

degree. This represents an error, dR/R , approximately 3 percent at 100 cm and 0.4 percent at 16.7 cm. These measurements were performed under ideal conditions and under actual use the *maximum* error can be considered to be at least 2 to 3 times larger than this because of scattering causing an unnoticed change in the course of the particle, to cloud-chamber turbulence, and to operator fatigue. However, the *mean deviation* certainly should be no greater than 3 percent at 100 cm, for example. Tracks which are bent because of a single scattering event are usually detected if the scattering is large enough because the track image cannot be made continuous over its entire length for a single value of θ . Such tracks can be measured by using only the segment of the track which lies on one side or the other of the scattering point.

For a track whose radius of curvature is less than 7 cm the radius is measured by direct comparison of the image with arcs scribed on the white base plate. This makes the instrument capable of measuring radii in the range from 0.5 cm to 100 cm.

In actual use the instrument has measured as many as 150 tracks per hour and at present the speed of

observation and recording is limited by a recorder's ability to record the data accurately by voice transmission from an observer.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. D. W. Kerst and Dr. H. W. Koch for their many helpful suggestions and criticisms rendered.

The author also wishes to express his appreciation to the large number of people who helped in construction and successful operation of the equipment; especially to Dr. C. D. Curtis for his work on the photographing-reprojecting system and to Donald Vermillion for his work as an aid throughout the program.

Figure 2 was obtained through the courtesy of Dr. Philip C. Fisher. The curvature-measuring device of Fisher shown by Fig. 2 is an improved model of the original device constructed by the author. The improvements were made by lighting the scribed points from underneath by means of a pilot light and two Lucite light pipes, and by placing the scale and vernier system in a more convenient location for reading.

A High Precision Electron-Diffraction Unit for Gases

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(Received August 18, 1953)

An electron-diffraction unit incorporating a rotating sector has been developed which makes possible the accurate and objective measurement of the intensity of electrons diffracted by free atoms and molecules. The diffraction data afforded are sufficiently precise to permit the calculation of the distribution of electrons in atoms and the amplitude of vibration of atoms in molecules, as well as interatomic distances that are comparable in accuracy in suitable cases to those obtained by microwave spectroscopy. A description of the essential components of the unit is given together with some data on performance and discussion of the use of the apparatus.

ELECTRON diffraction has been the best generally applicable tool for determining interatomic distances in free molecules for over twenty years. It continues to hold an important place in molecular structure investigations, the brilliant success of the new microwave techniques in spectroscopy notwithstanding, for it is possible to study by diffraction molecules that are not amenable to spectroscopic treatment, and recent techniques in diffraction give a precision comparable to that of microwave methods in determinations of the structure of simple polyatomic molecules. In addition, electron diffraction is capable of yielding information about nuclear motion in molecules and electron distribution in atoms.

The older methods of recording and interpreting electron-diffraction patterns, however, are not sufficiently reliable to provide answers for many questions of current chemical interest. Analyses of structure require the precise characterization of molecular interference terms which manifest themselves only as small deviations from the smooth background of scattered electrons, and the background itself falls off with such extreme rapidity as the scattering angle increases that it is difficult to record and measure the pattern accurately. This difficulty has been overcome by the use of a rotating sector to compensate for the precipitous drop in intensity by suitably screening the electrons before they reach the photographic emulsion used to record the pattern, and by the measurement of the resulting photographic records with a sensitive

