Para-ortho hydrogen conversion: Solving a 90-year old mystery

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Abstract
Almost ninety years have passed since the experiments of Farkas and Sachsse [Z. Phys. Chem. B 1933; 23:1] on para-ortho hydrogen conversion catalyzed by paramagnetic species such as O2, but a detailed and quantitative understanding of the conversion process and its temperature dependence was still lacking. Here, we present a complete and quantitative theoretical treatment of this catalytic process. Both interactions causing the conversion are included: the magnetic dipole-dipole coupling between the electron spin of O2 and the nuclear spins in H2 and the Fermi contact coupling from spin densities at the H-nuclei induced by O2. The latter were extracted from ab initio electronic structure calculations. State-to-state conversion cross sections and rate coefficients are obtained from quantum mechanical coupled-channel calculations including the full anisotropic O2-H2 interaction potential and by treating both the spin-dependent couplings perturbatively. The total rate coefficient agrees with the experimental value recently measured by Wagner [Magn. Reson. Mater. Phys., Biol. Med. 2014; 27:195] in O2-H2 gas mixtures and explains the temperature dependence observed in the 1933 measurements mentioned above.

INTRODUCTION

Hydrogen is best known as a clean fuel, but also arises in other important applications. One of them is in nuclear magnetic resonance (NMR), a technique that is widely used to determine the structure of (bio)molecules and materials, and in magnetic resonance imaging (MRI) used for medical diagnostics. As explained below, normal hydrogen is a mixture of ortho-hydrogen and para-hydrogen in the ratio of 3 to 1, which interconvert so slowly that they can be considered as distinct species. For the application in magnetic resonance, one needs pure or substantially enriched para-hydrogen. The incorporation of para-hydrogen in molecules studied by NMR or MRI can increase the sensitivity of these techniques by four to five orders of magnitude1–5 through the effect of para-hydrogen induced polarization (PHIP). This hyperpolarization method not only reduces the number of transients required to obtain an NMR spectrum or image, but can also reveal previously undetectable species present in solution. The transfer of the singlet nuclear spin configuration of para-hydrogen (explained below) to the molecules studied by NMR can occur either via a catalytic hydrogenation reaction or through formation of a transient complex in which the para-hydrogen molecule and the molecule to be measured associate as ligands to a transition-metal complex.5

The rate of ortho-para hydrogen conversion is strongly enhanced not only by special catalysts, but also by collisions with paramagnetic molecules in the gas phase. This paper presents the first complete and quantitative theoretical treatment of the conversion process in collisions with a paramagnetic molecule, oxygen. Before describing our approach, based on first principles, we briefly outline the theoretical and historical background.

The reason why the conversion between ortho-hydrogen (oH2) and para-hydrogen (pH2) is extremely slow is that they have different nuclear spin states. Nuclear spins interact so weakly with other properties of matter that these spin states are conserved in almost any process, including chemical reactions. A fundamental postulate in quantum mechanics is that the wave functions of indistinguishable particles must be symmetric or antisymmetric under the exchange of their position and spin coordinates. Hydrogen nuclei, protons, with nuclear spin 1/2, are fermions and thus...
the wave functions of the two protons in H₂ must be antisymmetric. In pH₂, the two proton spins are coupled to total spin \( I = 0 \). The \( I = 0 \) nuclear spin wave function is antisymmetric, which implies that the spatial wave functions of pH₂ must be symmetric and that the molecule can only possess rotational states with even values of the angular momentum quantum number \( j \). By contrast, the three nuclear spin wave functions of oH₂ with the proton spins coupled to \( I' = 1 \) and \( M' = -1, 0, 1 \) are symmetric and so its spatial wave functions must be antisymmetric and its rotational quantum numbers \( j \) are odd. The equilibrium ratio of about 1 to 3 of pH₂ and oH₂ at room temperature (293 K) is determined by the multiplicity of their nuclear spin wave functions with \( I = 0 \) and \( I' = 1 \), respectively. The \( j = 1 \) ground state of oH₂ is higher in energy than the \( j = 0 \) ground state of pH₂ by about 120 cm⁻¹ (173 K). By passing the mixture of pH₂ and oH₂ over a suitable catalyst at liquid hydrogen temperature (20 K), one can convert it completely into the more stable pH₂ in the rotational ground state with \( j = 0 \). Although strongly out of equilibrium at room temperature, this pure pH₂ can be kept for several weeks in special gas cylinders and used in NMR or MRI to bring also the nuclear spins of other nuclei in a sample out of equilibrium and thereby strongly enhance the measured signals.

