The Dispersion of Standard Air*

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By combining Barrell and Sears' measurements in the visible and Koch's and Traub's in the ultraviolet, a dispersion formula for standard air has been derived, viz.,

\[(n-1)10^8=6432.8+2949.810(146-\sigma^2)^{-1}+25.540(41-\sigma^2)^{-1},\]

\(\sigma\) being vacuum wave number in \(\mu^{-1}\), which should satisfy all needs of precision spectroscopy, in particular for converting wavelengths in air into vacuum values.

INTRODUCTION

THE standard wavelengths, on which all spectroscopic measurements are based, are by definition referred to "standard air," viz., dry air, containing 0.03 percent by volume of \(\text{CO}_2\), at normal pressure\(^{\dagger}\) and a temperature of 15°C. On the other hand, atomic and molecular energy levels derived from these measurements, and all energy relationships in spectra, must be expressed in wave numbers\(^{\ddagger}\) in vacuum,

\[\sigma_{\text{vac}}=1/\lambda_{\text{vac}}=1/n\lambda_{\text{air}},\]

\(\sigma\) being the refractive index of standard air. For the conversion of wavelengths in air into wave numbers in vacuum spectroscopists have been using almost universally for the past 27 years Kayser's \(\textit{Tabelle der Schwingungszahlen}\),\(^{1}\) which is based on the dispersion formula of Meggers and Peters.\(^{2}\)

During 1934–1939 three independent and remarkably accurate determinations of the refraction of air for visible radiations were published by Kösters and Lampe,\(^{3}\) Pérand,\(^{4}\) and Barrell and Sears.\(^{5}\) The dispersion formulas derived show a reasonably good mutual agreement throughout the wavelength region that was actually covered by observations. In comparison with these results Meggers and Peters' formula gives refractivity values which are too low by an amount ranging approximately from 50 to 100\(\times\)10\(^{-5}\) within the visible region. The significance of this discrepancy may be judged by recalling that wavelength measurements are now approaching an accuracy of one part in 50 000 000, thus calling for the same accuracy in the refractive index of air, that is \(\pm 2\times 10^{-5}\). It is evident, therefore, that Meggers and Peters' formula is no longer

1 H. Kayser, \textit{Tabelle der Schwingungszahlen etc.} (B. G. Teubner, Leipzig, 1925).
sufficiently accurate, and precision spectroscopists have for some time been faced with the problem of finding an adequate substitute, covering not only the visible range but also the ultraviolet. A solution to this problem is proposed here.

**SELECTION OF OBSERVATIONAL MATERIAL**

In the choice between the recent dispersion formulas, viz., Kösters and Lampe’s (b), Pérard’s (c), and Barrell and Sears’ (d), it should be observed that usual criteria would give a weight to (d) nearly ten times higher than that of (c), while the weight of (b) cannot be stated with certainty because the necessary details have never been published. By comparing the three formulas (see Fig. 2), one finds for the visible region that (c) and (d) agree very closely as to dispersion but differ in absolute values by an amount of approximately 8.5×10⁻⁸. This difference seems to be considerably larger than the uncertainty in Barrell and Sears’ measurements as estimated from the detailed description of their experiments, and remains unexplained as long as the relevant data for Kösters and Lampe’s experiments are unknown. In this situation I have preferred to choose Barrell and Sears’ results rather than a weighted mean of the different formulas.

Recently, Dr. E. Engelhard of the Physikalisch-Technische Bundesanstalt, Braunschweig, kindly informed me that Kösters and Lampe, as far as he knew, had been using a “synthetic” air obtained by mixing the pure components of air according to its average percentage composition. He pointed out, that a possible reason for the difference between the NPL and the PTR results could be the presence of impurities such as moisture, carbonoxides, hydrocarbons, or, principally, vapors of heavy hydrocarbons. Dr. Engelhard also reported several details showing that the relative values of Kösters and Lampe should be at least as accurate as those of Barrell and Sears. It is gratifying, particularly in view of this information, that the two formulas are practically identical as regards dispersion.

It is obvious from the general shape of the dispersion curve (n−1=A+B/X²+C/X⁴+⋯) that an extrapolation toward shorter wavelengths is definitely precarious (see Fig. 2). For instance, with σ² (=1/X²) as the appropriate abscissa, any one of the curves (b), (c), or (d) would have to be extrapolated 4 times its observed length to reach 2500Å. It is clear that any reliable extension of the dispersion curve in that direction has to be based on actual observations in the region concerned.