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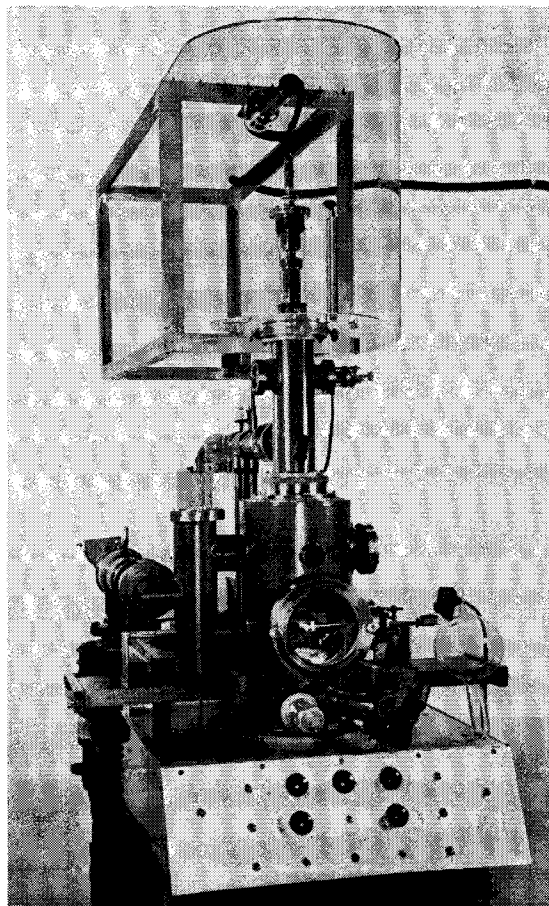


FIG. 1. Photograph of electron-diffraction unit.

recording microphotometer. Although the rotating sector-microphotometer method has been in use since 1939,¹ it has only recently realized its full potential in practice. Several laboratories are now using this method exclusively in electron-diffraction investigations of molecular structure.

The attainment of high precision in molecular structure investigations is thus essentially a problem in instrumentation and since the older electron-diffraction units for which a detailed description exists in the literature are not well adapted for modification to the newer techniques it was felt desirable to describe a new apparatus which was designed expressly for use with the rotating sector. This apparatus, illustrated in Figs. 1 and 2, is noteworthy in its combination of simplicity and high performance. Careful attention has been paid to ease and reliability of operation and versatility of function. It was with this instrument that the distribution of electrons in atoms was first studied by electron diffraction.² Precision of a few thousandths of an angstrom unit has been attained in

the measurement of interatomic distances and nuclear vibrational amplitudes in gas molecules. The instrument is also suitable for high resolution diffraction studies with solid specimens.

DESCRIPTION OF INSTRUMENT

Electron Optical System

A self-biased hot cathode gun is used for the electron source. The filament can be centered in the grid sheath by a fine screw motion device which tilts the filament support. A second device raises or lowers the filament along the electron-optical axis. Experience with commercial guns sealed with hard wax led to the selection of metal-to-glass seals instead of wax both for the glass envelope enclosing the gun parts and for the electrical leads into the gun. Unlike some self-biased electron guns, this gun is exceptionally stable in current output at low filament currents as well as at the normal operating plateau current. The plateau of the emission current can be varied during operation by varying either the bias resistance or the distance of the filament from the grid aperture.

The divergent beam from the gun is focussed on the plane of the photographic plates by a single magnetic lens. One lens has proved sufficient for even high resolution diffraction work because the fineness of the source of electrons at the gun makes it possible to obtain a beam less than twenty microns in diameter at the focus. The fineness of the effective emission source is due to the electrostatic focussing action of the gun optics rather than to a defining aperture, so that a very intense beam can be obtained with a modest total emission current. The output from the gun is contained within a small solid angle with less than one-half of the electrons diverging as much as $\frac{1}{3}$ of a degree from the axis of the beam when the beam has reached its plateau current. At smaller space currents, and therefore smaller bias voltages, the direct beam is much wider.

An electrostatic shutter between the gun and lens is used in association with an electronic timing circuit to regulate exposure times from a fraction of a second to many seconds. Easily accessible platinum apertures are located at the shutter, lens, and nozzle, with the shutter or lens aperture serving as the limiting aperture of the system. The limiting aperture is chosen to make the beam about 0.1 mm in diameter at the nozzle when the nozzle is 10 cm from the photographic plate. The beam current is measured beneath the nozzle by a metal probe with a depression 8 mm deep to trap the electrons. The probe is always withdrawn from the beam during exposures so that no shadow can be cast upon the diffraction pattern.

