

These results specify  $D_2$  symmetry for the group interchanging the molecules in the unit cell. The spacing of the levels in Figure 4 is due to the different projections of the molecules onto the direction perpendicular to the 110 face.<sup>29</sup> The ratio of the  $E_b$  to  $E_a$  splittings is  $3.21 \pm 0.03$ , whereas the ratio of the projections of the C=O bond onto the **b** and **a** axes is 3.21 from X-ray diffraction.<sup>34</sup>

### Isomerization in Excited States

One of the most powerful traditional uses of dipole moments in structural chemistry is as a device for distinguishing isomers, one of which is more polar than the other. It is fitting to end this summary with the analogous structural identification of excited-state isomers. When all *trans*-2,2'-bispyridine is used to form a dilute solid solution in a biphenyl host lattice, one can observe in the low-temperature spectra some rather sharp lines around 3200 Å that correspond to what appears to be two separate  $n\pi^*$  absorption systems.<sup>35</sup> Actually one of the systems shows a Stark splitting and the other does not, indicating that one system is due to polar molecules and the other is not.<sup>36</sup> These mixed crystals are prepared by Bridgman techniques from a melt and the relative amounts of oriented polar and nonpolar forms in the dilute mixed crystal are presumably determined by the crystal growth kinetics.

### Conclusions

Table I contains the complete list of data, as of November 1972, using the techniques described here

(34) E. B. Fleischer, N. Sung, and S. Hawkinson, *J. Phys. Chem.*, **72**, 4311 (1968).

(35) R. D. McAlpine, *J. Mol. Spectrosc.*, **38**, 441 (1971).

(36) R. M. Hochstrasser and A. H. Zewail, unpublished work.

(see ref 20–24, 26, 28, 29, 31, 33, 36–41). A trend at present is to probe higher order effects and investigate the influence of electric fields on dynamical processes in molecular solids. In this Account I have described how to extract from electric-field experiments various parameters relating to the anisotropy of the charge distributions of molecules and crystals. In so doing I left virtually no space to discuss the use of these parameters in interpreting the structure and behavior of excited states. Such a discussion will await a considerable enlargement of the scope of Table I and will require a pooling of information from numerous other sources of these excited-state parameters.<sup>42</sup>

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(37) R. M. Hochstrasser and T. S. Lin, *J. Chem. Phys.*, **49**, 4929 (1968).

(38) A. P. Marchetti, *J. Chem. Phys.*, **56**, 510 (1972).

(39) R. M. Hochstrasser and A. P. Marchetti, *J. Mol. Spectrosc.*, **35**, 335 (1970).

(40) D. A. Wiersma, *Chem. Phys. Lett.*, **16**, 517 (1972).

(41) R. M. Hochstrasser and A. H. Zewail, *Chem. Phys. Lett.*, **11**, 157 (1971).

(42) Note Added in Proof. We have recently studied the second-order Stark effect on the visible absorption spectra of *p*-benzoquinone using modulation techniques (R. M. Hochstrasser, L. W. Johnson, and H. P. Trommsdorff, *Chem. Phys. Lett.*, in press). These studies confirm the presence of at least two close lying electronic  $n\pi^*$  states being mixed by the field. Intensity changes, energy shifts (both positive and negative polarizabilities), and Stark induced spectra were observed. Stark modulation clearly provides a powerful new method for the study of the excited electronic states of molecules.

## Determination of Mechanistic Information from Nuclear Magnetic Resonance Line Shapes for Intramolecular Exchange

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The rates of chemical processes under equilibrium conditions can be obtained from temperature-dependent nmr line shapes. Activation parameters of varying degrees of accuracy have been presented in a continuously broadening stream of publications since

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the early work of Gutowsky and Holm.<sup>1</sup> More recently efficient computational techniques for the analysis of line shapes in complex spin systems have made it possible to extract quite detailed mechanistic information in certain cases, in addition to the conventional rate data.

One of the earliest kinetic studies was the elegant work of Whitesides and Mitchell<sup>2</sup> on  $(\text{CH}_3)_2\text{NPF}_4$

(1) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(2) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969).

where it was shown that the  $^{31}\text{P}$  nmr spectrum could exhibit two types of line-shape behavior with temperature: one for mechanisms in which the two axial fluorines in the trigonal-bipyramidal structure exchanged simultaneously with the two equatorial fluorines, and one for mechanisms in which they exchanged independently. The experimental results showed unequivocally that the former process was dominant.

In general, a chemical system undergoing rapid exchange spends most of its time near the equilibrium low-energy configurations. This means that the line shapes can be calculated using a "jump" model, and, as a consequence, we get no information on the actual physical pathway which takes the molecule from its configuration before exchange to its configuration after exchange. Thus any physical process (including the classical Berry process<sup>3</sup>) which simultaneously exchanges the axial and equatorial fluorines in  $(\text{CH}_3)_2\text{NPF}_4$  is consistent with the experimental data.

A further development in this field, brought about by the ability to analyze nmr line-shape effects in complex spin systems, has been the application of group theoretical methods to the determination of the extent of the mechanistic information which is contained in the exchange-broadened spectra.