Para-ortho conversion of hydrogen by interaction with gas phase paramagnetic species was reported in 1933 in three papers in the same issue of the Zeitschrift für Physikalische Chemie. Two of them, by Farkas and Sachsse, described measurements of the para-ortho H₂ conversion rate in gas mixtures with paramagnetic molecules such as O₂, NO, and NO₂, see Figure 1. The third was a theoretical paper contributed by Eugene Wigner. He argued that the magnetic dipole of a paramagnetic molecule produces an inhomogeneous magnetic field that in a nearby H₂ molecule may be different at the positions of its two H nuclei. The nuclear spins of these two nuclei interact with this field, which makes them inequivalent. This breaks the exchange symmetry and causes para-ortho H₂ conversion. From an estimate of the frequency of collisions of H₂ with the paramagnetic molecule, the time they stay in each other’s vicinity, the strength of the different nuclear spin interactions at an estimated distance of closest approach, Wigner obtained a realistic estimate of the para-ortho H₂ conversion rate. A more qualitative discussion of para-ortho conversion in H₂ and D₂ by paramagnetic species and, in particular, of how to determine the ratio of the proton and deuteron magnetic moments from this process was presented in 1935 by Kalckar and Teller.

The subject of para-ortho H₂ conversion attracted more attention again when it was discovered in 1997–5 that para-H₂ is an important species in NMR and MRI. Since O₂, which is one of the few stable small molecules with an open-shell ground state and a nonvanishing electron spin (\( S = 1 \)), is abundant in air and under pressure dissolves in water and other liquids, this also caused renewed interest in para-ortho H₂ conversion by interactions with O₂. A recent remeasurement of the conversion rate coefficient in O₂-H₂ gas mixtures by Wagner was triggered by the need to understand the detrimental effect of oxygen when applying para-hydrogen induced enhancement methods in NMR and MRI.

Over the years the magnetic dipole-dipole coupling mechanism proposed by Wigner was invoked in several qualitative theoretical model studies of para-ortho H₂ conversion on various catalyst surfaces and in solid or liquid hydrogen with impurities, which accompanied experimental work on this subject. Ilisca and Sugano and Minaev and Ågren suggested in 1986 and 1995, respectively, that para-ortho H₂ conversion is also caused by another mechanism that they believed to be much more effective than the one proposed by Wigner. Their idea was that the exchange interaction between a spin triplet (\( S = 1 \)) molecule such as O₂ and a nearby H₂ molecule induces spin density in the latter by mixing a small amount of its lowest triplet (\( S = 1 \)) excited state into its closed-shell (\( S = 0 \)) ground state. In asymmetric collisions this causes a different electron spin density at the two H nuclei which, via the Fermi contact interaction, leads to para-ortho H₂ conversion. Both mechanisms were included in subsequent model studies of H₂ adsorbed on clean Ag surfaces and on Ag surfaces with co-adsorbed O₂, and it was concluded that the Fermi contact interaction is nearly as effective as the magnetic dipole-dipole coupling when O₂ and H₂ are close to each other on the surface, while it is less effective when the...
adsorbed molecules are further apart. In our description of the couplings, we explain this distance effect. With the aid of density-functional theory (DFT) electronic structure calculations, order of magnitude estimates of the conversion time were given\(^1\) and it was found that the presence of \(\text{O}_2\) on the Ag surface accelerates the conversion. The only more quantitative theoretical study of the catalyzing effect of gas phase \(\text{O}_2\) on para-ortho \(\text{H}_2\) conversion is the 1967 paper by Nielsen and Dahler.\(^2\) These authors employed scattering theory based on a hard-sphere isotropic intermolecular potential to model the \(\text{O}_2\)-\(\text{H}_2\) interactions, which allowed them to write the scattering wave functions analytically, but neglects the scrambling of the rotational states of \(\text{O}_2\) and \(\text{H}_2\) that also takes place during the collision. Only the rotational ground states of \(\text{O}_2\) and \(\text{H}_2\) were included and only the leading term of the magnetic dipole-dipole coupling was taken into account. These rather crude approximations and the absence of the Fermi contact coupling mechanism caused their rate coefficients calculated at 77.3 and 86 K to be smaller than the experimental values of Farkas\(^3\) by a factor of 3 to 4. So, in spite of all the work carried out since 1933 a complete and quantitative explanation of the para-ortho hydrogen conversion by paramagnetic molecules was still lacking. Also the gas phase measurements\(^4\) did not provide insight into the processes occurring during \(\text{O}_2\)-\(\text{H}_2\) collisions or on the conversion mechanisms.

