A Calibration Method for Infra-Red Prism Spectrometers[1]

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A method of high accuracy applicable to various prisms in infra-red spectrometry has been used to calibrate NaCl and KBr prisms. The method requires only a small number of experimental bands, is practically independent of resolving power, provides an extensive wave-length range, and permits a tabulated calibration without the necessity of drawing calibration curves. The procedure is described in detail with an example.

INTRODUCTION

THE principal method used in recent years for calibrating infra-red rocksalt spectrometers between 5 and 15 microns has been that of Oetjen, Kao, and Randall.[3] Their method employs some 150 points from the spectra of NH_3, CO_2, and H_2O vapor measured on both a prism and a grating spectrometer, with the resolving power of the latter adjusted to that of the prism instrument. Under these conditions, wave-lengths of the bands calculated from the grating characteristics are transferable directly to the prism instrument being calibrated.

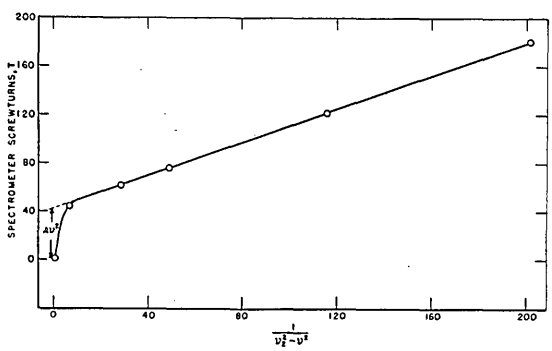

FIG. 1. Relationship between spectrometer screw-turns, T, and $1/(\nu_2^2-\nu^2)$ for research-type NaCl spectrometer from 0.6 to 15.0 microns; C_2H_2, C_2H_4, C_6H_6, and NaD calibration points.

The original calibration of a research spectrometer at the Chemistry Department of Carnegie Institute of Technology was based on 20 points calculated by Cross[4] from the dimensions of his instrument and refractive index values for rocksalt. Precise interpolation between Cross' points was not possible because of doubt as to the proper curvature of the line. Accordingly, it was decided to search for an empirical equation which could be used to carry out this interpolation. The equation found proved to be of sufficient accuracy to describe the whole curve, from the visible region to 15 microns, without relying on refractive index data which might be in error because of impurities in the rocksalt sample used to obtain the data.

EQUATION

The empirical equation is based on the curve (Fig. 1) obtained from six spectral bands by plotting for each band the spectrometer screw-turn value, T, *vs.* $1/(\nu_2^2-\nu^2)$, where ν is the corresponding frequency and ν_2 is a Restrahlen or neighboring frequency of the prism material. The curve is a straight line from about 3.5 to 15 microns. Curvature in the short wave-length region is attributed to absorption of NaCl in the ultraviolet region, for which a correction term has to be applied. The obvious form of the correction would correspond to the above frequency term, namely, $1/(\nu_1^2-\nu^2)$, in which ν_1 would be the frequency of the absorption band

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[2] Initial work on this subject submitted in partial fulfillment of the requirements for the degree of Doctor of Science at Carnegie Institute of Technology.

[3] R. A. Oetjen, Chao-Lau Kao, and H. M. Randall, Rev. Sci. Inst. **13**, 515 (1942).

[4] P. C. Cross, Rev. Sci. Inst. **4**, 197 (1933).

TABLE I. Spectral data for NaCl calibration. ($\nu_2 = 125$ cm^{-1}).

	Compound	Wave-length in microns[a]	Frequency in cm^{-1} [a]	Screw-turn T[b]	$\frac{1}{\nu_2^2-\nu^2}$	$\frac{B}{\nu_2^2-\nu^2}$	$A\nu^2$	T_0
I	Na	0.5890	16,969	2,166.6	$-0.37431\cdot10^{-8}$	−2.222	390.744	−1778.08
II	H_2O	2.673	3,741	1,740.6	$-7.15335\cdot10^{-8}$	−45.774	18.991	−1777.38
III	CO_2	4.225	2,367	1,670.0	$-17.8984\cdot10^{-8}$	−114.532	7.603	−1776.93
IV	H_2O	5.463	1,830	1,590.2	$-30.0005\cdot10^{-8}$	−191.973	4.544	−1777.63
V	H_2O	6.107	1,637	1,541.1	$-37.5355\cdot10^{-8}$	−240.190	3.636	−1777.65
VI	H_2O	6.784	1,474	1,483.9	$-46.3596\cdot10^{-8}$	−296.656	2.948	−1777.61
VII	NH_3	8.490	1,177.9	1,313.1	$-72.8957\cdot10^{-8}$	−466.460	1.883	−1777.68
VIII	NH_3	9.057	1,104.1	1,247.5	$-83.0971\cdot10^{-8}$	−531.739	1.654	−1777.58
IX	NH_3	9.876	1,012.6	1,145.9	$-99.0360\cdot10^{-8}$	−633.733	1.391	−1778.25
X	NH_3	10.540	948.8	1,056	$-113.0459\cdot10^{-8}$	−723.382	1.222	−1778.56
XI	NH_3	11.206	892.4	959.5	$-128.081\cdot10^{-8}$	−819.594	1.081	−1778.01
XII	NH_3	12.075	828.2	823.6	$-149.189\cdot10^{-8}$	−954.663	0.931	−1777.34
XIII[c]	CO_2	13.875	720.7	507.5	$-198.498\cdot10^{-8}$	−1270.191	0.705	−1776.99
XIV	CO_2	14.97	668.0	293.1	$-232.235\cdot10^{-8}$	−1486.074	0.606	−1778.57

