

Spin Catalysis of Ortho–Para Hydrogen Conversion

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We propose a new mechanism for paramagnetically catalyzed ortho–para conversion in molecular hydrogen. In this mechanism, a $^3\Sigma_u^+$ excited-state character of H_2 is mixed into the ground state of a collisional complex, inducing spin-uncoupling and removal of antisymmetrization of the parts of the wave function localized to the hydrogen nuclei. This induces an effective Fermi contact hyperfine interaction between the ortho and para states. Using the collision complex $H_2 + O_2$ as model system, we show that the proposed mechanism is more than 2 orders of magnitude stronger than the traditional inhomogeneous magnetic field model.

1. Introduction

The spin-catalysis concept was recently introduced in order to describe and classify a wide range of phenomena in which chemical reactions are promoted by substances assisting to overcome spin prohibition.^{1,2} This concept is based on the crucial role of the electron spin in the control of reaction channels in the region of activated complexes. Catalysts can change the rate of a reaction by a spin switch with the catalysant in the complex. There are two very effective ways to accomplish these changes: (1) by supplying electrons with non-totally quenched orbital angular momentum to the activated complex of the common system (spin-orbit coupling induced spin catalysis) and (2) by supplying nonpaired electrons to the activated complex of the common system (paramagnetic spin catalysis).

When the paramagnetic substance produces a catalytic action upon a diamagnetic substrate reaction, the spin change can easily occur because of the intermolecular exchange interaction. Paramagnetic species which accelerate the rate of cis–trans isomerization reactions, enhance decarboxylation of malonic acids, etc., constitute examples of homogeneous spin catalysis of the second type. Singlet (S) to triplet (T) state mixing in organic molecules induced by exchange interaction with paramagnetic catalysts is responsible for the lowering of the activation energy.² The ortho–para hydrogen conversion catalyzed by O_2 could be considered as a physical process of similar nature. In order to induce a nuclear spin flip the paramagnetic catalyst should first produce spin-uncoupling in the electronic shell, since it is most sensitive to catalytic perturbation. The triplet excited-state contamination to the ground singlet state in the H_2 molecule induced by collision with paramagnetic oxygen can give a nonzero matrix element for Fermi contact interaction between ortho and para states. It is well-known that the S–T state mixing by Fermi contact interaction is the most important contribution to the spin–spin coupling constant in the NMR spectrum of the HD molecule.³ On this ground we propose and evaluate a new model for ortho–para hydrogen conversion catalyzed by molecular oxygen.

Eyring et al. paid attention to spin changes in chemical kinetics already 50 years ago.^{4,5} They interpreted the gas-phase thermal cis–trans isomerization reactions of substituted ethylenes on the basis of absolute rate theory of “singlet and triplet

mechanisms” according to whether the reaction proceeds entirely via the singlet (S) state potential energy surface (PES) or involves a switch to the triplet (T) state PES at $\gamma \approx 90^\circ$, where γ is the torsion angle.⁴ At the same time Eyring et al.⁵ tried to explain the effect of paramagnetic substances in catalyzing these cis–trans isomerizations by the account of nonhomogeneous magnetic fields created by the catalysts, which would act differently on each of the two spins. This was the mechanism that Wigner⁶ first proposed for paramagnetic catalysis of ortho–para (o–p) conversion of molecular hydrogen. However, in the context of paramagnetic catalysis of cis–trans isomerization it was later argued that the magnetic field mechanism could not be as effective as ordinary electronic intermolecular interaction.⁷ By means of configuration interaction calculations we have recently shown this to be the case in the catalytic complex $C_2H_4 + O_2$.² It is therefore natural to suggest that the traditional nonhomogeneous magnetic field perturbation mechanism is not the main driving force for the catalysis of the ortho–para (o–p) conversion in hydrogen. Experimental data also indicate that Wigner’s mechanism underestimates the rate for catalyzed o–p conversion by 2 orders of magnitude.^{8–11}

2. Paramagnetic Spin Catalysis of Ortho–Para Hydrogen Conversion

The proton spins of ortho– H_2 are mutually parallel (triplet state) and those of para– H_2 are antiparallel (singlet state). The o–p conversion is very important for the storage of condensed hydrogen. At low temperatures the uncatalyzed o–p interconversion is relatively slow and a nonequilibrium mixture can exist. The energy released on converting normal hydrogen (the equilibrium 3:1 mixture) to para-liquid hydrogen is sufficient to vaporize 64% of the original liquid.¹² For this reason, catalysts have been developed that rapidly convert normal to para hydrogen, thereby facilitating the storage of liquid H_2 .¹²

