optical axis of the instrument. The detector for the fringe system is a photomultiplier cell, and the optical path is different because it is necessary to place the photomultiplier behind the second slit. Small changes in the plane of the grating on scanning, or other changes, will alter the position of the maxima of the fringe system with respect to the absorption lines and thus will produce erratic absolute measurements.

A method of measurement which leads to high precision is to use noble gas spectra for calibrating the fringe system of the Fabry-Perot interferometer, and then to use the fringe system as a comparison spectrum. A detailed description of this method of measurement is given in this paper.

2. Experimental Method

In order to make measurements of high precision, a grating spectrometer was used for the dispersing instrument. The grating, which is about 8 in. wide and 5 in. high, has rulings of 7,500 lines/in. The optical arrangement of the spectrometer [7] and of the radiation sources is shown in figure 1. The source of radiation for the infrared measurements in the region from 1 to 3 μ is a Western Union enclosed arc of 300-w capacity. The radiation source of the interferometer is a 100-w Western Union arc. The radiation sources for the standard wavelengths are Westinghouse enclosed arcs which pass about 3 or 4 amp. The detector was a PbTe

[1] Figures in brackets indicate the literature references at the end of this paper.

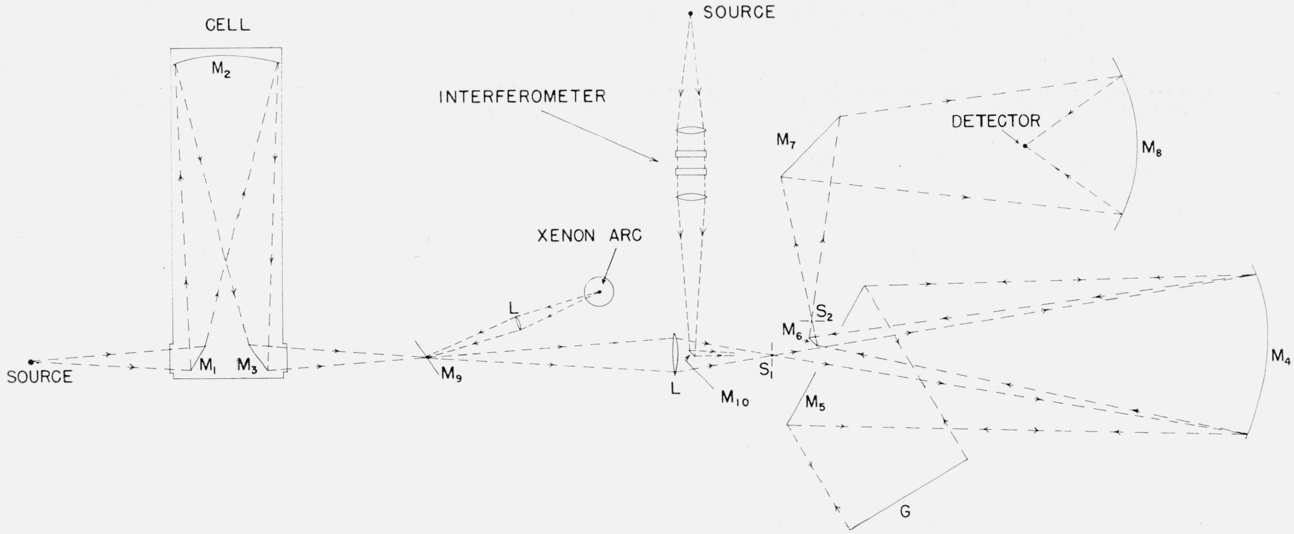

FIGURE 1. *A diagram showing the optical arrangement of the spectrometer, the standard sources, and the interferometer.*

cooled cell. The fringe system was detected by a 1P28 photomultiplier which was placed behind the second slit. A small plane mirror was placed near the top of the second slit, and the radiation of the fringe system was reflected on the photomultiplier which was located above the slit. The small mirror covered about one fifth of the total slit, and the energy from the Nernst source or Western Union arc passed through the other part of the exit slit.