Now, a critical study of existing literature has revealed two sets of measurements, and only two, which may be judged as acceptable for this purpose. They are by J. Koch (Uppsala, 1912), range 5460–2378Å, and W. Traub (Tübingen, 1920), range 5460–1854Å. Both investigators used a method, based on the Jamin refractometer, which is of intrinsically high accuracy, and the careful execution is testified by small scattering and by close agreement as to dispersion in overlapping regions, both mutually and with Barrell and Sears. Koch and Traub give the relative number of interference fringes s passing in different wavelengths when the pressure is changed from atmospheric to zero value. These s values are derived directly from fringe positions on photographic spectrum plates covering in one exposure the whole wavelength region investigated and are independent of pressure and temperature measurements. The refractivities are proportional to λ×s and can be obtained as soon as the value is known for one of the wavelengths observed.

I have derived refractivity values from the s values given by Koch and Traub by choosing the proportionality factor so as to get the best possible fit to Barrell and Sears’ observations in the common region, 5460–4358Å. The data are collected in Table I, referred to dry, CO₂ free air at 760 mm Hg and 15°C. Barrell and Sears’ values were obtained by multiplying the figures labeled “adjusted” in Table VII of their paper by the factor 720.8826, obtained from their formula (5.12). Koch’s measurements were then adjusted to the

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same scale by means of the relation

\[(n - 1)10^8 = 5.08665\lambda s,\]

where \(\lambda\) is expressed in \(\mu\) in vacuum, and correspondingly for Traub \((n - 1)10^8 = 5.08689\lambda s\). In this way 46 different observed values of \(n - 1\) (Barrell and Sears 8, Koch 24, and Traub 14) at 38 different wavelengths, ranging from 6438 to 1854A, have become available for determining the dispersion curve.

**DERIVATION OF THE DISPERSION FORMULA**

When trying to derive a formula fitting the observed values in Table I, one finds immediately that the Cauchy form, \(n - 1 = a + b/\lambda^2 + c/\lambda^4\), is not able to cover this extended region without undue systematic deviations. Theoretically a dispersion formula should have, the form \(n-1 = \sum A_i (\sigma_i^2 - \sigma^2)^{-1}\), where \(\sigma_i\) are resonance frequencies of the gas. It was used by Koch and Traub with 2 terms (4 adjustable parameters). Although Traub's formula represents fairly well his observations from 5460 to 1854A, it is impossible to get a perfect fit for the entire set of observations with only two terms. When a 3-term formula is used it turns out, however, that one of the resonance frequencies will become very large, and that an equally good result is obtainable when \(\sigma^2\) is neglected in one of the terms. Besides, the values for \(\sigma_i\) need to be given to 2 or 3 significant figures only. The following formula was finally accepted as the simplest and the best representation of the observed values:

\[
\frac{n - 1}{10^8} = 5.08665 \lambda s - 2.949330 + \frac{25536}{146 - \sigma^2} + \frac{25536}{41 - \sigma^2},
\]

(1)

\(\sigma\) being the vacuum wave number expressed in \(\mu^{-1}\). The values calculated with this formula are shown in the last column of Table I.

The deviations of the 46 individual observations from the formula are plotted against wave number in Fig. 1. The diagram will serve to indicate the accuracy of the observations and of the formula fitted to them. The last two points, at \(\lambda 1850\), fall outside the region of immediate interest and are of lower accuracy than the rest, according to Traub. Some of Koch's values show relatively large deviations. It is interesting to note that if one would choose the wavelengths recently published by Burns, Adams, and Longwell\(^9\) for natural mercury instead of those from the M.I.T. compilation\(^10\) which were actually used in computing the product \(\lambda s\), the two largest deviations, namely for \(\lambda 2675\) and \(\lambda 2400\), would be reduced from \(+3.5\) to \(2.4\) and from \(-3.8\) to \(-2.7\), respectively. In general, however, the uncertainty of \(\lambda\) has no significant influence on the values of \(n - 1\) in Table I. As judged from the diagram it seems justified to assume that formula (1) gives the refractivity through the visible and ultraviolet down to at least 2000A with an accuracy of about \(\pm 1 \times 10^{-8}\) as regards relative values. The uncertainty in the absolute values, depending directly on Barrell and Sears' data, should not be much larger. A small constant error would in any case be of secondary importance as affecting only the magnitude of the wave-number unit. When converting wavelengths into vacuum by means of the relation \(\lambda_{vac} = n\lambda_{air}\), an error \(dn = \pm 1 \times 10^{-8}\) would cause the corresponding errors \(d\lambda = n d\lambda_{air}\) or \(d\sigma = -\sigma dn\), the magnitudes of which are illustrated by the following figures (\(K = cm^{-1}\)):

