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Infra-Red and Raman Spectra of Polyatomic Molecules

I. An Automatic Prism Spectrometer for the Infra-Red

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A spectrometer has been constructed which contains two prisms, one of NaCl, the other of KBr, each in a Wadsworth-Littrow mounting. The prisms may be interchanged in the optical train without opening the spectrometer housing or disturbing the calibration. The recording system includes a Barnes-Matossi type amplifier using a photronic cell. The recording is done stepwise, so that the zero of the amplifying system, the intensity of the source and the intensity of transmitted radiation are measured at each setting of the prism table, which is moved by a ratchet device.

THE design of the spectrometer to be described was largely determined by the purpose it was meant to fulfill. The spectrometer is one of a number of different types of apparatus whose combined function is to determine the thermodynamic properties of organic molecules. An instrument was desired that would be capable of determining the fundamental vibration frequencies of these molecules, require as little attention as possible and at the same time be sufficiently flexible to permit the use of absorption cells of many different sizes and the heating of these cells if necessary.

Since practically all of the molecules in which we are interested have fundamental vibrations of lower frequencies than can be reached with a rocksalt prism, it was necessary to use a prism of potassium bromide in addition. A considerable advantage in economy of construction and operation has been achieved by incorporating both prisms into the same mounting and housing by means of a rotating top on the prism table. This and the noncontinuous type of recording which has been employed are the principal new features of the instrument.

The spectrometer is designed after the combination Wadsworth-Littrow type, in which the radiation passes through the prism twice at approximately minimum deviation. Fig. 1 shows schematically the optical arrangement. L_1 is

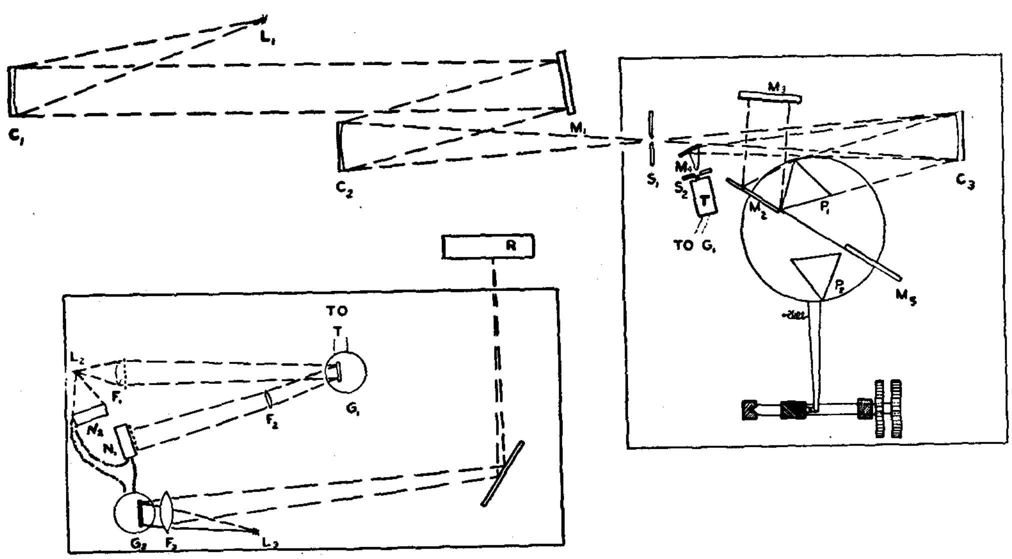

FIG. 1. Diagram of apparatus.

the light source, which is a Globar.[1] It was found that a completely satisfactory mounting for the Globar could be constructed by using the full 6″ length with the standard commercial spring clip terminals. A brass frame was built to hold the spring terminals and the assembly was inserted into an iron pipe 4″ in diameter, which was wound with copper tubing through which water is circulated. Good contact between the pipe and tubing was secured by means of a cement of water glass and magnesia. A slit in the pipe permits radiation to emerge. C_1 is a concave mirror which gives a beam of parallel light into which the absorption cells are inserted. L_1 and C_1 are fixed with respect to each other and mounted on a base that may be moved with respect to M_1, so that different size cells may be inserted. M_1 is a plane mirror and C_2 a concave mirror which focuses the light on the entrance slit S_1.

