Precision Infrared Spectroscopy*

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SINCE the end of World War II tremendous advances have been made in the study of infrared spectra at wavelengths longer than 1.2μ. The availability of microwave sources as the result of the development of radar has produced a fantastic increase in our knowledge of the details of molecular spectra. These microwave spectra, in which frequency is measured, allow previously undreamed of precision to be obtained in determination of certain molecular constants. The microwave techniques up to the present time have been used at wavelengths in excess of 0.57 mm. In the hands of Professor C. H. Townes, Professor Walter Gordy, and their collaborators, the subject of microwave spectroscopy has been developed to the state where, indeed, extremely high precision can be obtained.

This paper, however, is concerned primarily with advances in near-infrared spectroscopy in the region of 1 to 5μ where wavelength is the experimentally measured quantity. Here again progress was dependent on certain technological advances. The development of the photoconducting detectors, particularly PbS and PbSe and more recently the photovoltaic detector InSb, has provided the experimentalist with detecting devices whose sensitivity is of a different order of magnitude when compared to the sensitivity of previously available detectors.

Almost simultaneously with the development of the new infrared detectors, tremendous advances have been made in the art of ruling large diffraction gratings of high perfection.

The first of the large so-called modern gratings was produced by Babcock and Babcock[1] at Mt. Wilson. Almost simultaneously, David Richardson at the Bausch and Lomb Optical Company was able to rule gratings of comparable size and perfection. In addition Richardson and the Bausch & Lomb Company were able to develop a replication technique which preserves the quality and precision of the original rulings. The perfection and success of the replication technique has resulted in the ready availability of high-quality diffraction gratings. More recently Harrison and Stroke[2] have ruled diffraction gratings of even higher degree of perfection by making use of interferometric control of the ruling engine. Harrison and Stroke have produced rulings in excess of 10 in. in width.

About a decade ago, Dr. Wiggins and the author found that modern gratings were sufficiently good so that resolution in the infrared could be increased by double passing the diffraction grating. More recently in this laboratory it has been demonstrated[3] that by double passing a 10-in. Harrison grating, higher resolution can be obtained than is theoretically possible for single pass at wavelengths as short as λ4358 Å. Throughout the 2 to 5μ region we have been able to obtain lines whose half-intensity width is 0.025 cm^{-1} or slightly less, making use of an 8-in. Harrison echelle grating. This line half-intensity width is approximately equal to the half-intensity room-temperature Doppler width of Hg lines at λ4000 Å.

The ability of the best modern instruments to produce lines of 1/40 cm^{-1} half-intensity width introduces a problem with regard to the measurement of line centers. It was found that rotation of a diffraction grating with the requisite smoothness was probably nearly mechanically impossible. In this laboratory we have devised the so-called "wedge scanner" to traverse a small region of the spectrum with both linearity and the requisite smoothness so as to obtain all the information optically available.[4–6] The schematic diagram of the wedge scanner can be seen in Fig. 1.

The infrared spectra which are most easily observable and of the most general interest are absorption spectra. The wavelength standards formerly avail-

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[1] Harold D. Babcock and Horace W. Babcock, J. Opt. Soc. Am. **41**, 776 (1951).

[2] George R. Harrison and George W. Stroke, J. Opt. Soc. Am. **50**, 1153 (1960).

[3] D. H. Rank, D. P. Eastman, G. D. Saksena, T. K. McCubbin, and T. A. Wiggins, J. Opt. Soc. Am. **50**, 1045 (1960).

[4] D. H. Rank, E. R. Shull, J. M. Bennett, and T. A. Wiggins, J. Opt. Soc. Am. **43**, 952 (1953).

[5] J. N. Shearer and T. A. Wiggins, J. Opt. Soc. Am. **45**, 133 (1955).

[6] D. H. Rank, D. P. Eastman, B. S. Rao, and T. A. Wiggins, J. Opt. Soc. Am. **51**, 929 (1961).

able consist of emission lines located in the region from λ4000 Å to 10,000 Å. Recently Humphreys and Paul[7] have made interferometric measurements on a considerable number of atomic lines in the 1 to 3μ region. In a few cases the very precise wavelengths of Humphreys and Paul have been verified by Peck[8] and his collaborators using a totally different interferometric technique.

