Investigating Catalytic Processes with Parahydrogen: Evolution of Zero-Quantum Coherence in AA′X Spin Systems

J. Natterer,* O. Schedletzky,† J. Barkemeyer,* J. Bargon,* and S. J. Glaser†,[1]

*Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstr. 12, D-53115 Bonn, Germany; and
†Institute of Organic Chemistry, J. W. Goethe-University, Marie-Curie-Str. 11, D-60439 Frankfurt, Germany

A systematic outline for the elucidation of the nature of hydrogenation intermediates with a lifetime too short to be directly detectable with standard NMR methods is presented. The method takes advantage of the special nature of the parahydrogen density operator and its inherent enhancement factor. The key aspect of these experiments is the evolution of zero-quantum coherence which is contained in the parahydrogen density operator. Analytical coherence transfer functions have been derived which describe the evolution of this zero-quantum coherence in spin systems consisting of three spins 1/2 that form an AA′X spin system. The analytical expressions presented form a basis for a thorough investigation of crucial catalytic steps.   © 1998 Academic Press

Key Words: PHIP effect; catalysis; density operator theory; coherence transfer functions; parahydrogen; PASADENA.

INTRODUCTION

Performing a hydrogenation with parahydrogen yields NMR signals of the two former parahydrogen nuclei in the product molecule that are enhanced by several orders of magnitude as compared to proton signals at thermal equilibrium. This so-called PASADENA (*1, 2*) or PHIP (*3*) effect stems from the breakdown of the parahydrogen symmetry in the product molecule. This effect has been used for a wide range of investigations of hydrogenations, the most recent work covering the transfer of polarization to heteronuclei (*4–6*), the rapid characterization of organometallic compounds with modified HMQC (*7*) or NOESY (*8*) pulse sequences, the study of hydrogenation intermediates (*9, 10*), and studies of the reversibility of catalytic steps (*11*).

Early on in the study of the PHIP phenomenon it was realized that the polarization spectra of the product molecule contain information about hydrogenation intermediates (*12*). This was proven by showing that the structure of the polarization spectra depends crucially on the catalyst and substrate used (*13*). Hence, the PHIP phenomenon also reveals information about hydrogenation intermediates with a lifetime much too short to be directly detectable by NMR spectroscopy. This effect was explained in terms of a nu-

clear S/T_0 mixing phenomenon at the catalyst, that is, a mixing of the initially pure nuclear singlet state S with the nuclear triplet state T_0. This process alters the population differences as well as the transition probabilities in the product spin system and hence the appearance of the spectra. It was, however, quickly realized that this effect only occurs if the two former parahydrogen nuclei are strongly coupled in the product molecule. The S/T_0 mixing was analyzed for hydrogenations into symmetric substrates, that is, into substrates where only the natural content of ^{13}C isotopes breaks the symmetry of parahydrogen. In these substrates, the relevant spin systems were of AA′X character (*14*). It was further shown that in these spin systems, dramatic polarization phenomena can also be observed on the hetero nucleus X (*15*). These effects were analyzed based on the populations of the energy levels of the AA′X spin system (*16*). Generally, no flip angle dependence can be derived if only population differences are considered. This is a major disadvantage, as it turns out that the polarization spectra obtained in strongly coupled spin systems depend crucially on the flip angle applied. Furthermore, an analysis based on population differences is only valid if sufficiently small flip angles are used (*17*), which was not the case in the studies quoted. In this paper we present a theoretical framework for the analysis of the polarization spectra based on a complete density matrix treatment. We limit our discussion to the case of AA′X spin systems. We explain the origin of polarization on the hetero nucleus X and present an outline for a systematic investigation of crucial catalytic steps using parahydrogen.