A detailed diagram of the Fabry-Perot interferometer is shown in figure 2. The two plates in the center are aluminized to about 50-percent transmission and are separated 2 mm by three invar pins. The maxima of the fringe system are separated about 0.3 cm^{-1} at 4.5 μ. The plates are held together by spring attachments, with pressure being applied directly in line with the three separators. The entire interferometer is placed within a vacuum cylinder to eliminate the effects of the index of refraction of air. In the ends are placed the lenses which collimate the light through the interferometer. The plates, separators, and spring attachments are assembled and attached to the cylinder head, where they can be removed as a single unit. The vacuum is held by means of an O-ring represented by two black dots in the figure. On using the Fabry-Perot interferometer in vacuum, it is possible to use silver reflecting surfaces on the plates rather than aluminum, since the silver will not tarnish.

Figure 3 shows the high orders of the emission lines of the krypton arc in the spectral region of 3.3 μ. All the lines of good intensity have been identified, and they are useful in calibrating the spectrometer. If all of the regions of the spectrum have a sufficient number of lines at close intervals, they can be used as the calibrating spectrum without the interferometer. However, sufficient lines are not known in all regions, and the interferometer gives a more precise scale. In order to use a spectral line as a standard in the infrared region, its wave-

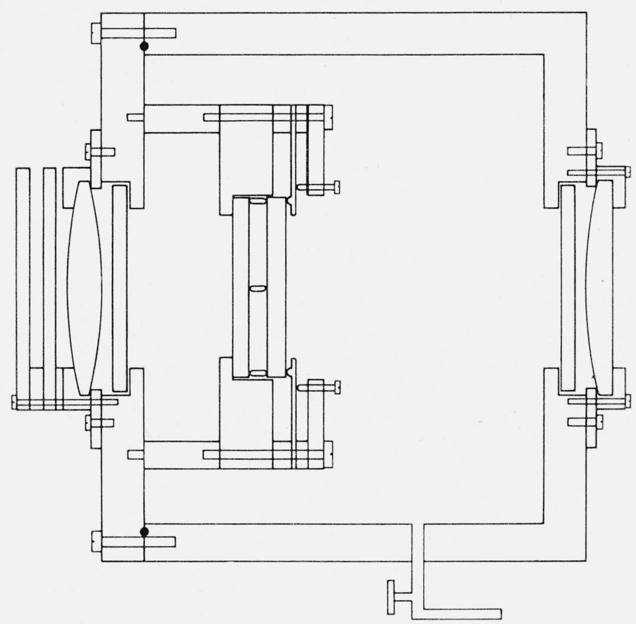

FIGURE 2. *A diagram of a Fabry-Perot interferometer within a vacuum system.*

On the left is a holder for the standard filters.

length must be known to a high precision. Only the lines with wavelengths less than 1 μ are known with such precision, and in order to use the lower wavelength lines of krypton in the 1-to 6-μ region, it is necessary that they be observed in the higher orders. To provide a greater number of standard lines, many emission lines of krypton and xenon have been measured recently in the 1-to 2-μ regions. A table listing the wavelengths of these infrared lines, measured in this laboratory and useful as standards, will be given further in this paper (see table 4).

Figure 4 shows the interferometer fringes simultaneously recorded with the emission lines. This

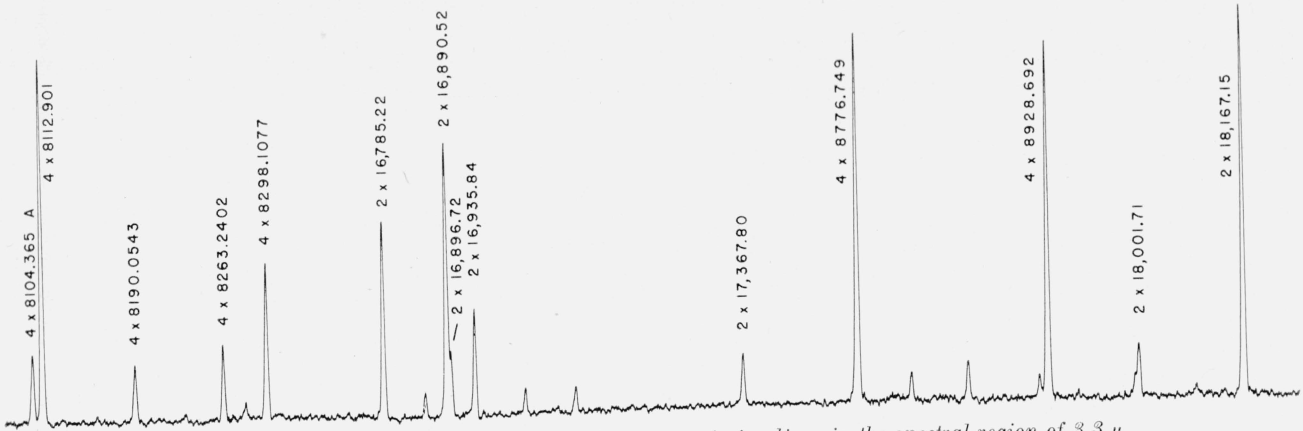

FIGURE. 3 *A record of higher orders of krypton emission lines in the spectral region of 3.3 μ*