We restrict ourselves in this Account to systems undergoing mutual intramolecular exchange, the high-resolution Hamiltonian being the same before and after exchange except for the permutation of spins, *i.e.*, only one chemical isomer is present in significant concentrations. The possible exchange processes in a given case can be represented by a set of permutations.

In the following, we illustrate some of the recent advances in the methods of determining mechanistic information from nmr line shapes using examples taken from our own work on transition metal hydrides.

### Determination of the Number of Distinguishable Temperature Dependent Nmr Line Shapes or Basic Sets

Consider the case of a cis iron or ruthenium dihydride<sup>4,5</sup> with the reference-labeled configuration as shown in Figure 1. A specific mutual exchange is denoted in Figure 1a. The arrows indicate only the overall permutation and should not be taken to imply an actual path or mechanism for the reaction. The permutation in this case is

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 3 & 2 & 1 & 4 & 5 & 6 \end{pmatrix} \text{ or } (13)$$

In general, the cycle  $(ijkl\dots)$  will be taken to mean the ligand at position  $i$  moves to position  $j$ , the ligand at position  $j$  moves to position  $k$ , etc.

The possible configurations of a labeled *cis*- $\text{H}_2\text{MP}_4$  system comprises a group of order  $4! \times 2!$ , *i.e.*,  $S_4(\text{P}) \times S_2(\text{H})$ , where  $S_4$  is the symmetric group repre-

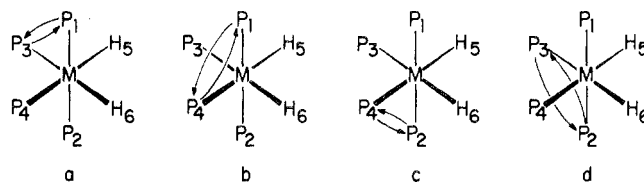


Figure 1. Schematic representation of one of the basic sets of permutations for a labeled  $\text{H}_2\text{ML}_4$  molecule.

sending all possible permutations of the phosphorus nuclei among themselves and  $S_2$  is the symmetric group representing all possible permutations of the hydrogens among themselves.

In analyzing the temperature-dependent nmr line shapes, it is not necessary to carry out separate calculations for each of the 48 possible permutations. This can be seen from Figure 1. The  $\text{H}_2\text{MP}_4$  skeleton belongs to the  $C_{2v}$  point group and, as a consequence, the four permutation reactions shown are equivalent; by symmetry, they must all occur at the same rate. We call such a set of permutations a "basic permutational set." Mathematically, two permutations,  $p_i$  and  $p_j$ , belong to the same permutational set if, for some permutation  $g_k$  in the permutational point group  $G$  of the molecule

$$p_i = g_k p_j g_k^{-1} \quad (1)$$

In the alternative nomenclature of Klemperer,<sup>6</sup>  $p_i$  and  $p_j$  are said to be "indistinguishable permutational isomerization reactions in a totally symmetric environment." Clearly, all members of a basic permutational set must be included together in the line-shape calculations for that set.

Using the labeling in Figure 1, the permutational subgroup of  $S_4(\text{P}) \times S_2(\text{H})$  generated by the molecular point group of the molecule ( $C_{2v}$ ) is

$$g_1 = E = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 1 & 2 & 3 & 4 & 5 & 6 \end{pmatrix} = (1)(2)(3)(4)(5)(6)$$

$$g_2 = C_2 = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 1 & 4 & 3 & 6 & 5 \end{pmatrix} = (12)(34)(56)$$

$$g_3 = \sigma_v = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 1 & 3 & 4 & 5 & 6 \end{pmatrix} = (12)(3)(4)(5)(6)$$

$$g_4 = \sigma_v' = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 1 & 2 & 4 & 3 & 6 & 5 \end{pmatrix} = (1)(2)(34)(56)$$

In this case,  $G$  is isomorphic with  $C_{2v}$  and the elements of  $G$  are labeled with the corresponding symmetry operators of  $C_{2v}$  (in general,  $G$  and the molecular point group are only homomorphic;  $G$  may have fewer elements than the molecular point group).

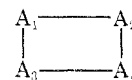
All of the permutations  $p_i, p_j$  related by eq 2 for

$$p_i = h_k p_j h_i \quad (2)$$

some  $h_k, h_l$  in  $\mathcal{K}$ , where  $\mathcal{K}$  is the effective permutational group of the nmr Hamiltonian,<sup>7</sup> would, if

(6) W. G. Klemperer, *J. Chem. Phys.*, **56**, 5478 (1972).

(7) Often  $G$  and  $\mathcal{K}$  are isomorphic and equivalent, but, in general,  $G$  is a subgroup of  $\mathcal{K}$ . Consider the case of a spin system of the type



with  $D_{2d}$  symmetry. The spin system is said to be of the  $A_4$  type since all of the chemical shifts are equal. The effective group of the nmr Hamiltonian is  $S_4$  rather than  $D_{2d}$ , reflecting the experimental indeterminability of the coupling constants in solution.

(3) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(4) P. Meakin, E. L. Muettterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971).