The following parts, which constitute the spectrometer proper, are all enclosed in a well-insulated box[2] represented by the solid frame in Fig. 1: the entrance slit S_1, the collimating mirror C_3, the two prisms P_1 and P_2 the two Wadsworth mirrors M_2 and M_5, the Littrow mirror M_3, the small plane mirror M_4, the exit slit S_2 and the thermopile T. The slits may be operated from outside the thermostat by rods that run through tightly fitting rubber tubing. The thermopile, which is attached to the exit slit S_2, is enclosed in an evacuated glass jacket and surrounded by an iron pipe and is lagged with felt. The leads from the thermopile to the galvanometer G_1 are single lengths of copper wire, twisted and run through a copper tube. G_1 is surrounded by shields of copper and soft iron and is lagged with cotton waste and felt. The prism table can be set in either of two positions 180° apart from outside the thermostat by means of strings. The prism table is turned by means of an arm 10″ long which is held by a spring against a flat on a long nut which moves on a 1″ diameter, 1 mm pitch screw. The nut has a tail which runs in a groove and keeps it from rotating. The screw is turned by a ratchet and pawl driven from outside the spectrometer by a string. All the strings that run into the spectrometer pass through $\frac{1}{8}''$ copper tubing packed with heavy grease, which seals the inner box from the atmosphere. One notch on the ratchet moves the prism table 10″ of arc. The screw is geared to a Veeder counter outside the thermostat. One notch on the ratchet corresponds to one Veeder number. The prism table may be moved continuously instead of stepwise by the shaft that runs to the Veeder counter.

The two-prism design that is used is made possible by the properties of the Wadsworth-Littrow mounting. In this mounting the radiation that passes through the exit slit has passed through the prism at minimum deviation. This means that the radiation is leaving the prism at the same angle at which it entered it. Accordingly, one may replace this prism by any other prism of a different material (provided that both prisms are isosceles) and all the mirrors will still be in line and in focus. The radiation passing through the exit slit will still be that which has passed through the prism at minimum deviation and the only difference will be that the radiation will be of a different wave-length. We have made use of this property in the following manner: The two Wadsworth mirrors have been accurately aligned so that when the table is rotated 180° M_5 is exactly where M_2 was and *vice versa*. This alignment was made by mounting the mirrors on a single casting which has a flat surface in a plane perpendicular to the top of the prism table and passing through the center of rotation. M_2 is held against the flat surface over a square opening and M_5 against a flat plate held against the flat surface of the casting with openings so that most of the surface of the mirror is exposed. There are two separate prism holders. The table is set in one of its two positions and C_3, P_1, M_3, M_4 and S_2 are adjusted so that the radiation entering S_2 is that which has passed through the prism at minimum deviation. This is done with the sodium D lines. The table is then rotated to the other position and it is only necessary to adjust P_2 so that radiation of the desired wave-lengths can reach S_2 within the possible rotation of the prism table (about 10°). There is no reason why this mounting cannot be

[1] We are indebted to the Globar Corporation for the gift of this item.

[2] This box was originally used as a double-walled air thermostat. The use of a thermostat was discontinued when it was found that the periodic fluctuations (±0.01°) of the thermostat at equilibrium were picked up by the thermopile.

extended to include as many prisms as one may wish. It takes only a few seconds to switch from the NaCl to the KBr prism or back again.

The concave mirrors are 5 cm in diameter with focal lengths about 33 cm. The face of the rocksalt prism is 4 cm×6 cm so that the effective aperture is a little less than $f:7$. For the KBr prism the aperture is not as favorable because the prism is only 4×4 cm. The mirrors are all arranged so as to minimize astigmatism.[3] The maximum angle between beams approaching and leaving the mirrors is 17°.

