

vaporization and ejection of large amounts of lunar and meteoritic material, or with any other mechanism that transports material out of a crater. This further indicates that only partial isostatic compensation has occurred. The highland ridges produce local relative, positive accelerations at these low altitudes. (These features had been lost in the broad negative background observed previously at higher altitudes.) The best example is the +20-mgal "ridge" at +15° longitude. This correlates closely with throwout shown on the preliminary lunar geological map of the U.S. Geological Survey. A low-altitude (25 to 50 km) subsatellite with S-band transponder would permit one to map large portions of the lunar surface to a resolution which is capable of producing geophysically significant information and correlations with other lunar data.

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"Polywater": Possibility of p-Electron Delocalization

Abstract. *p-Electron delocalization may be important in determining the stability of the symmetric hydrogen bonds in a recently proposed model of "polywater."*

Lippincott *et al.* (1) have suggested a model for "polywater" in which symmetrical hydrogen bonds (O...H...O) are the basic components for constructing planar networks of hexagonal units. This model was criticized by Donohue (2) on the basis that eight different

Table 1. Calculated stabilization energy and bond order.

Calculation	Energy stabilization, O...H...O bond unit (kcal/mole)	Bond order, O...H
1	16.1	0.60
2	118.9	0.78

forms of ice and numerous hydrates have an angle between adjacent hydrogen bonds very near the tetrahedral angle, and hence that the 120° angles proposed by Lippincott *et al.* are unsatisfactory. However, similar reasoning, based on the observation of many thousands of aliphatic hydrocarbons, would lead one to conclude that ethylene is an unlikely species.

The symmetrical hydrogen bonds were postulated (1) on the basis of infrared spectra of "polywater" and by analogy to the bifluoride ion. In the case of the bifluoride ion (FHF⁻) a theoretical study and calculation by McLean and his co-workers (3) show that delocalization of the "lone-pair" *p*-electrons on the fluorine atoms takes place. This suggests that π -bonding is partially responsible for the unusual stability of the bifluoride hydrogen bonds.

This same sort of *p*-electron delocalization is possible in the model of polywater proposed by Lippincott *et al.* (1). The delocalization of the *p*-electrons on oxygen can be thought of as being transmitted by a hydrogen atom between any two oxygen atoms. This requires that the hydrogen atoms have some *p*-character. In the calculations for FHF⁻ hydrogen was indeed found to have such *p*-character (3).

The model, consisting of planar networks of hexagonal units (1), seems to be an ideal circumstance for the delocalization of the *p_z* electrons on the oxygens throughout the network to form a *p*- π band. This is analogous to what occurs in graphite, except that the bandwidth and occupation of the band would be different. On the basis of this model the electronic conductivity of "polywater" is expected to be significantly larger than that for normal water. Unfortunately, no conductivity measurements on "polywater" have been reported to date.

The prior theoretical calculations on "polywater" have been of the CNDO/2 (4) and INDO (5) types of semiempirical calculations, proposed by Pople and his co-workers (6), and have not

made it possible to determine whether the *p*-character of the hydrogens is important.

In the work reported here very approximate assessment was obtained of the importance of *p*-character in the hydrogen bonds. Calculations of the CNDO/2 type were modified to allow specifically for *p*-character in the hydrogens (7). The calculations for the (H₂O)₆ hexagonal unit are summarized in Table 1. In calculation 1 the O...O distance was taken as 2.3 Å with the internal hydrogens placed symmetrically between the oxygen atoms. For a symmetrical hydrogen bond a distance between the two oxygen atoms of 2.3 Å gives a minimum in the energy. The external hydrogens were placed at 0.96 Å from the oxygen (the experimentally observed O-H distance in normal H₂O). All angles were taken to be 120°. Calculation 1 was a normal CNDO/2 calculation. Calculation 2 was identical to calculation 1 except that an extra basis function (a *p_z* orbital) was centered on the hydrogen atoms involved in hydrogen bonds.

Calculation 2 (Table 1) leads to a very large increase in stabilization. This large increase could be very much in error, however, because the basis set on hydrogen has been increased (by the addition of a *p_z* orbital) whereas the set of orbitals on the oxygens has been kept fixed. This procedure leads to an unbalanced basis set which can lead to an overestimation of the charge density in the vicinity of the hydrogen atom. Since the CNDO/2 method with the use of extended basis sets has not been calibrated against *ab initio* calculations in any published studies, it is difficult to estimate the error involved in the procedure used here. Although the numerical values obtained are certainly not quantitatively correct, the qualitative feature that *p*-electron delocalization can have a stabilizing effect could indeed be correct.

The stabilization energy is calculated by taking one-sixth of the difference between the binding energy of the (H₂O)₆ unit and six times the quantity (the binding energy of the H₂O unit, with no *p_z* orbitals on the hydrogens, at the experimentally determined geometry of an isolated H₂O).