The lens and sector axis positions are mechanically fixed for stability of operation. Alignment is accomplished by bending the beam with electrostatic deflector plates and by moving the gun itself. An intermediate viewing screen above the lens serves in the rough

¹ P. P. Debye, *Physik. Z.* 40, 404 (1939); Finbak, Hassel, and Ottar, *Arch. Math. Naturvidenskab.* 44, No. 13 (1941).

² L. S. Bartell and L. O. Brockway, *Phys. Rev.* 90, 833 (1953).

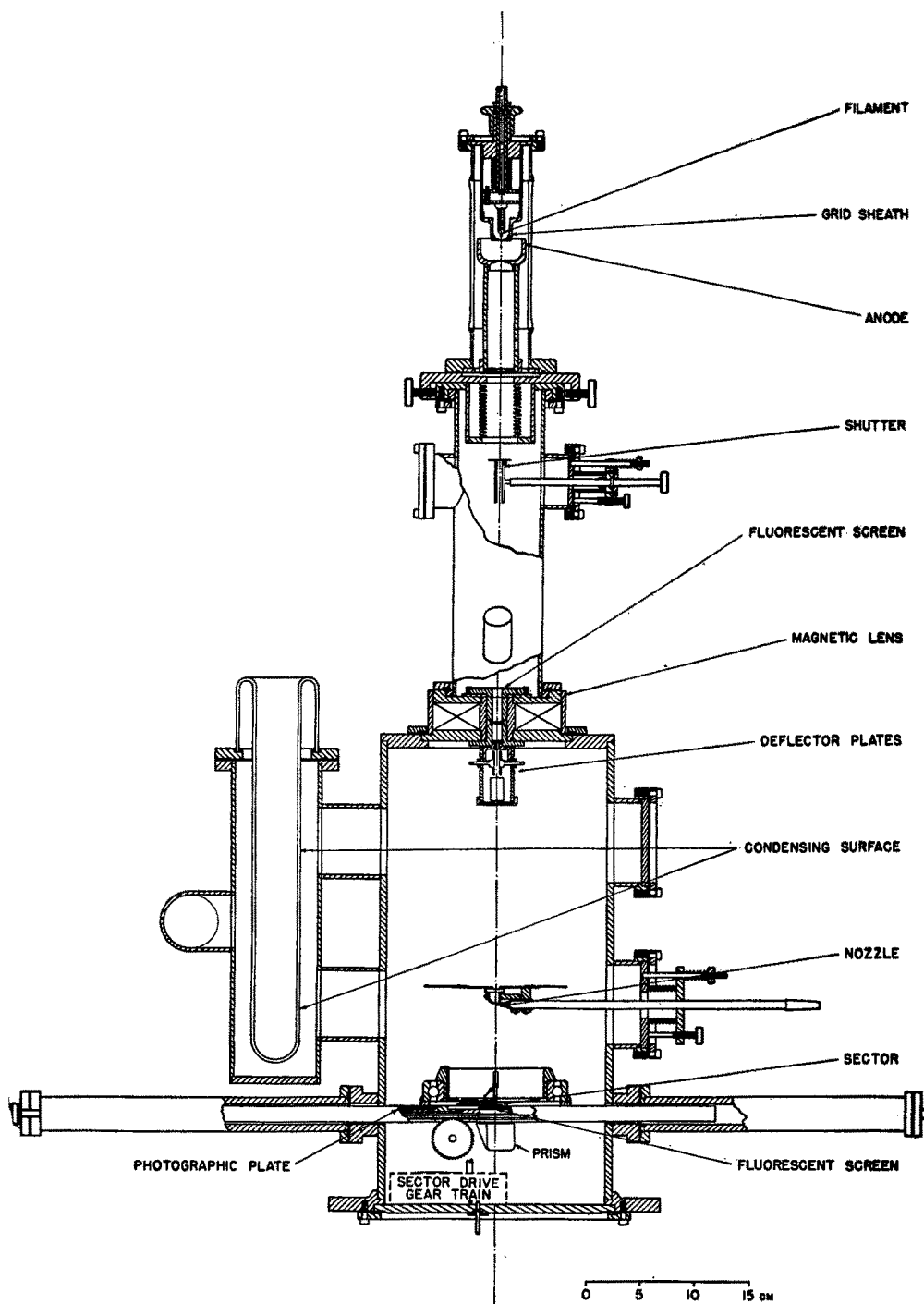


Fig. 2. Sectional drawing of electron-diffraction unit.