The receiver is a 26 junction Ag-Bi linear thermopile, constructed by Coblentz about 1915. While a more modern type of thermopile would probably increase the sensitivity and permit the use of narrower slits and thus increase the resolving power, the instrument as it stands seems to have enough resolving power for our purposes. It clearly resolves the ethylene bands at 1400 cm^{-1} into the envelopes of the P, Q and R branches.

The amplifying system is also shown in Fig. 1. It is similar to that described by Barnes, Brattain and Seitz,[4] except that N_1 and N_2 are Weston photronic cells which oppose each other. This eliminates errors due to fluctuations in the intensity of the light source. The part of the amplifying system enclosed in the solid frame is mounted on a concrete pier which is independent of the building. R is a portable light tight box which contains the paper moving mechanism. This is simply an old typewriter carriage and roller, with the original gear replaced by one three times as fine, so that the paper moves 1.2 mm for each notch of the ratchet. The ratchet is activated by a string from an eccentric on the same shaft as the devices that move the cell holders, shutter and table, which will be described below.

The type of recording system used is adapted from one described by Fahrentholz.[5] The prism table is moved one step at a time and while it is stationary the zero of the amplifying system, the intensity of the light source and the intensity of the transmitted radiation are recorded. The cell

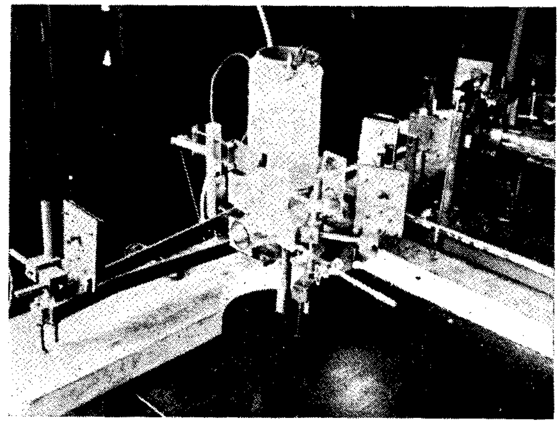

FIG. 2. Photograph of part of spectrograph.

holder is an aluminum casting and is mounted on the end of a piston which is raised by a cam. The photograph, Fig. 2, shows this and the rest of the optical train outside the spectrometer housing. When the piston rests on the circular quadrants of the cam the shutter is open and when it is rising or falling the shutter is closed. The cell holder supports two cells, one containing the substance under investigation, the other evacuated. When the piston is rising, the ratchet driving the table and that moving the photographic paper are moved one notch by means of eccentrics on the same shaft as the cam. This shaft turns at 2 r.p.m. through a 900–1 reduction box connected to an 1800 r.p.m. synchronous motor. The shutter is also moved by an eccentric which is geared to move twice as fast as the cam, so that it opens and closes twice in each cycle, recording the zero twice. The shutter is mounted so that it moves in front of the slit horizontally. Thus, even though it is moving continuously, the actual time of opening or closing is of very short duration compared to the time that it is open or closed. (The shutter moves through 5 cm, while the slit width is never greater than 1.5 mm.)

Figure 3 shows the kind of record that is made by this spectrometer. The records are easily measured by means of a simple device, shown in Fig. 4. A triangle with one side equal to 10 cm (and graduated in mm) has been marked on a transparent celluloid 30°–60°–90° triangle. A narrow strip of celluloid with a straight line ruled on it is pivoted so that the line rotates with the apex opposite to the ruled side of the tri-

[3] (a) Czerny and Turner, Zeits. f. Physik **61**, 792 (1930); (b) Czerny and Plettig, ibid. **63**, 590 (1930).
[4] Barnes, Brattain and Seitz, Phys. Rev. **48**, 582 (1935).
[5] Fahrentholz, Zeits. f. tech. Physik, 67 (1936).

