Keggin structures.[14] When a $[PO_4W_9O_{30}]^{9-}$ "half-unit" is made from a Keggin structure by plucking off three WO_6 octahedra[10] (caption, Figure 1), the PO_4 tetrahedron is free to move a little closer to the remaining W atoms. Thus in $[P_2W_{18}O_{62}]^{6-}$, formed by joining two of the 9-tungsto half-units, the P-O-W distances remain slightly shorter than in $[PW_{12}O_{40}]^{3-}$. According to recent very accurate crystal structures, the average P-O-W distance[14] in the PW_{12} complex is 3.97 Å; the average P-O-W distance[15] for the six "capping" W atoms in the P_2W_{18} complex is 3.94 Å; and the average P-O-W distance[15] from each P atom to the six "belt" W atoms closest to it is 3.90 Å. These averages are more accurate than the individual distances.

The fact that the $^2J_{P\text{-}O\text{-}W}$ values are larger for the $[P_2W_{18}O_{62}]^{6-}$ than for the $[PW_{12}O_{40}]^{3-}$ is consistent with the slightly shorter P-O-W distances in the former complex. The sharpness and simplicity (owing to $I = \frac{1}{2}$) of the spectra which yield the respective J values, as well as the differences in the δ values for the structurally very similar W atoms in these two complexes, emphasize the clarity and potential sensitivity of ^{183}W NMR for elucidating subtle structural differences.

Acknowledgments. We are grateful to the National Science Foundation for support under Grant No. CHE76-05887 and to the Spanish Fulbright Commission for partial support of one of us (R.A.). We appreciate Dr. O. A. Gansow's private communication of his results for Na_2WO_4, WF_6, and WCl_6.

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Received October 6, 1978

Optical Activity as a Mixed Parity Phenomenon

Sir:

It has been suggested that natural optical activity provides a subtle example of broken symmetry, originating in the loss of the inversion symmetry of the medium as a whole.[1] The argument rests on the requirement that an ideal stationary state (one that has an infinite lifetime and is independent of the previous history of the system) must be an eigenstate of the parity operator since it must have the full symmetry of the complete Hamiltonian of the system. Consequently, a molecule in an ideal stationary state cannot show optical activity because the corresponding rotational strength vanishes. This is because the rotational strength involves the scalar product of an electric dipole and a magnetic dipole transition moment between the same initial and final molecular states, and the electric and magnetic dipole moment operators have opposite parity. A gedanken experiment was proposed in which, on taking a resolved enantiomer of a small optically active molecule in the gas phase and doing everything possible to eliminate intermolecular interactions and increase the resolution in energy, the optical activity might disappear abruptly, signaling the observation of transitions between ideal stationary states.[2] While it may be necessary to abandon the molecular structure hypothesis in order to savor fully the implications of such a hypothetical experiment,[1,2] it is worth pointing out for the benefit of the perplexed stereochemist that, by utilizing the concept of mixed parity quantum states that are quasi-stationary in the sense that they are only stationary on the time scale of our measurements, the molecular structure hypothesis allows an individual, resolvable, chiral molecule to show optical activity.

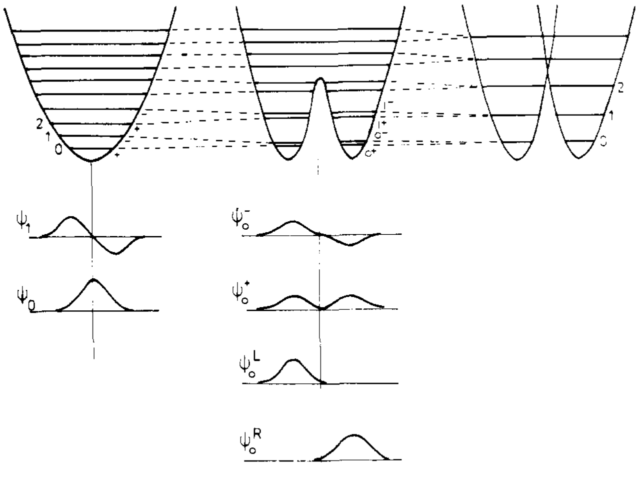

Figure 1. The vibrational states of a molecule that can invert between two equivalent configurations. $\psi_o{}^+$ and $\psi_o{}^-$ are two definite parity states for which there is complete uncertainty, and $\psi_o{}^L$ and $\psi_o{}^R$ are two mixed parity states for which there is complete certainty, about whether the molecule is in the left or right well.

