JOURNAL OF THE OPTICAL SOCIETY OF AMERICA VOLUME 62, NUMBER 8 AUGUST 1972

Dispersion of Air*

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(Received 18 February 1872)

New measurements of the infrared dispersion of air are reported. They agree with series I of the 1962 data of Peck and Khanna, but lie below Edlén's 1966 formula. A two-term Sellmeier formula suffices to fit the resulting infrared (ir) data as well as the data selected by Edlén in the visible and ultraviolet (uv), being valid down to nearly 0.23 μm. Other possible Sellmeier fits are discussed, including extension to 0.185 μm.

Index Headings: Dispersion; Refractive index; Infrared.

In 1966, Edlén[1] published a comprehensive review article on the refractive index of air. This included a normalization of experimental data from Svensson,[2] Erickson,[3] Rank *et al.*,[4] and Peck and Khanna[5] (herein to be abbreviated P & K); a new dispersion formula; a study of the dependence of refractive index on pressure and temperature; and consideration of the effects of carbon dioxide and water vapor. The dispersion formula contains five parameters,

$$(n-1)\times 10^8 = 8342.13 + \frac{2\,406\,030}{130-\sigma^2} + \frac{15\,997}{38.9-\sigma^2}. \quad (1)$$

It applies to standard air at 15°C, with 0.033% content of CO_2. The wave number σ is here to be expressed in reciprocal μm. Edlén allowed this formula to rise higher in the ir than any of the data points in order to favor the accurate data of Erickson,[3] which cover the range from 0.3985 to 0.6440 μm. He stated that the average deviation of the data below the 1966 formula was 0.7×10^{-8}. This situation left a question about the ir region and indicated that further data would be of interest. This paper presents new measurements at eight ir wavelengths from 0.7247 to 1.53 μm, all of which lie below the 1966 formula. In addition, we re-examine the data of P & K[5] under the hypothesis of some contamination by water vapor in series II of the data of that paper. Series I measurements of P & K are in close agreement with the new data. We find it possible to represent the entire range of valid data from 0.23 to 1.69 μm by a new Sellmeier formula having only four parameters. Five parameters are necessary, however, for any extension to shorter wavelengths.

NEW DATA

The new data are measurements of the refractivity ratio, $(n-1)/(n-1)_{0.5462}$, for air in the ir, made using the corner-cube interferometer, read-out equipment, and the method previously described.[5,6] The path of light in the gas was effectively doubled, compared to the previous work, by the addition of a second gas cell in the previously empty arm of the interferometer. Like the first cell, this has a length of 24.14 cm. The two cells being equal in length to within 0.001 cm, the double-cell design provides compensation over drifts due to changing density of ambient air. A typical measurement involved simultaneous evacuation of one cell and filling of the other. This was usually paired with the reverse operation to minimize drift errors. Because the light traverses each cell twice, the effective path length in the gas is 96.5 cm. Another significant change in the equipment concerned the dehumidifying of the air samples. Outdoor air, drawn from a point far from vehicular traffic in the small city of Moscow, Idaho, was first filtered through ten inches of glass wool and then passed through a millipore filter with pore size of 10 nm. The air next traversed a copper cold trap 127 mm long and 38 mm in diameter, completely submerged in a bath of solid CO_2 and acetone. Finally, it passed through a coil of glass tubing also immersed in CO_2–acetone. Of these two drying units, only the second was employed for the measurements of P & K.

Table I contains the new measurements. Ratio values had an internal consistency indicated by standard deviations in the mean of many runs, usually about 15 per wavelength, ranging from 1.6×10^{-6} to 3.6×10^{-6}. The refractivity values are computed from these refractivity ratios by multiplication with the absolute value of $27\,789.88\times 10^{-8}$ taken by Edlén for the mercury wavelength 0.5462 27 μm. The standard deviations for the mean refractivity values run then from 0.05×10^{-8} to 0.11×10^{-8}. The last column of Table I shows the deviations of these data from the 1966 formula of Edlén. These average -0.38×10^{-8}, and all are negative.

COMPARISON WITH PREVIOUS DATA

Eight of the values of refractivity of air reported in the 1962 paper of P & K[5] and quoted by Edlén in 1966

Table I. New data on ir refractivity of air, and comparison with Edlén's formula.