The characteristic density operator of parahydrogen is given by

$$\rho(0) = \frac{1}{4}\mathbf{1} - \mathbf{I}_1\mathbf{I}_2 = \frac{1}{4}\mathbf{1} - I_{1z}I_{2z} - (ZQ)_x, \qquad [1]$$

with the zero-quantum term

$$(ZQ)_x = I_{1x}I_{2x} + I_{1y}I_{2y}. \qquad [2]$$

If the spin system after hydrogenation forms an AA′X system, the free evolution Hamiltonian $\mathcal{H}$ has the form

$$\mathcal{H} = \mathcal{H}' + \mathcal{H}'' \qquad [3]$$

with the coupling terms

$$\mathcal{H}' = 2\pi J_{12}\mathbf{I}_1\mathbf{I}_2 + 2\pi J_{13}I_{1z}I_{3z} + 2\pi J_{23}I_{2z}I_{3z} \qquad [4]$$

and the offset terms

$$\mathcal{H}'' = \Omega_A(I_{1z} + I_{2z}) + \Omega_X I_{3z}. \qquad [5]$$

As $[\mathcal{H}', \mathcal{H}''] = 0$ and furthermore $[\mathcal{H}'', \rho(0)] = 0$, $\mathcal{H}''$ is irrelevant for the evolution of $\rho(0)$ under the Hamiltonian $\mathcal{H}$. In the nomenclature introduced in Ref. (18), the remaining term $\mathcal{H}'$ corresponds to an *ILL* coupling topology, where the spins 1 and 2 are isotropically (I) coupled, and where longitudinal coupling terms (L) exist between spins 1 and 3, and between spins 2 and 3.

The term $1/4\,\mathbf{1} - I_{1z}I_{2z}$ of the initial density operator $\rho(0)$ commutes with $\mathcal{H}'$ and thus remains invariant under the action of this Hamiltonian. Hence, the evolution of the initial parahydrogen polarization $\rho(0)$ in an AA′X spin system can be reduced to the evolution of the zero-quantum term $(ZQ)_x$ under the action of the *ILL* Hamiltonian $\mathcal{H}'$. The equation of motion for $\rho(t)$ is given by the Liouville–von Neumann equation

$$\frac{d}{dt}\rho(t) = -i[\mathcal{H}', \rho(t)]. \qquad [6]$$

Starting from $(ZQ)_x$, only the zero-quantum antiphase terms $\{2(ZQ)_yI_{3z}\} = \{2(I_{1y}I_{2x} - I_{1x}I_{2y})I_{3z}\}$ and $(I_{1z} - I_{2z})I_{3z}$ are created. Hence, $\rho(t)$ can be expressed as

$$\rho(t) = \frac{1}{4}\mathbf{1} - I_{1z}I_{2z} - a(t)(ZQ)_x$$
$$- b(t)2(ZQ)_yI_{3z} - c(t)(I_{1z} - I_{2z})I_{3z}. \qquad [7]$$

Application of the Liouville–von Neumann equation results in the following set of differential equations for the time-dependent coefficients $a(t)$, $b(t)$, and $c(t)$:

$$\frac{d}{dt}a(t) = \pi(J_{13} - J_{23})b(t)$$

$$\frac{d}{dt}b(t) = -\pi(J_{13} - J_{23})a(t) + 2\pi J_{12}c(t)$$

$$\frac{d}{dt}c(t) = -2\pi J_{12}b(t). \qquad [8]$$

The density operator $\rho(0)$ corresponds to the initial conditions $a(0) = 1$ and $b(0) = c(0) = 0$, for which the solution of Eq. [9] is given by

$$a(t) = \sin^2\phi + \cos^2\phi\,\cos(2\pi J't)$$
$$b(t) = -\cos\phi\,\sin(2\pi J't)$$
$$c(t) = 2\cos\phi\,\sin\phi\,\sin^2(\pi J't) \qquad [9]$$

with

$$\sin\phi = \frac{J_{12}}{J'}, \quad \cos\phi = \frac{J_\Delta}{J'} \qquad [10]$$

and

$$J_\Delta = \frac{J_{13} - J_{23}}{2}, \quad J' = \sqrt{J_{12}^2 + J_\Delta^2}. \qquad [11]$$

The time-dependent coefficients $a(t)$, $b(t)$, and $c(t)$ are proportional to the expectation values $\langle(ZQ)_x\rangle$, $\langle 2(ZQ)_yI_{3z}\rangle$, and $\langle(I_{1z} - I_{2z})I_{3z}\rangle$, respectively.