In 1933 Farkas and Sachsse¹³ found that paramagnetic molecules (O_2 , NO) induce interconversion of ortho- and parahydrogen in the gas phase and that diamagnetic molecules do not influence such a reaction. Wigner⁶ gave the following explanation of this S–T transition in the nuclear spin system. The nuclear wave function of a hydrogen molecule consists of two parts, corresponding to spin and rotation. The nuclear spin functions can be written in the usual form

$$\Omega_{\text{ortho}} = 2^{-1/2}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (1)$$

$$\Omega_{\text{para}} = 2^{-1/2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (2)$$

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The relative phase of the spin and rotation components is important. The singlet para spin state is antisymmetric upon permutation of the two protons, and hence the Pauli principle requires the rotational wave function to be symmetric. The rotational quantum number l must be even. Similarly, the triplet ortho spin state is symmetric upon permutation and is associated with odd l values. The lowest para state ($l = 0$) is lower in energy than the corresponding ortho state ($l = 1$) by a rotational quantum $B = 60.8 \text{ cm}^{-1}$. Hence the spin symmetry leads to a large energy splitting of the ortho and para states. To cause the o-p transition this energy must flow to dynamic variables. In Wigner's theory of homogeneous paramagnetic gas catalysis the decrease of energy is connected with the kinetic energy of the molecules. Several authors^{8,14-17} extended Wigner's theory to studies of o-p conversion at solid magnetic surfaces. They included the energy flow to the spin system of magnetic impurities but did not change the main feature of Wigner's theory—the driving force of the o-p conversion.

The magnetic field created by the catalyst is inhomogeneous on the scale of the hydrogen molecule; the spins of the two protons (I_1 and I_2) experience different magnetic fields (B_1 and B_2). The nuclear Zeeman Hamiltonian is given by

$$H_Z = \beta_N \sum_i (I_{1,i} B_{1,i} + I_{2,i} B_{2,i}) = 0.5 \beta_N \sum_i [(I_{1,i} + I_{2,i})(B_{1,i} + B_{2,i}) + (I_{1,i} - I_{2,i})(B_{1,i} - B_{2,i})] \quad (3)$$

where β_N is the magnetic moment of the proton and $i = x, y, z$. A spin operator of the type $(I_{1,i} - I_{2,i})$ can mix S and T nuclear spin functions (1) and (2). But the magnetic field, created by the paramagnetic catalyst at an intermolecular distance of the order 3 Å, is very weak (the difference of magnetic field strengths at the two hydrogen nuclei is even less). For gas-phase catalysis by molecular oxygen the best orientation of the H_2 and O_2 molecules would in this model correspond to a collinear collision, which implies maximum magnetic field difference at the hydrogen nuclei. *Ab initio* calculations predict that such a geometry constitutes one of the most stable structures of the complex.¹⁸ At the restricted open-shell Hartree-Fock (ROHF) level there is a local minimum for the linear $H_2 + O_2$ complex, although the trapezoid-like complex is slightly more stable (6-311 G** basis set results).¹⁸ The optimized intermolecular O-H distance between the nearest neighbors in the linear complex is 3.04 Å in the ROHF approximation¹⁸ and the $\langle \text{ortho} | H_Z | \text{para} \rangle$ matrix element of perturbation (3) is easily estimated as 0.064 MHz. At any other collisional geometry the perturbation energy would be smaller and equal to zero at the symmetrical (C_{2v} group) trapezoid complex.

The alternative mechanism of paramagnetic spin catalysis for the ortho-para hydrogen conversion is prompted by the experience from investigations of the oxygen influence on the enhancement of optical S-T transitions¹⁸ and of the O_2 induced spin catalysis.² For example, the vertical $T_1 \leftarrow S_0$ absorption in ethylene is strongly enhanced by collision with molecular oxygen. Because the O_2 molecule has a triplet ground state ${}^3\Sigma_g^-$ ¹⁹ all states of the collision complex $C_2H_4 + O_2({}^3\Sigma_g^-)$ can be triplet states (the T + T collision can give singlet, triplet, and quintet states).²⁰ In the collision complex the ground triplet state is mixed by intermolecular exchange interaction with the ethylene excited triplet state,²⁰ so the S-T transition in the ethylene moiety is not spin-forbidden any more. The efficiency in the removal of spin-forbiddenness depends on the intermolecular exchange interaction. Configuration interaction studies²¹ of the complex gave a good explanation for the 10^5 times intensity enhancement of the $T_1 \leftarrow S_0$ transition in ethylene.

