

Orbital processes in O-P H₂ conversion on noble metals

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 297

(<http://iopscience.iop.org/0953-8984/4/1/041>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 11:02

Please note that [terms and conditions apply](#).

Orbital processes in o-p H₂ conversion on noble metals

E Ilisca

Laboratoire de Magnétisme des Surfaces, Université Paris 7, 2 Place Jussieu, 75251 Paris
Cédex 05, France

Received 3 June 1991, in final form 18 September 1991

Abstract. EELS experiments of H₂ physisorbed on noble metals at low temperature have indicated that the ortho-para (o-p) conversion can be very fast on non-magnetic catalysts. Two processes are described in which the molecular nuclear angular momenta are dissipated by the emission of metal electron-hole pairs through a metal-molecule spin-orbit coupling. Both processes rely on electron momentum transfer to the metal but in the second one the virtual electron jump—back and forth from the metal to the molecule as induced by the electron Coulomb interaction—considerably strengthens the o-p rate and brings it close to the experimental values observed on Cu catalysts.

1. Introduction

Since Wigner in 1933 [1], it has been established that the physical ortho-para (o-p) conversion of hydrogen molecules occurs through a magnetic nuclei decoupling induced by a nearby impurity electron spin. Astonishingly, in 1982, Avouris *et al* [2] and then Andersson *et al* [3] observed fast conversion rates on non-magnetic pure noble metals, respectively Ag and Cu, although it was demonstrated that the H₂ adsorption remained physical. Quite recently, we have interpreted the Ag(111) o-p rate on the basis of the emission of electron-hole (e-h) triplet pairs. In this mechanism the ortho-nuclei angular momenta are transferred to the (e-h) electron spins [4]. The purpose of this paper is to examine different mechanisms where singlet (e-h) pairs dissipate the molecular momenta through an electron momentum transfer parallel to the surface. We shall first detail the nuclear spin-electron momentum coupling already suggested by Yucel as being possibly operative on Cu catalysts [5]. However, we find this process gives rise to very long conversion times (10–140 hours). In contrast, when we include the metal-molecule Coulomb interaction, which couples metal band states with the molecule antibonding excited state, we obtain much shorter times (less than half an hour).

We consider an H₂ molecule physisorbed on a noble metal surface, at a low temperature ($T \approx 10$ –50 K), a distance d away ($d \approx 3.5$ Å). The two H₂ electrons occupy the σ_g (1s) spin orbitals denoted by g (and \bar{g} —a bar on the top of the spin orbital will indicate, from now on, a spin down). The metal in its ground and initial state, is described by a conduction band which is assumed to be completely filled up to the Fermi level (small temperature effects are neglected). It is composed of N doubly degenerate one-electron Bloch states denoted k (and \bar{k}). The electron system is thus described in its ground and coupled metal-molecule state by a Slater determinant of $2N + 2$ one electron

states: $|S_i\rangle = |g\bar{g} \dots k\bar{k} \dots\rangle$ which represents its initial state. We consider small energetic excitations where one electron is transferred from a state k below, to a state χ above the Fermi level. The hole k couples to the electron χ to build E-H pair states. We denote by $^1[k\chi] = |k\bar{\chi} - \bar{k}\chi\rangle/(2)^{1/2}$ the spin singlet one and by: $|S_f\rangle = |g\bar{g} \dots ^1[k\chi] \dots\rangle$ the final state of the electron system. The nuclear system involves the spin and position coordinates of the molecular protons, adsorbed on the metal surface. It is described by a set of ortho (L odd, $I = 1$) and para (L even $I = 0$) states where, as usual, L and I denote the rotational and nuclear spin angular momenta of the H_2 molecule.

2. The orbital process

The hydrogen O-P conversion rate, relative to the orbital process, O, is simply obtained from the golden rule formula

$$P_{o \rightarrow p}(O) = \frac{2\pi}{\hbar} \sum_{k\chi} |\langle S_f, p | H(O) | S_i, o \rangle|^2 \delta[\varepsilon_\chi - \varepsilon_k - \varepsilon_{op}] \quad (1)$$

where $H(O)$ denotes the Hamiltonian which couples the electron and nuclear systems through the spin-orbit process, ε_χ (ε_k) being the energy of the excited (ground) electron and ε_{op} the O-P energy.