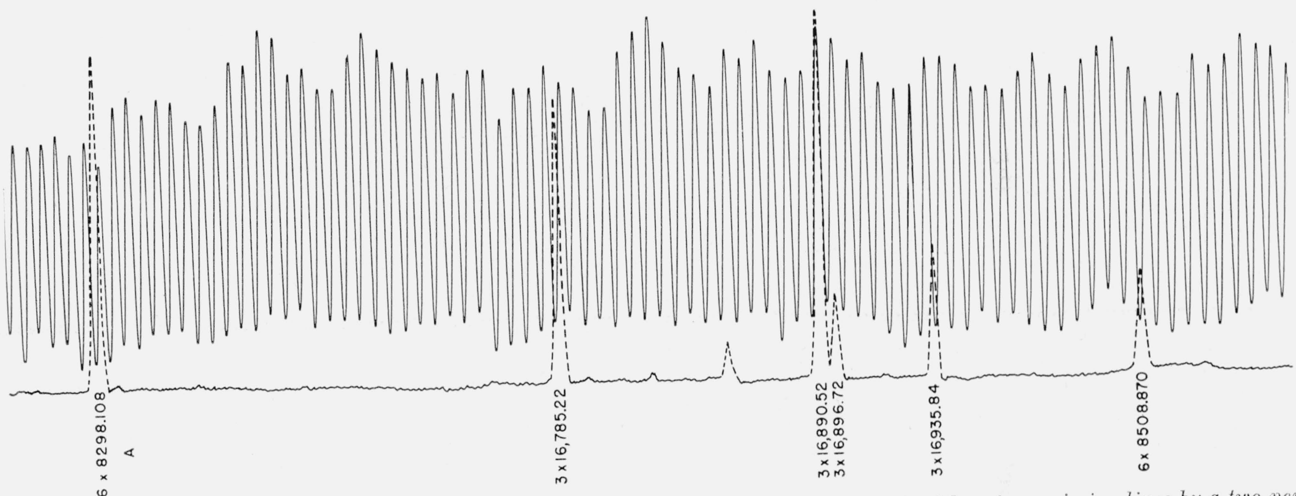

FIGURE 4. *Tracing of a record of interferometer fringes simultaneously recorded with standard krypton emission lines by a two-pen recorder.*

record was made on a two-pen recorder, with one pen recording the fringe system as detected by a 1P28 photomultiplier; the other pen records spectral lines as detected by a cooled PbTe cell.

For the record shown in figure 4, the mirror, M–9 (see fig. 1), has been thrown in position, so that the krypton lamp is being employed as a source. When the mirror, M–9, is removed, the absorption spectrum of the gas will be recorded by one pen, and the fringes of the interferometer will be recorded by the other pen. In the measurement of the absorption spectrum, at least two standard atomic lines are recorded, preferably one before the beginning and one at the end of the absorption band. The radiation from the krypton lamp travels along the same path as the radiation through the absorption cell, and in this way any shift of wavelengths between the two systems is avoided. The interferometer fringes are used as a comparison spectrum, and are given wave-number values after being calibrated with the standard lines.

The fringes are formed of white light; consequently in the region from 1 to 6 μ, it is necessary to observe the fringes in higher orders. Table 1 is a list of Corning glass filters, with narrow bands of transmission, which are employed in conjunction with the 1P28 photomultiplier that has an upper limit of sensitivity of 0.62 μ. When a narrow range of the spectrum is desired, two filters can be used. For example, the transmission of Corning filters, 5543 and 3385, extends over the spectral range of 0.47 to 0.51 μ. The cut-off region of the filters is sufficiently

TABLE 1. *A list of Corning glass filters which are used with the interferometer*

Filter number	Band width in microns [a]	Filter number	Band width in microns [a]
5970	0.30 to 0.42	3385	0.47 to 0.62
5031	.30 to .60	3384	.49 to .62
5030	.31 to .55	X–8	.50 to .62
5562	.33 to .54	3486	.51 to .62
4303	.34 to .62	3484	.53 to .62
5543	.35 to .51	3482	.54 to .62
3389	.42 to .62	2434	.55 to .62
3387	.435 to .62	3480	.56 to .62
		2424	.57 to .61

[a] The band width is determined by the filter and the long-wavelength cutoff of the 1P28 photomultiplier.