Odd Parity Observables and Mixed Parity States. Although eigenstates of opposite parity can never be exactly degenerate since they can never constitute a basis set spanning a degenerate irreducible representation, nonetheless they can often be sufficiently close in energy so as not to be resolvable in particular experiments, in which case the system appears to be in a state of mixed parity. Measurements on a system in a state of definite parity can reveal only observables with even parity, examples being electric charge, magnetic dipole moment, electric quadrupole moment, etc., whereas measurements on a system in a state of mixed parity can reveal, in addition, observables with odd parity, examples being linear momentum, electric dipole moment, etc.[3] A famous example of a system that can be observed in states of mixed parity is the hydrogen atom: although the states with $n = 2$, $l = 0$ and $n = 2$, $l = 1$ are not exactly degenerate because of a small relativistic splitting, in all but the weakest electric fields[1] the first excited state of the hydrogen atom shows a first-order Stark effect, one interpretation of which is that the first excited state possesses a permanent electric dipole moment.[4]

The optical rotatory parameter is a pseudoscalar[5] and so has odd parity. It is easy to see that the optical rotation experiment conserves parity because, if one inverts the entire experiment (the light beam plus the active medium), the resulting experiment is also realized in nature.[6] Consequently, resolved chiral molecules exist in quantum states of mixed parity.

Mixed Parity States of a Chiral Molecule. The origin of these mixed parity states can be appreciated by considering

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the vibrational wave functions of a molecule such as NH_3 which inverts between two equivalent pyramidal configurations (Figure 1).[7] If the planar configuration were the most stable, the electronic potential would have the parabolic form shown on the left with simple harmonic vibrational energy levels equally spaced. If a potential hill is raised gradually in the center, the two pyramidal configurations become the most stable and the energy levels approach each other in pairs. For an infinitely high potential hill, the pairs of energy levels are exactly degenerate, as shown on the right. The rise of the central potential hill modifies the wave functions as shown, but does not destroy their parity. The even and odd parity wave functions ψ^+ and ψ^- describe ideal stationary states in all circumstances. It can be seen that the wavefunctions $\psi_o{}^L$ and $\psi_o{}^R$, corresponding to the system in its lowest state of oscillation and localized completely in the left and right wells, respectively, are obtained from symmetric and antisymmetric combinations of the even and odd parity wave functions:

$$\psi_o{}^L = \frac{1}{\sqrt{2}}(\psi_o{}^+ + \psi_o{}^-)$$

$$\psi_o{}^R = \frac{1}{\sqrt{2}}(\psi_o{}^+ - \psi_o{}^-)$$

In fact $\psi_o{}^L$ and $\psi_o{}^R$ are simply the time-independent part of the general wave function[7]

$$\psi_o = \frac{1}{\sqrt{2}}(\psi_o{}^+ + \psi_o{}^- e^{i\omega t})e^{iW_o{}^+t/\hbar}$$

taken at $t = 0$ and $t = \pi/\omega$, where $\hbar\omega = W_o{}^- - W_o{}^+$ is the energy separation of the two parity states (the tunneling splitting). Thus, if the system is prepared at $t = 0$ in the left well, after a time $t = \pi/\omega$ it will be found in the right well, ω being the frequency of a complete inversion cycle. The tunneling splitting is determined by the height of the potential barrier, and is zero if the barrier is infinite.