The collision complex between the O_2 and H_2 molecules has also been studied as the simplest example of perturbations produced by a diamagnetic molecule on the oxygen spectra and as a theoretical model for solvent induced emission of molecular ${}^1\Delta_g$ oxygen.^{18,21,22} Though the problem of the $T_1 \leftarrow S_0$ transition enhancement in the hydrogen molecule ($a^3\Sigma_u^+ \leftarrow X^1\Sigma_g^+$) by collision with oxygen has no importance and has not been studied by experimentalists, it is related (indirectly) to the catalysis of o-p conversion. Both problems are determined by spin-uncoupling in the electronic shell of the H_2 molecule, which is a measure of electronic singlet and triplet state mixing. In the $H_2 + O_2$ complex the ground triplet state

$${}^1\Sigma_g^+(H_2) + {}^3\Sigma_g^-(O_2) \quad (4)$$

has an admixture of the triplet component of the configuration

$${}^3\Sigma_u^+(H_2) + {}^3\Sigma_g^-(O_2) \quad (5)$$

Such a mixing has been obtained in previous CI calculations of nonsymmetric collision complexes^{18,23} and is studied in detail in this paper. The admixture is extremely small, but nevertheless it is important for spin catalysis of ortho-para hydrogen conversion. The ground state of the collision complex $H_2 + O_2$ can be represented by the wave function

$${}^3\Psi_0 = {}^3({}^1\Sigma_g^+(H_2) * X^3\Sigma_g^-(O_2)) + C_1 ({}^3\Sigma_u^+(H_2) * {}^3\Sigma_g^-(O_2)) \quad (6)$$

Here * means the proper antisymmetrization product of the wave functions. The electronic wave function (6) can be used for calculation of the Fermi contact hyperfine coupling operator matrix element for ortho-para conversion.

$$a = \langle {}^3\Psi_0 \Omega_{\text{ortho}} | H_F | {}^3\Psi_0 \Omega_{\text{para}} \rangle = 2C_1 \langle {}^1\Sigma_g^+(H_2) \Omega_{\text{ortho}} | H_F | {}^3\Sigma_u^+(H_2) \Omega_{\text{para}} \rangle \quad (7)$$

here H_F is the Fermi contact hyperfine coupling operator

$$H_F = \sum_{k,N} \xi_N \delta(\mathbf{r}_{k,N}) \mathbf{s}_k \cdot \mathbf{I}_N \quad (8)$$

where

$$\xi_N = 16\pi\mu_B \hbar \gamma_N / 3 \quad (9)$$

Conventional notations are used. The last integral in eq 7 is equal to

$$\langle {}^1\Sigma_g^+ \Omega_{\text{ortho}} | H_F | {}^3\Sigma_u^+ \Omega_{\text{para}} \rangle = -(\xi_H / \sqrt{2}) [\langle 1\sigma_g | \delta_a | 1\sigma_u \rangle - \langle 1\sigma_g | \delta_b | 1\sigma_u \rangle] \quad (10)$$

where δ_a is a one-electron δ -function on the a nucleus and $1\sigma_g$ and $1\sigma_u$ are the bonding and antibonding MOs of the hydrogen molecule in a simple representation of the lowest triplet ${}^3\Sigma_u^+$ repulsive state

$${}^3\Sigma_u^+ = (1/\sqrt{2}) [1\sigma_g(1)1\sigma_u(2) - 1\sigma_g(2)1\sigma_u(1)] \omega_t \quad (11)$$