Vacuum wavelength, μm	$(n-1)\times 10^8$	[Data−Eq. (1)] $\times 10^8$
1.5300 153	27 326.41	−0.46
1.3722 3271	342.52	−0.38
1.3507 884	345.31	−0.21
1.0142 5728	410.78	−0.48
0.9660 4341	426.28	−0.48
0.9227 0299	442.66	−0.18
0.9125 4707	446.43	−0.51
0.7247 1632	557.42	−0.13

involved a weighting of two sets of measurements there called series I and series II. Series II measurements differed systematically from series I, being on the average 0.38×10^{-8} lower. The weighting scheme adopted by P & K favored series II by 5 to 3. The two series were reported separately as well, in the belief that the systematic difference might be significant in regard to the seasonal composition of the outdoor air between winter, January and February, when series I was performed, and spring for series II. We now believe that the difference between series is indeed due to a change in the air sample in the simplest way, the absolute humidity of the air in winter being much less than in the spring. As mentioned above, only a single drying unit was used in the work of P & K, whereas two units operating in series were employed in the present work, with the aim of reducing the danger of contamination by water vapor. We think it reasonable to suppose that the single cooling coil was adequate to remove the moisture from winter air, but that in spring enough water was trapped that the frost in the cooling coil extended above the level of the coolant on the outlet side. A rough calculation indicates that a realistic partial pressure of water can account for the difference between series I and series II. From Fig. 4 of Edlén's 1966 paper, we estimate that the difference between the refractive indices of water and air, $(n_{H_2O}-n_{air})$, changes by very roughly -0.13×10^{-8} per torr from 0.546 to 1.3 μm. The average deviation of -0.38×10^{-8} between the two series corresponds then to about 3 torr of water vapor, or a dew point of −6°C. Perhaps it is a rough check that the absolute value of the index of air at 0.5462 μm, as reported by P & K from series II only, was low by about 5×10^{-8}, suggesting 1 torr of water contamination. With a properly operating drying chamber at the dry-ice temperature of −78°C, there would be only the negligible partial pressure of 0.00056 torr.

The supposition that the air was effectively dried for series I data is suggested by their agreement with the new measurements. Table II reproduces the series I data, renormalized from their original reference value of $27\,790.10\times10^{-8}$ at the mercury-green wavelength to Edlén's newer value of $27\,789.88\times10^{-8}$. The renormalization amounts to subtraction of 0.22×10^{-8} from the values published by P & K. The deviations of these figures from Edlén's 1966 formula are given. Again, all are negative. Of the four lines common to Tables I and II, the mean deviation of the new data from the 1966 formula is -0.40×10^{-8} compared with -0.35×10^{-8} for series I. The mean deviation of all the new data from the 1966 formula is -0.38×10^{-8} compared with -0.46×10^{-8} for all of series I. These figures agree to within the expected precision of the data. The last column of Table II shows the differences (series I—new data) for the four common lines. These have an algebraic mean of 0.04×10^{-8}, and an rms value of 0.14×10^{-8}.

We now put forward the data in Tables I and II as a consistent set of 16 independent measurements of dry air at twelve wavelengths ranging from 0.7247 to 1.6945 μm. They are so treated in the following section on curve fitting. It is noteworthy that the only other ir datum included in Edlén's 1966 selection, Table 2 of his paper,[1] also falls below the 1966 formula, by 0.77×10^{-8}.

TABLE II. Renormalized data of Peck and Khanna, series I. Comparison with Edlén's formula and with new data.

Vacuum wavelength, μm	$(n-1)\times10^8$	Ser. I—Eq. (1) $\times10^8$	Ser. I—new data $\times10^8$
1.6945 208	27 314.00	−0.72	
1.5293 544	326.56	−0.37	
1.4756 503	331.28	−0.53	
1.3722 3271	342.34	−0.56	−0.18
1.3507 884	345.38	−0.14	+0.07
1.1290 4974	381.47	−0.64	
1.0142 5728	410.87	−0.39	+0.09
0.9125 4707	446.62	−0.32	+0.19

It appears, from the agreement between series I of P & K and the new measurements, that for the near ir the dispersion of outdoor air in Moscow, Idaho, is indistinguishable from that in Evanston, Illinois, at least to a precision of the order of 0.2×10^{-8}. This is remarkable in view of an altitude difference of some 600 m, and the fact that Moscow, unlike Evanston, does not lie on a lake shore. The time span of about 10 years between the two experiments may be favorable in the comparison because of the increasing air pollution near large cities such as Chicago.