The present paper describes the first complete and quantitative theoretical calculation of the para-ortho \(\text{H}_2\) conversion rate due to collisions with \(\text{O}_2\) from first principles. Both the Fermi contact coupling and the magnetic dipole coupling between the electron spin of \(\text{O}_2\) and the nuclear spins in \(\text{H}_2\) are evaluated as functions of the geometry of the \(\text{O}_2\)-\(\text{H}_2\) collision complex. The spin density at the two H-nuclei induced by the exchange interaction with \(\text{O}_2\) that appears in the formula for the Fermi contact coupling is obtained from \textit{ab initio} electronic structure calculations. Both couplings are then included in nearly exact quantum mechanical coupled-channel (CC) scattering calculations\(^5\) for the collisions between \(\text{O}_2\) and \(\text{H}_2\), which also include the full anisotropic \(\text{O}_2\)-\(\text{H}_2\) potential surface\(^6\) and yield the para-ortho \(\text{H}_2\) conversion cross sections and rate coefficients for temperatures up to 400 K. The latter are compared with the rate recently measured in \(\text{H}_2\)-\(\text{O}_2\) gas mixtures at room temperature\(^7\) and with the older experimental data\(^8\) measured for a range of temperatures.

Also para-ortho \(\text{H}_2\) conversion by an exchange reaction with H atoms or \(\text{H}^+\) and \(\text{H}_2^+\) ions has been studied theoretically and experimentally, see Ref.\(^9\) and references therein. This is of interest especially in astrophysical environments where free H atoms and \(\text{H}^+\) or \(\text{H}_2^+\) ions are abundant, but it is not the subject of the present paper.

### PARA-ORTHO \(\text{H}_2\) COUPLINGS

The anisotropic \(\text{O}_2\)-\(\text{H}_2\) interaction potential leads to rotationally inelastic collisions of the \(\text{pH}_2\) and \(\text{oH}_2\) species, but since it depends only on the spatial coordinates of the molecules and \(\text{pH}_2\) and \(\text{oH}_2\) have different nuclear spin functions, it does not produce any \(\text{pH}_2\)-\(\text{oH}_2\) conversion. Interactions that do lead to conversion must also act on the nuclear spin functions. Since the exchange (\(P_{12}\)) parities of the \(\text{pH}_2\) and \(\text{oH}_2\) nuclear spin functions are opposite to each other, they must be antisymmetric under exchange of the spin coordinates of the nuclei \(\text{H}_1\) and \(\text{H}_2\). And since the rotational wave functions of \(\text{pH}_2\) and \(\text{oH}_2\) have opposite parities as well, these interactions must also be antisymmetric under exchange of the \(\text{H}_1\) and \(\text{H}_2\) spatial coordinates.

The magnetic dipole-dipole coupling between the electron spin of a paramagnetic molecule (\(\text{O}_2\) in our case) and the proton spins in \(\text{H}_2\) proposed as a conversion mechanism by Wigner\(^10\) can be written as follows

\[
\hat{V}^{dd} = \frac{\mu_0}{4\pi} g_e g_p \mu_B \mu_N \left[ \hat{l}(\text{H}_1) \cdot T^{(2)}(\text{R}_1) \hat{S} + \hat{l}(\text{H}_2) \cdot T^{(2)}(\text{R}_2) \hat{S} \right],
\]

where \(g_e = 2.0023193\) and \(g_p = 5.5856947\) are the gyromagnetic factors of the electron and the proton, respectively, \(\mu_B\) is the bohr magneton, \(\mu_N\) the nuclear magneton, and \(\mu_0\) the vacuum permeability. The vector operator \(\hat{S}\) with components \((\hat{S}_x, \hat{S}_y, \hat{S}_z)\) is the electron spin operator of \(\text{O}_2\), and the vector operators \(\hat{l}(\text{H}_i)\) are the nuclear spin operators of the nuclei \(\text{H}_i\) (\(i = 1, 2\)) in \(\text{H}_2\). The symbol \(T^{(2)}(\text{R}_i)\) denotes the second rank dipole-dipole interaction tensor (in Cartesian components a \(3 \times 3\) matrix), which depends on the length \(\text{R}_i\) and the direction of the vector \(\text{R}_i\) pointing from the center of \(\text{O}_2\) to the nuclei \(\text{H}_i\). The Fermi contact term proposed as a coupling mechanism by Ilisca and Sugano\(^11\) and by Minaev and Ågren\(^12\) reads

\[
\hat{V}^{fc} = -\frac{2}{3} \mu_0 g_e g_p \mu_B \mu_N \left[ \sigma(\text{H}_1) \hat{l}(\text{H}_1) \cdot \hat{S} + \sigma(\text{H}_2) \hat{l}(\text{H}_2) \cdot \hat{S} \right]
\]

with \(\sigma(\text{H}_i)\) being the spin density at nucleus \(\text{H}_i\) (\(i = 1, 2\)).