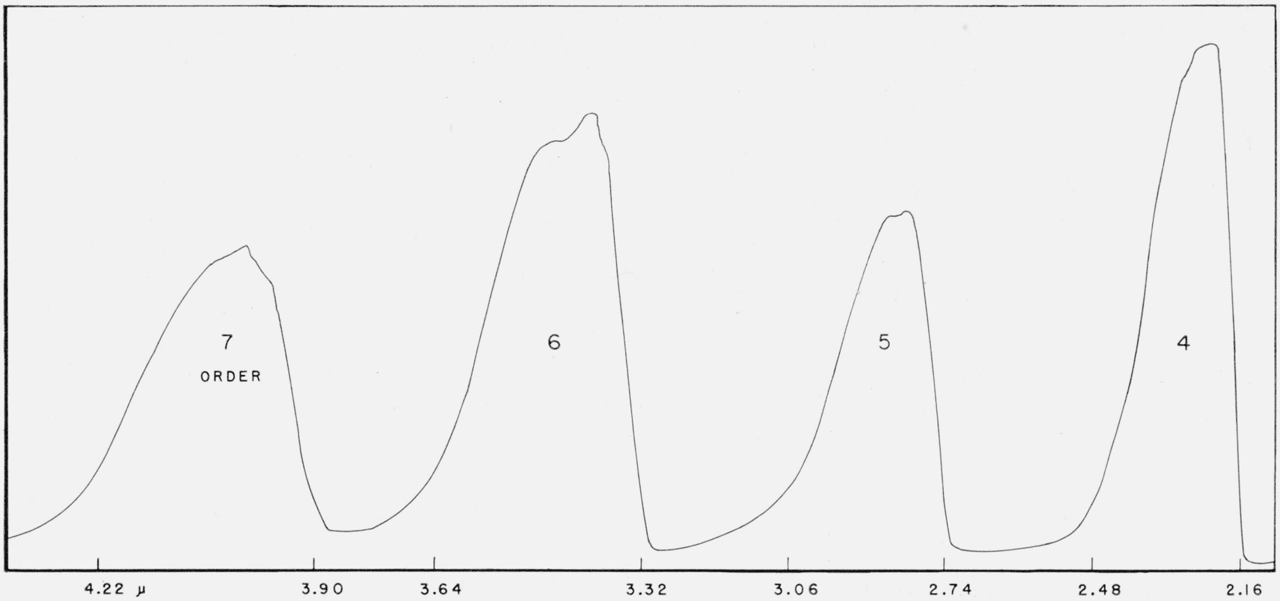

FIGURE 5. *A portion of the unresolved fringe system showing the 4th, 5th, 6th, and 7th orders.*

This fringe system is produced by white light in the spectral range from 0.54 to 0.62 μ.

sharp, so that there is no overlapping of different orders. From 1.5 to 1.8 μ, the third order of the visible fringes is used. This is done by employing Corning glass filter, 8X, which begins transmitting at 0.5 μ; and since the detecting limit of 1P28 photo cell is about 0.62 μ, this limits the band to 0.50 to 0.62 μ in the first order or 1.50 to 1.86 μ in the third order. At 6 μ the 10th or 11th order of the visible fringes is used. To produce fringes which have a change between maxima and minima of 40 percent or better, it is sometimes necessary to shift the width of the fringe band with another filter or combination of filters.

Figure 5 shows four orders of unresolved fringe systems using Corning filter number 3482, which, in conjunction with the cutoff of the photomultiplier, transmits the spectral region from 0.54 to 0.62 μ. The intensity of the fringe system varies with the spectral order and the characteristics of the grating. Figure 5 is typical of a particular grating; the intensity of the orders will not have the same value for other gratings, but with the same set of filters, the maxima of the fringe system will occur at the same wavelengths for all gratings. All of the spectral region from 1- to 6-μ can be measured by observing the fringe system in different orders.