TWO-TERM DISPERSION FORMULA

It remains to show that the set of ir data points, the new, the newly revised, and the datum of Rank *et al.*[4] are consistent with the entire body of precise refractivity measurements, in the sense that a reasonable dispersion formula can be found to produce a good fit over the whole range of wavelengths down to the ultraviolet. The senior author, with help from Charles Mansfield and William Rasmussen, has developed computer programs for fitting formulas of the Sellmeier type with up to three terms. These programs involve no assumption about absorption wave numbers. The seventeen ir points discussed above were included in computing the fit; and the ten points of Erickson[3] were each entered twice, to double their weight. A few of the other data that had large deviations from all formulas including Eq. (1) were omitted from the computation. We conclude that a two-term formula, with only four parameters, is satisfactory for representing all of the data, from the farthest ir measurements to nearly 0.23 μm. Such a formula is

$$(n-1)\times10^8=\frac{5\,791\,817}{238.0185-\sigma^2}+\frac{167\,909}{57.362-\sigma^2}. \qquad (2)$$

Table III and Fig. 1 show in detail how the new formula compares with the data and with Eq. (1). The

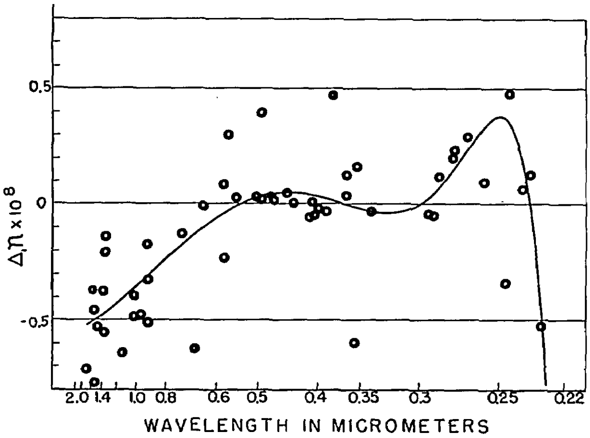

FIG. 1. Data points of Table III, and the new two-term dispersion formula for air, Eq. (2), plotted relative to Edlén's 1966 formula, Eq. (1). The widely deviant points marked "b" in Table III are omitted.

table includes all of the points listed in Table 2 of Edlén's[1] paper, except (i) the points of P & K at 2.0856 91 and 0.7034 35 μm are omitted as being only in series II and showing anomalies; (ii) the point at 0.4078 98 μm, which was not measured but only interpolated by Rank *et al.*[4] Additional data points in the ir are from our new measurements. The old data from P & K are entirely the renormalized series I, as given also in Table II. Figure 1 omits the wide points marked "b" in Table III.

Comparison of the new formula, Eq. (2), with Edlén's 1966 formula, Eq. (1), can best be made statistically. The conclusions are the same whether the rms deviation or the mean absolute deviation of the data is chosen as a figure of merit for the formula. The former was chosen as being more frequently used. For N points whose deviations are x_i, the rms deviation is defined by $(N^{-1}\sum_{i=1}^{N} x_i^2)^{\frac{1}{2}}$. Table IV shows these rms deviations for all of the data and for selected sets of points, along with the mean algebraic deviations, which give a measure of systematic differences.

The selections of data in Table IV require explanation. The first groupings exclude the ir, because the primary question to be examined is whether the inclusion of the ir data in the computation of the formula causes a poor fit elsewhere. From the entire set of 42 visible and uv points, we next try removing five whose deviations exceed twice the rms deviation. Then we remove three more points whose deviations are still about twice the improved rms deviation. The resulting rms values of 0.17×10^{-8} to 0.19×10^{-8} seem to represent the precision of the bulk of the data in these regions, from below 0.7 μm to 0.23 μm. One more point, at 0.23 μm, was omitted finally, to leave the group of 33 points, just because it happens to be low and favors our Eq. (2) more than Edlén's formula, Eq. (1). In all of these groups, Eq. (2) compares well with Eq. (1), being

TABLE III. Refractivity of standard air at 15 °C in the wavelength range 1.69–0.23 μm. The data and the predictions of Eq. (2) are tabulated along with differences between data, Eq. (2) and Eq. (1).