The operators in Equations (1) and (2) are invariant under the permutation \(P_{12}\) that interchanges the coordinates of the nuclei \(\text{H}_1\) and \(\text{H}_2\), but each operator can be split into two terms in which the spatial and spin operators individually are symmetric and antisymmetric under \(P_{12}\), respectively. The antisymmetric terms given in Equations (S1) and (S2) of the Supporting Information contain the spin operator \((\hat{l}(\text{H}_1) - \hat{l}(\text{H}_2))\) that couples the \(l = 0\) nuclear spin state of \(\text{pH}_2\) with the three \(l' = 1\) functions of \(\text{oH}_2\) and the antisymmetric spatial operators \((T^{(2)}(\text{R}_1) - T^{(2)}(\text{R}_2))\) and \((\sigma(\text{H}_1) - \sigma(\text{H}_2))\) couple their rotational functions with even and odd \(j\).

Both the Fermi contact interaction from the spin densities induced at the two H-nuclei by the interaction with \(\text{O}_2\) and the magnetic dipole coupling between the electron spin of \(\text{O}_2\) and the nuclear spins in \(\text{H}_2\) are evaluated for a large number of geometries of the \(\text{O}_2\)-\(\text{H}_2\) collision complex.
and then fitted to different analytic forms. The spin densities at the H-nuclei in $O_2-H_2$ were obtained from ab initio electronic structure calculations at the complete-active-space self-consistent field (CASSCF) and multi-reference configuration-interaction (MRCI) levels with the program package Molpro.\textsuperscript{26} Details are given in the Supporting Information. Dipole-dipole coupling is a long-range interaction and the interaction tensors $T^{(2)}(R_i)$ in Equation (1) depend on $R_i$ as $R_i^{-3}$. The H-nuclei are relatively close to one another compared to the $O_2-H_2$ distance $R$, and the difference tensor $[T^{(2)}(R_i) - T^{(2)}(R_j)]$ decays as $R^{-4}$. The induced spin density and, therefore, also the Fermi contact interaction is an overlap effect which decays exponentially with $R$. Hence, the magnetic dipole-dipole interaction dominates at long range, the Fermi contact interaction at short range.

**PARA-ORTHO H$_2$ CONVERSION BY COLLISIONS WITH O$_2$**

Collisions between molecules that lead to (de-)excitation of the rotational states of one or both of the molecules can be studied in detail experimentally in a crossed molecular beam setup. By preparing the molecules before the collision in specific states and state-specifically detecting them after the collision, one can measure state-to-state cross sections, which are proportional to the probabilities that specific (de-)excitation processes occur. Also $O_2-H_2$ collisions have been studied in this way\textsuperscript{24, 27–29} and these measurements were accompanied by quantum mechanical coupled-channels (CC) calculations with the use of an $O_2-H_2$ interaction potential computed in Ref.\textsuperscript{[25].} Good agreement was found between the calculated and measured collision cross sections, which shows that the interaction potential is accurate. The $PH_2-oH_2$ conversion cross sections that correspond to transitions between rotational states of $PH_2$ with even $j$ and of $oH_2$ with odd $j$, or vice-versa, are about twelve orders of magnitude smaller (see below) than those of the observed rotational transitions within the even and odd $j$ manifolds.\textsuperscript{27} Hence, no $PH_2-oH_2$ conversion can be detected in a crossed-beam setup. Neither was it predicted in the CC calculations,\textsuperscript{24, 27–29} because the latter did not include the required coupling terms given above. To our knowledge, the only experimental data available on $PH_2-oH_2$ conversion by collisions with $O_2$ is the rate coefficient recently measured at room temperature in $O_2-H_2$ gas mixtures\textsuperscript{12} and the older data\textsuperscript{9} measured for a range of temperatures. These measurements do not provide any insight into the processes occurring during $O_2-H_2$ collisions or on the conversion mechanisms. Therefore, such information has to be provided by theory, which is the aim of the present paper.

Coupled-channel calculations as carried out for rotationally inelastic $O_2-H_2$ collisions\textsuperscript{24, 27–29} are not feasible for $PH_2-oH_2$ conversion. In addition to the anisotropic $O_2-H_2$ potential one has to include the hyperfine interaction operators in Equations (1) and (2), which act both on the spatial and spin coordinates. The channel bases containing the rotational states of $O_2$ of $PH_2$ with even $j_{H_2}$ and those of $O_2-oH_2$ with odd $j_{H_2}$ would have to be combined and extended with the three electron spin functions of $O_2$ ($S = 1$) and the nuclear spin functions of $PH_2$ ($I = 0$) and $oH_2$ ($I' = 1$). This would increase the size of the channel basis by more than a factor of 10, the required computer memory by more than a factor of 100, and the cpu time by more than a factor of 1000, which implies that CC calculations become impractical.