3. Results

To test the precision of the measurements, well-known wavelengths of krypton lines have been measured in higher orders. The fringe system was calibrated by two known lines, and other lines were measured from the fringes. The atomic lines used as standards in these measurements are listed in table 2. The difference in wavenumbers between the two known lines is divided by the number of fringes between the two lines, thus giving a constant, the value of which depends on the spectral order of the fringe system. This constant is equal to the separation in wavenumbers between adjacent maxima of the fringe system, and is used to determine the wavenumber of any line. The distance of the atomic line from the neighboring maximum of the fringe system is determined by direct measurement to one hundreth of an inch. Table 2 shows the differences in measurements taken in this way compared with the published values [8] of these lines. The two sets of wavelengths check to about 1 part in 500,000.

The infrared spectrum of mercury was explored more than 40 years ago by Paschen and by Volk [9]; the former reported 23 lines from 10140 to 40159 A and the latter 21 lines from 10140 to 23253 A. The wavelengths of 22 lines between 13210 and 19200 A

TABLE 2. *A comparison of present measurements with known standards, Krypton*

Meggers and Humphreys 1st order	Order meas.	Meggers and Humphreys	Present work	Difference	Standards used 1st order
λ Air	n	$n\lambda$ Air	$n\lambda$ Air		
A		*A*	*A*	*A*	
7601.545	4	30406.18	30406.31	+0.13	9923.198 Xe 9799.697 Xe
8104.365	4	32417.46	32417.51	+.05	8776.749 Kr 8112.902 Kr
8104.365	5	40521.83	40521.89	+.07	8112.902 Kr 8928.692 Kr
8263.240	5	41316.20	41316.20	.00	8112.902 Kr 8928.692 Kr
8776.749	5	43883.74	43883.73	−.01	8112.902 Kr 8928.692 Kr
8928.692	4	35714.77	35714.68	−.09	7601.545 Kr 8776.749 Kr
8928.692	6	53572.15	53572.31	+.16	9162.652 Xe 8776.749 Kr
9751.759	5	48758.80	48758.96	+.16	8190.057 Kr 7601.545 Kr

were recently refined by Humphreys [10]. Since the spectrum of mercury has many lines of high intensity in the region from 1 to 2 μ, it was thought desirable to survey the region from 2 to 5 μ with the possibility of detecting other lines. In this region Paschen found 8 lines, and we have found 6, only 2 of which are identifiable with his. The results of the present work are shown in table 3. The wavelengths of four lines are in good agreement with the values calculated from the energy levels. The differences between the observed and calculated wavelengths are greater than the errors in the observed values. This difference may arise from the lack of interferometer values for the derivation of the "odd" energy levels in the transitions.

The third order of the line at 15295.63 A of mercury occured close to the first order line at 45122.04 A. It was also measured and checked with the high resolution measurements of Humphreys, who found a value of 15295.82 A.

The emission lines of neon, argon, krypton, and xenon are used for calibrating the fringe system. They are observed from Westinghouse enclosed arcs, operated on about 3 amp. Interferometric measurements on many of the lines of these gases have been made by Meggers and Humphreys [8]. The intense lines can be observed in the higher orders, and they have been used for calibration to 6 μ. In table 4 there are listed the more intense lines for each gas. The lines at wavelengths less than 10000 A have all been selected from the paper of Meggers and Humphreys.

The standards are only valid in standard air (15° C and 760 mm). If measurements are made in air of different density serious errors can be introduced by multiplying uncorrected wavelengths by 4, 5, or 6, if measured in the 4th, 5th or 6th order, to get the "apparent" value in the infrared region. At the time the measurements on the krypton lines, reported in this work, were made, the temperature was 22° C, and the pressure was 750 mm. The correction for standard conditions to the wavelengths is of the order of 0.001 A. If a line is used in the sixth order the correction would be 0.006 A, and this value is about one-third the error in our observations. However, when values of highest precision are desired, the wavelengths of all lines should be reduced to standard conditions.

There are many intense lines of krypton and xenon between 1 and 2 μ, as shown by the exploratory work of Humphreys and Plyler [11], of Sittner and Peck [12], and of Humphreys and Kostkowski [13]. These lines have not been measured with an interferometer and, therefore, could not be used as standards. Some of these lines have been measured in the present work and are also listed in table 4. Some gratings have low intensities in certain orders, and by having additional standard lines available from 1 to 2 μ, it is possible to measure in the entire region from 1 to 6 μ.