Vacuum wave-length in μm	Data $\times10^8$	Eq. (2)	Data source[a]	Data −Eq. (2)	Data −Eq. (1)	Eq. (1) −Eq. (2)
1.6945 208	27 314.00	27 314.19	I	−0.19	−0.72	+0.52
1.5300 153	326.41	326.37	N	+0.04	−0.46	+0.50
1.5299 77	326.1	326.37	R	−0.27	−0.77	+0.50
1.5293 544	326.56	326.43	I	+0.13	−0.37	+0.50
1.4756 503	331.28	331.32	I	−0.04	−0.53	+0.49
1.3722 3271	342.34	342.42	I	−0.08	−0.56	+0.47
1.3722 3271	342.52	342.42	N	+0.10	−0.38	+0.47
1.3507 884	345.38	345.05	I	+0.33	−0.14	+0.47
1.3507 884	345.31	345.05	N	+0.26	−0.21	+0.47
1.1290 4974	381.47	381.71	I	−0.24	−0.64	+0.41
1.0142 5728	410.87	410.90	I	−0.03	−0.39	+0.36
1.0142 5728	410.78	410.90	N	−0.12	−0.48	+0.36
0.9660 4341	426.28	426.42	N	−0.14	−0.48	+0.34
0.9227 0299	442.66	442.52	N	+0.14	−0.18	+0.31
0.9125 4707	446.62	446.64	I	−0.02	−0.32	+0.31
0.9125 4707	446.43	446.64	N	−0.21	−0.51	+0.31
0.7247 1632	557.42	557.37	N	+0.05	−0.13	+0.18
0.6909 66[b]	586.4	587.62	S	−1.22	−1.37	+0.15
0.6718 29[c]	606.4	606.89	S	−0.49	−0.62	+0.13
0.6440 2492	27 638.195	27 638.092	E	+0.103	+0.001	+0.102
0.6236 10[b]	664.8	663.79	S	+1.01	+0.93	+0.08
0.6125 19[b]	677.8	678.88	S	−1.08	−1.15	+0.07
0.6074 39[b]	687.2	686.07	S	+1.13	+1.06	+0.07
0.5792 264	729.8	729.67	R	+0.13	+0.09	+0.04
0.5771 195.	733.0	733.20	R	−0.20	−0.23	+0.04
0.5677 47	749.7	749.37	S	+0.33	+0.30	+0.03
0.5462 2707	789.880	789.843	E	+0.037	+0.029	+0.009
0.5017 074	891.528	891.525	E	+0.003	+0.030	−0.026
0.4961 52[b]	905.0	906.27	S	−1.27	−1.24	−0.03
0.4923 304	916.709	916.714	E	−0.005	+0.027	−0.032
0.4917 45	918.7	918.34	S	+0.36	+0.40	−0.03
0.4714 462	978.608	978.623	E	−0.015	+0.027	−0.042
0.4679 4587	898.846	989.866	E	−0.020	+0.024	−0.044
0.4472 732	28 062.084	28 062.082	E	+0.002	+0.050	−0.048
0.4359 5623	106.304	106.335	E	−0.031	+0.016	−0.048
0.4359 56	106.5	106.34	R	+0.16	+0.21	−0.05
0.4109 33	218.4	218.50	S	−0.10	−0.06	−0.04
0.4047 7144	249.536	249.611	E	−0.075	−0.040	−0.036
0.4047 71	249.5	249.61	R	−0.11	−0.08	−0.04
0.3985 09	282.8	282.85	S	−0.05	−0.02	−0.03
0.3889 751	28 336.787	28 336.843	E	−0.056	−0.033	−0.023
0.3802 73[c]	390.5	390.04	S	+0.46	+0.47	−0.01
0.3655 874	489.6	489.47	R	+0.13	+0.13	+0.00
0.3651 190	492.9	492.86	R	+0.04	+0.04	+0.00
0.3562 24[c]	559.5	560.08	S	−0.58	−0.60	+0.01
0.3544 43	574.4	574.22	S	+0.18	+0.16	+0.02
0.3391 68	705.9	705.90	S	0.00	−0.03	+0.03
0.2926 30	29 264.3	29 264.37	S	−0.07	−0.04	−0.02
0.2894 47	314.4	314.49	S	−0.09	−0.05	−0.04
0.2857 79	374.8	374.75	S	+0.05	+0.12	−0.07
0.2760 59	548.7	548.64	S	+0.06	+0.20	−0.14
0.2753 60	562.1	562.02	S	+0.08	+0.24	−0.15
0.2675 75	719.8	719.74	S	+0.06	+0.29	−0.23
0.2577 11	945.5	945.74	S	−0.24	+0.10	−0.33
0.2464 82	30 245.7	30 246.41	S	−0.71	−0.34	−0.36
0.2447 65	297.3	297.17	S	+0.13	+0.48	−0.35
0.2379 11	514.4	514.50	S	−0.10	+0.06	−0.16
0.2346 17	628.3	628.14	S	+0.16	+0.13	+0.03
0.2302 89[d]	787.6	787.68	S	−0.08	−0.53	+0.45

[a] E, Erickson; S, Svensson; R, Rank *et al.*; I, series I of P&K; N, new data.