The magnetic coupling of a nuclear spin I with the orbital momentum $L_\alpha = r_\alpha \times p_\alpha$ of an electron α located at r_α and of momentum p_α can be represented by a Hamiltonian: $H_\alpha = (\mu/\hbar) I \cdot L_\alpha/r_\alpha^3$, where $\mu = 8.1 \times 10^{-8}$ au. With two protons a and b located at distances ar_α and br_α (from electron α) much larger than their distance ab , we may retain the first order term in the series expansion

$$(br_\alpha/br_\alpha^3) - (ar_\alpha/ar_\alpha^3) = (ab \cdot \nabla)(r_\alpha/r_\alpha^3) + \dots \quad (2)$$

and write the inhomogeneous magnetic coupling of an electron α with the H_2 nuclear protons as

$$H_\alpha(O) = (\mu/2\hbar) i \cdot [(ab \cdot \nabla)(r_\alpha/r_\alpha^3) \times p_\alpha] \quad (3)$$

where the electron position vector r_α is referred to the molecular centre of mass chosen as the origin, and the nuclear spin difference is expressed by $i = I(b) - I(a)$. To obtain a simpler form of the magnetic coupling (3) we express the operators in terms of irreducible tensors in spherical basis and apply the gradient formula [6] which leads to

$$H_\alpha(O) = (2\mu/\hbar)(-\pi)^{1/2} i^1 \cdot \{[ab^1 \times \{Y^2(r_\alpha)/r_\alpha^3\}]^1 \times p_\alpha^1\}^1. \quad (4)$$

After uncoupling and recoupling the four irreducible tensors and summing over all the electrons α , the hyperfine orbital Hamiltonian can be expressed as a sum of products of separate electron and nuclei tensors: E^j, N^j .

$$H(O) = \sum_\alpha \sum_{j=1,2} a_j N^j \cdot E^j(\alpha) \quad (5a)$$

$$N^j = (i^1 \times ab^1)^j \quad (5b)$$

$$E^j(\alpha) = [(Y^2(r_\alpha)/r_\alpha^3) \times \nabla^1]^j \quad (5c)$$

$$\alpha_j = \mu\{(4j + 1)/5\pi\}^{1/2}. \tag{5d}$$

The calculation and summation of the nuclear matrix elements products gives

$$\sum_{ii'} \langle p | N_{\mu}^j | o_{ii'} \rangle \langle o_{ii'} | N_{-\nu}^k | p \rangle = \delta_{j,k} \delta_{\mu,\nu} (-)^{j-\mu} (ab)^2 / 3 \tag{6}$$

where $o_{ii'}$ is one ortho substate $|I = 1, L = 1, m, m_i\rangle$, and the $2N + 2$ electron matrix elements can be reduced to one-electron ones as

$$\left\langle S_i \left| \sum_{\alpha} E_{\mu}^j(\alpha) \right| S_i \right\rangle = (2)^{1/2} \langle \chi | E_{\mu}^j | k \rangle. \tag{7}$$

Thus, bringing together (5), (6), (7) and inserting in the conversion rate (1), we obtain

$$P_{O \rightarrow P}(O) = \frac{4\pi^2(ab)^2\mu^2}{15\hbar} \sum_{k\chi} \sum_{j\mu} (4j + 1) |\langle \chi | E_{\mu}^j | k \rangle|^2 \delta(\epsilon_{\chi} - \epsilon_k - \epsilon_{op}). \tag{8}$$

The summation over the electron band states k, χ in the close vicinity of the Fermi level can be simply worked out by noticing that $\epsilon_{op} \approx 14.7$ meV is much smaller than the Fermi energy ϵ_F (referred to the bottom of the band) and thus the energy variation $k(E)$ might be neglected over ϵ_{op} . Then the sum over the Dirac functions contribute by a factor $N^2(\epsilon_F)\epsilon_{op}$ ($N(\epsilon_F)$ being the electron density of states at ϵ_F), whereas the angular average over all orientations of the wavevectors k, χ parallel to the surface plane leads to

$$I(k) = \left\langle \sum_{j\mu} (4j + 1) |\langle \chi | E_{\mu}^j | k \rangle|^2 \right\rangle = 10 \int_0^{2k} \lambda^2 (4k^2 - \lambda)^{1/2} L^2(\lambda) d\lambda \tag{9a}$$

$$L(\lambda) = \int_{-\infty}^{+\infty} dz \Phi^2(z) e^{-\lambda z} \tag{9b}$$

where $\Phi(z)$ is the z -dependence, perpendicular to the surface, of the electron wavefunction. Inserting (9) in (8) leads to the conversion rate

$$P_{O \rightarrow P}(O) = (4\pi^2(ab)^2/15\hbar)\mu^2 N^2(\epsilon_F)\epsilon_{op} I(k_F) \tag{10}$$

where k_F represents the component parallel to the surface of the band wavevector at the Fermi level. The conversion rate, relative to the orbital process, is thus found to be proportional to the square of the density of states at the Fermi energy, as arising from the considered band. It is also directly related to the Laplace transform of the metal layer electron density: $L(\lambda)$ through the average $I(k_F)$ which contains all the characteristics of the surface electron distribution.