alignment of the gun and shutter aperture. Precise focussing and alignment are facilitated by observation of the beam on the fluorescent screen through a 20-power microscope with a calibrated reticle. Since the microscope must focus on the fluorescent screen from below, two prisms are used in the optical system, one directly beneath the fluorescent screen (Fig. 2) and one

between the objective lens and eyepiece, to enable the operator to observe the screen from a comfortable position. The microscope is an 8-power elbow telescope used with an additional element in the objective lens, and can be seen just under and slightly to the right of the center of the main port in Fig. 1.

It is essential for high-quality diffraction records that

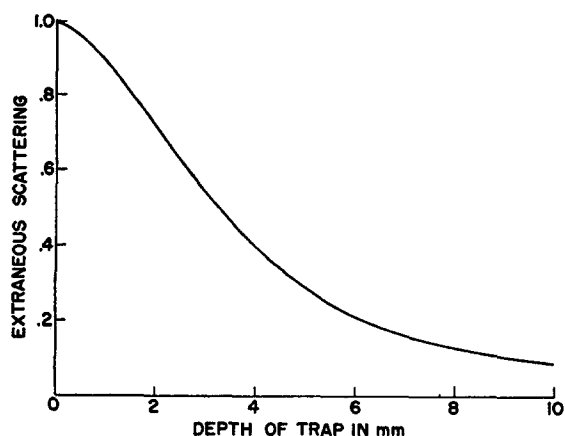


FIG. 3. The effectiveness of a beam trap as a function of the depth of its trapping hole. The diameter of the trapping hole is 2 mm.

the undiffracted beam be thoroughly trapped before it can strike the photographic emulsion. When an electron beam is stopped, secondary electrons are emitted along with x-rays which in turn eject photoelectrons. This extraneous radiation can fog the photographic emulsion unless steps are taken to trap it. We have observed that the outer portion of a photographic plate is fogged about twenty times more heavily if the emulsion is struck by the direct beam than if the beam is stopped above the emulsion by a flat metal plate. Even a well-grounded flat metal plate several hundred times wider than the beam is not an adequate trap, for it will generate an extraneous intensity comparable to the diffracted intensity at large scattering angles if the pressure of the gas specimen is sufficiently low to prevent appreciable multiple scattering. A deep depression in the trap is required for the effective trapping of the beam. Figure 3 shows how the extraneous scattering decreases as the depth of the trapping hole is increased. In the apparatus, a trapping tube over 20 mm deep is mounted on the sector, and the hole through the sector which permits observation of the beam on the main fluorescent screen is closed during

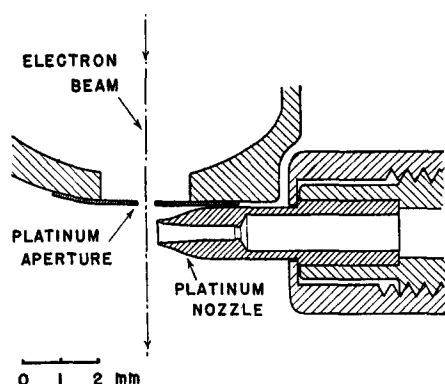


FIG. 4. Section through specimen injection system. The nozzle has a circular throat, and is made of platinum so that it can be kept scrupulously clean.

the recording of diffraction patterns through the action of a device operating by centrifugal force.