Here ω_t is an electronic triplet spin state wave function of type 1. The configuration (11) is a main component of the lowest excited triplet state of the hydrogen molecule at the equilibrium ground-state distance $r_e = 0.75 \text{ Å}$. Small admixtures of other configurations ($1\sigma_u 2\sigma_g$ and $1\sigma_g 2\sigma_u$) do not change the qualitative conclusion of this simple analysis, which strictly applies for a minimal basis set. In that case the $1\sigma_g$ and $1\sigma_u$ MOs can be represented in the form

$$1\sigma_g = \frac{1}{\sqrt{(2 + 2S_{a,b})}}[\psi_a + \psi_b] \quad (12)$$

$$1\sigma_u = \frac{1}{\sqrt{(2 - 2S_{a,b})}}[\psi_a - \psi_b] \quad (13)$$

where ψ_a is 1s atomic orbital on nucleus a. For these MOs it is easy to get, neglecting small two-center integrals,

$$\langle 1\sigma_g | \delta_a | 1\sigma_u \rangle - \langle 1\sigma_g | \delta_b | 1\sigma_u \rangle = \frac{1}{2\sqrt{(1 - S_{a,b}^2)}} |\psi_{1s}(0)|^2 \quad (14)$$

The integral (7) is now equal to

$$a = - \frac{C_t \xi_H}{\sqrt{2(1 - S_{a,b}^2)}} |\psi_{1s}(0)|^2 \quad (15)$$

The density of the 1s wave function on the nucleus is a well-known parameter.²⁴ The proposed mechanism crucially depends on the admixture of the hydrogen triplet state wave function, C_t , induced by collision with molecular oxygen. In order to compare the paramagnetic spin catalysis of this type with Wigner's mechanism we have estimated the electronic spin-uncoupling coefficient C_t by direct calculations of the collision complexes $H_2 + O_2$.

3. Calculations

We have performed configuration interaction (CI) calculations using orbitals optimized for the $O_2 + H_2$ complex at different geometries. The orbital optimization was carried out using the restricted open-shell Hartree-Fock (ROHF) method and an extended split 6-311 G** basis set augmented by polarization p orbitals on the hydrogen atoms and d orbitals on the oxygen atoms.²⁵ The ground-state configuration reads

$${}^3\Phi_0 = |1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\sigma_g^2(H_2) 3\sigma_g^2 1\pi_u^4 1\pi_g^2| \quad (16)$$

Though the molecular orbitals (MOs) of the nonsymmetric complex are mixed, it is possible to make an approximate assignment using the $D_{\infty h}$ notations of the individual molecules. The hydrogen MO in expression (16) has a special label, and all other MOs belong to oxygen. In the CI approach the inner-shell MOs are kept frozen. The main results (R, CI admixture coefficients) were found insensitive to freezing also the two first valence MOs, $2\sigma_g$ and $2\sigma_u$. So all results discussed here include the following multireference CI: the first four orbitals were kept frozen; the next six MOs determine the complete active space for ten electrons. All single and double excitations from these 15 reference states of the complete active space to the 15 lowest unoccupied MOs were taken into account, which corresponds to 37 590 configuration state functions (CSF:s). The unoccupied MOs above the main ground-state configuration (16) include two σ_u , two σ_g , and π_u orbitals on hydrogen together with three vacant σ_u , two σ_g , and π_g , π_u MOs on oxygen. The corresponding multireference CI (MRCI) for the separated molecules have also been performed including different interatomic distances. For the O_2 molecule the MRCI basis includes 6085 CSFs. The calculations for hydrogen correspond to a single-reference CI with 28 CSFs.

The admixture coefficient, C_t , strongly depends on the geometry of the collision complex. At the trapezoid-like geometry with C_{2v} symmetry¹⁸ the mixing (6) is forbidden. The mixing is allowed for the linear complex; the intermolecular distance dependence has been studied here for such a linear collision (the enhancement of $b^1\Sigma_g^+ - a^1\Delta_g$ transition in O_2 ,