Since $\psi_o{}^L$ and $\psi_o{}^R$ are states of mixed parity, the origin of the mixed parity states of a resolved enantiomer is now obvious, for a potential energy diagram with a very high barrier separating the left and right wells can be drawn for any resolvable chiral molecule.[8] If such a state is prepared, but the tunneling splitting is finite, its energy will be indefinite because it is a superposition of two parity states of different energy. Using $\Delta W = \hbar/T$, where T is the average lifetime and ΔW is the width of the level corresponding to a quasi-stationary state,[9] the splitting of the two definite parity states is seen to be proportional to the inverse of the L to R conversion time (cf. the previous paragraph). A crucial point is therefore the relation between the time scale of the optical activity measurement and the lifetime of the resolved enantiomer. A manifestation of the uncertainty principle appears to arise here which may be stated loosely as follows. "If, for the duration of the measurement, there is complete certainty about the enantiomer, there is complete uncertainty about the parity of its quantum state. If there is complete uncertainty about the enantiomer, there is complete certainty about the parity of its quantum state." Thus experimental resolution of the definite parity states in an enantiomer of tartaric acid, say, which has a lifetime probably greater than the age of the universe, is impossible unless the duration of the experiment is virtually infinite, whereas for a nonresolvable chiral molecule such as H_2O_2, spectroscopic transitions between states of definite parity are observed routinely.

Nonresolvable chiral molecules can be regarded as "self-racemic" since the *single* molecules exist in states of definite parity. On the other hand, definite parity states of resolvable chiral molecules must embrace *two* opposite enantiomers, which accords with the usual concept of a racemic mixture. The states of the neutral K meson have been likened to the four possible states of a chiral molecule, the particle and antiparticle states corresponding to $\psi_o{}^L$ and $\psi_o{}^R$, with "racemic" states corresponding to $\psi_o{}^+$ and $\psi_o{}^-$.[10] However, since *single* neutral K mesons can exist in definite parity (more precisely, CP) states with different energies, the analogy would appear to be with a self-racemic chiral molecule such as H_2O_2. The analogue of a resolved enantiomer would appear to be a left or right circularly polarized photon because such a photon is in a state of mixed parity and only the combined states of *two* such photons can have definite parity[3] (this analogy is not exact because the parity operations are carried out in the combined momentum–polarization space of the photon). The use of mixed parity states appears to be essential in any discussion of the symmetry aspects of reactions involving chiral molecules, and interesting parallels with certain elementary particle reactions can be expected.

Although the existence of mixed parity quantum states is a necessary condition for both a permanent electric dipole moment and optical activity, it is not sufficient since a molecule can possess a permanent electric dipole moment without being optically active, and point group symmetry arguments must be introduced to distinguish the two situations. The essential distinction is that, while both the electric dipole moment and the optical rotatory parameter have odd parity, the first is a polar vector while the second is a pseudoscalar. This is why an isotropic collection of molecules can show no bulk electric dipole moment, but can show optical rotation.

Acknowledgments. I thank Dr. R. G. Woolley and Dr. J. K. Tyler for stimulating discussions, and a referee for helpful comments.

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Oxygen Transfer from Ligands: Cobalt Nitro Complexes as Oxygenation Catalysts

Sir:

Recently, catalytic oxidations of phosphines to phosphine oxides[1] and isonitriles to isocyanates[2] and co-oxidation of Ph_3P and terminal olefins to Ph_3PO and 2-alkanones[3] have been demonstrated using metal peroxo complexes. In these oxidations, the formation of strong P═O and RNC═O bonds is an important driving force. Since all known peroxo complexes contain oxidizable ligands, co-oxidation of the ligands cannot be avoided.[17] In addition, coordinatively unsaturated metal complexes which can be easily oxidized or reduced tend to initiate nonspecific Haber–Weiss radical autooxidations.[4]

To avoid these problems, we would like to offer a new approach which involves oxidation of organic substrates via an oxygen atom transfer from a *ligand* of the metal complex. The

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