(5) P. Meakin, E. L. Muettterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **95**, 75 (1973).

they could occur alone, give the same temperature-dependent nmr line shapes. All of the basic permutational sets comprised of elements related by (2) will give the same calculated nmr line shapes and are said to be *indistinguishable basic permutational sets* (the line shapes will, however, be different from those calculated for any of the individual permutations). If all of the elements of two or more basic permutational sets are related by eq 3 for

$$p_i = g_k p_j g_i \quad (3)$$

some  $g_k, g_i$  in  $G$ , then these permutational sets and all linear combinations of them will give the same calculated nmr line shapes; we term them *equivalent basic permutational sets*.

The minimum number of basic permutational sets needed to calculate all possible temperature dependences of the nmr line shapes can be determined systematically as follows. Choose one of the possible permutations  $p_j$  (48 in the example given above) and find all of the permutations satisfying eq 1. From this set calculate the equivalent basic sets satisfying eq 3; these sets will all give the same calculated line shapes. Now, choose another permutation not already generated from  $p_j$  by (1) and (3) and repeat the process using the new permutation. The overall procedure is repeated until all 48 permutations are accounted for. In this way, we find that there are five different possible types of temperature-dependent line shapes<sup>8</sup> which correspond to the five "*nonequivalent basic permutational sets*."<sup>4,5</sup>

We have written a computer program which evaluates the number of distinguishable basic permutational sets given the number of ligands of each type and the generators of the permutational group  $G$  formed from the point group of the molecule. The results for the  $H_2MP_4$  case are given in Table I. Klemperer<sup>6</sup> has presented analytical formulas which may be used to determine the distinguishable basic permutational sets without the aid of a computer. The approach is based on the enumeration and combinatorial methods of Polya.<sup>9</sup>

**Examples.** Since we are concerned mainly with the interpretation of nmr spectra in solution, we will need to evaluate only the number of distinguishable basic sets in a totally symmetric environment. Klemperer<sup>6</sup> has considered, in addition, the effect of a chiral environment. In this case the number of nonequivalent basic sets can be obtained by using the permutational group  $R$  generated by the proper rotational subgroup of the molecular point group in place of  $G$ , i.e., the permutations,  $p_i$  and  $p_j$  belong to non-equivalent basic sets in a chiral environment if

$$p_i \neq r_k p_j r_l \quad (4)$$

for any  $r_k, r_l$  in  $R$ .

**HML<sub>4</sub> Systems.** Most hydrides of the type HML<sub>4</sub> (L is a trivalent phosphorus ligand) have  $C_{3v}$  symmetry in solution<sup>10</sup> and may be described either as

(8) We include the identity set  $E$ , consisting of the permutations which are elements of  $G$  in all cases, even if  $G$  contains only proper rotations. This set corresponds to those permutations which do not affect the line shapes.

(9) G. Polya, *Acta Math.*, **68**, 145 (1937).

(10) P. Meakin, E. L. Muettterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972).

**Table I**  
Basic Permutational Sets for a *cis*- $H_2MP_4$  System in a Symmetric Environment<sup>a</sup>

Set	Equivalent Sets		
E (1 2) (3 4) (5 6)	(1) (2) (3) (4) (5) (6)	(3 4) (5 6)	(1 2)
I (1 4) (2 3) (5 6)	(1 3) (2 4)	(1 3 2 4) (5 6)	(1 4 2 3)
	(1 3) (2 4) (5 6)	(1 4) (2 3)	(1 4 2 3) (5 6)
II (1 2) (3 4)	(5 6)	(4 3)	(1 2) (5 6)
III (1 4) (5 6)	(1 2 4 3)	(1 2 4) (5 6)	(1 4 3)
	(3 2) (5 6)	(1 3 4 2)	(1 3 2) (5 6)
	(2 4) (5 6)	(1 4 3 2)	(1 4 2) (5 6)
	(1 3) (5 6)	(1 2 3 4)	(1 2 3) (5 6)
IV (1 4)	(1 2 4 3) (5 6)	(1 2 4)	(1 4 3) (5 6)
	(2 3)	(1 3 4 2) (5 6)	(1 3 2)
	(2 4)	(1 4 3 2) (5 6)	(1 4 2)
	(1 3)	(1 2 3 4) (5 6)	(1 2 3)

<sup>a</sup>The permutations are given with respect to the reference labeling shown in Figure 1.

distorted trigonal bipyramids with the hydride ligand in an axial position or as a tetrahedral arrangement of the four phosphorus ligands with the hydride ligand in one of the faces. In solution, there are only two distinguishable basic permutational sets (including the identity) for both the proton noise-decoupled <sup>31</sup>P nmr spectra and the <sup>1</sup>H or <sup>31</sup>P spectra without decoupling. Accordingly, there is no mechanistic information in the nmr line shape changes.

**H<sub>2</sub>ML<sub>4</sub> Systems.** Complexes of the form *cis*- $H_2FeL_4$  are the only systems which are sufficiently complex such that the number of distinguishable types of line-shape behavior cannot easily be obtained by inspection, while at the same time the temperature-dependent nmr line shapes have been measured and analyzed.<sup>4</sup> In this case there are five distinguishable basic permutational sets (see previous discussion and Table I).