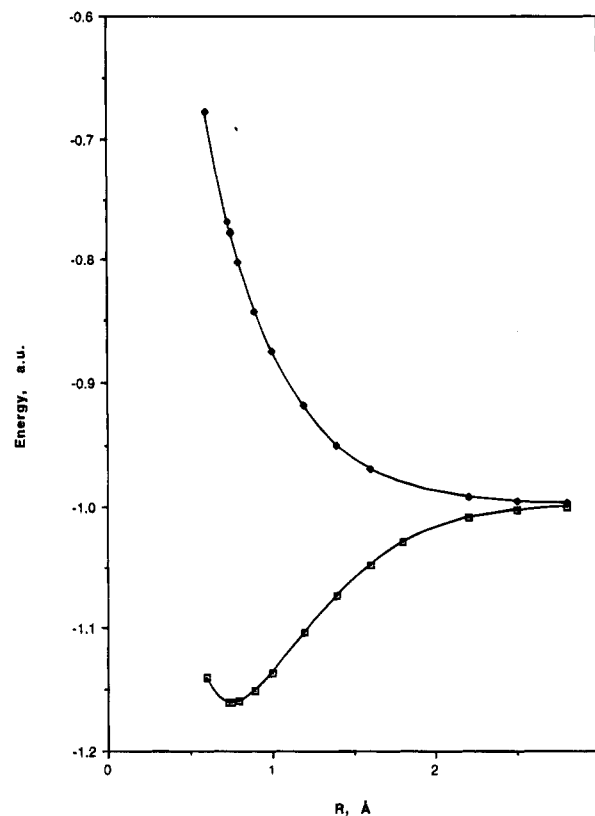


Figure 1. Potential energy curves for the lowest singlet $X^1\Sigma_g^+$ and triplet $b^3\Sigma_u^+$ states of the H_2 molecule.

which was studied previously,¹⁸ is forbidden at linear collision; so this complex was not described in ref 18). A few nonsymmetrical collisions have also been calculated in order to get some qualitative conclusion about averaging of random collision geometries.

4. Results

To discuss the quality of the CI approach and to verify the nature of the collisional perturbation, it is necessary to study the ability of the calculations to reproduce the spectra of the separated molecules. Important for the purpose of our work is to reproduce the energy difference between the lowest triplet $b^3\Sigma_u^+$ and the ground singlet $X^1\Sigma_g^+$ states in the hydrogen molecule ($\Delta E_{T,S}$). The potential curves for these states are shown in Figure 1. The total energy of the hydrogen molecule at the internuclear distance ($r = 0.741$ Å) is only -1.1611 hartrees in our calculation, to be compared with the value of Kolos and Wolniewicz, -1.1744 hartrees,²⁶ (full CI in the basis set gives -1.1677 hartrees). The $\Delta E_{T,S}$ value, 10.60 eV, is, however, in excellent agreement with the precise data of Kolos and Wolniewicz (10.62 eV).²⁶ Other excited states of the H_2 molecule being of some Rydberg character are reproduced with less accuracy. The calculated spectroscopic constants for few important states of O_2 and H_2 are compared with experimental data in Tables 1 and 2, respectively. The quality of calculated potentials is moderate, but they reproduce the qualitative features of the spectra. Energies of the pure Rydberg states $E^1\Sigma_g^+$, $a^3\Sigma_g^+$ in H_2 disagree notably with experimental energies. Fortunately, this is not important for our final result; we use a semiempirical estimation of the Fermi contact interaction in the ground state and the extension of the basis set is not necessary for this purpose.

Calculations of the collision complex $H_2 + O_2$ in this approach give the most stable linear geometry with a nearest O-H distance $R = 2.92$ Å. We use the fixed equilibrium r_e

TABLE 1: Experimental and Calculated Spectroscopic Constants for a Few Triplet States of the Oxygen Molecule

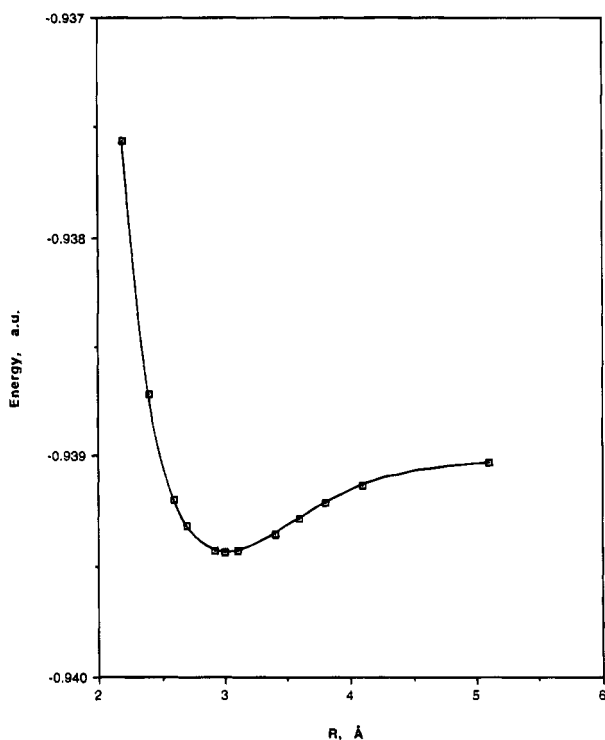
term	adiabatic excitation				vertical excitation	
	r_e (Å)		T_e (eV)		E (eV)	
	expt ^{a,b}	MRCI ^c	expt ^{a,b}	MRCI ^c	expt ^{a,b}	MRCI ^c
$X^3\Sigma_g^-$	1.208	1.213	0	0	0	0
$A^3\Sigma_u^-$	1.513	1.558	4.307	3.887	~6	6.039
$A^3\Sigma_g^+$	1.520	1.562	4.389	3.964	~6	6.188
$B^3\Sigma_u^-$	1.604	1.620	6.174	6.605	8.6	9.852