<table>
<thead>
<tr>
<th>(\lambda(A))</th>
<th>(d\lambda(A))</th>
<th>(\sigma(K))</th>
<th>(d\sigma(K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 000 ± 0.00010</td>
<td>10 000 ± 0.0001</td>
<td>10 000 ± 0.0001</td>
<td>10 000 ± 0.0001</td>
</tr>
<tr>
<td>5 000 ± 0.00005</td>
<td>20 000 ± 0.0002</td>
<td>20 000 ± 0.0002</td>
<td>20 000 ± 0.0002</td>
</tr>
<tr>
<td>2 000 ± 0.000002</td>
<td>50 000 ± 0.00005</td>
<td>50 000 ± 0.00005</td>
<td>50 000 ± 0.00005</td>
</tr>
</tbody>
</table>

These errors are clearly below present error limits of spectroscopic wavelength determinations. The possibility of hidden, systematic errors may, of course, not be overlooked. The assumption that \(n - 1\) is proportional to \(\lambda s\) presupposes that the density factor, \(p(1 + \beta p)(1 + 15\alpha)/760(1 + 76\beta)(1 + a\delta)\), is independent of wavelength, which may not be strictly true. However, even if \(\alpha\) and \(\beta\) would, unexpectedly, be subject to some dispersion, this would have a very small effect in the present case because Koch and Traub had chosen


\(^10\) M.I.T. Wavelength Tables (New York, 1939).
TABLE II. Recurring intervals in the spectrum of Hg 198 calculated by means of dispersion formula (2) from wavelength measurements by Meggers and Kessler and by Burns and Adams.

<table>
<thead>
<tr>
<th>Pair of lines $\lambda\lambda$</th>
<th>Interval, cm$^{-1}$</th>
<th>M and K B and A Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 046 -4 358</td>
<td>1 767.2183 7.2174 7.2179</td>
<td></td>
</tr>
<tr>
<td>2 967 -3 131.5</td>
<td>7.2173 7.2204 7.2189</td>
<td></td>
</tr>
<tr>
<td>2 752 -2 893</td>
<td>7.2190 7.2201 7.2195</td>
<td></td>
</tr>
<tr>
<td>4 358 -5 460</td>
<td>4 630.6765 0.6786 0.6776</td>
<td></td>
</tr>
<tr>
<td>3 131.8 -3 663.2</td>
<td>0.6785 0.6754 0.6770</td>
<td></td>
</tr>
<tr>
<td>3 131.5 -3 662.8</td>
<td>0.6779 0.6748 0.6764</td>
<td></td>
</tr>
<tr>
<td>3 125 -3 654</td>
<td>0.6777 0.6789 0.6783</td>
<td></td>
</tr>
<tr>
<td>2 893 -3 341</td>
<td>0.6791 0.6767 0.6779</td>
<td></td>
</tr>
<tr>
<td>2 655 -3 027</td>
<td>0.6811 0.6740 0.6775</td>
<td></td>
</tr>
<tr>
<td>3 663.2 -5 790</td>
<td>10 025.7678 5.7678 5.7678</td>
<td></td>
</tr>
<tr>
<td>3 654 -5 769</td>
<td>5.7677 5.7685 5.7681</td>
<td></td>
</tr>
<tr>
<td>3 027 -4 347</td>
<td>5.7687 5.7692 5.7689</td>
<td></td>
</tr>
</tbody>
</table>

From Koch's$^{11}$ measurements on CO$_2$, the conversion factor is found to be constant to the required accuracy over the whole wavelength range and equal to 1.000162. The formula for standard air then finally becomes

\[
(n-1)10^8 = 6432.8 + \frac{25540}{146-\sigma^2} + \frac{41-\sigma^2}{41-\sigma^2}.
\]

THE COMBINATION PRINCIPLE

Meggers and Kessler$^{12}$ applied the combination principle to their measurements in the Hg 198 spectrum, using two different dispersion formulas, and found deviations that could be explained as arising only from errors in these formulas. The application of this test on the present formula (2), using the same lines as were used by Meggers and Kessler, is shown in Table II. The recent observations by Burns and Adams$^{13}$ are also included. The intervals come out constant to complete satisfaction, especially from the mean of the two measurements, in which case the close agreement must indeed be partly fortuitous. In this connection it should be remembered that while a correct dispersion formula must of course stand the test of the combination principle, one may not conclude from this test alone that a formula is correct. This is due to the obvious fact that wave-number errors of the form $\Delta \sigma = a \sigma + b$, corresponding to errors of refractive index of the form $\Delta n = a + b/\sigma = a + b \Lambda$, cannot be revealed in this way.

