pensated by shortening of metal-oxygen interatomic distances involving O(6) atom (Table 2).

The formula inferred from the microprobe analysis presented by Nicholls and Carmichael (*3*) was confirmed by the crystal structure analysis, which revealed the crystallochemical formula

$$(Na,K)_2^{VI}\ (Fe^{+3})_2^{VI}\ (Fe^{+2})_2^{IV}\ Si_{12}O_{30}\cdot H_2O$$

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Interstellar Scintillations of Pulsar Radiation

Abstract. *Time fluctuations in the intensity of pulsed radiation from CP 0834, CP 1133, AP 1237, and CP 1919 have been investigated. Power spectra, modulation indices, frequency distributions, and decorrelation frequencies are consistent with scintillation theory. If it is assumed that these scintillations are due to irregularities in the interstellar medium that travel at a velocity of 20 kilometers per second, the irregularities have a scale size on the order of 10^4 kilometers and a distance from the earth of approximately 70 parsecs. These interstellar scintillations would not have been observed if the apparent angular diameters of the pulsars were larger than 0.3×10^{-5} second of arc, and they would cause even a point radio source to have an apparent angular diameter of approximately 10^{-3} second of arc at 318 megahertz.*

Recent observations of the time fluctuations in the intensity of pulsar radiation are consistent with the predictions of scintillation theory. These observations reinforce the evidence (*1*) for an interstellar plasma between the earth and the pulsars. If we assume that the scintillations are interstellar (*2*), the size of the diffracting irregularities and their distance from the earth may be calculated.

Pulsars CP 0834, CP 1133, AP 1237, and CP 1919 were observed at Arecibo Ionospheric Observatory. Radiometers were used with 10-msec time constants and the following combinations of radio frequency and bandwidth: 111 Mhz–125 khz, 195 Mhz–500 khz, 318 Mhz–500 khz, and 430 Mhz–1 Mhz. The 111- and 430-Mhz antennas were circularly polarized, and the 195- and 318-Mhz antennas were linearly polarized.

Pulse intensities (ON intensities) were calculated by integrating the power within windows of data which were 200 msec wide and centered on each pulse. Intensities due to system noise (OFF intensities) were similarly calculated for windows centered midway between pulses. A more complete description of the method of calculating these intensities is given by Lovelace and Craft (*3*).

In order to minimize the noise contribution to the ON intensities, the intensity data were smoothed by replacing each intensity point with the average of the 50 succeeding points. Power spectra of the fluctuations of the ON intensities about the mean value were then measured on arrays of 4096 points of intensity (Fig. 1). A similar spectrum for the OFF intensities was undetectable on the scale of Fig. 1. The spectra of CP 1133, AP 1237, and CP 1919 have widths which are proportional to $\lambda^{1.0 \pm 0.2}$, where λ is the wavelength. These widths give time scales for the fluctuations which are in agreement with the more qualitative results of other observers (*3–6*). A study of other features in the spectra of CP 1919 has also been made (*7*).

Some examples of the frequency histograms calculated for the ON and OFF intensities are shown in Fig. 2. After calculating the average intensity of the ON data, $\bar{I}_{ON}$, I formulated these histograms by counting the number of times an intensity I fell within the interval $I \pm (\bar{I}_{ON}/20.0)$. Although the ON frequency distribution is actually the convolution of the pulse frequency distribution with the OFF frequency distribution, the OFF histogram is narrow enough to show that an exponential distribution of pulse intensities is consistent with the observed data. Also shown in Fig. 2 is the relative root-mean-square value M of the intensity fluctuations about the mean intensity. This modulation index and the parameter ξ, which measures the skewness of the ON distribution, were calculated according to the procedure of Cohen *et al.* (*8*). An exponential distribution of intensities, and values of M and ξ