For the ensemble of spin systems, the time t between hydrogenation and the application of the first radio-frequency pulse varies in the range $0 \le t \le \tau_h$, where τ_h is the time during which hydrogenation occurs. If a constant probability of hydrogenation is assumed during $0 \le t \le \tau_h$, then for $\tau_h \gg (1/J')$,[2] the averaged density operator $\bar{\rho}_i$ is given by

$$\bar{\rho}_i = \frac{1}{4}\mathbf{1} - I_{1z}I_{2z} - \bar{a}(ZQ)_x$$
$$- \bar{b}\,2(ZQ)_yI_{3z} - \bar{c}(I_{1z} - I_{2z})I_{3z}, \qquad [12]$$

with

$$\bar{a}(t) = \sin^2\phi = \left(\frac{J_{12}}{J'}\right)^2$$

$$\bar{b}(t) = 0$$

$$\bar{c}(t) = \cos\phi\,\sin\phi = \frac{J_{12}J_\Delta}{(J')^2}. \qquad [13]$$

CREATION OF POLARIZATION ON THE HETERO NUCLEUS X

With the results of Eqs. [12] and [13], the creation of polarization signals on the hetero nucleus X can be understood. The application of a pulse along the y axis to the hetero nucleus X with a flip angle α transforms the two-spin order terms (I_{1z}

[2] In practical cases, this condition is always met. Usually, the hydrogenation proceeds for a few seconds before the detection pulse is placed (i.e., $\tau_h \approx 3$ s); J' is for normal systems greater than 10 Hz.

$- I_{2z})I_{3z}$ with a scaling factor of sin α into single-quantum antiphase terms of the form $(I_{1z} - I_{2z})I_{3x}$. These terms evolve under the J_{13} and J_{23} couplings into detectable I_{3y} magnetization. No other terms that are generated by the pulse can evolve into detectable magnetization during acquisition.

$$(I_{1z} - I_{2z})I_{3x} \xrightarrow{\mathcal{H}'t} (I_{1z} - I_{2z})I_{3x}\cos(\pi J't)$$
$$+ \left(\left(\frac{1}{2}I_{3y} - 2I_{1z}I_{2z}I_{3y}\right)\cos\phi\right.$$
$$\left. - 2Z(Q)_y I_{3x}\sin\phi\right)\sin(\pi J't). \quad [14]$$

The sine modulation of the expectation value of the detectable operator I_{3y} gives rise to an antiphase signal at the resonance frequency of spin 3 with a splitting of J'. In the nomenclature of (14), the two multiplet lines correspond to the transition between the states $S'\alpha$ and $T'_0\beta$, and the transition between the states $S'\beta$ and $T'_0\alpha$. If the antiphase signals are well resolved, that is, if no mutual cancellation of the antiphase signals occurs, the signal amplitudes are proportional to the product of the prefactors $\bar{c}$, cos ϕ, and sin α. Except for the trivial scaling factor sin α, the flip angle α has no influence on the observed antiphase multiplet. Hence, the same dependence of the signal amplitudes is expected as derived before, based on the populations of the energy levels of the AA'X spin system (15). The maximum signal amplitude (which is obtained for the flip angle $\alpha = \pi/2$) is proportional to

$$\bar{c}\cos\phi = \cos^2\phi\sin\phi. \quad [15]$$

Maximum signal intensity is obtained for $\cos\phi = \sqrt{2/3}$, which corresponds to $|J_\Delta/J_{12}| = \sqrt{2}$. This condition is identical to the results found by Barkemeyer *et al.* (15).

ANALYSIS OF THE INFLUENCE OF THE CATALYST

If the product of hydrogenation forms an AA'X spin system, its spectrum also provides information about hydrogenation intermediates. In the simplest case, the two protons form an isolated weakly coupled two-spin system in the intermediate.[3] For simplicity, we first assume that there is an intermediate with a lifetime τ_{cat} that is identical for all molecules in the ensemble. Under the influence of the weak coupling Hamiltonian of the two-spin system, the initial density operator of parahydrogen, $\rho(0)$, evolves during the lifetime τ_{cat} of the intermediate to

$$\rho(\tau_{cat}) = \frac{1}{4}\mathbf{1} - I_{1z}I_{2z} - \cos(\Delta\Omega_{cat}\tau_{cat})(ZQ)_x$$
$$- \sin(\Delta\Omega_{cat}\tau_{cat})(ZQ)_y, \quad [16]$$