[a] Values for points IV and XIII inclusive obtained from R. A. Oetjen, C. L. Kao, and H. M. Randall, Rev. Sci. Inst. 13, 515 (1942).
[b] All screw-turn values corrected for small, uncompensated temperature shifts, etc., using 4.225μ CO_2 band as base point.
[c] The 13.417μ NH_3 band was included formerly, but because of unreproduceability due to broadness it has been omitted.

in the ultraviolet. Since these data could not be found in the literature and since it is desirable not to introduce another parameter into the equation, the first two terms of the expansion are used: $1/(\nu_1^2-\nu^2) = \text{constant} + A\nu^2 + \cdots$. The final form of the equation is

$$T + T_0 = A\nu^2 + B/(\nu_2^2 - \nu^2),$$

where B is the slope of the straight-line portion of T *vs.* $1/(\nu_2^2-\nu^2)$, $A\nu^2$ is the correction term for ultraviolet absorption, and T_0 is a nearly constant term which varies slightly with wave-length. There is notable similarity between this equation and the refractive index equation:

$$n^2 = 1 + (e^2/\pi m)\sum_i N_i/(\nu_i^2 - \nu^2).$$

Calibration involves first the simple evaluation of constants A and B as illustrated below. Then the nearly constant T_0 terms are calculated for each experimentally determined absorption band and the values plotted against corresponding wave-lengths. Lastly, the spectrometer screw-turn value T can be calculated for any chosen frequency and a complete calibration obtained.

The slight variation of T_0 values is attributed to deviation of the apparently straight-line portion of T *vs.* $1/(\nu_2^2-\nu^2)$ from perfect linearity. The original T_0 curve, using five absorption bands and the NaD line, is curve *a* of Fig. 2. In order to minimize errors, the total spread of T_0 values is decreased by using a better method for calculating the constant B and by changing ν_2 from one Restrahlen frequency, 192.5 cm^{-1}, to the principal Restrahlen frequency at 184 cm^{-1}. The resulting curve *b* gives a total spread of T_0 values equivalent to only 0.006 micron at 10 microns. The S-shape of the curve was somewhat dubious but has been verified on another research instrument using the same experimental points, and also on a Perkin-Elmer spectrometer at the Bureau of Mines using 13 selected bands from the spectra of NH_3, CO_2, and H_2O vapor by Oetjen, *et al.*, and the NaD line. The T_0 curve obtained for the latter conditions is shown in Fig. 3. The calibration range in this case has been extended to the 14.97μ CO_2 band with the production of another minimum in the curve. For the Perkin-Elmer instrument 125 cm^{-1} is

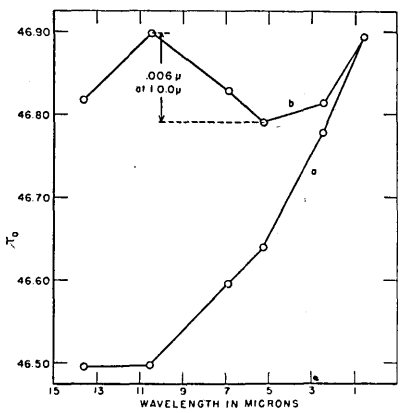

FIG. 2. T_0 curves for research-type NaCl spectrometer; C_2H_2, C_2H_4, C_6H_6, and NaD calibration points. Curve *a*: $\nu_2 = 192.5$ cm^{-1}, B calculated from 10.5 and 13.7μ bands. Curve *b*: $\nu_2 = 184$ cm^{-1}, B calculated from 2.5 and 13.7μ bands.

TABLE II. Spectral bands for KBr calibration.