In order to illustrate this orbital process we have modelled the Ag (111) surface band, observed by angle-resolved-photoelectron-spectroscopy [7], which is known to be fairly well reproduced within the nearly-free electron approximation [8], and obtained

$$\Psi(r) = e^{ik_{\parallel} \cdot r} \Phi(z) \tag{11a}$$

$$\Phi_m(z) = 0.077 e^{-0.0446z} \cos(0, 7z - 0.23) \tag{11b}$$

$$\Phi_v(z) = 0.088 e^{0.56z} \tag{11c}$$

where the indexes m, v correspond to metal and vacuum wavefunctions, matched at $z_0 = 0.36 \text{ \AA}$ outside the jellium background (all numbers being given in atomic units and the wave-functions being normalized to a unit surface cell area). This surface band crosses the Fermi level at $k_F \approx 0.074$ where the average $I(k_F)$ has been calculated

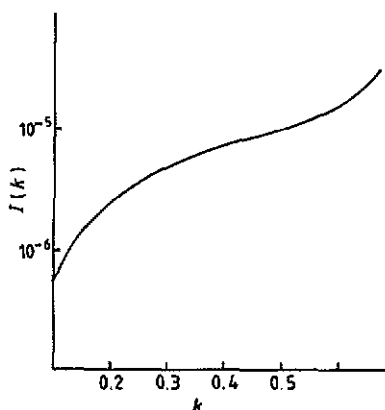


Figure 1. Momentum transfer integral $I(k)$ (defined by (9)), as a function of the metal electron wavevector k parallel to the surface. (Numerical values are taken from the Ag(111) surface band.)

numerically and found equal to 2.4×10^{-7} au when the molecule stands at a distance of 3.56 \AA [9] from the first metal atomic layer. With a corresponding density of states of the order of 0.12 eV^{-1} state/surface ion we obtained a conversion rate of the order of $P_{\text{op}} = 2 \times 10^{-6} \text{ s}^{-1}$ that is, a conversion time of about 140 h. It seems, therefore, that the surface band remains inefficient in performing the momentum transfer, mainly because of its very small value of k at the Fermi level. We have computed the average $I(k)$ as a function of k to examine the possible influence of bulk bands, and represented its variation in figure 1. We remark that the average $I(k)$ rises rather sharply with increasing momentum transfer parallel to the surface and could strengthen the conversion rate by two orders of magnitude, bringing the conversion time to about one and a half hours which is still too long compared with experimental results. Another point is worth noticing: the extremely slow variation of $I(k)$ with the metal–molecule distance which makes this process operative at long distances may occur in molecular multilayers adsorbed on a metal surface.

3. The Coulomb-orbital process

In search of a more efficient process we investigate, in the following, a two-step process in which a Fermi electron k is first virtually transferred to the molecular antibonding orbital $u = \sigma_u$ ($1s$) through the electron orbit–nuclear spin interaction $H(0)$ given by (5). In a second virtual step the Coulomb interaction C brings the electron back to the metal in an excited state χ . By considering also the reverse process, the O–P conversion rate, relative to this Coulomb–Orbital process (UO) takes the form

$$P_{\text{O} \rightarrow \text{P}}(\text{UO}) = \frac{2\pi}{\hbar} \sum_{kx} \sum_{i,l} |\langle S_f, p | C | S_v, q \rangle \langle S_v, q | H(0) | S_i, o_{il} \rangle + \langle S_f, p | H(0) | S_v, q \rangle \langle S_v, q | C | S_i, o_{il} \rangle|^2 \delta(\epsilon_\chi - \epsilon_k - \epsilon_{\text{op}}) / \Delta^2 \quad (12)$$

where $\Delta = E_v - E_i$ is the virtual transition energy, $|q\rangle$ one of the $|L = 1 m_l, I = 0\rangle$ and $|L = 0, I = 1 m_i\rangle u$ eigenstates and $|S_v\rangle = |g\bar{g} \dots [ku] \dots |$ the singlet virtual intermediate

state. The orbital matrix element is obtained by applying the Hamiltonian (5) to the eigenfunction u which, in a first order expansion in spherical basis, is written as

$$u(r) = f(r)Y^1(\widehat{ab}) \cdot Y^1(\widehat{r}) \tag{13}$$

where $f(r)$ is a known radial function. By applying the electron tensor E^j given by (5c) to u , we obtain