In careful studies of atomic scattering at large scattering angles by noncondensable samples, it is advisable to have an aperture in addition to those illustrated in Figs. 2 and 4 which should be somewhat smaller than the aperture at the nozzle and should be located about 2 cm above the nozzle at the bottom of an ample trapping funnel. In molecular structure investigations the omission of this extra device to reduce extraneous scattering has no effect on the measurement of interatomic distances and leads to an estimated error in the measurement of vibrational amplitudes of nuclei in molecules of less than 0.0002 Å.

Specimen Injection

Two ports are provided for introducing the specimen into the electron beam, one at 10 cm and one at 25 cm from the photographic plates. The shorter distance is appropriate for studies of moderate to wide-angle scattering by gases and the longer distance is useful for examination of small-angle scattering by gases and for diffraction by solid specimens.

The turning of a stopcock which has been provided with a cam and microswitch simultaneously admits a gas sample into the system and triggers the electronic shutter timing circuit. The sample is sprayed into the electron beam from a fine nozzle 0.3 mm away from the center of the beam. A platinum nozzle is used for it was found to be impossible to keep brass or stainless steel nozzles sufficiently clean to prevent them from disturbing the beam.

The pressure of the gas in the sample reservoir is adjusted to strike a balance between multiple scattering which occurs at high pressure and extraneous scattering which is relatively worse at low pressures. The pressure in mm, p , that is used with a nozzle of the dimensions and shape illustrated in Fig. 4 is

$$p \sim 3 \times 10^4 / \sum_i Z_i^2,$$

where Z_i is the atomic number of the i th atom in the molecule being investigated. Thus, a pressure of 25 mm would be used for CCl_4 . Pressures as low as one one-hundredth of this magnitude have given usable diffraction records.

If the instrument is properly aligned and exposure times are kept under 0.2 second, very clean diffraction patterns with little evidence of diffuseness of gas sample can be obtained without the use of a cold trap to condense the specimen as it streams from the nozzle. This is fortunate because it means that high quality patterns can be obtained with noncondensable gases as well as with condensable gases. The diffraction patterns have an index of resolution of 0.9 to 1.0; that is, the ratio of the amplitude of the molecular diffraction terms to the magnitude of the smooth background (atomic plus extraneous) upon which the

molecular terms are superposed is 0.9 to 1.0 times that given by theory for a perfect pattern. Measurements of the distribution of gas pressure in the vicinity of the nozzle have been made by passing the gas diffraction pattern produced by an extremely narrow electron beam through a slit a few microns wide. The distribution of intensity received by the photographic plate when the slit is well off the axis of the beam is a direct measure of the distribution of specimen concentration. The observed spread of gas is so slight that it introduces no perceptible error into measurements of interatomic distances and affects measurements of the amplitude of vibration of atoms in molecules by only a few ten-thousandths of an angstrom unit.

Recording System

The recording system is built into the diffraction chamber to allow easy access of the parts through the large main port. It consists of a rotating sector mechanism and a photographic plate unit.

It has been found appropriate to use a sector with an angular opening increasing as the cube of the radius in all molecular structure studies. In recording low angle atomic scattering at $s = (4\pi \sin \frac{1}{2}\theta)/\lambda$ values from less than one to eight a sector with an angular opening increasing as the square of the radius is more satisfactory. It is convenient to use a heart-shaped sector with the two halves made separately to allow the narrow portion of the slit to be accurately figured and finished.

A peripheral mounting for the sector was chosen to avoid the shadow that an axial support would cast on the diffraction records because the records are spun about their centers while being measured by the recording microphotometer. All details of the sector support (Fig. 5) were arranged to avoid any shadow other than that of the sector. The rotating part of the mount is the inner ring of a carefully demagnetized Norma Hoffman XLS series ball bearing with a bore of $3\frac{1}{4}$ inches. The outer ring is clamped rigidly in place on the sturdy track which guides the photographic plate holder. The inner ring is provided with a counterbalance for the sector so that it will not tend to vibrate while rotating, and with a flange for engaging a friction drive wheel (Figs. 5 and 6). A small motor of variable speed output transmits rotary motion through a modified Wilson seal in the vacuum wall. A 12:1 step-up gear train is used inside the vacuum system to impart high speed to the rubber rimmed wheel driving the sector without overtaxing the vacuum seal which admits the drive shaft. The sector rotates at about 1200 rpm.