[3] The discussion can easily be extended to an arbitrary network of weakly coupled nuclei.

where $\Delta\Omega_{cat}$ represents the difference of the precession frequencies of the two protons at the catalyst. This corresponds to a mixing of the initial singlet state $|S\rangle = (|\alpha\beta\rangle - |\beta\alpha\rangle)/\sqrt{2}$ and the triplet state $|T_0\rangle = (|\alpha\beta\rangle + |\beta\alpha\rangle)/\sqrt{2}$ with the complex amplitudes $c_S = \exp\{i\varphi\}\cos(\Delta\Omega_{cat}\tau_{cat}/2)$ and $c_{T0} = i\exp\{i\varphi\}\sin(\Delta\Omega_{cat}\tau_{cat}/2)$, respectively, and arbitrary phase φ. Hence, the S/T_0 mixing angle is $\varphi_{S/T_0} = \Delta\Omega_{cat}\tau_{cat}/2$ and the relative weights of S and T_0 are given by $\|c_S\|^2 = \cos^2(\Delta\Omega_{cat}\tau_{cat}/2)$ and $\|c_{T_0}\|^2 = \sin^2(\Delta\Omega_{cat}\tau_{cat}/2)$. In principle, therefore, a total conversion of the initial state S to the state T_0 can take place at the catalyst.

After the S/T_0 mixing process during the lifetime τ_{cat} of the intermediate, the density operator $\rho(\tau_{cat})$ (Eq. [16]) evolves in the substrate in an AA'X spin system. The difference between $\rho(0)$, the evolution of which is given in Eq. [7], and $\rho(\tau_{cat})$ is the scaling of the term $(ZQ)_x$ by a factor of $\cos(\Delta\Omega_{cat}\tau_{cat})$ and the additional zero-quantum term $\sin(\Delta\Omega_{cat}\tau_{cat})(ZQ)_y$. As the zero-quantum term $(ZQ)_y$ commutes with $\mathcal{H}''$, its evolution is solely determined by the *ILL* Hamiltonian $\mathcal{H}'$. Upon action of this Hamiltonian on $(ZQ)_y$, only the terms $\frac{1}{2}(I_{1z} - I_{2z})$ and $2(ZQ)_x I_{3z}$ are generated. Hence, the evolution of $(ZQ)_y$ yields a density operator $\rho_y(t)$ which can be expressed as

$$\rho_y(t) = d(t)(ZQ)_y + e(t)\frac{1}{2}(I_{1z} - I_{2z}) + f(t)2(ZQ)_x I_{3z}. \quad [17]$$

The solution for the time-dependent coefficients $d(t)$, $e(t)$, and $f(t)$ can be derived with the help of a system of differential equations similar to the one in Eq. [8]. For the initial conditions $d(0) = -\sin(\Delta\Omega_{cat}\tau_{cat})$, $e(0) = 0$, and $f(0) = 0$, the following time dependencies are obtained:

$$d(t) = -\sin(\Delta\Omega_{cat}\tau_{cat})\cos(2\pi J't)$$
$$e(t) = -\sin(\Delta\Omega_{cat}\tau_{cat})\sin\phi\sin(2\pi J't)$$
$$f(t) = -\frac{1}{2}\sin(\Delta\Omega_{cat}\tau_{cat})\cos\phi\sin(2\pi J't). \quad [18]$$

Following the reasoning leading to Eq. [12], these coefficients must be averaged in time to yield an averaged density operator. Quite evidently, the time averages of the coefficients $d(t)$, $e(t)$, and $f(t)$ are all equal to zero. Hence, the zero quantum term $(ZQ)_y$ in the density operator ρ_{cat} cannot affect the spectrum of the product molecule. Overall, therefore, the presence of the intermediate changes the time averaged density operator of the product from $\bar{\rho}_i$ (cf. Eq. [12]) to

$$\bar{\rho}'_i = \frac{1}{4}\mathbf{1} - I_{1z}I_{2z} - \cos(\Delta\Omega_{cat}\tau_{cat})$$
$$\times (\bar{a}(ZQ)_x + \bar{b}2(ZQ)_y I_{3z} + \bar{c}(I_{1z} - I_{2z})I_{3z}). \quad [19]$$