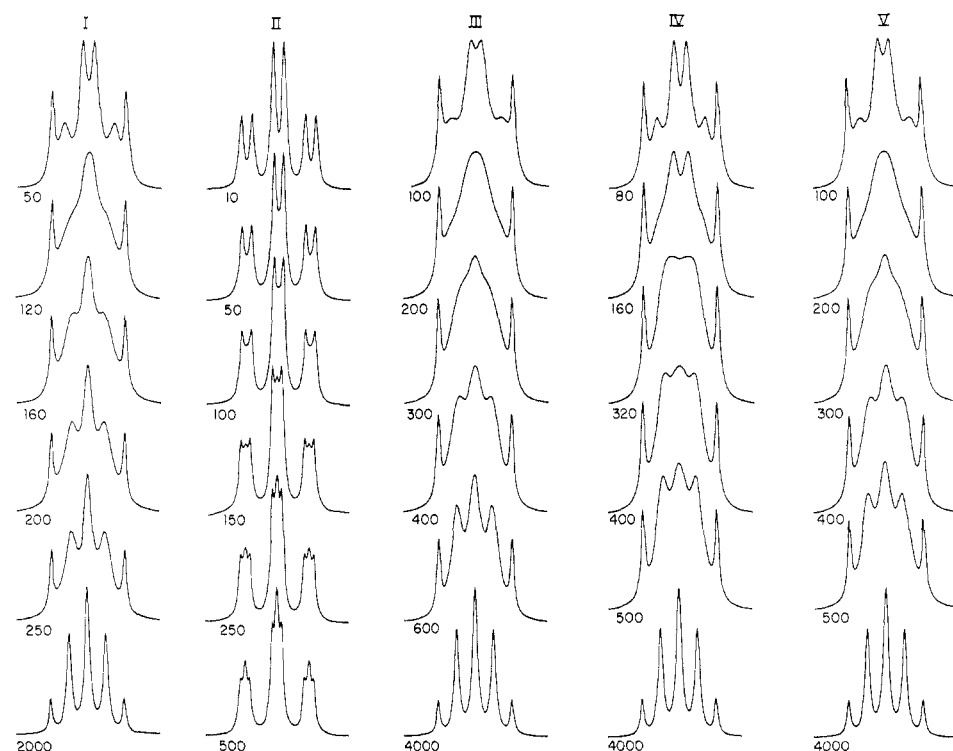
The proton noise-decoupled <sup>31</sup>P nmr spectra can be analyzed by simply ignoring the protons. The group of possible permutations for the phosphorus nuclei is  $S_4(P)$  with 24 elements and the permutational group generated by the point group is  $E = (1)(2)(3)(4)$ ,  $C_2 = (12)(34)$ ,  $\sigma_v = (12)$ ,  $\sigma_v' = (34)$ . There are now only three distinguishable basic permutational sets and much of the mechanistic information has been lost (in this particular case, the experimental situation is such that almost all the mechanistic information has been lost<sup>4</sup>).

**H<sub>3</sub>ML<sub>4</sub> Systems.** This class is the only member of the  $H_nML_4$  series ( $n = 1-4$ ) for which stereochemical nonrigidity has not yet been investigated. Assuming the complexes have  $C_{3v}$  symmetry with one phosphorus ligand and the metal atom on the  $C_3$  axis, the number of basic permutational sets is seven for the <sup>1</sup>H hydride spectrum in solution and two for the proton noise-decoupled <sup>31</sup>P system.

**H<sub>4</sub>ML<sub>4</sub> Systems.** Temperature-dependent nmr line shapes have been observed for several complexes of this type where  $M = Mo$  or  $W$ <sup>11-13</sup> and the structure

(11) P. Meakin, E. L. Muettterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 5261 (1971).

(12) B. Bell, J. Chatt, G. J. Leigh, and T. Ito, *J. Chem. Soc., Chem. Commun.*, **34** (1972).



**Figure 2.** Line-shape simulations for the basic permutational sets I-IV for  $H_2ML_4$  systems with coupling constants appropriate to the case where  $M = Fe$ . V is a random exchange situation (a linear combination of I-IV).

of one of them ( $H_4Mo[P(C_6H_5)_2CH_3]_4$ ) has been determined.<sup>13</sup> The complex has a trigonal dodecahedral structure with  $D_{2d}$  symmetry, the hydrogens occupying the A sites.<sup>14</sup> The number of basic permutational sets in solution is  $20^{13}$  for the  $^1H$  hydride spectrum. The noise-decoupled  $^{31}P$  spectrum consists of a single line (there is only one  $^{31}P$  chemical shift) and contains no mechanistic information. The slow-exchange limit nmr spectrum is invariant to all permutations of the nuclei, the effective permutational group of the nmr Hamiltonian being  $S_4$ .

If the average geometry in solution has  $T_d$  symmetry (a tetrahedral arrangement of phosphorus atoms with hydrogens in all four tetrahedral faces) the number of distinguishable basic permutational sets is five.