^a Huber and Herzberg.¹⁹ ^b Slinger and Cosby.²⁹ ^c This work.

TABLE 2: Experimental and Calculated Spectroscopic Constants for the Hydrogen Molecule

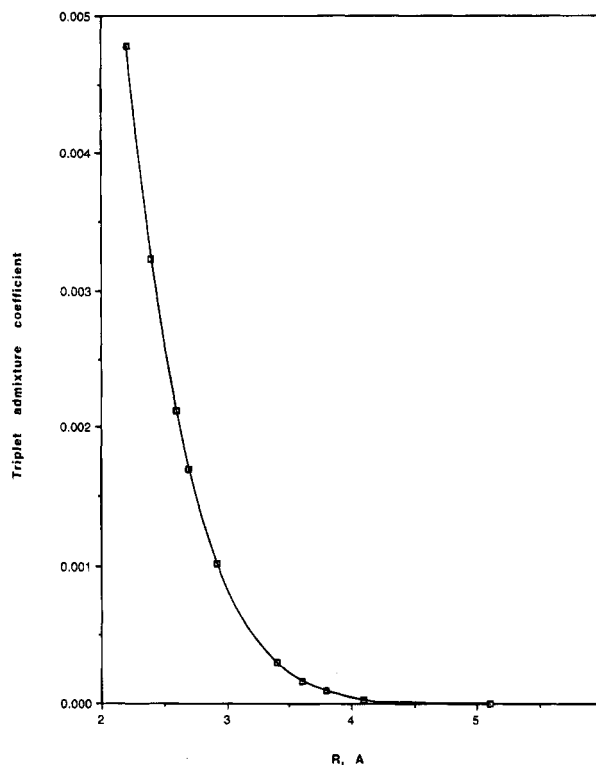
term	adiabatic excitation		vertical excitation	
	r_e (Å)		T_e (eV)	
	expt ^a	MRCI ^b	expt ^a	MRCI ^b
$X^1\Sigma_g^+$	0.741	0.750	0	0
$B^1\Sigma_g^+$	1.289	1.276	11.37	12.15
$F^1\Sigma_g^+$	2.315	2.320	12.51	13.34
$a^3\Sigma_g^-$	0.989	0.981	11.90	14.72

^a Huber and Herzberg.¹⁹ ^b This work.

**Figure 2.** Potential energy curve for the lowest $^3\Sigma^-$ state of the linear complex between the H_2 and O_2 molecules.

values for O_2 (1.2132 Å) and H_2 (0.7505 Å) obtained by the multireference CI calculations, because the total geometry optimization at the ROHF level showed only small changes of these quantities upon the complex formation.¹⁸ A partial geometry optimization at the MRCI level definitely shows that the linear complex is more stable than all other geometrical structures. The intermolecular potential for the linear collision is shown in Figure 2. The calculated dissociation energy of the complex, $D_e = 86.6 \text{ cm}^{-1}$, obtained as an energy difference at $R = 10 \text{ Å}$ and at R_e distances, is rather approximate.

