sary to choose an ion, such as ruthenium(II), whose Δ is high but whose oxidation potential is sufficiently low such that a d-π^* state becomes the lowest excited state in the molecule. Finally, to obtain π-π^* emission one must select a system with a substantial crystal-field splitting (in order to keep the d-d levels high in energy) and with an oxidation potential of the central ion that is high enough to prevent a d-π^* state from becoming the first excited configuration. The lowest excited state in the molecule then becomes π-π^* in nature, and the characteristic π-π^* emission appears.

Although in the past all three types of emission have been observed from molecules containing ions with a d^6 configuration, it has been necessary to change the central metal ion in order to obtain the oxidation potentials and ligand-field splittings necessary for a proper disposition of the excited levels. Recently, however, we have been able to obtain a d-d, a CT, or a π-π^* emission from complexes of the same metal ion, iridium(III), by a chemical modification of its ligand environment.

In Fig. 1 we have plotted the absorption and luminescence spectra of three different iridium complexes, all containing *o*-phenanthroline or substituted *o*-phenanthroline as part of the ligand system. In each molecule the iridium ion feels a potential dictated by the total ligand environment. Excitation of any of the three species at 77°K in a glass results in a luminescence which has been plotted in Fig. 1. We see that the photoluminescence observed from these three molecules is radically different in nature. In curve a the luminescence has structure and decays with a measured mean life of 190 ± 5 μsec. This luminescence occurs in a region of the spectrum that is very close to the emission from the 5,6-dimethyl-1,10-phenanthroline molecule itself, and we assign it to a π-π^* emission. The slight red shift (~ 400 cm^{-1}) from the luminescence of the solvated ligand is due to the perturbation of the π-π^* state by interaction with d-π^* states and the metal ion. In curve b the emission has a prominent vibrational progression and decays in 6.92 ± 0.05 μsec at 77°K. A quantum-yield measurement shows the radiative life to be ~ 14 μsec (*6*). These properties are characteristic of the emission observed from complexes of ruthenium(II) at 77°K; the latter are known to be CT transitions. We thus believe that the lowest excited state in this iridium(III) molecule is d-π^* in nature. Curve c shows the emission from the tetrachloro(1,10-phenanthroline)iridium(III) complex ion. Here the observed luminescence band is broad, structureless, almost gaussian in shape, an indication that the emission originates at an excited d-d level.

Figure 1 demonstrates that it is possible to change the nature of the low-lying excited states of the complexes of the same metal ion in the same oxidation state from π-π^* to d-π^* to d-d by a suitable chemical modification of the environment of the central species. We have also achieved π-π^* emission from the porphyrin and dibenzoylmethide complexes of iridium(III) and d-d emission from several iridium(III) species containing pyridine and halides as ligands.

The present study shows that it is possible to design luminescent materials of a single metal ion that have predetermined optical properties. By a proper choice of ligands and chemical structures one can "tune" the frequency and characteristics of the emitted light. There is every reason to believe that this kind of molecular design can be carried out for many other ions to yield a host of luminescent materials having varied but selected optical properties.

A second implication of this work lies in the field of photochemistry. Since the lowest-lying excited states certainly must be involved in some of the photochemical reactions that inorganic complexes undergo, these results demonstrate that it is possible to design molecules containing the same metal ion in which the lowest-lying excited states are substantially different in nature. One may then be able to use such molecules as photochemical energy donors or even possibly as subjects for the study of the photochemistry of inorganic materials.

A further area of research that could be guided by these principles is the field of analysis by fluorescence or phosphorescence. The results presented here establish guidelines for developing new sensitive luminescent indicators.

Finally, the demonstration above clearly shows the efficacy of using several spectroscopic parameters, such as mean decay time, quantum yield, and band structure as diagnostic tools for assigning the orbital natures of the excited states of complexes. For many molecules the results are far less ambiguous than assignments based on absorption spectroscopy alone.

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How Did Venus Lose Its Angular Momentum?

Abstract. *Venus now has a retrograde and negligible spin, but it very likely started with a typical planetary spin: prograde and with a 10- to 20-hour period. The usually assumed mechanism of solar tidal friction is quite insufficient to remove this angular momentum. Instead, we postulate capture of a moonlike object from an initially retrograde orbit: it would despin Venus and suddenly transform the planet's rotational kinetic energy into internal heat, which would lead to volcanism and the liberation of large amounts of volatiles. The moon would disappear by crashing into the surface of Venus.*

The planet Venus occupies a quite anomalous position in the solar system by having a spin angular momentum that is clearly retrograde. Since the first radar measurements at the Jet Propulsion Laboratory in 1962 by Carpenter and Goldstein, it has become apparent that Venus has a sidereal period of 243.09 ± 0.18 days; the rotation vector is retrograde and inclined by 1.2° from the normal to the orbit plane and by 2.2° from the normal to the ecliptic (*1*). All other objects in the solar system have rotation periods measured in terms of hours, with two exceptions: (i) Mercury, whose spin period is believed to have been affected by solar tides until it became nearly 59 days, precisely two-thirds of its orbital period, where it is now locked in by a resonance effect (*2*); (ii) Pluto, which has a period of about 6.4 days, possibly explained by the hypothesis that Pluto is an escaped satellite of Neptune (*3*).