It would be desirable to have many standards in the infrared region, and certain lines should be measured by the interferometer directly, as has been done in the visible and near infrared regions. The method of measurement in the infrared region would be similar to that used in the photographic

TABLE 3. *Selected lines in the infrared spectrum of mercury*

Present work		Calculated from atomic energy levels		Designation
λ Air	ν (vac)	λ Air	ν (vac)	
A	*CM*$^{-1}$	*A*	*CM*$^{-1}$	
22493.28	[a] 4444.56 ±0.01	22492.85	4444.64	$7p^3p^\circ_0-8s\ ^3S_1$
23253.07	4299.33 ±0.02	23252.63	4299.41	$7p^3p^\circ_1-8s\ ^3S_1$
32148.06	3109.76 ±0.02	32151.32	3109.44	$7p^1p^\circ_1-8s\ ^1S_0$
36303.03	2753.84 ±0.002	36303.78	2753.79	$7p^3p^\circ_2-8s\ ^3S_1$
39283.61	2544.90 ±0.042	--------	-------	--------------
45122.04	2215.63 ±0.027	--------	-------	--------------

[a] The average deviation of six measurements.

TABLE 4. *A list of intense atomic lines of neon, argon, krypton, and xenon for infrared calibration*

λ in air	λ in air	λ in air	λ in air	λ in air
		NEON		
A	*A*	*A*	*A*	*A*
4422.519	4827.587	5820.148	6678.2766	8679.491
4424.800	4837.3118	5852.4880	6929.4678	8681.920
4488.0928	4884.915	5881.8950	7024.0508	8771.70
4537.68	4892.090	5944.8343	7032.4134	8780.6223
4537.751	4957.0334	5965.474	7173.9389	8783.755
4538.31	5005.160	5974.628	7245.1668	8853.867
4575.060	5037.7505	5975.5339	7438.8990	8865.759
4645.416	5144.9376	6029.9970	7488.8722	8919.50
4656.3923	5145.01	6074.3377	7535.7750	9148.68
4678.218	5330.7766	6096.1630	7943.1802	9201.76
4704.395	5341.091	6143.0624	8082.4580	9220.05
4708.854	5343.284	6163.5937	8136.4060	9300.85
4712.06	5400.5620	6217.2811	8266.076	9313.98
4715.344	5562.769	6266.4950	8300.3258	9326.52
4749.572	5656.6585	6304.7893	8377.6068	9425.38
4752.7313	5719.2254	6334.4280	8418.4274	9459.21
4788.9258	5748.299	6382.9914	8495.3600	9486.680
4817.636	5764.4182	6402.2455	8591.2584	9535.167
4821.924	5804.4488	6506.5278	8634.6480	9547.40
4827.338	5811.42	6598.9528	8654.3835	9665.424
		ARGON		
6965.4302	7383.9800	7891.075	8115.3115	9122.9660
7030.262	7503.8676	7948.1754	8264.5209	9224.498
7067.2170	7514.6510	8006.1556	8408.208	9354.218
7147.0406	7635.1053	8014.7856	8424.647	9657.7841
7272.9357	7723.7597	8053.307	8521.4407	9784.5010
7372.117	7724.2064	8103.6922	8667.9430	10470.051
		KRYPTON		
7486.862	8104.3642	8776.7490	[a] 14347.69	[a] 16896.72
7587.4130	8112.902	8928.6920	[a] 14426.67	[a] 16935.84
7601.5443	8190.0543	9751.759	[a] 14734.42	[a] 17367.80
7685.2460	8263.2398	[a] 13634.28	[a] 15239.67	[a] 18001.71
7694.5395	8281.0495	[a] 13738.94	[a] 15334.92	[a] 18167.15
7854.8217	8298.1077	[a] 13883.15	[a] 16785.22	[a] 21902.51
8059.5038	8508.8700	[a] 13924.11	[a] 16890.52	
		XENON		
7119.598	7643.91	8231.6336	8908.73	9799.697
7285.301	7802.651	8280.1162	8930.83	9923.198
7312.452	7881.320	8346.8217	8952.2506	[a] 12623.36
7316.272	7887.3898	8409.1894	8987.57	[a] 13657.22
7386.003	7967.342	8648.54	9045.4460	[a] 14241.23
7393.793	8057.258	8739.372	9162.6520	[a] 14732.88
7584.680	8061.339	8819.411	9374.76	[a] 15418.12
7642.025	8206.336	8862.32	9513.377	

[a] Measured in present work

region, except that a semiconductor cell would be employed to scan the Haidinger fringe pattern.

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