The results presented in Table 1 may be compared with the estimates of Lippincott *et al.* (1) of a stabilization energy of 60 to 100 kcal/mole and a bond order of 2/3. The effect of *p*-electron delocalization also explains the recently

obtained proton magnetic resonance spectra of polywater (8), since the ring current causes a deshielding of the end protons which will produce a downfield shift of the right magnitude. A definitive and quantitative assessment will require that *ab initio* calculations, with balanced basis sets of the type carried out for the bifluoride ion system (3), be performed on these models of "polywater" to ascertain fully the importance of the effect discussed here.

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Vocal Imitation and Individual Recognition of Finch Calls

Abstract. American goldfinch females recognize individual males by their individually distinctive flight calls. Goldfinches and other cardueline finch species are also capable of learning new flight calls by imitation during pair and flock formation. Vocal imitation can occur between members of different species as well as between members of the same species. Learning of new flight calls differs in several respects from typical passerine song learning.

Traditionally, bird vocalizations have been classified as songs or calls. Most songs are rather long, complex, territorial defense, and mate-attracting signals primarily sung by males in reproductive condition; calls are generally shorter, simpler signals, and many calls are neither restricted to a given season nor to a given sex (1). Normal song development in many passerines involves learning (2). Such song learning is generally characterized by: (i) a predisposition to learn the species-typical pattern, (ii) a "critical period" in the young male's first year when learning must occur, and

(iii) the absence of further modification of song pattern once song has "crystallized" and the critical period has passed (3). In contrast to song, bird calls are generally considered to be inherited, unlearned species-specific signals (2), although a few apparent exceptions are recorded (4). In this report I present evidence that several species of cardueline finches learn new flight calls by imitation. Unlike song learning, the learning of new flight calls is not restricted to a critical period; an individual bird continues to learn new calls throughout its lifetime.

I recorded and analyzed on the sound spectrograph changes in the flight calls of individual adult European siskins *Carduelis pinus*, American goldfinches *Carduelis tristis*, and pine siskins *Carduelis pinus* (5). All three finches possess flight calls which a field observer usually hears when flocks or isolated individuals are in flight but which may also be given when the birds are perched. When perched, these birds usually give flight calls just before or after flight, although these calls may also occur in other perched situations, such as during courtship feeding (6). Flight calls are species-specific, but, within the constraints of species specificity, they are also individually variable. For example, sonograms of representative flight calls of 24 male American goldfinches recorded from populations breeding in fields near Ithaca, New York, and Oxford, Ohio, revealed that each male possessed one to three versions of the flight call, at least one of which was individually distinctive. This individual variation in flight call patterns of goldfinches permits individual recognition, which facilitates the coordination of the reproductive behavior of nesting pairs.

Individual vocal recognition can be demonstrated in the field with free-flying, breeding adults. During the nesting season, incubating and brooding female goldfinches are regularly fed at the nest by their mates. By vocal and postural display these females solicit immediately prior to and during a bout of feeding, and the male's flight call is one of the stimuli that evokes this soliciting. The following field experiment tested whether a given female goldfinch solicits only in response to her mate's flight call, or to the calls of other males. Fourteen experimentally naive incubating females were tested by playback of tapes that presented 10 seconds of the mate's flight call (a sequence of five calls); 30 seconds of silence; and then, as a control, 10 seconds of five flight calls from a different male (7). The occurrence of female soliciting during or immediately following playback of a given sequence of five flight calls was scored as a positive response; silence during and immediately following playback of a sequence of five calls was scored as no response. All fourteen females failed to respond to the flight call of the control male, but seven of these females responded positively to playback of their mate's flight call. Females discriminate between the flight call of their mate and those of other

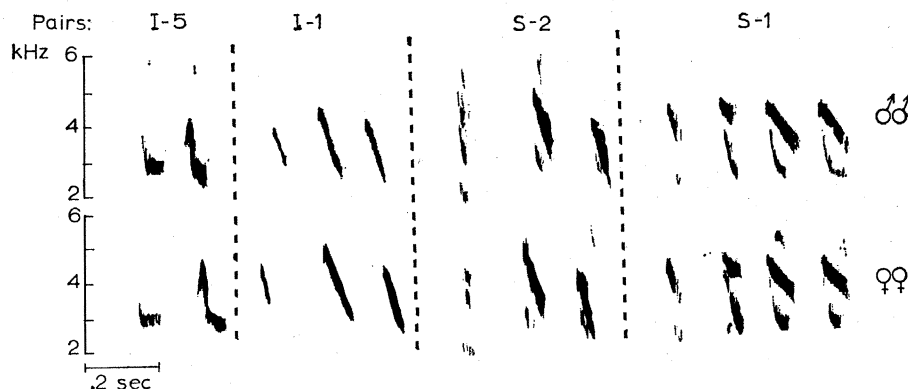


Fig. 1. Similarity of call pattern within pairs of wild American goldfinches. All pairs nested in 1967 in fields near Ithaca, New York. Pairs I-5 and I-1 were neighbors in one field, and S-2 and S-1 were neighbors in a second field. The spectrographic analysis of sounds illustrated in this and following figures presents frequency along the ordinate and time along the abscissa.