![Fig. 2. Various dispersion formulas minus formula (2) versus $\sigma^2$.](image-url)

Note that vertical scale is 10 times smaller than in Fig. 1.

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This, incidentally, invalidates Barrell’s14 arguments regarding the accuracy of his proposed formula. It is of interest to note that the original formulas of Koch and Traub as well as that of Kösters and Lampe all satisfy the combination principle when applied to the lines of Table II.

**CONCLUSIONS**

A comparison of various dispersion formulas is displayed in Fig. 2, where the deviation from formula (2) of the present paper is plotted against $\sigma^2$. After having been reduced, when necessary, to the appropriate conditions (15°C, 0.03 percent CO₂) the formulas shown in Fig. 2 are:

Meggers and Peters

\[(n-1)10^8=27.264.3+122.95\sigma^2+3.560\sigma^4\], (a)

Kösters and Lampe

\[(n-1)10^8=27.274.7+150.19\sigma^2+1.835\sigma^4\], (b)

Pérand

\[(n-1)10^8=27.286.0+140.14\sigma^2+2.998\sigma^4\], (c)

Barrell and Sears

\[(n-1)10^8=27.258.5+154.37\sigma^2+1.293\sigma^4\], (d)

Barrell (mean of b, c, d)

\[(n-1)10^8=27.272.9+148.23\sigma^2+2.041\sigma^4\] (e)

\[\sigma = \text{vacuum wave number in } \mu^{-1}\].

For convenient comparison the first 3 terms in the series development of formula (2) are \[27.259.9+153.58\sigma^2+1.318\sigma^4\]. This simplified form is identical with (2) within \(1 \times 10^{-8}\) for wavelengths longer than 5000A.

The graph demonstrates the impossibility of a trustworthy extrapolation toward shorter wavelengths of formulas based on observations in the visible only. At the same time it shows that long waves can be reached arbitrarily by a short and comparatively safe extrapolation. This would be even more evident if instead of $\Delta n$ one would plot the spectroscopically more relevant $\Delta\sigma$, in which case all curves would run quickly together with increasing wavelength. Of existing refractivity observations in the infrared there is none that can be judged as sufficiently accurate to furnish any improvement on the extrapolation from formula (2).

The curve referring to Meggers and Peters’ formula is of special interest in view of the enormous amount of spectroscopic measurements that have been reduced with that formula. The deviation ranges from $\Delta n = -106 \times 10^{-8}$ around 3700A to $+155 \times 10^{-8}$ at 2000A. The corresponding wave-number error ranges from $\Delta\sigma = +0.031$K to $-0.078$K. It cannot be expressed in a simple form. In order to preserve the usefulness of Kayser’s *Tabelle der Schwingungszahlen*, the corrections have been computed and collected in Table III in a convenient form, corresponding to the accuracy of Kayser’s table.

Table for the vacuum correction, $\Delta\lambda = \lambda_{air}(n-1)$, have been computed in order to facilitate the use of formula (2). The larger one, “Vacuum corrections for wavelengths from 2000 to 13 500A,” gives $\Delta\lambda$ to 5 decimals for every angstrom from 2000 to 10 000A, and to 4 decimals for every 10 angstrom from 10 000 to 13 500A. In the great majority of spectroscopic work, however, a 3-decimal accuracy is ample. For that purpose a more convenient table has been prepared, “Vacuum corrections to three decimal places for $\lambda=2000-13 900$A.” It is constructed so as to avoid all interpolation. Mimeographed copies of these tables are available.