The estimation of the D_e value and the search of the real minima on the potential energy surface (PES) is not the aim of this study. From present and previous¹⁸ studies one can infer that the PES is quite flat until the intermolecular distance $R \approx$

**Figure 3.** Intermolecular distance dependence of the C_1 coefficient (6).

3 Å with a shallow ditch around the O_2 molecular at this distance. Few local minima separated by very small barriers have been obtained at the single and double CI level. The most important aspect for the present study is the decomposition analysis of the CI wave function and the admixture of the configuration $^3(^3\Sigma_u^+(H_2) * ^3\Sigma_g^-(O_2))$

$$^3\Phi_1 = |1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\sigma_g^1(H_2) 3\sigma_g^2 1\pi_u^4 1\pi_g^2 1\sigma_u^1(H_2)| \quad (17)$$

For this and for the largest CI contributions the results are found negligibly sensitive to addition of triple and quadrupole excited configurations.

Few random types of collision geometries have been calculated at different R by the MR CI approach. For all of them the intermolecular distance between the nearest H and O atoms is very close to 3 Å. The interatomic distance in oxygen was kept fixed (1.2132 Å) throughout all calculations; for hydrogen it was varied slightly in the vicinity of 0.75 Å. The largest CI admixture (6) was obtained at the linear collision geometry.

Figure 3 shows the admixture coefficient (6) as a function of intermolecular distance for the linear collision $H_2 + O_2$. At the equilibrium distance $R_e = 2.92 \text{ Å}$ it is close to 0.001 and increases rapidly at shorter R . Its behavior is typical for other collision-induced properties which depend on the intermolecular exchange interaction (singlet-triplet and cooperative transition intensities, intermolecular spin-orbit coupling perturbation, spin polarization etc.).^{18,21} It has been shown that such properties are also very sensitive to charge-transfer interactions.^{18,21} There is some correlation between charge polarization inside the molecules at large distances, charge transfer (from oxygen to hydrogen) at shorter distances ($R < 3.5 \text{ Å}$), and the C_1 coefficient. Though there are great many charge-transfer (CT) configurations in the CI expansion we can discern some dependence between the most important CT admixtures and the triplet state (6) contribution.

Accounting for the computed C_1 admixture at the equilibrium R_e distance we obtain the ortho-para hydrogen transition matrix

element (7) equal to 1.5 MHz. Here we used the experimentally adjusted value $\xi_{\text{H}}|\psi_{1s}(0)|^2 = 1420 \text{ MHz}$.³ The matrix element of the nuclear Zeeman perturbation (3), which is used in Wigner's theory, is only 0.072 MHz at the same distance. So the ratio of the squares of the two matrix elements is over 400, which corresponds to the ratio of the rate constants for the ortho–para conversion, determined by the two mechanisms. The dynamic part of Wigner's theory could be applied further without changes. It means that the energy of rotational quanta which corresponds to the ortho–para transition can dissipate through translational movements of the two molecules.

5. Conclusions

A great amount of experimental studies of ortho–para hydrogen conversion catalyzed by paramagnetic impurities in homogeneous or heterogeneous catalysis have been analyzed in terms of the theory of Wigner.⁶ The energy balance provided by the kinetic energy in the gas phase has been augmented by magnons in the case of catalysis by magnetic surfaces.^{8,14–17} Nevertheless, all experimental data indicate that Wigner's mechanism underestimates the rate for catalyzed o–p conversion by 2 orders of magnitude.^{8–11} Backed by *ab initio* calculations we have shown that the nonhomogeneous magnetic field perturbation proposed by Wigner is not the main driving force behind the catalysis of the o–p conversion in hydrogen. The most important mechanism is rather the spin-uncoupling mechanism, induced in the electronic shell by collision with the paramagnetic catalyst, and which corresponds to the triplet-state admixture to the ground state of the H₂ moiety. Similar mechanisms are realized in many other spin-catalytic processes.² Such spin-uncoupling removes the proper antisymmetrization of those parts of the wave function which are localized in the vicinity of the hydrogen nuclei and induces therefore an effective Fermi contact hyperfine interaction between the ortho and para states. By comparison of matrix elements we have shown that the proposed mechanism is much more effective than the traditional one proposed already in 1933.⁶ Finally, we note that the necessity of inclusion of electronic orbital degrees of freedom has recently been realized for H₂ o–p conversion on nonmagnetic metal surfaces,^{27,28} where Wigner's theory cannot be applied. It was proposed that the o–p energy dissipates by

metal electron–hole triplet pairs.^{27,28} In some way this mechanism is similar to the mechanism considered in the present work.

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