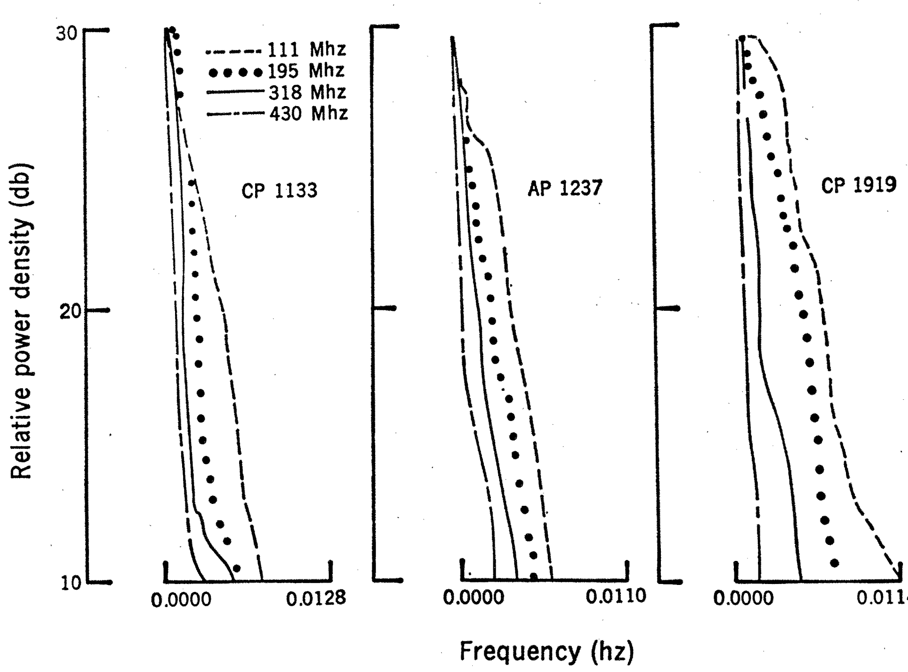

Fig. 1. Power spectra of the fluctuations in the pulse intensity of pulsars about the mean intensity. The frequency resolution is approximately 0.00025 hz, and the effective Nyquist frequency is approximately 0.01 hz.

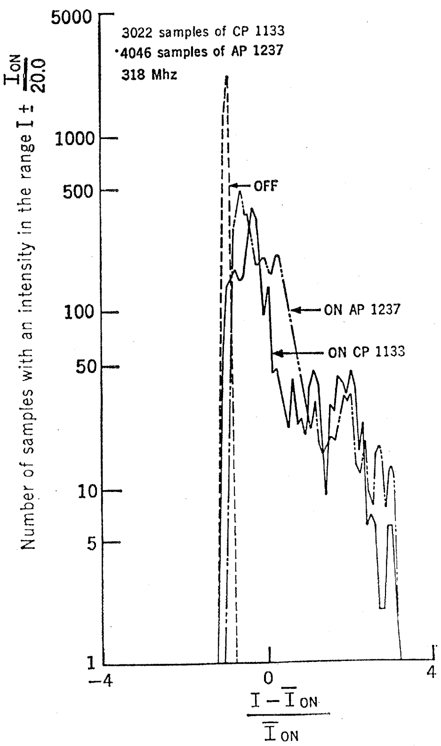

Fig. 2. A frequency histogram representing the probability density function of pulsar radiation intensity; $M \approx 0.8$ and $\xi \approx 1.0$, both values having been computed as described by Cohen *et al.* (*8*).

of 1.0 ± 0.2, were observed for CP 1133, AP 1237, and CP 1919 at all four radio frequencies (111, 195, 318, and 430 Mhz). Because only a few noisy pulses were detected during observation of CP 0834, the data did not allow reasonable estimates of the power spectra and frequency distributions for this pulsar.

In order to interpret the observations, let us assume that the observed intensity fluctuations are caused by randomly distributed phase-changing irregularities of size a in an extended medium located at a distance z from the earth along the line of sight between the observer and the pulsar. The phase deviations are assumed to have a Gaussian autocorrelation function and are characterized by the root-mean-square value ϕ_0.

If we assume that the irregularities are drifting at a velocity V transverse to the line of sight, and that turbulent velocities are small compared with this drift, then the conventional theories which explain the spatial diffraction pattern of a phase screen may be used to predict the temporal variations of the pulsar intensity detected by a fixed antenna (*9*). If observations are made at a wavelength λ, and if $z \gg a^2/\lambda$ the modulation index will be on the order of unity, and the intensity fluctuations will have a Gaussian power spectrum whose full width to half maximum is equal to $\sqrt{2}\phi_0 V/a$. In addition, the probability distribution of intensities will be exponential. When ϕ_0 is much larger than unity, these conclusions hold under the less stringent requirement [see (*9*)] that

$$z > 2\pi a^2/\lambda\, \phi_0^{2/3}$$

Because the root-mean-square phase deviation of a plasma is proportional to λ, each power spectrum should have a width which is proportional to λ. The spectra shown in Fig. 1 have widths which are consistent with this prediction. The observed modulation indices and frequency distributions are also consistent with theoretical predictions. Each spectrum, however, has a non-Gaussian tail, and the second moment will differ from the theoretical value. The same anomaly is found in the spectra of interplanetary scintillations near the sun (*10*).