In our approach, we take advantage of the large difference in coupling strength between the anisotropic terms in the $O_2-H_2$ interaction potential that couple the rotational states of $O_2$ and $H_2$ (but not those with even and odd $j_{H_2}$), and the much weaker hyperfine terms in Equations (1) and (2). We use the CC method to compute the wave functions for the rotationally inelastic collisions exactly, but separately for $PH_2$ and $oH_2$, without including the hyperfine coupling terms. Next, we compute the cross sections for $PH_2-oH_2$ transitions from the matrix elements of the hyperfine coupling terms over these scattering wave functions. This method is known as the distorted-wave Born approximation (DWBA),\textsuperscript{30} and since both the Fermi contact coupling and the magnetic dipole-dipole coupling are about a million times smaller than the anisotropy in the $O_2-H_2$ interaction potential, it is extremely accurate in this case. Calculating matrix elements involving scattering wave functions is also demanding, but we made use of an efficient algorithm developed in our group.\textsuperscript{31}

One problem remains, however. The spatial part of the magnetic dipole-dipole coupling in Equation (1) is a second rank tensor, which means that it couples wave functions with total angular momentum quantum numbers $J$ that differ by up to two quanta. In the Supporting Information we show that one can do the calculations for single $J$ values by making a minor approximation for some radial integrals. This, together with the DWBA makes the calculations practically feasible.

We applied this procedure to all initial rotational states $n_{O_2}$ of $O_2$ and $j_{H_2}$ of $PH_2$ that are thermally occupied at room temperature and calculated state-to-state $PH_2-oH_2$ conversion cross sections $\sigma_{n_{O_2}j_{H_2} \rightarrow n'_{O_2}j'_{H_2}}(E)$ and the corresponding rate coefficients for transitions to all open final states $n'_{O_2}$ of $O_2$ and $j'_{H_2}$ of $oH_2$. Summation over all final states accessible at a given collision energy $E$ and Boltzmann averaging over the initial states then yields the total conversion rate coefficients as a function of temperature.

**RESULTS AND DISCUSSION**

The $O_2$ molecule with total spin $S = 1$ in its electronic ground state has two unpaired electrons. They are coupled by a spin-spin coupling term of about 4 cm\textsuperscript{-1} and the total spin is coupled to the rotational angular momentum $n_{O_2}$ by a much smaller spin-rotation coupling term to produce the total angular momentum $j_{O_2}$. These internal $O_2$ spin couplings are very small in comparison with the energy gaps of at least 120 cm\textsuperscript{-1} between the states of $PH_2$ and $oH_2$, so we expect that their effect on the $PH_2-oH_2$ conversion rate will be negligible. They might have some effect at low
FIGURE 2  State-to-state conversion cross sections for transitions from the j = 0 state (closed lines) and the j = 2 state (dashed lines) of pH2 to the j' = 1 state of oH2, accompanied by transitions from nO2 = 1, 9 to n'O2 = 1, 5, 9, 13. Panel (a) is for initial nO2 = 1, panel (b) for initial nO2 = 9. The different curves are labeled with n'O2,j'H2 ← nO2,j'H2.

temperatures, where scattering resonances occur (see below), but where the conversion rate is insignificantly small. Hence, we use the bare rotational states of O2 labeled by nO2 in our CC calculations, while the electron spin S = 1 of O2 provides the weak couplings with the nuclear spins of H2 discussed in Section "Para-Ortho H2 Couplings" and treated with the DWBA. Since the 16O-nuclei are bosons with nuclear spin I = 0 and the 3Σ− electronic wave function is antisymmetric under exchange of the nuclear coordinates, the rotational functions must be antisymmetric as well, and the quantum number nO2 adopts only odd values. We start with pH2 with even jH2 and compute the transitions to oH2 with odd jH2.

Plots of the thermal populations of the O2 and H2 states obtained from Equation (S64) in the Supporting Information are shown in Figure S3. Although the jH2 = 2 state is higher in energy than the jH2 = 0 ground state by about 360 cm⁻¹ (518 K), its population at room temperature is not much smaller than that of the ground state, because of the multiplicity factor 2jH2 + 1 = 5. The initial states that we take into account are those with jH2 = 0, 2 and nO2 = 1, 3, ..., nmax, with nmax = 15 for jH2 = 1 and nmax = 13 for jH2 = 2. When jH2 = 0 and O2 is in its ground state with nO2 = 1 there is an energy threshold of about 120 cm⁻¹ to get to the lowest state of oH2 which gradually decreases for increasing nO2. For jH2 = 2 there is no threshold to get into the lowest jH2 = 1 state of oH2, but there is a threshold of about 360 cm⁻¹ to reach the final state with jH2 = 3.