The photographic plates are held in place by gravity and are brought into position by a rack and pinion device which automatically moves the fluorescent viewing screen out of the way. The design allows the sector to approach to within 5 mm of the photographic plates. In some previous designs the sector has been

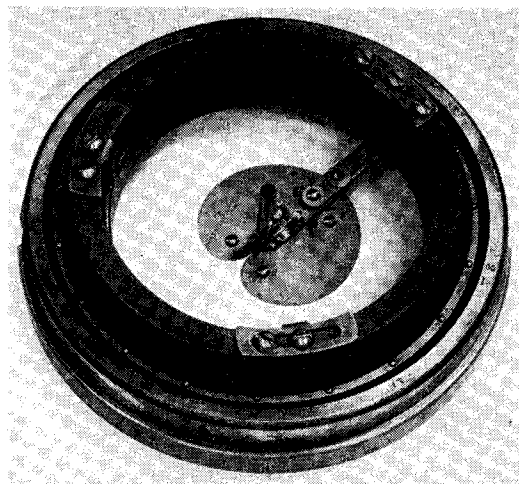


FIG. 5. Sector mounted on the inner ring of a ball bearing. The beam trap can be seen directly over the sector on the axis of rotation.

located much farther from the plates, with the consequence that the undesirable effects of edge scattering, electrostatic charging, magnetism of bearings, and finite size of beam at the sector have been magnified. The unit is provided with a daylight-loading plate holder which accommodates up to 14 inches of $3\frac{1}{4}$ -inch wide plates. Masks mounted directly beneath the sector are used to control the size of exposures. Three to six exposures are commonly made with one loading.

Care is taken to use high quality photographic plates that are uniform in flatness and thickness as well as in emulsion characteristics because variations of several thousandths of an inch, if not checked individually, would be a major source of error in precise determinations of interatomic distances. Ports are provided for viewing and measuring the position of the nozzle and photographic plates in order to determine the camera geometry.

Vacuum System

Opposite each specimen-introduction port is a high vacuum lead directed toward a cold trap which is evacuated by a high-speed oil diffusion pump backed by a fast mechanical pump. The cold finger is removed

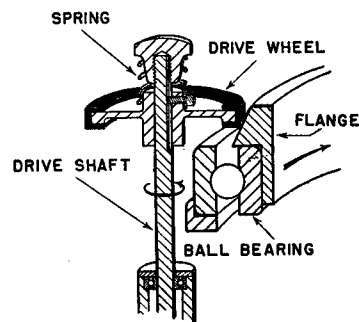


FIG. 6. Section through sector drive mechanism. The wheel is keyed to the shaft and is free to slide vertically under gentle pressure from the spring.

from the trap to improve the pumping speed if the specimen is noncondensable. The chamber above the lens is evacuated by an independent pumping system and is isolated from the diffraction chamber except for a small aperture in the lens, with the result that even a relatively large burst of gas can be admitted into the specimen chamber without discharging the electron gun. The apparatus is evacuated to 10^{-5} mm for gas diffraction studies.

An excellent design for a high-vacuum valve to be used between the diffusion pump and the vacuum chamber was obtained from A. Risberg in the Chemical Institute of the University in Oslo. As illustrated in Fig. 7 its effective opening is nearly as large as the internal diameter of the tubular housing. A circular disk carries a rubber "O" ring in a channel on the rim, and the ring is squeezed against the wall of the tube when the disk stands across the tube. The disk is hinged through two links to the push rods providing a positive action for opening and closing the valve. The push rods have glands sealed with smaller "O" rings.

The valve in the closed position provides a vacuum-tight seal against an atmosphere pressure and is especially well adapted for use between a vacuum system and a cold trap above the diffusion pump. Its simplicity of construction and operation and its low

impedance make it well suited for vacuum operations in lines of any moderate size.

