valence band into the defect level. Such transitions would lead to the monotonic increase in absorption with photon energy that we observed. The strength of the absorption observed [a cross section of 6×10^{-17} cm^2 per exposed molybdenum atom (*7*)] is consistent with other similar defects if every surface site undergoes transitions.

These data on the electronic structure of the edge surface have important implications for our understanding of catalysis in the transition metal sulfides. Such reactions are known to occur on the edge surface (*17*) and are correlated with the optical absorption we have observed (*7*). The presence of reduced molybdenum species such as Mo^{3+} at the surface is consistent with the "sulfur vacancies" that are often hypothesized as catalytically active sites (*18*). In fact, W^{3+} (which is isoelectronic with Mo^{3+}) has been correlated with activity in sulfide catalysts in electron spin resonance studies (*19*).

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Solar Irradiance Change and Special Longitudes Due to *r*-Modes

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Sluggish global oscillations, having a periodicity of months and trapped in the sun's convection zone, modulate the amount of energy reaching Earth and seem to impose some large-scale order on the distribution of solar surface features. These recently recognized oscillations (*r*-modes) increase the predictability of solar changes and may improve understanding of rotation and variability in other stars. Most of the 13 periodicities ranging from 13 to 85 days that are caused by *r*-modes can be detected in Nimbus 7 observations of solar irradiance during 3 years at solar maximum. These modes may also bear on the classical question of persistent longitudes of high solar activity.

Two solar problems of high interest early this century were never solved. The challenging observations had no convincing explanations. Perhaps as a consequence, their study became unfashionable at the main research centers. First, solar activity (sunspots and flares) tends to occur at certain preferred longitudes, and second, it seems multiperiodic, at periods other than the 11- or 22-year cycle. Although few investigators thought that many true periods were plausible, some did accept the evidence for preferred (*1*) and rigidly rotating (*2*) longitudes, in spite of the paradoxical nature of this idea in a gaseous sphere whose surface so clearly fails to rotate rigidly. Today, new explanations are possible that involve convection and global oscillations of its mass (*3*). These oscillations rotate like rigid bodies, creating special longitudes with their nodes and antinodes. The sun's heat rises by convection through a layer thought to occupy at least the outer 25% of its radius. At depth, these flows are massive and have the energy to dominate the thin surface layers, affecting the local brightness and the number and location of surface blemishes. All this can be modulated by a system of global oscillations that corresponds with measured periods in the sun's irradiance and is consistent with rotation of large surface features. Our results demonstrate that periodic global oscillations, called *r*-modes, are indeed strong enough to modulate convection, making irradiance and surface blemishes similarly periodic in longitude and time.

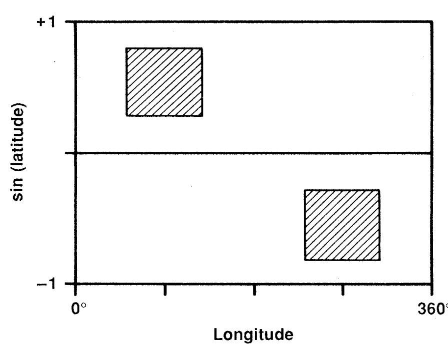

Fig. 1. Map of a complete solar surface showing schematically the areas (shaded) of atypical brightness where convection tends to be enhanced by a family of *r*-modes. The pattern rotates rigidly at a known rate. Smaller scale structure is ignored because of its lesser influence on irradiance, which is an integral over a solar hemisphere.

An *r*-mode (*4*) is a toroidal oscillation of swirling horizontal motions whose period is at least as long as the star's rotation period. "*r*-Modes," "Rossby waves," and "inertial oscillations" are basically the same physical phenomenon differing in geometric approximations or history of derivation. The restoring force (Coriolis) conserves angular momentum while other forces (compression and buoyancy) are negligible. Such modes have been studied for a uniformly rotating star (*5–7*) and specifically for the sun (*8*). Their strong interaction with convection is almost certain because the size, vorticity, and period of the *r*-mode are all comparable (*8*) with that of large deep convection cells. This would cause the sun's total luminous output to fluctuate and parts of its surface to change brightness on long time scales derivable from *r*-modes, contradicting the widespread assumption that convection is stochastic over intervals that much exceed the turnover time of a typical cell (*9*). As a test, one can ask: Does solar energy reaching Earth display periodicities consistent with the surface distribution of *r*-modes and their rotation law?