[b] Point of the set of five first removed from calculation of the rms deviation.

[c] Point of the set of three next removed from calculation of the rms deviation.

[d] Point last removed from calculation of the rms deviation.

generally a little more precise, but never appreciably worse.

Next, the ten points of Erickson[3] are isolated for examination, although they were included in the foregoing sets: for Eq. (1) was stated[1] to have been designed for good fit of these. Here Eq. (1) does have a small advantage in rms error, 0.030×10^{-8} vs 0.047×10^{-8}, although it is slightly worse in mean deviation. Probably these differences are all so small as to be without significance. Most of the advantage for Eq. (1) accrues from the two extreme points of Erickson's range of data.

Now unlike Eq. (1), Eq. (2) was computed with inclusion of the ir data, and it fits the 17 ir points well, as Table IV shows. Its precision here is as great as for the good data of the other regions, namely, 0.17×10^{-8} rms, whereas Eq. (1) runs an average of 0.43×10^{-8} too high, with correspondingly large rms deviation. This lack of fit for Eq. (1) in the ir results naturally in poor over-all precision for the combined sets of 59, 54, and 51 points. Equation (2) fits over the whole range, from 1.7 to 0.23 μm, with a uniform rms deviation of about 0.2×10^{-8}, which is presumably the precision of the better data.

Of course, Eq. (2) is not unique. Small variations of the constants are possible, provided that they are properly related, with little change of the results. Equation (2) is actually a simplified version of the formula yielded by the computer. With numbers at most of 7 digits as parameters, it yields the same values as the computer-derived formula to a maximum difference of 1.4 in the eighth digit. More significantly, use of different input data, or weighting, or choosing a fit with rms deviation slightly above minimum, changes the formula appreciably. For example, we obtained another equally valid formula whose differences with Eq. (2) run to about 0.03×10^{-8} or less over most of the range of Table III, but peak sharply at 0.10×10^{-8} at 0.25 μm and then proceed to diverge from Eq. (2) indefinitely, in the opposite sense from the peak, below 0.22 μm. In this case, the constants representing squares of fictitious absorption wave numbers both decreased, the first by 2.5%, the second by 0.6%. It is to be noted, however, that the extreme difference of 0.10×10^{-8} over the valid range of the formulas is well within the scatter of the data.

TABLE IV. Statistical comparison of the new dispersion formula, Eq. (2), with Edlén's 1966 formula, Eq. (1). The factor of 10^{-8} is understood.

Spectral region	Number of points	rms deviation of data from Eq. (2)	rms deviation of data from Eq. (1)	Mean algebraic deviation of data from Eq. (2)	Mean algebraic deviation of data from Eq. (1)
Visible and	42	0.45	0.46	−0.05	−0.02
ultraviolet	37	0.22	0.25	−0.01	+0.03
0.69–0.23 μm	34	0.18	0.19	+0.00	+0.05
	33	0.18	0.17	+0.00	+0.07
Infrared					
1.69–0.72 μm	17	0.17	0.47	−0.02	−0.43
Visible					
(Erickson)					
0.64–0.39 μm	10	0.047	0.030	−0.006	+0.013
Entire region	59	0.39	0.46	−0.04	−0.14
1.69–0.23 μm	54	0.21	0.33	−0.02	−0.12
	51	0.17	0.31	−0.00	−0.11

TABLE V. Far-uv refractivity of standard air. Data of Traub, recalculated for 15 °C and 0.033% CO_2 content, normalized to $27\,789.88\times10^{-8}$ for 0.5462 27 μm, and compared with Eqs. (3), (2), and (1).