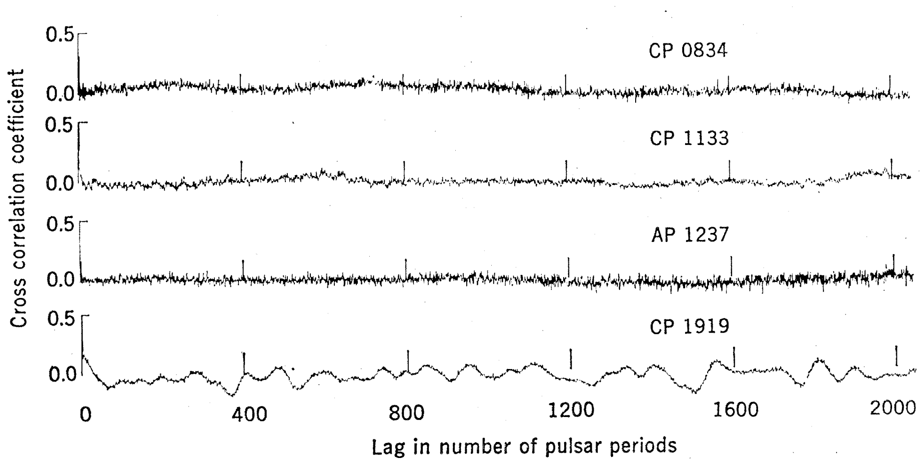

Fig. 3. Cross correlations of pulse intensities detected by radiometers with 500-khz bandwidths, 10-msec time constants, and radio frequencies of 111 and 195 Mhz.

Although some pulsars have a correlation of pulse intensities over a broad range of frequencies [see (*4*) and Fig. 3], most of this correlation will be lost if the observed intensities are averaged over several pulses. Correlations over such a large frequency range will be important in the consideration of theoretical models for pulsar radiation (*11*). Because the cross-correlation functions shown in Fig. 3 are less than unity, however, it is plausible that there will be some decorrelation over some smaller frequency difference.

The scintillation theory predicts little correlation between the intensity fluctuations seen at radio frequencies whose separation $\Delta\nu$ is given by

$$\Delta\nu > 2\pi a^2 c/\lambda^2 \phi_0^2 z$$

where c is the velocity of light (*9*). Estimates of $\Delta\nu$ have been made by Rickett (*12*), based upon observations made at 408 Mhz. By using pulse intensities averaged over 1 minute, he obtained values of $\Delta\nu \approx 4 \pm 2$ Mhz for CP 0834 and CP 1919, and $\Delta\nu \approx 10 \pm 4$ Mhz for CP 1133. If we assume that the dispersing electrons are isotropically distributed about the earth, Rickett's measurements indicate this separation is inversely proportional to $z\phi_0^2$.

Cross correlations have been made between the intensities of 4096 pulses simultaneously recorded with six radiometers, each of which had a 10-msec time constant, a 500-khz bandwidth, and a radio frequency near 318 Mhz. When the ON intensity data were averaged over 50 pulses, pulsars CP 0834, CP 1133, AP 1237, and CP 1919 each had cross-correlation coefficients of 1.0 ± 0.01, 0.7 ± 0.1, 0.5 ± 0.2, 0.4 ± 0.1, and 0.2 ± 0.1 when the radio frequencies of two radiometers were separated by 0.0, 0.5, 1.0, 1.5, and 2.0 Mhz, respectively. Consequently, $\Delta\nu \approx 1.5 \pm 0.5$ Mhz for these pulsars. Although Faraday rotation effects could contribute to about 10 percent of the observed $\Delta\nu$ coherence loss, CP 0834, CP 1133, and CP 1919 do not exhibit any detectable Faraday rotation at 111 Mhz (*13*). The measurements of $\Delta\nu$ at 318 and 408 Mhz are, within the limits of error, consistent with the expected λ^{-4} dependence of $\Delta\nu$.