The apparent (synodic) rotation rate of an *r*-mode is (*8, 10*)

$$\nu = \nu_s \left[1 - \frac{2}{\ell(\ell + 1)}\right] - \nu_e \qquad (1)$$

where ν_s is the mean sidereal rotation rate of the sun's envelope, $\nu_e = 31.7$ nHz is the orbital rate of Earth and ℓ is the principal

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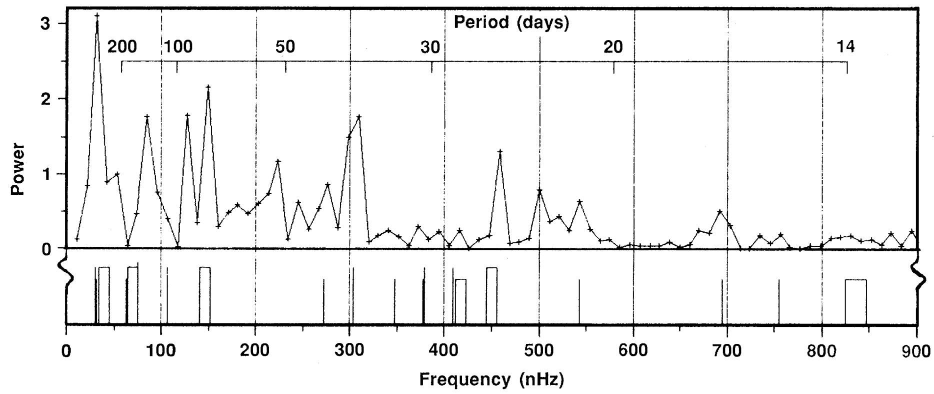

Fig. 2. The power spectral density of solar irradiance residuals near solar maximum (upper panel) is locally high at almost all 13 *r*-mode frequencies (lower panel) lying in the less complex region above 135 nHz. The *r*-modes appear responsible for a major fraction of the variance in irradiance.

index of the spherical harmonic defining the mode. The azimuthal index, m, is not included in Eq. 1 because the calculations presented here require an accuracy of only three significant figures and no high radial harmonics. Therefore, modes having the same value of ℓ will appear to be one rigidly rotating entity, or "family," whose special longitudes cause luminous fluctuations to regularly face Earth at the rates $m\nu$ ($m = 1, 2, \ldots \ell$). These have been called repetition rates (*8*). Those rates for $m < 3$ give the largest rotational modulations since irradiance is an integral of the entire visible hemisphere. Moreover, a study of *r*-modes originally excited by a large convection cell at mid-latitudes (*11*) shows that the largest scale symmetry possessed by any family with a low ℓ value can be represented schematically by Fig. 1 (*12*). One of the two shaded areas in Fig. 1 can be more effective. Clearly, such a brightness distribution modulates irradiance at ν and 2ν as it rotates (*13*). For these reasons, ν and 2ν are used in the analysis. There is some evidence for the families $\ell = 2$ and 3 during the maximum phase of most solar cycles in this century (*14*).

Solar energy reaching Earth varies. Irradiance has been monitored since 16 November 1978 by the cavity pyrheliometer of the earth radiation budget (ERB) experiment aboard the Nimbus 7 satellite (*15*). It senses about 1370 W m^{-2} at mean distance from the sun. The instrument is regularly calibrated by using an internal heater, and the readings have remained stable for more than 7 years (*16*). Four-day averages of the irradiance have high precision in almost every point and show real changes from week to week of ~0.1%. Uncertainty is caused mainly by truncation in the spaceborne electronics. The truncation error in almost every 4-day average is less than ±0.02%. This data set also contains a mean linear trend of about −0.016% per year, perhaps due in part to a decline in the present 11-year cycle. Subtracting the linear trend from the 4-day means leaves "residuals"—the actual quantity to be scanned for periodicity. The first 3 years of residuals lie at the maximum of the 11-year cycle where irradiance fluctuations are strong and frequent. After the maximum, fluctuations decline. Only years of solar maximum will be analyzed to avoid mixing data of differing character and because data from other maximums seem to show *r*-modes. The Fourier spectrum of the residuals for the 3-year interval after mid-November 1978 is shown at the top of Fig. 2. Strong periodicities between 37 and about 400 days are obvious as well as some noticeably higher power at other periods. Many spectral lines are only one resolution element wide, so, whatever their physical cause, it must have persisted nearly 3 years or longer.