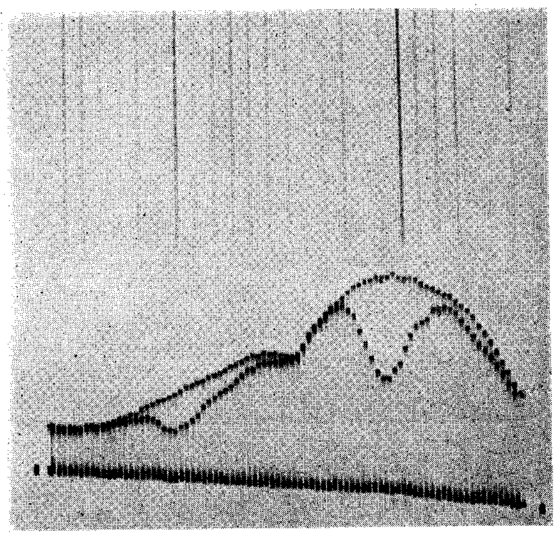

FIG. 3. A sample record (ethylene from 1650 to 5000 cm^{-1}) showing the CO_2 absorption of the atmosphere, the maximum of intensity of the source, and several ethylene bands.

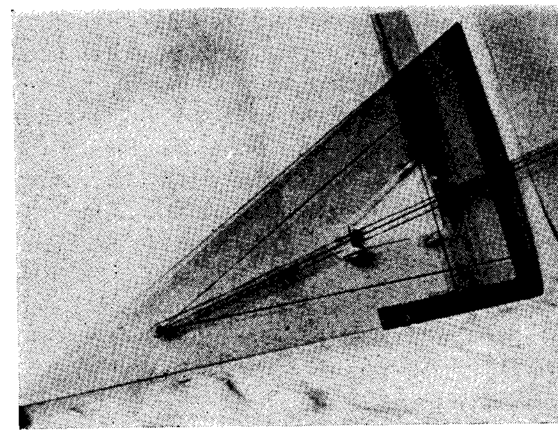

FIG. 4. Photograph of device for reading records.

angle as its center of rotation. If the instrument is placed so that the ruled edge is at the right parallel to the galvanometer deflections, the lower side of the triangle made to intersect the lowest point of a set, the upper side intersecting the highest point and the movable line set to intersect the middle point, then the intersection of this line with the ruled side will give the ratio of the smaller deflection to the larger one.[6]

This type of recording has many advantages over the usual continuous type. It eliminates uncertainties due to drift of the zero, change of intensity of the source of radiation and absorption by water vapor and carbon dioxide in the atmosphere. Such phenomena are indicated in Fig. 3. This discontinuous recording also eliminates any possibility of shifts in the recorded maxima due to time lag in the thermopile-recording system. It has the possible disadvantage that it takes more time to run through the spectrum, but this is, in our opinion, more than compensated for by the added accuracy. To go from 3300 cm^{-1} to 700 cm^{-1} in steps of 3 Veeder numbers (this corresponds to about 30 cm^{-1} at 2000^{-1} and 3 cm^{-1} at 1000 cm^{-1}) takes about four hours and two feet of photographic paper. It takes only two or three minutes to change the instrument from automatic to hand recording by substituting a scale in place of R.

[6] We are indebted to Dr. W. H. Avery for the design and construction of this measuring instrument.

The rocksalt prism was calibrated empirically by means of the absorption bands of C_2H_4, C_2H_2, C_2H_6 and C_6H_6. The potassium bromide prism was also calibrated with these bands and the calibration extended to 400 cm^{-1} (25μ) by means of the known indices of refraction of KBr. While these indices are not known with great accuracy, the error introduced is less than 1 cm^{-1} at 500 cm^{-1}, due to the wide spread of the dispersion on a wave number scale.

The spectrometer table and screw were constructed by Mr. D. W. Mann of the physics department shop. We wish to acknowledge our gratitude to Professor D. C. Stockbarger of the Massachusetts Institute of Technology for the gift of several crystals of KBr and to Professor George B. Kistiakowsky for advice and encouragement. Part of this investigation has been supported by a grant from the Milton Fund of Harvard University.