### Analysis of Nmr Line Shapes

The nonequivalent basic permutational sets can now be used to obtain calculated line shapes based on a jump model. In most cases, the density matrix approach of Kaplan<sup>15</sup> and Alexander<sup>16</sup> is employed. This method involves the solution of the phenomenological density matrix equation of motion

$$d\rho/dt = 2\pi i[\rho, H] + (d\rho/dt)_{relax} + \sum_i (P_i^+ \rho P_i + P_i \rho P_i^+ - 2\rho) / 2\tau_i \quad (5)$$

for the conditions of slow passage, high temperature, and weak radiofrequency fields,  $\rho$  is the mean spin density matrix,  $H$  is the mean spin Hamiltonian in-

cluding interaction with the radiofrequency field, and  $(d\rho/dt)_{relax} = -\rho_{ij}/T_2$  for density matrix elements one off diagonal in  $I_z$  (the  $z$  component of total nuclear angular momentum) is a relaxation term which determines the line width in the absence of exchange. The  $P_i$  are exchange matrices corresponding to the permutations  $P_i$  defined by  $\psi'(t) = P_i\psi(t)$ , where  $\psi(t)$  and  $\psi'(t)$  are the spin wave functions before and after the exchange process (permutation of spins).  $\tau_i$  is the average time between exchanges of the  $i$ th type and the summation is over the members of a basic permutational set. In the appropriate Liouville space, eq 5 can be written as<sup>17,18</sup>

$$d\varrho/dt = -i\mathcal{L}\varrho + \mathbf{R}\varrho + \sum_i \alpha_i \varrho \quad (6)$$

where  $\varrho$  is now the density vector in Liouville space,  $\mathcal{L}$  is the Liouville operator,  $\mathbf{R}$  is the relaxation operator, and the  $\alpha_i$ 's are the exchange operators.

The techniques used to solve eq 6 and 7 have been reported in the literature.<sup>4,17,19-21</sup> With the advent of the numerical techniques developed by Gordon and McGinnis,<sup>19</sup> Binsch,<sup>17</sup> and Schirmer, Noggle, and Gaines,<sup>20</sup> and the symmetry-factoring procedures of Kleier and Binsch<sup>21</sup> and ourselves,<sup>4</sup> it is now possible to simulate the temperature-dependent nmr line shapes for quite complex non-first-order systems whose nmr spectra may contain several hundred lines.

In obtaining mechanistic information from temperature-dependent nmr line shapes, we must ana-

(13) P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **95**, 1467 (1973).

(14) J. L. Hoard and J. V. Silvertown, *Inorg. Chem.*, **2**, 235 (1963).

(15) J. I. Kaplan, *J. Chem. Phys.*, **28**, 278 (1958); **29**, 462 (1958).

(16) S. Alexander, *J. Chem. Phys.*, **37**, 967, 974 (1962); **38**, 1787 (1963); **40**, 2741 (1964).

(17) G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969).

(18) U. Fano in "Lectures on the Many Body Problem," Vol. 2, E. R. Caianiello, Ed., Academic Press, New York, N. Y., 1964, p 217.

(19) R. G. Gordon and R. P. McGinnis, *J. Chem. Phys.*, **49**, 2455 (1968).

(20) R. E. Schirmer, J. H. Noggle, and D. F. Gaines, *J. Amer. Chem. Soc.*, **91**, 6240 (1969).

(21) D. A. Kleier and G. Binsch, *J. Magn. Resonance*, **3**, 146 (1970).

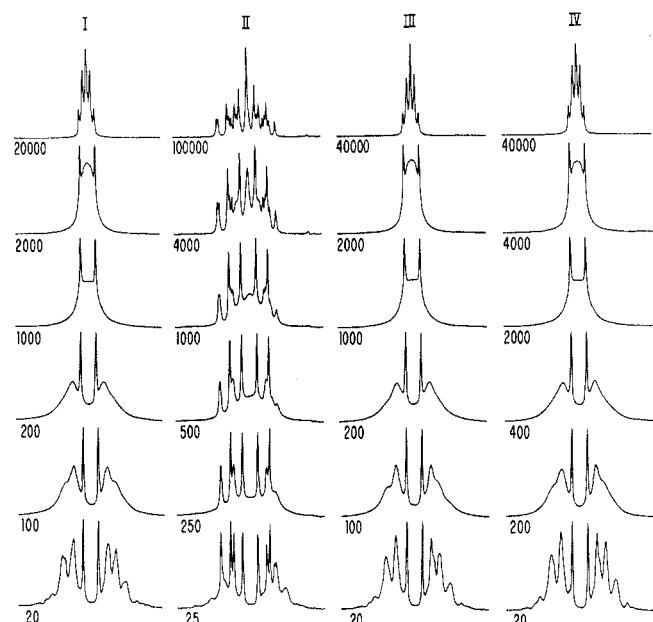


Figure 3. Line-shape simulations for the basic permutational sets I-IV for  $H_2ML_4$  systems with coupling constants appropriate to the case where  $M = Ru$ .