State-to-state cross sections

Some typical cross sections for pH2-oH2 conversion from the j = 0 ground state and the j = 2 excited state of pH2 to the j' = 1 ground state of oH2 are depicted in Figure 2, a more complete set is shown in Figures S1 and S2 of the Supporting Information. They are about twelve orders of magnitude smaller than the cross sections for rotationally inelastic collisions within pH2 or oH2, cf. Figure 10 of Ref. [24]. These figures also illustrate the energy thresholds for pH2(j = 0)-oH2 conversion: 120 cm⁻¹ when the O2 collision partner stays in its ground state with n = 1, and higher when O2 is simultaneously excited. The threshold vanishes when O2 is initially excited to n = 9 and gets de-excited to n' = 1, because of energy exchange between the collision partners. The cross sections for transitions from the excited j = 2 state of pH2 to the j = 1' state of oH2 look similar to those for the jH2 = 0 → 1 transitions, but they are smaller. They mostly have no energy threshold, so they yield a substantial contribution to the overall pH2-oH2 conversion rate coefficient.

The cross sections for jH2 = 0 → 3 transitions are not shown; they are smaller than those in Figure 2 by more than three orders of magnitude, because of the much larger energy gap of nearly 720 cm⁻¹. Moreover, such transitions occur only for collision energies above this gap, which makes their contribution negligible. The cross sections for jH2 = 2 → 3 transitions are smaller than those for jH2 = 2 → 1 transitions by about one order of magnitude and they have an energy threshold of about 360 cm⁻¹, so they yield a small but nonnegligible contribution to the conversion rate coefficient.

The two panels in Figure 2 also illustrate that the cross sections are largest for Δn = n'O2 − nO2 = 0. The more complete set of cross sections depicted in Figures S1 and S2 of the Supporting Information shows that they systematically decrease with increasing |Δn|. It is noteworthy that the cross sections for similar values of Δn exhibit similar values for different initial O2 states. This implies that the sums of the state-to-state cross sections σ(n'O2,j'H2 ← nO2,j'H2) over all final states n'O2 are nearly the same for all initial nO2. We return to this point in our discussion of the rate coefficients.

Another feature that can be seen in Figure 2 are the narrow peaks in the cross sections for collision energies just above the threshold. They correspond to scattering resonances, but have only a small effect on the rate coefficients except at temperatures below 50 K.
FIGURE 3  pH$_2$-oH$_2$ conversion rate coefficients for initial $j_H^2 = 0$ (closed lines with crosses) and 2 (dashed lines with circles) at three different temperatures for all initial $n_{O_2}$ values, summed over all final states $j_H^{'}_{H_2}$, $n_{O_2}^{'}$. The curves are quadratic fits to these coefficients.

FIGURE 4  $T$-dependent pH$_2$-oH$_2$ conversion rate coefficients for initial $j_H^2 = 0$ and 2 (blue and red dashed lines), and the total rate (closed black line) obtained by Boltzmann averaging over these initial states. The value measured by Wagner$^{12}$ is indicated by a circle with error bars, the older experimental values of Farkas and Sachsse$^{6}$ by diamonds.

Rate coefficients

State-to-state rate coefficients for conversion of pH$_2$ into oH$_2$ for temperatures up to 400 K were obtained from the $ab$ initio calculated state-to-state cross sections by numerical integration over the collision energy, cf. Equation (S63) in the Supporting Information. By exponential extrapolation of the integrand in Equation (S63) they can even be extended to higher temperatures.