Emission standards have many shortcomings when used to measure absorption spectra. The atomic standards are very far apart necessitating special interpolation techniques if high precision with grating spectrographs is desired. An elegant interpolation method employing channel fringes produced with the aid of a Fabry-Perot interferometer has been invented by Douglas and Sharma.[9] This interpolation method is capable of giving precision of the order of a few hundredths of a wave number. We have occasionally used a modification of the Douglas and Sharma method combined with the "wedge scanner" and obtained measurements to a few thousandths of a wave number precision.

It is well known that when using diffraction gratings, wavelength errors (displacements) can, and usually do, occur when the standards are generated by a different source from that used to produce the spectra which are to be measured. The reasons for the occurrence of these "displacement errors" are several and will not be explored in this paper. In any event it is convenient and desirable to use a single light source to produce both standards and the spectrum to be measured.

Some years ago in collaboration with my students we embarked upon a program to develop methods, and make wavelength measurements on infrared absorption-band lines with the aid of the Fabry-Perot interferometer. The techniques involved in the use of the Fabry-Perot interferometer for this purpose are moderately complicated. The experimental problems which were necessary to solve were quite different from those encountered in the use of the Fabry-Perot interferometer in the photographic region of the spectrum. We were able to measure a relatively large number of lines in the 002–000 band of HCN located at 1.5μ.[10] Similar measurements were made on the 2–0 band of CO at 2.4μ.[11] We believe the absolute accuracy of the wavelengths measured is about one part in five million and the relative accuracy of the lines within a single band considerably higher.

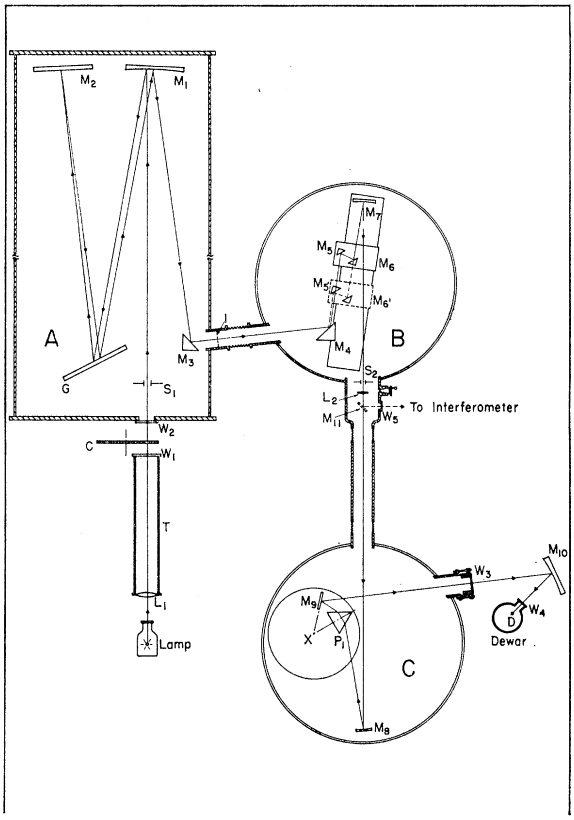

FIG. 1. Schematic diagram of the Echelle spectrograph. The schematic diagram for the primary monochromator is portrayed in Sec. A of the figure. M_1 is a spherical mirror of 5-m focal length. M_2 is the plane mirror used to double pass the grating. The spectrum comes to a focus at the position indicated by I. Section B is the schematic diagram of the "wedge scanner." M_7 is a spherical mirror used at its center of curvature. The purpose of the spherical mirror M_7 is to transfer the spectrum imaged at I to the exit slit S_2. The scanning of the spectrum is accomplished by translating the pair of mirrors M_5 and M_6 in the manner indicated in the figure. L_2 is a fluorite field lens and M_{11} an auxiliary mirror which can be inserted into the beam at will for use with an interferometer. Section C shows the secondary monochromator or (order sorter). The LiF prism P_1 is in a Wadsworth mounting which requires only a pure rotation of the prism mirror assembly to present the various wavelengths to the detector D. M_{10} is an off-axis parabola. The windows and lenses indicated are constructed of fluorite.