Earth and Mars have rotation periods of the order of 24 hours; Jupiter, Saturn, and Uranus, of the order of 10 hours; and Neptune, about 16 hours. It should be noted that Uranus has a spin axis that is inclined to the orbit plane by 98°, but all other objects show a prograde rotation. Alfvén has summarized the known rotation periods of the asteroids, which vary between 3 and 17 hours; in only three of the 27 cases does the rotation period vary by more than 50 percent from a mean value of about 8 hours (*4*). This uniformity of rate of rotation for most of the planets and large asteroids is remarkable in view of the wide variations in mass, orbits, and moments of inertia. It reinforces the currently popular theories of the origin of the solar system, whereby the planets were formed by accumulation of the material contained in a disklike nebula that orbited the sun. In these condensations, the planets would end with prograde spins—that is, with an angular momentum vector parallel to the orbital angular momentum. This conclusion depends critically on the angular velocity of the disk material as a function of distance from the sun, as well as on the shape of the original mass distribution (*5*).

If we then assume that Venus had a primordial spin period of between 10 and 20 hours and was spinning prograde, the question that immediately arises is how this angular momentum has been lost. This question has not attracted much detailed attention, since the greatest interest has focused on the possibility that the earth controls the present value of spin of Venus (*6*). It is most often assumed that the kinetic energy of rotation was dissipated by tidal friction due to gravitational tides raised on Venus by the sun (*7*). Yet, as we shall see, this explanation does not hold up under detailed examination.

It is convenient to use the earth-moon system as a model. The energy dissipated by earth tides per second, $\dot{E}$, can be calculated from the work done by the torque that the moon exerts on the earth's tidal bulges (*8*).

$$\dot{E} = -1.5\, k_2\, G\, m^2\, (R^5/a^6)\, (\omega - n) \sin 2\delta \tag{1}$$

Here k_2 is the tidal Love number, ~ 0.3; G, the gravitational constant; m, the mass of the moon; R and ω, the earth's radius and angular velocity, respectively; and a and n, the moon's semimajor axis and mean motion, respectively. Substituting numerical values gives

$$\dot{E} = -3.5 \times 10^{20} \sin 2\delta \quad \text{erg/sec} \tag{2}$$

and comparison with present tidal dissipation of 2.7×10^{19} erg/sec requires $2\delta = 4.5°$, or $Q = 12.5$.

Substituting Venus for the earth, and the sun for the moon, gives

$$\dot{E} = -4.46 \times 10^{20} \sin 2\delta \tag{3}$$

when the same value of ω is assumed. In general, with n negligible,

$$\dot{E} = -K_1\, \omega \sin 2\delta \tag{4}$$

where $K_1 = 6.12 \times 10^{24}$.

The value of $\sin 2\delta$ is uncertain. Its large value for the earth is very likely due to the large energy dissipation at the ocean-land boundaries. In the absence of liquid oceans on Venus, $\sin 2\delta$ may be one-tenth or less of the terrestrial value, which corresponds to $Q \geqq 125$; that is, $(\sin 2\delta)_V = 7.9 \times 10^{-3}$, where subscript V is Venus.

One further point is the dependence of $\sin 2\delta$ on the planet's angular velocity (*9*). If, instead of assuming a fixed value, we model the simplest linear dependence, then (neglecting n)

$$\sin 2\delta = K_2\, \omega \tag{5}$$

where $K_2 = 1.08 \times 10^2$, and

$$\dot{E} = -K_1 K_2\, \omega^2 = -6.6 \times 10^{26}\, \omega^2 \tag{6}$$

The kinetic energy of rotation is

$$E = \tfrac{1}{2}\, C\, \omega^2 \sim 0.2\, M\, R^2\, \omega^2 \sim 3.6 \times 10^{44}\, \omega^2 \tag{7}$$

where C is the polar moment of inertia and M is the mass of the planet. Finally, by combining Eqs. 6 and 7, we obtain

$$E(t) = E_0 e^{-\lambda t} \tag{8}$$

where $\lambda = 2\ K_1 K_2 / C = 1.83 \times 10^{-18}$ per second, which gives a "half-life" of $T_{\frac{1}{2}} = (\ln 2)/\lambda = 12$ billion years.

Even if we assume the much higher dissipation rates appropriate to oceans, we would have a half-life of 1.2 billion years, which gives a kinetic energy loss of 16, or a diminution in spin rate of about 4, during the history of the solar system. We conclude, therefore, that solar gravitational tides could not have slowed the spin of Venus to its present value and certainly could not have produced a retrograde spin (*10*). We must therefore look for another mechanism.

A planet's angular momentum can be altered by the capture of a "moon," here understood to be a massive body. (Our moon has a mass that is 1/81 that of the earth.) In studying the origin of our moon, I have used Urey's suggestion (*11*) that many moonlike objects were originally formed in the inner solar system, along with the planets. All but one have now disappeared by impacting on a planet; our moon narrowly missed this fate and by chance has been preserved (*9*).