Finally, a word may be said about the reduction to standard conditions of wavelength measurements made in uncontrolled air. The question has been thoroughly
discussed by Meggers and Peters,\textsuperscript{2} and recently by Babcock,\textsuperscript{18} using the elaborate density factor of Barrell and Sears.\textsuperscript{5} In work aiming a highest precision, the deviations from standard conditions of temperature and pressure are never extreme. Consequently in all practical cases the accuracy will be amply satisfied by the following simple relation:

$$\lambda_2^0 - \lambda_2 = \lambda_2^0 (n_2^0 - n_1^0) \left( \frac{p}{760} \frac{1 + 0.00367 \times 15}{1 + 0.00367 \times t} - 1 \right),$$  

where $\lambda_2^0$ is the unknown wavelength at standard conditions, $\lambda_2$ the same as actually measured, $n_2^0$ and $n_1^0$ the refractive index at standard conditions for unknown and reference wavelength, respectively, $p$ and $t$ actual pressure and temperature. This may also be written

$$\lambda_2^0 - \lambda_2 = (\Delta \lambda_2 - \Delta \lambda_1 \cdot \lambda_2 / \lambda_1) \left( \frac{0.0013882 p}{1 + 0.00367 t} - 1 \right),$$  

where $\lambda_1$ is the reference wavelength, and $\Delta \lambda_2$ and $\Delta \lambda_1$ are the vacuum corrections for $\lambda_2$ and $\lambda_1$ listed in the tables mentioned above. The direct calculation by means of this formula will very probably be found more convenient than using any kind of special tables. The value for the correction $\lambda_2^0 - \lambda_2$ will be slightly different when using Meggers and Peters' dispersion formula, and the difference will not always be negligible.

In high precision work an additional correction must be applied because of the water vapor in uncontrolled air. Following Barrell and Sears (reference 5, page 52) we may express the difference in refractive index between moist air, containing $f$ mm Hg of water vapor, and dry air at the same temperature and total pressure as follows:

$$\Delta n = \frac{(n)_{\text{moist air}} - (n)_{\text{dry air}}}{\lambda_1} = \frac{(a - b \sigma^2)}{(1 + a t)}.$$  

Inserting this value for $\Delta n$ in the general expression for the correction to a wavelength $\lambda_2$ measured at nonstandard conditions, we obtain the correction owing to water vapor:

$$\Delta \lambda = \lambda \left( \sigma \phi - \sigma_2 \phi \right) / (1 + a t),$$  

where $\sigma_2$ and $\sigma_1$ are the wave numbers of the unknown line and the reference line, respectively. Using the value for $\phi$ given by Barrell and Sears, $\phi = +0.068 \times 10^{-4}$, and approximating $1 + at$ to an average value, $1 + 20a = 1.07$, we have finally

$$\Delta \lambda \times 10^5 = +0.63 \times 1 + \lambda_2 / \lambda_1 (\sigma_2 - \sigma_1) f,$$

where $\lambda_1$ is expressed in angstrom and $a$ in $\mu^{-1}$. By way of illustration, assume that $\lambda_2 = 4046 \mu$ and $\lambda_1 = 2.47 \mu$ has been measured against $\lambda_1 = 6438 \mu$ in air containing $10$ mm water vapor, a usual value for laboratory conditions. Then the correction would be $\Delta \lambda \times 10^5 = +0.63 \times 1.63 \times 0.92 \times 10 = +9.4$, or $\Delta \lambda = +0.00009 \mu$.

Barrell and Sears' observations on moist air were confined to the range 6438-4358 $\mu$, and it would be hazardous to assume their differential dispersion factor, $a - b \sigma^2$, to hold for wavelengths far outside of these limits, especially to the short-wave side. A formula recently published by Newbound,\textsuperscript{16} who observed also in the ultraviolet, is in serious disagreement with that of Barrell and Sears. The difference seems difficult to explain, and it must be concluded that present knowledge of the dispersion of water vapor is insufficient for properly correcting ultraviolet wavelengths measured in moist air.

The dispersion formula discussed in the present paper was derived in the spring of 1951, and the tables were calculated in the summer of that year. A short abstract was published in the proceedings\textsuperscript{17} of a physics conference in Lund, June, 1951. At the meeting in Rome, September, 1952, the Joint Commission for Spectroscopy decided to recommend the formula for converting wavelengths in standard air to wavelengths in vacuum.

I am greatly obliged to Dr. Meggers, Dr. Barrell, Dr. Engelhard, and Mrs. Sitterly, who have read the manuscript of the present article and suggested several improvements that have been incorporated in the final issue.

\textsuperscript{17} Arkiv Fysik 5, 127 (1952).