Thus, we have produced absorption wavelength standards closely spaced and of high precision. Unfortunately, however, with ordinary diffraction gratings of 300 to 400 grooves per mm these standards are of very little use since they are located in only two small regions in the near infrared spectrum. Measure-

[7] C. J. Humphreys et al., Trans. Intern. Astron. Union, **10**, 211 (1960), Trans. Intern. Astron. Union, **11** (to be published).
[8] Edson R. Peck, J. Opt. Soc. Am. **50**, 512 A (1960). No wavelengths are given. The wavelengths will however be published in Trans. Intern. Astron. Union, **11** (to be published).
[9] A. E. Douglas and D. Sharma, J. Chem. Phys. **21**, 448 (1953).
[10] D. H. Rank, A. H. Guenther, J. N. Shearer, and T. A. Wiggins, J. Opt. Soc. Am. **47**, 144 (1957).
[11] D. H. Rank, A. H. Guenther, G. D. Saksena, J. N. Shearer, and T. A. Wiggins, J. Opt. Soc. Am. **47**, 686 (1957).

ment by interferometric methods of a sufficient number of band lines to have the same type of precision and close coverage of the 1 to 5μ region would be both a boring chore and involve a tremendous amount of labor.

We have circumvented this problem by the construction of the "echelle type" spectrograph shown in Fig. 1. The echelle grating is a Bausch & Lomb replica of a Harrison grating of very high perfection. The grating is 8 in. wide and has 73.25 grooves per mm. The grating is double passed and operates at over 60° angle of incidence which of course gives very high resolution. The overlapping orders are sorted at will by means of the LiF hind prism which is in a Wadsworth mounting. All but a small portion of the optical path source to detector is *in vacuo*.

Using the method of overlapping orders we have measured a very large number of band lines of HCN, N_2O and CO against the 002–000 band lines of HCN, and the 2–0 band lines of CO. The results of these measurements have been published in a recent paper.[6] We believe these measurements are good to about 0.001 cm.$^{-1}$ In Fig. 2 is displayed the coverage of the blaze of the echelle by the accurately measured band lines. In the 1 to 5μ region it is possible to measure any unknown wavelength against a known wavelength by interpolating using the "wedge scanner."

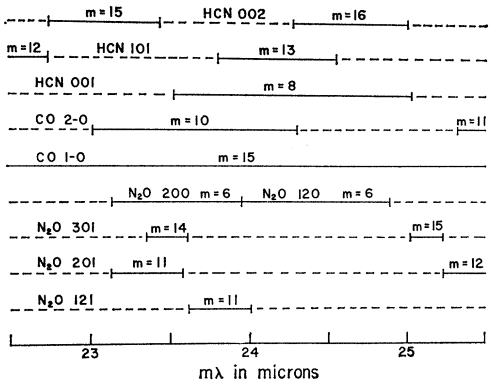

FIG. 2. Nomogram showing the distribution of accurately measured absorption wavelengths on the blaze of the echelle spectrograph. The bands, absorbing molecules, and order of diffraction m are indicated in the figure.

On the blaze of the echelle there are about 1200 absorption lines which can be used as wavelength standards.

In Tables I and V of reference 6 we have shown the satisfactory condition of the wavelength scale by showing the application of the combination principle to the groundstates of HCN and N_2O making use of the bands which we have measured accurately. These bands are scattered about in the 1 to 5μ region. We have also made use of the combination principle to derive information concerning vibration-rotation bands beyond 10μ.[12] The near-infrared bands permit multiple determination of these bands and the constancy obtained is a further indication of the correctness of the wavelength scale.

Band lines of linear or diatomic molecules have a further advantage as relative wavelength standards. The frequencies of the band lines fit simple accurate formulas which permit a smoothing of the measurements not possible with atomic spectra.