We do not explicitly show all the state-to-state rate coefficients $k_{O_2^{'}j_{H_2}^{'}n_{O_2}^{'}n_{H_2}^{O_2}}$, but we show in Figure 3 the rate coefficients at three different temperatures for initial pH$_2$(0) and pH$_2$(2) for each initial $n_{O_2}$, summed over all final $j_{H_2}^{'}$ and $n_{O_2}^{'}$ states. It is remarkable that these rates depend only weakly on the initial O$_2$ state, just as we noted for the corresponding cross sections summed over final $n_{O_2}^{'}$ states. The slight increase with $n_{O_2}$ can be perfectly fitted with a quadratic polynomial. The slope is relatively largest for initial $j_H^2 = 0$ at lower temperature, because the molecules have little kinetic energy and the excitation of O$_2$ helps to overcome the threshold. For initial $j_H^2 = 2$ there is no threshold and the curves are flatter. Overall pH$_2$-oH$_2$ conversion rate coefficients are obtained by summation over all initial O$_2$-pH$_2$ and final O$_2$-oH$_2$ states. The weights of the initial states in this summation are determined by the Boltzmann factors and the multiplicities in Equation (S64) of the Supporting Information. Figure 4 not only shows the total rates, but also the contributions from the initial states with $j_H^2 = 0$ and 2. One may observe that the rates for initial $j_H^2 = 0$ increase with the temperature, while those for initial $j_H^2 = 2$ are nearly temperature-independent. This is related to the energy threshold that the pH$_2$(0) states must overcome to convert into oH$_2$(1), while the pH$_2$(2) states mostly have no threshold. Wigner$^{8}$ already discussed this $T$-dependence. He only considered the initial pH$_2$ state with $j = 0$ and the final oH$_2$ state with $j = 1$ and he suggested an increase of the
As mentioned in Section Para-ortho H2 couplings, the Fermi contact interaction is a short range effect, while the magnetic dipole-dipole coupling affects also at larger O2-H2 distances. Figure S4 in the Supporting Information illustrates that this is reflected by the calculated cross sections: the magnetic dipole-dipole coupling contributes to the conversion for higher values of the total angular momentum \( j \) of the total angular momentum \( j \) of the reaction, the Fermi contact mechanism yields a substantial contribution but is not dominant, as suggested in Refs. [17, 18]. With the efficient algorithm — three orders of magnitude faster than the \( j_{\text{H}_2} = 0 \rightarrow 1 \) conversion rate coefficients by using the \( \text{H}_2 \) states with odd \( j_{\text{H}_2} \) as the initial states and those of \( \text{H}_2 \) with even \( j_{\text{H}_2} \) as the final states, and we found that our calculated rate coefficients agree even better with the value of 8 \( \pm \) 1 L mol\(^{-1}\) min\(^{-1}\). The latter value agrees even better with the value of 8.27 \( \pm \) 1.30 L mol\(^{-1}\) min\(^{-1}\) measured by Wagner, but we emphasize that it is less accurate according to theory because the CASSCF method takes less electron-electron correlation into account than the MRCl method.

Only the rate coefficients for the conversion of \( \text{H}_2 \) to \( \text{O}_2 \) are presented in this paper. The rates for the reverse process can easily be obtained by the detailed balance relation, Equation (S65) in the Supporting Information. We also computed some of the state-to-state \( \text{H}_2 \)-\( \text{O}_2 \) conversion rate coefficients by using the \( \text{O}_2 \) states with odd \( j_{\text{O}_2} \) as the initial states and those of \( \text{H}_2 \) with even \( j_{\text{H}_2} \) as the final states, and we found that our results accurately obey this relation.

### Conclusion

Finally, almost 90 years after the first measurement\(^6\) of para-ortho \( \text{H}_2 \) conversion in collisions with paramagnetic molecules such as \( \text{O}_2 \), a complete and detailed picture of this process has been obtained. \textit{Ab initio} computations of the nuclear-spin-dependent interactions that cause the conversion, the magnetic dipole-dipole coupling proposed by Wigner\(^8\) in 1933 and the Fermi contact coupling proposed later,\(^{17,18}\) and the inclusion of both these interactions in nearly exact quantum mechanical coupled-channel calculations yield state-to-state collision cross sections and rate coefficients that agree with the most recent measurements within the error bars. A complete characterization of the conversion process is thus obtained and the observed temperature dependence of the rate coefficients is explained. It is established that the Fermi contact mechanism yields a substantial contribution but is not dominant, as suggested in Refs. [17, 18]. With the efficient algorithm — three orders of magnitude faster than

### Table 1

| Temperature | dip-dip | Fermi contact |
|-------------|---------|---------------|
| 100 K       | 0.92    | 0.64          |
| 200 K       | 3.24    | 2.12          |
| 300 K       | 5.62    | 3.61          |

Conversion rate with temperature because of this energy threshold, which is more easily overcome when the temperature is higher and the colliding molecules have more kinetic energy. On the other hand, he also noted that there may be an opposite effect, because the collisions are shorter and probably less effective when the molecules move faster. It is clear now from Figure 4 that the \( j_{\text{H}_2} = 0 \rightarrow 1 \) rates are dominated by the threshold effect, while those for \( j_{\text{H}_2} = 2 \rightarrow 1 \) are nearly \( T \)-independent because the most dominant contributions do not experience any threshold. Also the overall \( \text{H}_2 \)-\( \text{O}_2 \) conversion rate increases with \( T \), but this is moderated at higher temperature by the contributions from the \( \text{H}_2(j = 2) \) state. The role of this \( \text{H}_2(j = 2) \) state was not previously considered, although its population at room temperature is nearly as high as that of the \( j_{\text{H}_2} = 0 \) ground state. Neither were the excited \( \text{O}_2 \) states that are substantially populated up to \( n_{\text{O}_2} = 15 \) at room temperature, while even higher \( \text{O}_2 \) states become excited during the collision. Both the magnitude of the conversion rate coefficient and its temperature dependence are significantly affected by the contributions from these excited states.