We can compare the observed spectrum with properties of the simplest *r*-mode families, $\ell = 1$, 2, 3, and 4. Table 1 lists their synodic rotation frequencies and periods. These values are derived from Eq. 1 by using $\nu_s = 455$ nHz, a synodic solar rotation period of 27.3 days. Equation 1 also shows that an infinite number of high ℓ families crowd into a finite frequency range. This possibly significant group of high harmonics, labeled H, consists of any power lying within one observational resolution element (11 nHz) of $\ell = \infty$. The five features in the table should influence irradiance at ten synodic rates (ν and 2ν) and ten beat frequencies. The beats, $\nu - \nu'$, are the rates at which active longitudes of any two families (ℓ and ℓ') overlap and interact nonlinearly as a result of their exchange of energy with convection. All 20 are plotted on the lower part of Fig. 2 at slightly different heights for clarity and with beats drawn 30% higher. For example, the lines at 348 and 695 nHz are caused by the $\ell = 3$ family, while the band covering 141 to 152 nHz is the beat between H and $\ell = 2$. Above 135 nHz there is excellent agreement with the observed spectrum. Most of the 13 theoretical frequencies here lie near the centroid of an observed power peak. Below 135 nHz agreement is not expected because of interference among closely spaced lines, especially the multitude (*17*) from *g*-modes (unresolvable here and omitted). In another report, we add in *g*-modes of low ℓ that produce new theoretical lines (*18*). Some lie between 200 to 300 nHz and near 520 nHz where power is not explained on Fig. 2.

Table 1. Apparent rotation of *r*-modes oscillating in the sun's convection zone.

ℓ	Rate (nHz)	Period (days)
1	−32	−365
2	272	42.6
3	348	33.3
4	378	30.6
H	412–423	28.1–27.3

Could the agreement be accidental? The following rather general test is suitable for multiperiodic systems. If some observed peaks are mere noise fluctuations but not known as such, the method statistically underestimates the quality of the model. In the region of interest above 135 nHz the observed spectrum has 21 maximums near or above a power level of 0.2. Of these, 19 seem to be single high points while two are more fairly viewed as broad. Of these two, the one at 300 nHz consists of two high points and the other near 825 nHz consumes, at most, five points of the spectrum. Thus spectral peaks occupy ≤(19 + 2+ 5) points out of a total of 72, making the probability, $P \leq 26/72 = 0.361$, that a randomly chosen frequency in this range will accidentally agree with an observed peak. Then, the binomial expression gives the probability that k frequencies out of a total of n will agree by accident

$$C = n!\ [k!(n-k)!]^{-1}\ P^k\ (1-P)^{n-k} \quad (2)$$

Before evaluating Eq. 2 for our system of 13 theoretical frequencies, one of its ten successful lines will be removed to account for the model's free parameter ν_s, which guarantees that one line can always be made to agree. This leaves $n = 12$ and $k = 9$ for which $C = 0.006$. Such a low probability means the agreement is real with a confidence level of about 3σ. Further confirmation of the model is now shown with an independent data set.

The irradiance time series responds to both true changes on the sun and the mere rotation into view of a constant surface feature with nonaverage brightness. Pure rotation (the five rates of Table 1) can be directly tested for with the extensive series of solar surface maps in the light of H_α constructed by McIntosh (*19*). The published sequence (*19*) of maps, superposed at epochs of 27.3 days for the years 1965 to 1974, dramatically shows the persistence of large-scale patterns whose rotation periods can be accurately measured if they are in the approximate range of 23 to 32 days. There are 11 prominent cases where the rotation period is constant for at least 1 year. Of these, four cluster about a rotation period of 30.3 days with a 3% spread from lowest to highest, closely corresponding to the family $\ell = 4$ in Table 1. Six others form a broader cluster (6% spread) centered on a 27.8-day period, agreeing with H in Table 1. The eleventh period, at 32 days, was hardest to measure accurately and agreed with nothing in the model. Thus, these maps contain good evidence for at least two preferred longitudes simultaneously rotating at different, constant rates agreeing with theory. Replotting the maps at longer epochs would allow testing for the lower ℓ families.