This expression was derived under the assumption that lifetime

τ_{cat} of the intermediate is identical for all molecules in the ensemble. In the more realistic case, where a distribution of lifetimes τ_{cat} exists, Eq. [19] is modified to

$$\bar{\rho}_i' = \frac{1}{4}\mathbf{1} - I_{1z}I_{2z} - \kappa(\bar{a}(ZQ)_x$$
$$+ \bar{b}2(ZQ)_yI_{3z} + \bar{c}(I_{1z} - I_{2z})I_{3z}), \quad [20]$$

where

$$\kappa = \langle\cos(\Delta\Omega_{cat}\tau_{cat})\rangle \quad [21]$$

represents the ensemble average of $\cos(\Delta\Omega_{cat}\tau_{cat})$. Hence, the general case with a range of lifetimes τ_{cat} cannot be distinguished from the special case with identical lifetimes τ_{cat} for all molecules in the ensemble and may be interpreted as an effective S/T_0 mixing with mixing angle $\varphi_{S/T_0}^{\text{eff}} = \arccos(\kappa)$.

If a pulse with flip angle β and phase y is applied to the protons 1 and 2, the density operator $\bar{\rho}_i'$ is transformed into $\bar{\rho}_f$, which is given by

$$\bar{\rho}_f' = d_1(I_{1x}I_{2z} + I_{1z}I_{2x}) + d_2(I_{1x} - I_{2x})I_{3z} + \ldots \quad [22]$$

with

$$d_1 = (1 - \kappa\bar{a})\sin\beta\cos\beta \quad [23]$$
$$d_2 = \kappa\bar{c}\sin\beta, \quad [24]$$

listing only those terms that evolve into detectable magnetization during acquisition. We consider the transitions C1–C8 with offsets

$$\nu_1 = -\nu_8 = (J' + J_{12} + J_\Sigma)/2$$
$$\nu_2 = -\nu_7 = (J' + J_{12} - J_\Sigma)/2$$
$$\nu_3 = -\nu_6 = (J' + J_{12} + J_\Sigma)/2$$
$$\nu_4 = -\nu_5 = (J' - J_{12} - J_\Sigma)/2 \quad [25]$$

relative to $\nu_A = \nu_{A'}$ and with $J_\Sigma = (J_{13} + J_{23})/2$. The individual integrals of these transitions are proportional to the transfer amplitudes $s_1, \ldots, s_8$, which can be derived with the help of the results of reference (19):

$$s_8 = s_7 = -s_2 = -s_1 = a(\beta), \quad [26]$$
$$s_3 = s_4 = -s_5 = -s_6 = b(\beta), \quad [27]$$

with

$$a(\beta) = ((1 - \sin\phi)(1 - \kappa\sin^2\phi)\cos\beta$$
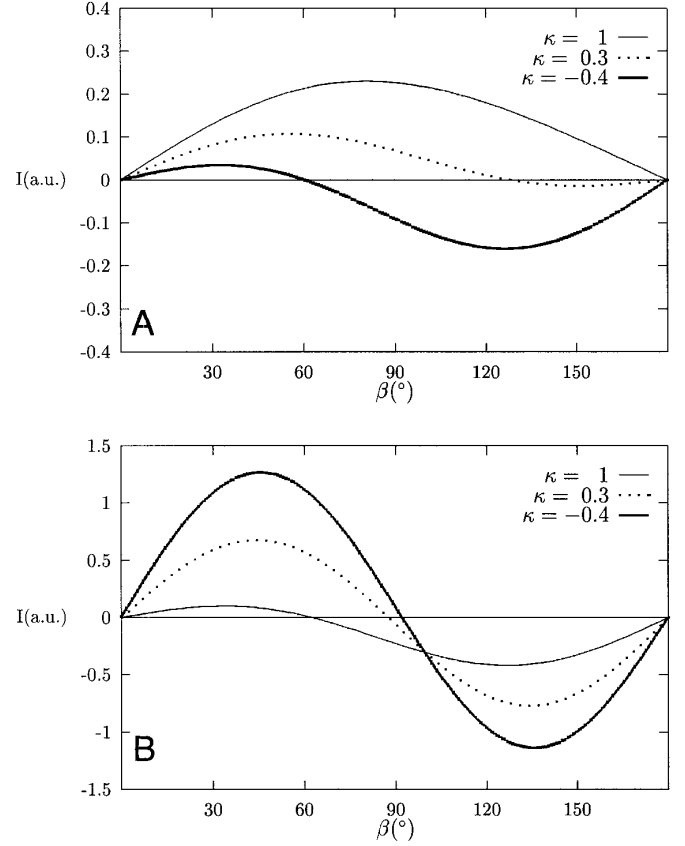$$+ \kappa\cos^2\phi\sin\phi)\sin\beta \quad [28]$$