lyze the low-temperature limit spectra. This first step may be the most difficult, particularly in those cases where the low-temperature limit spectrum is not well resolved. If only an envelope of the spectrum is observed, the usual procedures used to obtain the nmr parameters cannot be applied and a time-consuming trial and error approach must be employed.<sup>4,5</sup> Having analyzed the low-temperature limit spectra, the next step is to solve eq 5 and 6. The most efficient computer methods at the time of writing involve the diagonalization of a complex non-Hermitian matrix,<sup>4,17,19-21</sup> and the feasibility of the calculation depends mainly on the dimension of the largest submatrix into which this matrix may be factored.<sup>4,21</sup> In practice, the largest complex non-Hermitian matrix that can be conveniently diagonalized is of dimension  $\sim 50 \times 50$ . The actual dimension will depend on the spin system, the exchange process, and the degree of factoring.

If the matrices are too large, approximate methods must be used; thus, in cases where the low-temperature limit spectrum is well resolved, only the diagonal elements of the complex non-Hermitian matrix are needed to calculate the nmr line shapes for rates of exchange less than the separation between the lines. Mechanistic information can then be obtained from the relative broadening of spectral lines at slow exchange rates.<sup>22</sup> In other cases there will be many transitions of low intensity and the dimensions of the matrices may be reduced by eliminating them from the calculation.<sup>22,23</sup> Finally, indirect saturation techniques may be used to obtain mechanistic information<sup>24,25</sup> since a transition is only saturated if it is

(22) This is only true if the calculation has been set up in the basis in which the Hamiltonian is diagonal (in this basis, the Liouville operator  $\mathcal{L}$  is also diagonal).

(23) This is a dangerous approximation. As a check, the calculated high-temperature limit spectrum using this approximation must be correct and the calculated line shapes must be independent of the number of low-intensity lines omitted from the calculation.

(24) A. Forsen and R. A. Hoffman, *J. Chem. Phys.*, **40**, 1189 (1964); **39**, 2892 (1963); *Acta Chem. Scand.*, **17**, 1787 (1963).

exchanging (directly or indirectly) with the transition which is irradiated.

It is quite common that the differences between the nmr line shapes calculated for two or more basic permutational sets may be too small for them to be distinguished experimentally; the results of a detailed line-shape calculation are then quite disappointing.<sup>5</sup> Finally, it may be necessary to include linear combinations of the exchange operators (eq 6) corresponding to different basic permutational sets in cases where isomers other than the lowest energy species are involved as intermediates in the exchange process<sup>4,5</sup> or if more than one exchange mechanism is important.

**Examples.** Figures 2 and 3 show  $^1H$  spectra simulated using the low-temperature limit nmr parameters typical of the cis iron and ruthenium dihydrides, respectively, at 220 MHz for the basic permutational sets I-IV given in Table I.<sup>4,5</sup> For the case of the iron dihydrides, the spectra simulated for the "random-exchange" mechanism (labeled V), consisting of all four basic sets equally weighted, is also shown. Since the hydride region proton nmr spectra of the iron dihydrides are almost first order at 220 MHz, the first-order approximation was used in calculating the spectra. In the case of the ruthenium dihydrides, a complete density matrix calculation was required.

As can be seen from Figure 2, all five distinguishable basic permutational sets (including the identity set  $E$  corresponding to no temperature dependence) give calculated line shapes that can be readily distinguished. By contrast, the spectra simulated for the ruthenium dihydrides for the basic sets I, III, and IV (Figure 3) are virtually indistinguishable. This is attributed to the fact that the high-temperature limit spectrum for the ruthenium dihydrides consists of a quintet with quite small splittings. Unfortunately, the three basic sets I, III, and IV are those which correspond to the physically most reasonable exchange mechanisms,<sup>5</sup> and no useful mechanistic information can be obtained from the experimental spectra.

For the iron dihydrides only calculations using basic set IV give agreement with the observed spectra. An example is shown in Figure 4 for the hydride nmr of the molecule  $H_2Fe[P(OC_2H_5)_3]_4$  at 90 MHz (the difference between this case and the simulations in Figure 2 is that at 90 MHz the spectrum is no longer first order and a complete density matrix calculation must be used; at 220 MHz the spectra are first order and are similar to those shown under IV in Figure 2).

### Assignment of a Specific Physical Mechanism

Since the calculations described above are based on a jump model, they simply give information about the nuclear permutations which take place in the exchange process. There are, of course, an infinite number of physical pathways which can carry a labeled cis dihydride into a differently labeled cis dihydride. The final stage of the analysis is, therefore, to consider plausible physical mechanisms to see which are rigorously excluded on the grounds

(25) B. M. Fung, *J. Chem. Phys.*, **49**, 2973 (1968); **47**, 1409 (1967); *J. Amer. Chem. Soc.*, **90**, 219 (1968).