High Potential Supply

The accelerating voltage of forty kilovolts is filtered and regulated to about one part per ten thousand. The sum of the accelerating voltage and bias voltage can be read very accurately with a type K potentiometer which taps a known fraction of the 50-megohm bleeder resistance. This reading, when corrected for the relatively small bias (~ 300 volts), determines the experimental value of the de Broglie wavelength used in structure analysis computations.

Mounting

To minimize disturbance of the electron beam by external magnetic fields the instrument is mounted on a nonmagnetic table of welded aluminum construction. All alternating currents of appreciable magnitude are kept away from the control panel of the table by the use of relays operated from the control panel. The table is mounted on sponge rubber to keep the instrument free of vibrations. To prevent mechanical shock from being transmitted along the forepump leads to the instrument, flexible vacuum leads from the forepumps are connected to tubes rigidly attached to the wall, and from these tubes are run flexible leads to the diffusion pumps.

APPLICATION

After the electron optical system is thoroughly cleaned and aligned to ~ 0.03 mm, exposures are made under the conditions recommended above by injecting a burst of the sample into an electron beam of about 0.5 microampere. It is undesirable to use beams very much stronger than this because of the tendency of strong beams to charge surfaces, thereby enhancing extraneous scattering.

The density of the diffraction records should be kept well below the level of appreciable saturation of the emulsion (an optical density of ~ 0.8 for Kodak lantern slide plates) which can be determined by a suitable calibration procedure.³ The primary function of a rotating sector is to modify the intensity distribution of electrons received by the photographic plate so that the resulting exposure over the entire pattern lies in the most sensitive region of the emulsion and the microphotometer. It is essential for the most accurate work that a pattern be spun about its center while being scanned by the microphotometer, in order to average out irregularities in the emulsion. An averaged record of a good photographic plate is far freer from defects than a record along any one radius. Figure 8 shows microphotometer traces of diffraction records of carbon tetrachloride patterns taken at the 10-cm and 25-cm nozzle positions. (The sharp minimum

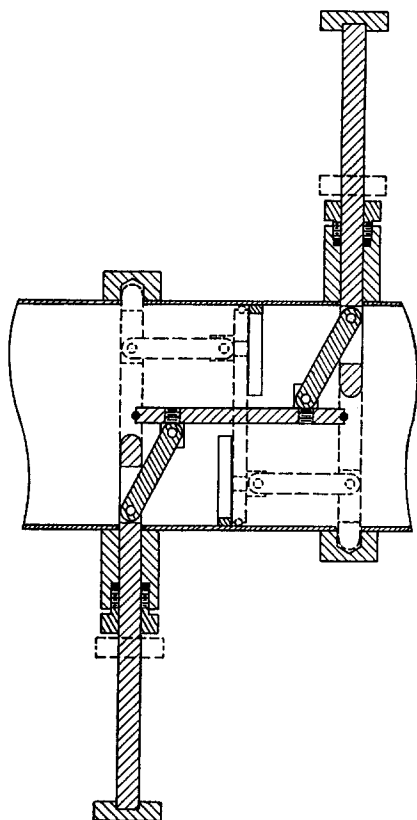


FIG. 7. Section through high-vacuum valve of simple operation and low impedance. Solid lines—open position; dashed lines—closed position.

³ L. S. Bartell and L. O. Brockway, *J. Appl. Phys.* **24**, 656 (1953).