We may distinguish two situations:

1) A direct impact of a moon on a planet. In this case the initial angular momentum of the moon is added directly to that of the planet (except for the angular momentum of escaping ejecta).

2) A close "impact," which results in capture of the moon into an orbit that is then modified by tidal perturbations. Calculations based on a frequency-dependent tidal theory indicate that an initially retrograde orbit will not preserve the moon but will shrink into an orbit that eventually intersects the planet.

An initially prograde orbit may develop in one of two ways, depending on the impact parameter: If smaller than a critical value, the orbit will shrink into one that intersects the planet; if greater than the critical value, it will first shrink into a tight circle and then expand—presumably the fate of our moon (*9*).

To remove the spin angular momentum H of a planet, the moon must have a retrograde orbit and therefore a negative (orbital) angular momentum h.

$$H \simeq 0.4\, M\, R^2\, \omega \tag{9}$$

$$h \simeq m\, v_0\, R_0 \tag{10}$$

Here R_0 is a distance, usually less than 2 or 3 times the planetary radius R, at which the tides are strong enough to produce complete capture of a moon from a nearly hyperbolic orbit. Thus the moon's angular momentum h is closely given by the product of escape velocity v_0 and pericentric distance R_0, where

$$v_0 = (2\,G\,M/R_0)^{1/2}$$

Finally,

$$h/H = \frac{(2\,G\,M\,R_0)^{1/2}\,m}{0.4\,M\,R^2\,\omega} \qquad (11)$$

By using values appropriate to Venus (that is, $M = 4.87 \times 10^{27}$ g; $R = 6.06 \times 10^8$ cm; $\omega = 1.46 \times 10^{-4}$ sec^{-1}; $R_0 \sim 2R$), we find that for $h/H \geqq 1$, we need

$$m \geqq 1.46 \times 10^{26} \text{ g} \qquad (12)$$

This value of m is roughly twice the moon's mass and is therefore a plausible value. A larger value would, in fact, produce a retrograde spin for the planet.

The moon is fated to crash into the planet's surface and will presumably disappear. Yet a "smile of the Cheshire cat" may remain. The whole capture process occupies a time span of the order of 100 years, during which all the kinetic energy of rotation of the planet Venus is dissipated, mainly by internal tidal friction. The average energy dissipated per gram is

$$\tfrac{1}{2}\,C\,\omega^2/M = 0.2\,R^2\,\omega^2 \qquad (13)$$

Numerically this works out to be $(10^9/P^2)$ erg/g, where P is the initial spin period measured in (24-hour) days. For example, an initial 6-hour period would correspond to 1.6×10^{10} erg/g, sufficient to melt most silicate rocks.

Should events have taken place in this manner, then capture of a moon may have provided the trigger for the internal melting of Venus, for the formation of a core, and for the copious production of an atmosphere through volcanic emissions (*12*).

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Celestial Rotation: Its Importance in the Development of Migratory Orientation

Abstract. *Three groups of indigo buntings were hand-raised in various conditions of visual isolation from celestial cues. When they had been prevented from viewing the night sky prior to the autumn migration season, birds tested under planetarium skies were unable to select the normal migration direction. By contrast, when they had been exposed as juveniles to a normal, rotating, planetarium sky, individuals displayed typical southerly directional preferences. The third group was exposed to an incorrect planetarium sky in which the stars rotated about a fictitious axis. When tested during the autumn, these birds took up the "correct" migration direction relative to the new axis of rotation. These results fail to support the hypothesis of a "genetic star map." They suggest, instead, a maturation process in which stellar cues come to be associated with a directional reference system provided by the axis of celestial rotation.*

The ontogenetic development of animal orientation abilities has received very little study. Early workers were impressed by the fact that the young of many species of birds migrate alone, setting out on a course they have never traveled before without the benefit of experienced companions. This suggested that directional tendencies must develop without any prior migratory experience and therefore must be entirely genetically predetermined (*1*).

Field studies, however, point to a dichotomy of navigation capabilities between young and adult birds. When birds of several species were captured and displaced from their normal autumnal migration routes, the adults corrected for this displacement and returned to the normal winter quarters but immatures (birds on their first autumnal migration) did not (*2*). Prior migratory experience improved orientation performance.

I arrived at a somewhat similar conclusion from studies of the migratory orientation of caged indigo buntings; the consistency and accuracy of the orientation exhibited by adults was greater than that of young, hand-raised birds. (*3*). Furthermore, young birds prevented from viewing celestial cues during their premigratory development showed weaker orientation tendencies than those exposed to the natural surroundings, including the day-night sky. I speculated that the maturation process was a complex one, which involved the coupling of stellar information with some secondary set of reference cues.

The following experiments were designed to test more precisely the ability of hand-reared birds to use celestial cues and to determine the possible importance of celestial rotation in providing an axis of reference for direction determination.

Twenty-six nestling indigo buntings between the ages of 4 and 10 days were removed from their nests and hand-raised in the laboratory, where their visual experience with celestial cues was carefully controlled. I housed the birds in 2 by 2 by 2 foot (65 by