These observations suggest that the widths of the power spectra and the decorrelation frequencies for CP 0834, CP 1133, and AP 1237, determined from averages over 50 pulse intensities, are accurate measurements of the parameters of a scintillating medium. Although the observations of CP 1919 result in similar values for these parameters, it is apparent from Fig. 3 that this source probably has long-term fluctuations in pulse intensity which arise both at the pulsar and in the intervening medium (*11*). During observations of these pulsars, scintillations due to irregularities in the solar wind caused very weak intensity modulations with time scales of less than a minute. Consequently, the interplanetary medium cannot account for the observed scintillations. If we assume that the scintillations are due to interstellar irregularities that travel at a velocity $V \approx 20$ km/sec, attributable to the relative motion of the pulsar or the medium, or both, with respect to the earth, then our measurement of $\sqrt{2} V\phi_0/a$ at 318 Mhz (Fig. 1) leads to $a/\phi_0 \approx 4 \times 10^4$ km. If we substitute $\Delta\nu =$ 1.5 Mhz at a radio frequency of 318 Mhz and $a/\phi_0 \approx 4 \times 10^4$ km into the equation for $\Delta\nu$, $z \approx 70$ parsecs. A reasonable estimate for the distance d of the pulsar from the earth would be $d \approx 2z \approx 140$ parsecs. This estimate for d is consistent with estimates of pulsar distance based on dispersion measurements (*1, 6, 14*). These interstellar scintillations would not have been observed if the apparent angular diameter of the pulsars were larger than $a/\phi_0 z \approx 0.3 \times 10^{-5}$ second of arc. The scintillations would cause even a point source to appear to have an angular size

$$\theta_{\rm scat} = \phi_0 \lambda / 2\pi a$$

of $\approx 10^{-3}$ second of arc at 318 Mhz. Interstellar scintillation may therefore establish an important limit to the detectable angular size of a radio source.

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Divalent Phosphate Electrode

Abstract. *Divalent phosphate ion activities can be measured in dilute aqueous solutions in the physiological* pH *range (7.0 to 7.5) with a liquid ion-exchange membrane electrode system; the organic ion exchanger consists of an amine chloride membrane. Reference solutions may be either aqueous chloride or bicarbonate solutions. An essentially Nernstian slope is obtained.*

We present here data for two liquid ion-exchange membrane systems which serve as electrodes selective for divalent phosphate in an activity range from 10^{-4} to $10^{-2}M$ monohydrogen phosphate in the presence of $10^{-2}M$ chloride. With no chloride present, sensitivities as low as $10^{-5}M$ divalent phosphate are obtained. The systems permit the direct determination of the activities of aqueous solutions of the divalent phosphate ion in certain mineral systems and in biological systems where the monovalent ion concentrations are below 10 meq/liter. Whereas earlier systems (*1*) have exhibited sensitivity and linearity but not selectivity for phosphate anions, our systems are both sensitive and selective in the ranges described.

The indicator electrode consisted of an Orion calcium electrode barrel (model 92-20) into which the appropriate organic ion exchanger and aqueous reference phases were inserted. An Orion membrane (model 92-20) was used to support the organic ion exchanger. The reference electrode was a saturated calomel cell.

The potentials of the calibration solutions were measured in the Orion microsample dish at ambient temperatures ($25° \pm 2°$C) with an Orion model 401 meter. The Beckman microassembly was used for *p*H determinations.

Calibration and reference solutions were prepared from reagent-grade chemicals and distilled water. Solutions of the potassium salts of mono- and dihydrogen phosphates, and of sodium chloride, were mixed to yield the desired anion concentrations at a *p*H of 7.2. Solutions were then stored anaerobically in capped Luer-Lok syringes. Under these conditions, the *p*H could be maintained for several days. Activities of the anions were computed from the extended Debye-Hückel equation and the mass action activity coefficients for phosphoric acid (*2*).

The first system consisted of a primary amine (Rohm & Haas XLA3) which was partially converted to the hydrochloride by the addition of one equivalent of concentrated HCl to 2.1 equivalents of the amine; the mixture was stirred at 50°C for 30 minutes. The temperature of the resulting emulsion was then raised gradually, during a period of an hour, to 110°C. The heat was removed, and the clear, oily product was injected immediately into the electrode chamber. The membrane became transparent. An aqueous NaCl reference solution ($0.025M$) was used, and the system was conditioned overnight in an external solution of the same composition.

The second system consisted of a quaternary amine chloride (General Mills Aliquat 336). The amine was used as received. The internal refer-

Table 1. Behavior of divalent phosphate electrodes at 25°C; electrode potential, millivolts; activity, *a*.

Ion exchanger (chloride salt)	Activity range of HPO_4^{2-} for linear response	Slope (mv/log *a*)
Primary amine (XLA3, Rohm & Haas)	2×10^{-4} to $1 \times 10^{-2}M$; 2×10^{-3} to $1 \times 10^{-2}M$ in the presence of 10 meq/liter of Cl^-	33
Quaternary amine (Aliquat 336, General Mills)	5×10^{-4} to $1 \times 10^{-2}M$ in the presence of 10 meq/liter of Cl^-	30