FIG. 1. Plot of the flip angle dependence of the signal group with intensity $a(\beta)$ (Eq. [28]) (A) and $b(\beta)$ (Eq. [29]) (B) for $\phi = 57°$ for various κ values. This value of ϕ corresponds to $J_{12} = 10$ Hz, and $J_{13} = 2$ Hz, $J_{23} = 15$ Hz. These are typical values for a coupling topology of two olefinic hydrogens and one carbon with a geminal $^2J_{CH}$ and a *trans* $^3J_{CH}$ coupling.

and

$$b(\beta) = ((1 + \sin\phi)(1 - \kappa\sin^2\phi)\cos\beta$$
$$- \kappa\cos^2\phi\sin\phi)\sin\beta. \quad [29]$$

For a given ϕ (Eq. [10]), the flip angle dependence of the line integrals $a(\beta)$ and $b(\beta)$ depends on κ, which in turn can be interpreted as a result of an effective S/T_0 mixing. In Figs. 1 and 2, the flip angle dependence of the signal integrals $a(\beta)$ and $b(\beta)$ is shown for three κ and two ϕ values, representing typical coupling constant networks for AA′X spin systems of practical interest. As can be seen, the nutation curve of the two signal groups a and b shows a significant dependence on the precise κ value. The nutation curves depend most sensitively on κ if the difference between J_{13} and J_{23}, that is, between the two J_{CH} coupling constants, is on the order of the proton–proton coupling J_{12}.

The extraction of κ by fitting the line integrals as a function of the flip angle β may fail if lines overlap and when consequently accurate line integrals cannot be determined. In this
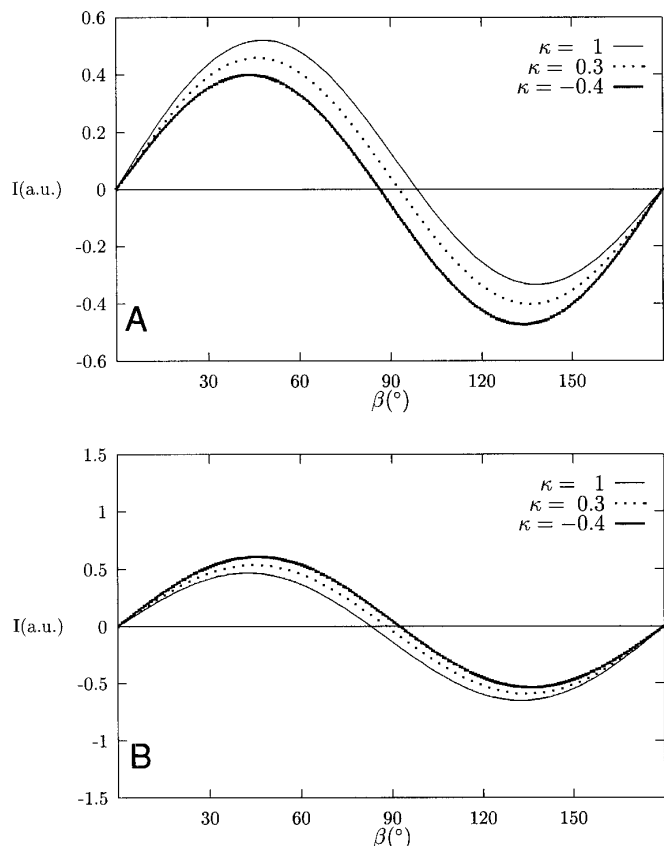
FIG. 2. Plot of the flip angle dependence of the signal group with intensity $a(\beta)$ (Eq. [28]) (A) and $b(\beta)$ (Eq. [29]) (B) for $\phi = 7°$ for various κ values. This value of ϕ corresponds to $J_{12} = 10$ Hz, $J_{13} = 2$ Hz, and $J_{23} = 150$ Hz. These are typical values for a coupling topology of two olefinic hydrogens and one olefinic carbon with a direct $^1J_{CH}$ and a geminal $^2J_{CH}$ coupling.