	Compound	Wave-length in microns	Frequency in cm^{-1}	Screw-turn[a] T
I	CO_2	14.970	668.0	1334.0
II	CO_2	16.181	618.0	1243.7
III	CH_3OH	18.215	549.0	1083.7
IV	H_2O	19.003	526.23	1016.0
V	H_2O	19.902	502.45	935.5
VI	H_2O	21.155	472.68	814.0
VII	H_2O	21.831	458.05	744.5
VIII	H_2O	23.854	419.20	518.5
IX	H_2O	25.137	397.81	363.0
X	H_2O	25.962	385.17	256.0
XI	H_2O	26.628	375.54	170.0
XII	H_2O	27.020	370.09	115.5

[a] 14.970μ CO_2 band used as base point for correction due to temperature shift, etc.

found to be the value of ν_2 most satisfactory for keeping the spread of T_0 values small. The ordinate in Fig. 3 is in terms of small divisions on the wave-length drum; the equivalent in microns is given at various wave-lengths to illustrate the magnitude of the variation.

CALIBRATION PROCEDURE FOR NaCl PRISM

The method of calibrating a Perkin-Elmer spectrometer with NaCl prism follows in detail. Complete sample data using the 14 points referred to above are given in Table I and in the necessary steps of the procedure.

1. *Rough A value:* Plot screw-turns, T, *vs.* $1/(\nu_2^2-\nu^2)$. Extrapolate linear part of curve and measure distance on T axis from the extrapolated portion to the NaD-line value as indicated in Fig. 1 for a research-type instrument. This quantity is the correction term for the NaD-line value, $A\nu_{Na}^2$, from which A is calculated: e.g., $T_{Na}-T_{intercept}=2166.6-1779=387.6=A\nu_{Na}^2$; $\therefore A=387.6\div 287{,}946{,}961=1.345\cdot 10^{-6}$. Calculate $A\nu^2$ for the first three wave-lengths.

2. *Final B value:* Solve simultaneous equations of $T+T_0=A\nu^2+B/(\nu_2^2-\nu^2)$ for B, using data from points III and XIII of the table (T_0 considered constant):

e.g., III: $1670.0+T_0=7.536-B\cdot\ 17.898\cdot 10^{-8}$

XIII: $\cdot 507.5+T_0=0.699-B\cdot 198.498\cdot 10^{-8}$

$B=6.3990\cdot 10^{+8}$.

Calculate $B/(\nu_2^2-\nu^2)$ for all points.

3. *Final A value:* Calculate T_0 from the equation for the first three points and plot T_0 *vs.* wave-length. Adjust A arbitrarily until a smooth curve is obtained. The value of A chosen for the present calibration is $1.357\cdot 10^{-6}$; if the difference between rough and final A values is appreciably greater than found here, it is desirable to recalculate B. Calculate $A\nu^2$ for all points.

4. *T_0 curve:* Calculate T_0 for all points and plot T_0 *vs.* wave-length (Fig. 3).

5. *Tabulated calibration:* Calculate T, screw-turns, for as many wave-lengths as the accuracy requires; get the necessary T_0 values from the T_0 *vs.* wave-length curve. Tabulate the data or draw a calibration curve if desired.

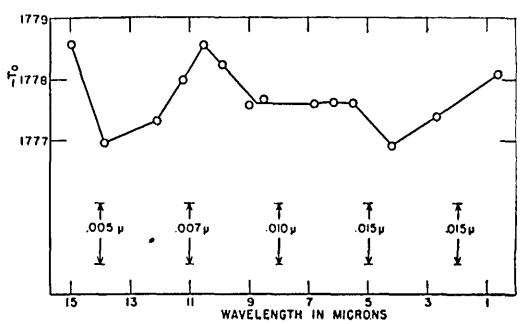

FIG. 3. T_0 curve for NaCl prism, Perkin-Elmer spectrometer; NH_3, H_2O, CO_2, and NaD calibration points. Wave-length equivalents of T_0 variations are indicated.

CALIBRATION OF KBr PRISM

The calibration of a KBr prism is simpler because there is no short wave-length curvature (Fig. 4) and, therefore, no necessity for the $A\nu^2$ correction term. The principal Restrahlen frequency of KBr, 115.2 cm^{-1}, is used for the term, ν_2. Experimental points from the spectra of CO_2, H_2O, and CH_3OH vapor are listed in Table II. Wave-lengths for the H_2O vapor points are obtained from the grating spectrum of Randall, *et al.*[5] The high resolution of this spectrum does not detract appreciably from the accuracy of the calibration since the bands selected are sufficiently symmetrical to obviate the use of

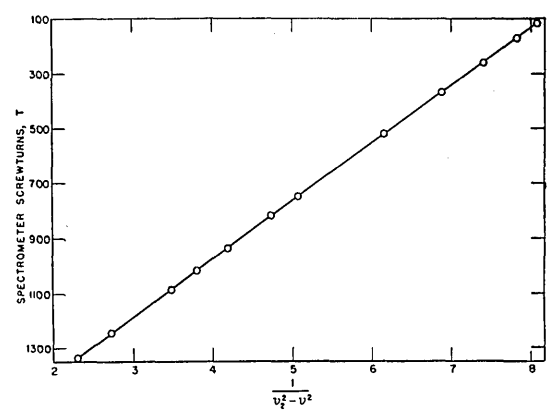

FIG. 4. Relationship between spectrometer screw-turns, T, and $1/(\nu_2^2-\nu^2)$ for KBr prism. Perkin-Elmer spectrometer, from 15 to 27 microns; CO_2, CH_3OH, and H_2O vapor calibration points.