We now come to the question, of what use to physics or other branches of science are these more or less sophisticated and complicated techniques just described? One can only answer this question by giving some results which have already been obtained by the employment of these techniques and developments.

1. The high resolution obtained has enabled us to show that l-type doubling constants of linear triatomic molecules do not depend completely on ν_2 but on ν_1 and ν_3, etc., as well.[13] This is probably a rather trivial observation but it was not in agreement with extant theory, and pertinent theory has not as yet been completely developed.

2. Three independent determinations of the velocity of light have been made using the band spectrum method. The molecules used for the c determination were HCN, CO, and DCl^{35}, respectively. The values obtained for the velocity of light were 299 793.2 $\pm$ 1.8 km/sec, 299 793.7 $\pm$ 0.7 km/sec and 299 793.1 $\pm$ 0.65 km/sec. The precision obtained is comparable to that obtained by other modern methods so far used for the determination of c and the result is in accord with the results obtained by other methods.

3. Jaffe[14] and his co-workers making use of some of these techniques (wedge scanner and double-passing) were able to demonstrate the J dependence of the pressure shifting of molecular band lines. This observation was in complete contradiction to the then current theories. Only several years after Jaffe's discovery has theory been able to partially explain the general features of this phenomenon. In Fig. 3 some of the results are shown which we have obtained with HCl gas perturbed by rare gases. The theory predicted that all lines of a rotation-vibration band should be shifted the same amount. It may be that

[12] D. H. Rank, G. Skorinko, D. P. Eastman, and T. A. Wiggins, J. Opt. Soc. Am. **50**, 421 (1960).
[13] J. N. Shearer, T. A. Wiggins, A. H. Guenther, and D. H. Rank, J. Chem. Phys. **25**, 724 (1956).
[14] S. Kimel, M. A. Hirshfeld, and J. H. Jaffe, J. Chem. Phys. **31**, 81 (1959).

when this phenomenon is better understood we shall gain considerable insight into the behavior of intermolecular forces in gases.

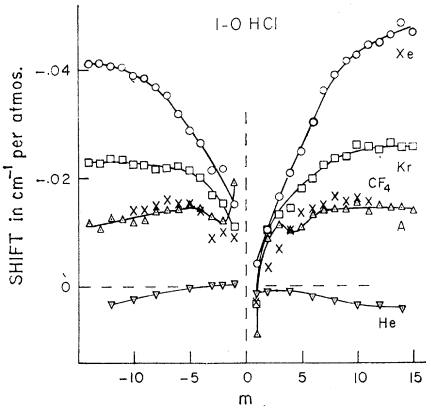

FIG. 3. Graphical display of the frequency shifts vs m ($m = -J$ for P branch and $J + 1$ for the R branch) for the 1-0 band HCl perturbed by various foreign gases.

4. In a recent paper[15] we have reported the results of our very precise measurements on the infrared rotation vibration bands of HCl^{35} and DCl^{35}. As the result of the theoretical analysis of the data it was found that the ground-state B value is perturbed from the result expected for a pure rotating vibrator. Making use of the known masses of H, D, and Cl^{35} it has been possible to derive a measure of the molecular magnetic moments of HCl^{35} and DCl^{35} from the data. This is (as far as we know), the only molecule for which the magnetic moment has been determined by infrared spectroscopy. At the present time no alternative method of measurement of the molecular magnetic moment is experimentally feasible for HCl.