case, however, the factor κ can still be extracted by considering the flip angles β_a and β_b, where $a(\beta_a) = 0$ and $b(\beta_b) = 0$. In addition to the trivial zero crossings for $\beta = n\pi$ with integer n, zero crossings are found for

$$\beta_a(\kappa, \phi) = \arccos\left(\frac{-\kappa \cos^2\phi \sin \phi}{(1 - \sin \phi)(1 - \kappa \sin^2\phi)}\right) \qquad [30]$$

$$\beta_b(\kappa, \phi) = \arccos\left(\frac{\kappa \cos^2\phi \sin \phi}{(1 + \sin \phi)(1 - \kappa \sin^2\phi)}\right). \qquad [31]$$

In Fig. 3, the functions $\beta_a(\kappa)$ and $\beta_b(\kappa)$ are shown for the same coupling networks as used in Figs. 1 and 2, respectively. As can be seen in Fig. 3, $\beta_a(\kappa)$ is most suitable for the detection of κ values smaller than about 0.4 and for negative values. $\beta_b(\kappa)$, on the other hand, is to be preferred for the analysis of κ values close to 1.

Accordingly, using either of the two approaches just outlined, valuable information about the amount by which the initial density operator of parahydrogen is modified at the catalyst can be extracted from the product spectrum.

CONCLUSIONS

In this article, we have presented a rigorous treatment of the evolution of the parahydrogen density operator in an AA′X spin system based on the density operator formalism. We have investigated the influence of the catalyst as well as the occurrence of polarization signals on the hetero nucleus X. We have validated the claim that assuming weak coupling at the catalyst, the processes at the catalyst can be described in terms of an effective S/T_0 mixing. Here, we have presented an analytical method to determine the degree of this effective S/T_0 mixing, which contains crucial information about the processes at the catalyst. Ultimately, the fingerprint the intermediate leaves on the polarization pattern of the product molecule should make it feasible to obtain a whole range of valuable information about the hydrogenation intermediate. It should, for instance, be possible to obtain information about the relative chemical shifts of the protons in the intermediates, about the lifetime of the intermediates, and also about their coupling topology with respect to other nuclei. Since the origin of the occurrence of this phenomenon lies in the specific nature of the parahydrogen density operator, and since the chances for actual detection of the effect rely on the inherent signal enhancement
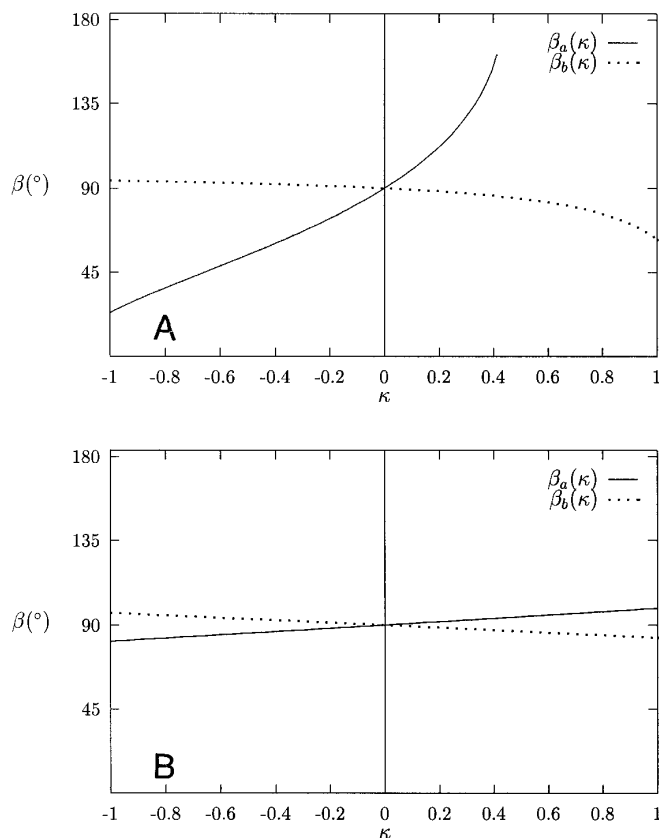

FIG. 3. (A) Plot of the functions $\beta_a(\kappa)$ and $\beta_b(\kappa)$ for $\phi = 57°$ (compare Fig. 1). (B) Plot of the functions $\beta_a(\kappa)$ and $\beta_b(\kappa)$ for $\phi = 7°$ (compare Fig. 2).

associated with parahydrogen, such detailed information about the catalytic processes cannot be obtained with any other NMR method.