In summary, global *r*-modes appear to have a strong influence on the outer layers of the sun. More than half the variance in irradiance at periods of 13 to 85 days could be attributed to *r*-mode families. Since only a single free parameter (ν_s) determines the value of all theoretical frequencies plotted on Fig. 2, the statistical significance of the agreement is rather high. This agreement confirms a preliminary detection (*14*) of two *r*-mode families in this century's sunspot area records. Also, evidence shows that *r*-modes with $\ell > 3$ cause persistent longitudes for large-scale surface features. By inference, *r*-modes have forced their periodicities onto convection, perhaps by assisting the initial growth. If this is true, a modification of convection theories on rotating bodies would be needed. If our identification of *r*-modes is correct, it determines a mean sidereal rotation rate for the sun's convective envelope of $\nu_s = 455 \pm 5$ nHz during the 3 years after 16 November 1978. This rate corresponds to a sidereal rotation period of 25.4 days (=27.3 days, synodic), and the above 1.1% uncertainty is the maximum deviation over which the agreement on Fig. 2 still holds.

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Correlation of Volcanic Activity with Sulfur Oxyanion Speciation in a Crater Lake

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The Yugama crater lake at Kusatsu-Shirane volcano, Japan, contains nearly 2200 tons (2800 parts per million) of polythionate ions ($S_nO_6^{2-}$, where n = 4 to 9). Analytical data on lake water sampled before and during eruptions in 1982 showed that the concentrations of polythionates decreased and sulfate increased in response to the preeruption activities of the subaqueous fumaroles. These changes were observed 2 months before the first phreatic explosion on 26 October 1982. The monitoring of polythionates and sulfate in crater lake water is a promising means of anticipating potential volcanic eruption hazards.

AS EMPHASIZED BY VERHOOGEN (*1*), it has been difficult to forecast volcanic eruptions because of many unknown factors controlling the time, place, and character of eruptions. Investigators have accumulated statistical records of volcanoes as well as their day-to-day vital signs in terms of earthquakes, surface deformation, temperature, and gas emissions. This report deals with dynamic formation and decomposition of sulfur oxyanions such as polythionates and sulfate ions in a crater lake in Japan. These anions exhibit sharp responses to the preeruption activities of the volcano. This reaction suggests that monitoring of the oxyanions can aid in forecasting possible volcanic hazards such as the disastrous mud streams that were triggered by a lake-bottom eruption, which killed more than 5000 people and damaged 104 villages, at Mount Kelud on Java Island in 1919 (*2*).

Kusatsu-Shirane is an active volcano located 153 km northwest of Tokyo. Many people visit the area for sight-seeing or skiing throughout the year. The volcano has three active craters, Mizugama, Yugama, and Karagama, from northeast to southwest (Fig. 1). A sequence of phreatic explosions at these craters has been recorded since 1805 (*3–5*). The central crater, Yugama, contains a lake, which has an average diameter of 270 m and is 27 m at the deepest point. Almost no vertical temperature variation was noted in the lake water (*6*). Molten sulfur was found at subaqueous fumarole vents where volcanic gases are violently discharged. The bottom temperatures at these gas vents have therefore exceeded 116°C (maximum observed temperature was 140°C) (*7*).

The lake water contains a variety of salts, fine particles of sulfur, and hydrochloric and sulfuric acids whose total acidity is almost 0.1*M* (Table 1). Major anions that have been detected in the water include chloride and sulfate. In analyses of the lake water, unidentified sulfur-containing anions have been expressed as equivalent to total sulfate after oxidation by hydrogen peroxide. Data for no. 1 of Table 1 show such an analysis with total equivalent sulfate (*8*).

In order to identify unknown sulfur compounds in the crater water, the water was analyzed by liquid chromatographic techniques. Detailed analytical conditions are described in the legend of Fig. 2. All the water analyzed was sampled at the fixed site on the lake shore without any pretreatment. No distinct difference in concentrations of the oxyanions has been detected among the samples taken at four to six other sites along the lake shore, but slightly higher concentrations of sulfur oxyanions were observed

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