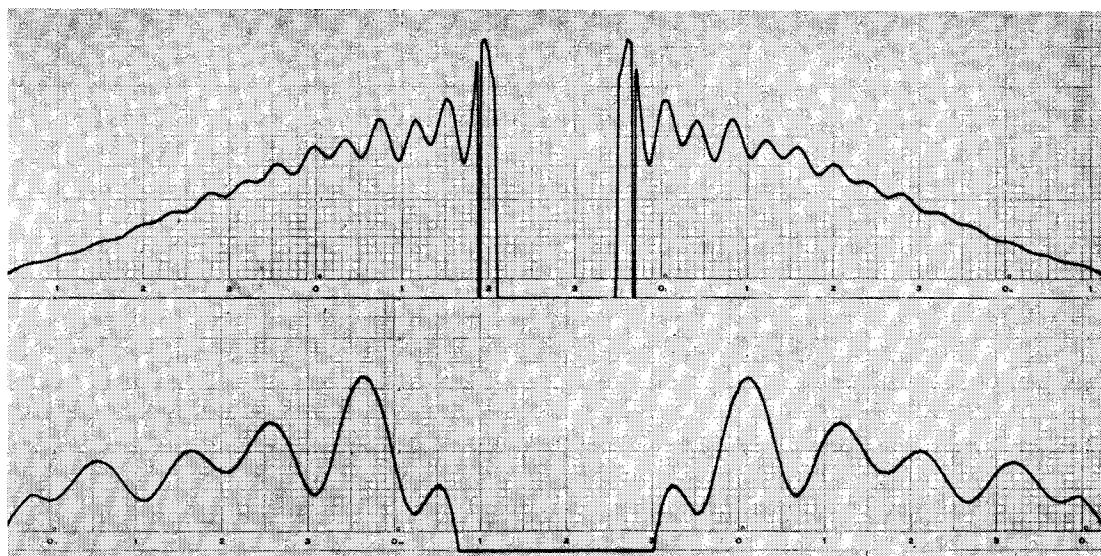


FIG. 8. Microphotometer traces of diffraction records of CCl_4 obtained with an r^3 sector. The lower pattern was recorded at the 25-cm nozzle position and shows the first five molecular interference maxima. The upper pattern was recorded at the 10-cm position and shows the maxima from the second through the fifteenth.

in the upper curve is due to a fine wire mounted across the opening of the sector near its center to provide a fiducial mark on the microphotometer record. The microphotometer is given a different arbitrary but known zero setting for recording different negatives, and the cutoff at low densities in the lower record occurs at a larger radius than in the upper record.) These may be compared to traces of unsectored patterns of the same substance made by Heston and Cutter.⁴

The traces are read at close intervals under about tenfold magnification with a suitable device for accurate interpolation, and these readings are converted to relative intensities.³ The averaged readings of several good plates should be sensitive to deviations from smoothness of the diffraction pattern of a few parts per ten thousand if the work is done carefully. The readings can be reduced to molecular structure parameters by any of several methods of analysis.⁵ Compounds which have already been the subject of study by this

equipment are a series of fluorine and chlorine substituted methanes and methyl silanes.⁶ An interesting example of the results is the observed decrease in the CF bond length in the fluoromethanes from 1.391 Å in CH_3F to 1.323 Å in CF_4 . The smallest uncertainty that can be expected with the present technique is about 0.002 or 0.003 Å.

ACKNOWLEDGMENTS

We wish to thank the Horace H. Rackham School of Graduate Studies of the University of Michigan for a grant for the construction of the apparatus and also for the grant of a research fellowship to L. S. Bartell. We are indebted to Dr. J. Karle and Professor S.H. Bauer for providing us with detailed information on the design of their diffraction equipment. We also wish to express our appreciation to Mr. Hermann R. Roemer of the Physics Instrument Shop and his exceptionally able staff whose skill and ingenuity contributed much to the success of the apparatus.

⁴ B. O. Heston and P. R. Cutter, *Rev. Sci. Instr.* **21**, 608 (1950).

⁵ H. Viervoll, *Acta Chem. Scand.* **1**, 120 (1947); O. Hassel and H. Viervoll, *ibid.* **1**, 149 (1947); I. L. Karle and J. Karle, *J. Chem. Phys.* **17**, 1052 (1949); J. Karle and I. L. Karle, *ibid.* **18**, 957 (1950); Brockway, Schwendeman, and Bartell (to be published).

⁶ A. C. Bond and L. O. Brockway, *J. Am. Chem. Soc.* (to be published); L. O. Brockway and C. G. Thornton, *J. Am. Chem. Soc.* (to be published).