5. We have very recently observed an induced Q branch in HCl and HBr fundamental bands by the use of only 2 to 5 atm pressure of rare gases as perturbers. The observation of the forbidden Q branch was made by Vodar[16] and his co-workers using high pressures (hundred of Amagats) and low resolution. Our experiments were performed at high resolution and low pressure and show a complicated unexpected fine structure which is distinctly different if argon, krypton, or xenon is used as the perturbing gas as is shown in Fig. 4. The theoretical explanation of the fine structure is not as yet completely clear but as a minimum conjecture we must assume that the

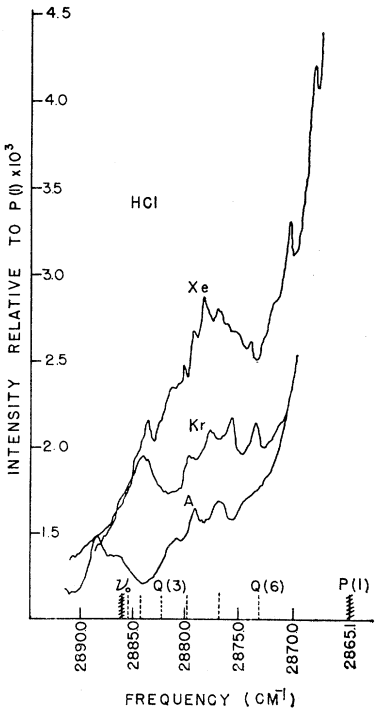

FIG. 4. Fine structure in the foreign gas-induced Q branch of the 1–0 band of HCl. Path length 90 cm, pressure of HCl 25 cm Hg, density of foreign gases argon, krypton, and xenon, 2.2, 1.7, and 1.9 Amagat, respectively.

molecular interaction results in some type of complex molecule formation.

6. Recently we were able to detect and measure accurately the 1–0 band of the quadrupole spectrum of the hydrogen molecule.[17] This spectrum might be considered to be the molecular rotation vibration analog of the Lyman series of the hydrogen atom. The intensity of this band is from 10 to 100 times as

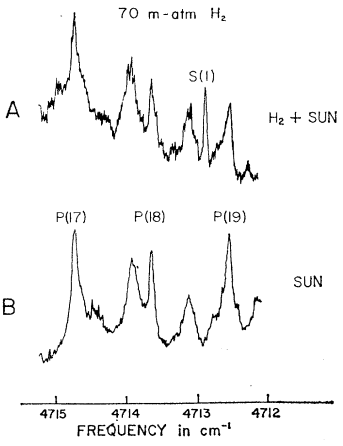

FIG. 5. (A). Reproduction of a small part of the solar spectrum after the sunlight has passed through a path length of 70 m atm of hydrogen. The strongest quadrupole line S(1) is indicated in the figure. (B). The same as (A) except the sunlight was not passed through the absorption tube. Lines indicated by P(17), P(18), and P(19) are telluric lines from the 201–000 band of N_2O.

great as expected from the observations of Herzberg on overtone bands. We are able to easily detect the

[15] D. H. Rank, D. P. Eastman, B. S. Rao, and T. A. Wiggins, J. Opt. Soc. Am. **52**, 1 (1962).

[16] R. Coulon, L. Galatry, B. Oksengorn, S. Robin, and B. Vodar, J. phys. radium **15**, 58 (1954).

[17] D. H. Rank, B. S. Rao, A. F. Slomba, P. Sitaram, and T. A. Wiggins, Nature (to be published).

strongest line S(1) with less than 10-m atm path. (In observing the first overtone band, Herzberg used a path of 10-km atm.) The width of the lines appears to be essentially the Doppler width even at 5 to 10 atm pressure. The measurements yielded the best molecular constants yet obtained for the $v = 1$ state of the hydrogen molecule.

The existence of this quadrupole spectrum may provide a very much more sensitive tool to the astrophysicist to probe the atmospheres of the planets and certain favorable regions of space for molecular hydrogen. Of course one should be naive indeed, if one did not recognize that the astrophysical application of the fundamental band even to the planets is not beset with experimental difficulties. However, with the development of interferometric techniques, these difficulties are probably not insurmountable at least for exploration of the atmospheres of the giant planets. In Fig. 5(B) a very small part of the solar spectrum is displayed. In Fig. 5(A) sunlight was passed through a large absorption tube containing hydrogen. Figure 5 demonstrates that the detection of the strongest quadrupole line S(1) suffers no interference from atmospheric absorption lines. It is also demonstrated that certainly less than 10-m atm of molecular hydrogen exists between the surface of the earth and the sun which of course is a result not unexpected.