[5] Randall, Dennison, Ginsburg, and Weber, Phys. Rev. 52, 160 (1937).

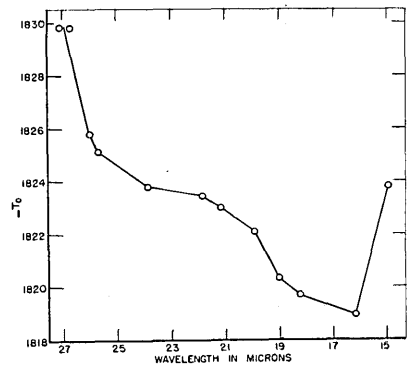

FIG. 5. T_0 curve for KBr prism, Perkin-Elmer spectrometer; CO_2, CH_3OH, and H_2O vapor calibration points.

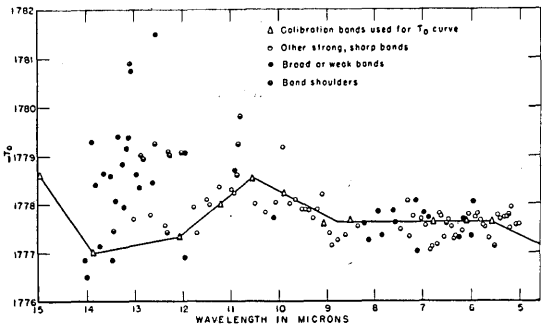

FIG. 6. Comparison of calibration methods: T_0 points, calculated from our spectra for all the NH_3 and H_2O bands used by Oetjen, *et al.*, are plotted together with portion of T_0 curve for the present calibration. Bands are arbitrarily classified according to strength or sharpness.

weighted averages for groups of resolved bands. Data from a spectrum of lower resolution, such as the KBr spectrum of H_2O by Weber and Randall,[6] would be preferable, but the accuracy of their work is insufficient. However, the tracing of the spectrum given in their article is very helpful in identifying the bands obtained on the Perkin-Elmer instrument. The T_0 curve (Fig. 5) follows somewhat the same pattern as the corresponding curve for NaCl.

Bands for H_2O vapor and the one band for CH_3OH vapor are obtained by simply placing a dish of the liquid in the small Perkin-Elmer housing with salt windows removed. Intensities of atmospheric H_2O vapor bands thus increase only slightly, but advantageously.

DISCUSSION

The chief advantages of the method are: (1) the extensive wave-length range, (2) the small number of bands required, (3) practical independence of resolving power since the bands chosen should be sufficiently sharp and symmetrical on most instruments, (4) accurate interpolation between experimental points because any number of points may be calculated, (5) applicability to various prisms, (6) tabulation of data without the necessity of drawing the usual complex calibration curve, and (7) exposure of doubtful points obtained from broad, weak, or unsymmetrical bands. The significance of the last item for a NaCl prism is shown in Fig. 6. The method of Oetjen, *et al.*, is compared with the present calibration by calculating from our spectra T_0 values for all NH_3 and H_2O points used by them. With one notable exception, all values for the bands which are arbitrarily classified as strong or sharp fall closely in line with those of the very sharp bands which determine the T_0 calibration curve. But, bands which are broad or which appear only as shoulders, because of our slightly lower resolving power, produce scattered T_0 values; this is particularly true for the longer wave-length NH_3 bands. Further, the 15μ CO_2 fine structure bands which are included in their calibration method, are detectable on the present instruments but are not reliable. A calibration curve drawn through such scattered points is questionable and not conducive to good accuracy.

Modifications of the method outlined are obviously possible. The T *vs.* $1/(\nu_2^2-\nu^2)$ curve in Fig. 1 is sufficiently linear between about 3.5 and 15 microns to permit an accurate calibration between these limits without dangerous interpolation and without evaluation of constants. Thus $1/(\nu_2^2-\nu^2)$ may be calculated for a whole range of frequencies, the values applied to the straight line, and the screw-turn values read off directly.

We wish to express our thanks to Ruth Borgman and Lois Pierce who carried out most of the measurements and calculations.

[6] L. Weber and H. M. Randall, Phys. Rev. **40**, 835 (1932).