The contributions from the magnetic dipole-dipole coupling in Equation (1) and the Fermi contact interaction in Equation (2) to the \( \text{H}_2 \)-\( \text{O}_2 \) conversion rates are listed in Table 1. It turns out that these contributions are of comparable importance, so the suggestion of Ilisca and Sugano\(^{17}\) and of Minaev and Ågren\(^{18}\) that the Fermi contact interaction is much more important than the magnetic dipole-dipole coupling is not correct.

As mentioned in Section Para-ortho \( \text{H}_2 \) couplings, the Fermi contact interaction is a short range effect, while the magnetic dipole-dipole coupling acts also at larger \( \text{O}_2 \)-\( \text{H}_2 \) distances. Figure S4 in the Supporting Information illustrates that this is reflected by the calculated cross sections: the magnetic dipole-dipole coupling contributes to the conversion for higher values of the total angular momentum \( J \) than the Fermi contact coupling. Table 1 shows, however, that this difference is not important for the temperature dependence of the conversion rate.

Also the rate coefficients measured at room temperature by Wagner\(^{12}\) in 2014, with error bars, and by Farkas and Sachsse\(^6\) for several temperatures are shown in Figure 4. Our \textit{ab initio} calculated value at room temperature lies just at the lower error bar of Wagner’s result. The much older and, in view of the applied methods, probably less accurate measurements of Farkas and Sachsse, yielded somewhat higher values and no error bars were given. Their value at room temperature is higher than Wagner’s more recent value and at all temperatures higher than our calculated values. It is satisfactory, though, that their measured temperature dependence of the rate is nicely reproduced by our calculated data. We cannot present error bars for our calculated rate coefficients, but we may quote some values at room temperature from different calculations. In the calculations by which all the results discussed are obtained, we assumed that the electron spin \( S = 1 \) of \( \text{O}_2 \) is localized at the center of the molecule. In alternative calculations for some initial and final states we placed two spins \( s = 1/2 \) at the \( \text{O} \)-nuclei. The rate coefficients from the latter calculations only differ from those presented here by about 1%. Another alternative considered was to use spin densities in the Fermi contact interaction in Equation (2) from \textit{ab initio} electronic structure calculations at the CASSCF level instead of the MRCl level. The room temperature rate coefficient with the MRCI calculated Fermi contact term is 6.94 L mol\(^{-1}\) min\(^{-1}\), with the CASSCF calculated term we estimate it to be 7.9 L mol\(^{-1}\) min\(^{-1}\). The latter value agrees even better with the value of 8.27 \( \pm \) 1.30 L mol\(^{-1}\) min\(^{-1}\) measured by Wagner, but we emphasize that it is less accurate according to theory because the CASSCF method takes less electron-electron correlation into account than the MRCI method.

In Table 1 the \( j \) states of \( \text{O}_2 \) with even \( j_{\text{O}_2} \) were not previously considered, although its population at room temperature is nearly as high as that of the \( j_{\text{O}_2} = 0 \) ground state. Neither were the excited \( \text{O}_2 \) states that are substantially populated up to \( n_{\text{O}_2} = 15 \) at room temperature, while even higher \( \text{O}_2 \) states become excited during the collision. Both the magnitude of the conversion rate coefficient and its temperature dependence are significantly affected by the contributions from these excited states.

| Temperature | dip-dip | Fermi contact |
|-------------|---------|---------------|
| 100 K       | 0.92    | 0.64          |
| 200 K       | 3.24    | 2.12          |
| 300 K       | 5.62    | 3.61          |
direct inclusion of the relevant spin-dependent coupling terms in CC calculations— and the software developed in this study, it will be also possible
to study the effects of paramagnetic molecules and ions other than O2 that may hinder the application of para-hydrogen induced polarization in
NMR and MRI. The early measurements6 have shown already that interesting and unexpected differences may occur, such as the observation that
NO with electron spin $S = \frac{1}{2}$ is four times more effective in converting pH2 into oH2 than O2 with spin $S = 1$.

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of the article.

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