ACKNOWLEDGMENTS

REFERENCES

1. C. R. Bowers and D. P. Weitekamp, *Phys. Rev. Lett.* **57,** 2645 (1986).

2. C. R. Bowers and D. P. Weitekamp, *J. Am. Chem. Soc.* **109,** 5541 (1987).

3. T. C. Eisenschmid, R. U. Kirss, P. A. Deutsch, S. I. Hommeltoft, R. Eisenberg, J. Bargon, R. G. Lawler, and A. L. Balch, *J. Am. Chem. Soc.* **109,** 8089 (1987).

4. J. Barkemeyer, J. Bargon, H. Sengstschmid, and R. Freeman, *J. Magn. Reson. A* **120,** 129 (1996); H. Sengstschmid, R. Freeman, J. Barkemeyer, and J. Bargon, *J. Magn. Reson. A* **120,** 249 (1996).

5. M. Haake, J. Natterer, and J. Bargon, *J. Am. Chem. Soc.* **118,** 8688 (1996).

6. J. Natterer, J. Barkemeyer, and J. Bargon, *J. Magn. Reson. A* **123,** 253 (1996).

7. M. Jang, S. B. Duckett, and R. Eisenberg, *Organometallics* **15,** 2863 (1996); S. B. Duckett, R. J. Mawby, and M. G. Partridge, *Chem. Commun.,* 383 (1996); S. B. Duckett, G. K. Barlow, M. G. Partridge, and B. A. Messerle, *J. Chem. Soc. Dalton. Trans.,* 3427 (1995).

8. C. J. Sleigh, S. B. Duckett, and B. A. Messerle, *Chem. Commun.,* 2396 (1996).

9. S. B. Duckett, C. L. Newell, and R. Eisenberg, *J. Am. Chem. Soc.* **116,** 10548 (1994); *J. Am. Chem. Soc.* **119,** 2068 (1997).

10. A. Harthun, J. Bargon, and R. Selke, *Tetrahedron Lett.* **35,** 7755 (1994); A. Harthun, K. Woelk, J. Bargon, and A. Weigt, *Tetrahedron Lett.* **51,** 11199 (1995); A. Harthun, R. Kadyrow, R. Selke, and J. Bargon, *Angew. Chem.* **109,** 1155 (1997).

11. A. Harthun, R. Selke, and J. Bargon, *Angew. Chem. Int. Ed. Engl.* **35,** 2505 (1996); A. Harthun, R. Giernoth, C. J. Elsevier, and J. Bargon, *Chem. Comm.,* 2483 (1996).

12. J. Bargon, J. Kandels, P. Kating, A. Thomas, and K. Woelk, *Tetrahedron Lett.* **40,** 5721 (1990).

13. J. Bargon, J. Kandels, and P. Kating, *J. Chem. Phys.* **98,** 6150 (1993); P. Kating, A. Wandelt, R. Selke, and J. Bargon, *J. Phys. Chem.* **97,** 13313 (1993).

14. M. Haake, J. Barkemeyer, and J. Bargon, *J. Phys. Chem.* **99,** 17539 (1995).

15. J. Barkemeyer, M. Haake, and J. Bargon, *J. Am. Chem. Soc.* **117,** 2927 (1995).

16. H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Can. J. Chem.* **35,** 65 (1957).

17. S. Schäublin, A. Höhener, and R. R. Ernst, *J. Magn. Reson.* **13,** 196 (1974).

18. S. J. Glaser, *J. Magn. Reson. A* **104,** 283 (1994).

19. L. E. Kay and R. E. D. McClung, *J. Magn. Reson.* **77,** 258 (1988).