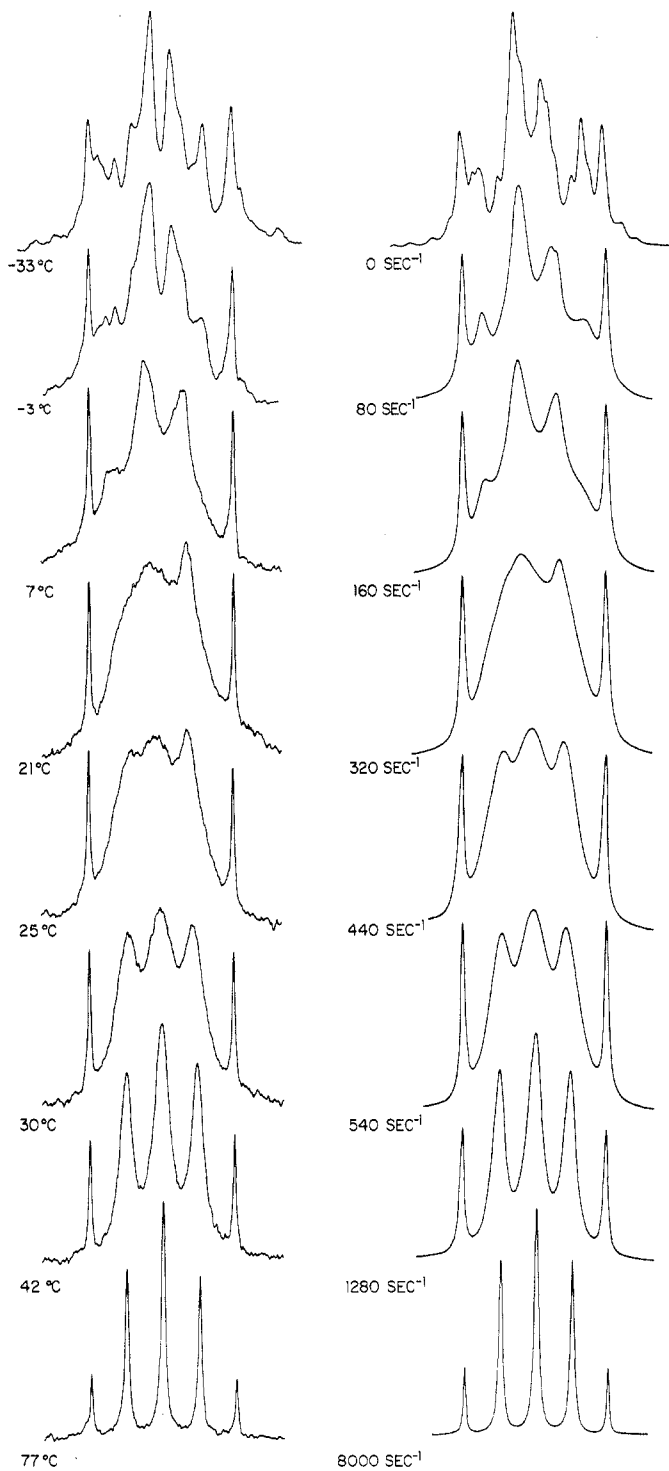


Figure 4. Observed 90-MHz hydride spectra for  $\text{H}_2\text{Fe}[\text{P}(\text{OC}_2\text{H}_5)_3]_4$  and calculated spectra using basic permutational set IV.

that they are permutationally incorrect and, of those which are permutationally correct, to select a mechanism or mechanisms which are most strongly supported by ancillary physical evidence.

Consider the trigonal twist mechanism which has been frequently discussed in the literature for intramolecular exchange in six-coordination.<sup>26</sup> The relationship between the two types of twist possible in  $\text{cis-H}_2\text{ML}_4$  molecules and the basic permutational sets is shown in Figure 5. It can be seen that twists

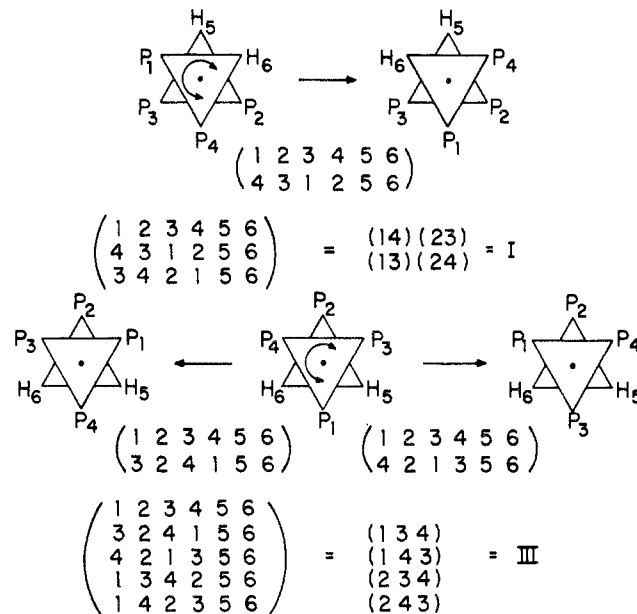


Figure 5. The correspondence between the two types of trigonal twist possible for  $\text{cis-H}_2\text{ML}_4$  molecules and the basic permutational sets I-IV.

about a PPH face correspond to basic set I and twists about a PPP face correspond to basic set III. Both these mechanisms are, therefore, rigorously excluded as concerted processes in  $\text{cis-H}_2\text{ML}_4$  molecules since, as we have seen in the previous section, only basic set IV agrees with experiment.