Wave-length in μm	Data $\times10^8$	Eq. (3)	Data −Eq. (3)	Data −Eq. (2)	Data −Eq. (1)
0.2145 06	31 496.8	31 496.6	+0.2	+5.5	−0.3
0.2026 05	32 214.8	32 217.4	−2.6	+18.8	−3.6
0.1990 52	32 479.5	32 478.5	+1.0	+32.7	−0.4
0.1935 85	32 939.7	32 937.5	+2.2	+60.4	−0.1
0.1862 77	33 697.4	33 702.7	−5.3	+129	−11.1
0.1854 73	33 805.5	33 801.4	+4.1	+152	−2.4

WIDER-RANGE DISPERSION FORMULAS

The existing data on the dispersion of air below 0.23 μm are probably of a lower order of precision than most of those quoted in Table III. Eventually, too, molecular absorption bands will set in to disturb the regularity of the dispersion. It is instructive nevertheless to investigate the possibility of extending a dispersion formula into this region. For this purpose, we have recalculated the six points of Traub[7] that are from 0.2145 down to 0.1854 μm. Table V shows these data, reduced to standard air at 15°C. In order to make them as accurate as possible, the correction from Traub's CO_2-free air to 0.033% CO_2 has been based upon an unpublished, three-term dispersion formula for CO_2. The 45 data points for that fit extended from 1.8 to 0.238 μm, so that extrapolation of the formula was necessary. Nevertheless the procedure was preferred to simple multiplication by a constant.

In what follows, we shall refer to spectral region A as that of Table III, and to region B as that of Table V; thus A and B are, respectively, higher and lower in wavelength than 0.23 μm. The five worst points in region A are omitted from consideration. The third column of Table V shows deviations of the data from Eq. (2), whereas Table VI gives rms deviations in region A, in region B, and in the combined region. Clearly our two-term fit of region A becomes totally unusable in region B. In fact, as Fig. 1 also shows, Eq. (2) is indeed falling rapidly relative to Eq. (1) already at 0.23 μm. The same was true of a three-term fit based entirely upon region A. Clearly, extrapolation is dangerous.

It was of interest next to try a two-term fit of the combined regions A and B. The result, as seen in Table VI, is an over-all rms error of 2.3×10^{-8}, with 4.9×10^{-8} for region B. However, this fit does no justice

TABLE VI. rms deviations from several dispersion formulas of the data over an extended wavelength range. The factor of 10^{-8} has been omitted.

Spectral region	Eq. (2)	Extended two term	Eq. (3)	Eq. (1)
Region A, 54 points 1.7–0.23 μm	0.21	1.8	0.23	0.33
Region B, 6 points below 0.23 μm	86	4.9	3.1	4.9
Combined A and B, 60 points	27	2.3	1.0	1.6

to the precision of the data in region A, having nine times the rms error of Eq. (2). Thus, two terms would be satisfactory over the wide range of A and B only if all of the data were of low precision, of the order of 2×10^{-8}. Even then, a systematic trend would be noticeable.

Finally, we obtained reasonable fits over the combined region A and B both in the form of Eq. (1) with 2.5 Sellmeier terms or five parameters, and also with three full terms. However, the six-parameter formula is not appreciably better than the five-parameter one. The rms deviations of the data from this five-parameter formula are 1.0×10^{-8} over all; 3.1×10^{-8} in region B, reflecting the scatter of the data; and 0.23×10^{-8} in region A, very slightly inferior to Eq. (2). Edlén's formula, Eq. (1), performs quite well in the combined region, except for the ir, yielding an over-all rms deviation of 1.6×10^{-8}, with 4.9×10^{-8} in region B. Thus, Eq. (1) may have been constructed with the extended region in view. See Table VI for a summary of the foregoing deviations.

The number of parameters required for a dispersion curve depends both on the range of the data and their precision. For air, four parameters suffice above 0.23 μm, but five are at present necessary and sufficient to include the less-regular data to 0.185 μm. Our five-parameter formula is

$$(n-1)\times10^8=8060.51+\frac{2\,480\,990}{132.274-\sigma^2}+\frac{17\,455.7}{39.32\,957-\sigma^2}. \quad (3)$$

We consider this to have temporary validity as a wide-range formula, but only until data of higher precision become available in region B. For the sake of completeness, Table V shows the deviations of the data in region B from Eqs. (1) and (3).

ACKNOWLEDGMENTS

We express our sincere thanks to Oshri Karmon and Jerry Latimer for their assistance in constructing a gas-manifold system for the interferometer. Most of the computing was done at the Computer Center of the University of Idaho. We are grateful for their patience and also for grants of computing time. The senior author also thanks the National Research Council of Canada for their hospitality in providing an office and computing facilities in Ottawa while the paper was being written.

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