Having ruled out the twist mechanisms, we must look for the chemically most plausible mechanism which corresponds to basic set IV. The  $\text{H}_2\text{FeP}_4$  skeleton of the molecule  $\text{H}_2\text{Fe}[\text{P}(\text{OC}_2\text{H}_5)_2\text{C}_6\text{H}_5]_4$ , taken from an X-ray crystal structure determination, is shown in Figure 6.<sup>27</sup> It can be seen that the  $\text{P}_4$  array is greatly distorted from an idealized octahedral structure; in fact, the P atoms are closer to the corners of a regular tetrahedron and the skeleton may be pictured approximately as a tetrahedron with the hydride hydrogens in two adjacent faces. The most plausible concerted mechanism appears to be one in which a single hydrogen (say  $\text{H}_5$  in Figure 6) moves from a PPP face ( $\text{P}_1\text{-P}_2\text{-P}_3$ ) through a PP edge (e.g.,  $\text{P}_3\text{-P}_2$ ) and into a previously unoccupied PPP face ( $\text{P}_2\text{-P}_3\text{-P}_4$ ), the configuration still being *cis* after exchange. An analysis similar to that in Figure 5 shows that, provided only one hydride ligand moves at a time, the mechanism corresponds to permutational set IV.<sup>4</sup> We have given the descriptive title "tetrahedral jump" to this mechanism and further support for it can be found in studies on five-coordinate hydrides.<sup>10</sup> Here the barriers to exchange are much lower and the four phosphorus ligands are much closer to the corners of a regular tetrahedron in the equilibrium geometry.<sup>10</sup>

Finally, it is necessary to consider the possibility of a two-step process involving a short-lived intermediate in addition to the concerted processes discussed above. In a few cases, *trans-H}\_2\text{ML}\_4* molecules have similar stability to the *cis* species and can be observed directly in the nmr.<sup>4,5</sup> This suggests that

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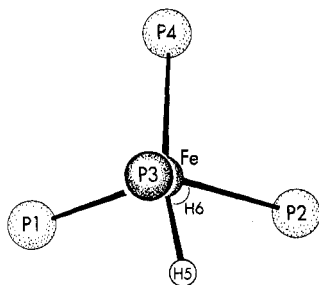


Figure 6. A perspective of the  $H_2FeP_4$  skeleton for the molecule  $H_2Fe[P(OC_2H_5)_2C_6H_5]_4$ , taken from an X-ray crystal structure determination.<sup>27</sup>

trans species are attractive possibilities as intermediates in the exchange processes. Several permutational alternatives exist for this type of mechanism and will not be discussed in detail here.<sup>5</sup> Suffice it to say that for one case the permutational analysis gives the linear combination  $2E + I + IV$  ( $E$  is the identity set and has no effect on the line shapes).<sup>5</sup> This combination gives fair agreement with the observed line shapes although it is less satisfactory than with  $IV$  alone. At this point in time, it is not possible to distinguish unambiguously between the concerted and two-step alternatives; in fact, strong arguments can be advanced, indicating that these closely relat-

ed alternatives merely represent two extremes of a continuum of potential surfaces, many of which may be actually realized in practice.<sup>5</sup>

### Conclusion

It is clear, with the introduction of the new mathematical approaches to computation, and with the application of group theoretical methods to the determination of the mechanistic information potentially present in the line shapes for a given exchanging system, that the field of nmr in dynamic systems has entered a new and exciting phase. Transition metal hydrides have been used as examples since this is the area in which the bulk of our research has so far been done. The methods can clearly be applied to any system undergoing mutual intramolecular exchange on the nmr time scale, provided it contains magnetic nuclei. The example of  $(CH_3)_2NPF_4$  has been mentioned; we have analyzed the spectra for, and are currently studying, cationic transition metal  $ML_5$  species where mechanistic information can be obtained.

Aside from the area of mutual intramolecular exchange it is likely that further diversification of the field will lead to mechanistic studies of non-mutual intramolecular exchange and of intermolecular exchange.

## Photochemistry of Aliphatic Azo Compounds in Solution

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Irradiation of aliphatic azo compounds with ultraviolet light may lead to any of three unimolecular chemical reactions: elimination of nitrogen, cis-trans isomerization, or tautomerization to a hydrazone.<sup>1</sup> Although bimolecular hydrogen abstraction has been observed in the aromatic series<sup>4</sup> and in azo esters,<sup>5</sup> the evidence for its occurrence in the azoalkanes is only very tentative.

Mechanistic investigations to date have focused primarily upon the first two reactions, nitrogen ex-

trusion and cis-trans isomerization. In some instances these have been complemented by studies of such photophysical processes as fluorescence and energy transfer. It is the purpose of this Account to present and evaluate some of the existing solution-phase photochemical data. Both the gas-phase photochemistry<sup>6</sup> and the thermal chemistry<sup>7</sup> of azo compounds are also under active investigation, and our

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