$$E^j u = \sum_{i=0,2} a_i(r) \left\{ \frac{Y^2(\widehat{r})}{r^3} \times [Y^1(\widehat{r}) \times Y^1(\widehat{ab})]^1 \right\}^j \tag{14a}$$

$$a_0(r) = (3)^{-1/2} (d/dr + 2/r)f(r) \tag{14b}$$

$$a_2(r) = -(2/3)^{1/2} (d/dr - 1/r)f(r). \tag{14c}$$

The tensorial algebra [6] allows to condense the spherical harmonics leading to

$$E^j u = \sum_{i=0,2} \frac{a_i(r)}{r^3} \sum_{k=0,2} \eta_k^{ij} [Y^k(\widehat{r}) \times Y^1(\widehat{ab})]^j \tag{15a}$$

$$\xi_k^{ij} = [3(2k+1)]^{1/2} (-)^{j+1} \begin{Bmatrix} 2 & i & k \\ 1 & j & 1 \end{Bmatrix} \tag{15b}$$

where

$$\eta_k^{ij} = \xi_k^{ij} \zeta_k^i \quad \zeta_2^0 = \zeta_0^2 = (4\pi)^{-1/2} \quad \zeta_2^2 = -(5/7 \times 2\pi)^{1/2}$$

and $\{ \}$ denotes the usual 6j symbol. In a similar procedure, we aggregate and condense the nuclear tensors and obtain

$$\sum_{j=1,2} \alpha_j N^j \cdot E^j u = F(r) Y^2(\widehat{r}) \cdot [i^1 \times Y^2(\widehat{b})]_0^2 \tag{16a}$$

$$F(r) = \sum_{i=0,2} \gamma_i a_i(r) / r^3 \tag{16b}$$

$$\gamma_i = \sum_{j=1,2} \eta_2^{ij} \alpha_j \lambda_j \tag{16c}$$

$$\lambda_j = \frac{ab}{\sqrt{10}} (2j+1) \begin{Bmatrix} 1 & 1 & j \\ 1 & 2 & 2 \end{Bmatrix} \tag{16d}$$

where α_j is given by (5d). We make now two simplifying assumptions of an axial band whose bottom lies in the vicinity of the Fermi level and whose eigenfunction vacuum tail $\Phi(z) \sim e^{\gamma z}$, ($z < 0$). Taking the Hermitian product of (16) with $\Phi(z)$, the orientation average leads to

$$\int e^{\gamma r \cos \theta} Y_m^2(r) \sin \theta \, d\theta \, d\varphi = \beta \delta_{m,0} G(\gamma r) \tag{17a}$$

$$G(x) = 4 \, sh \, x/x - 12 \, ch \, x/x^2 + 12 \, sh \, x/x^3 \tag{17b}$$

where the numerical constant $\beta = (5\pi/4)^{1/2}$. The function $F(r)$ is then integrated radially

$$\langle \Psi | H(0) | u \rangle = \Psi(L) \Theta [i^1 \times Y^2(\widehat{b})]_0^2 \tag{18a}$$

$$\Theta = \beta \int F(r) G(\gamma r) r^2 \, dr. \tag{18b}$$

The space integral Θ can be expressed analytically in terms of exponential integrals, in a lengthy but simple calculation, and then computed numerically. For the Ag(111) surface band(11), the resulting value is $\Theta \approx 4.43 \times 10^{-7}$ au. The nuclear operator in (18a) induces a simultaneous spin and rotation transition, from an ortho o_H state to the $|q\rangle = |L = 1 m = 0, I = 0\rangle u$ eigenstate, whose matrix element is obtained as

$$\langle I = 0, L = 1 m = 0 | [i^2 \times Y^2(b)]_0^2 | I = 1 m_i, L = 1 m_i \rangle = \delta_{m_i, -m_i} (m_i/2) (3/10\pi)^{1/2}. \quad (18c)$$

The Coulomb interaction which mixes metal and molecule electron states has already been estimated [4] and obtained as

$$\langle \Psi_g | c | u_0 g \rangle = 3.4 \Psi(I) \quad (19)$$

expressed in atomic units and u_0 denotes the rotational average $\langle L = 0 | u | L = 1 m = 0 \rangle$. Because of the axial symmetry the $m = 0$ rotational component is found to give the largest contribution in (17) and (19). Despite the small value of the metal eigenstate tail Φ_v at the molecular centre $I(\Phi_v(I) \approx 7 \times 10^{-3})$, the Coulomb integral (19) remains quite large (~ 0.65 eV). Therefore the Coulomb step considerably enhances the electron–nuclei interaction. Bringing together all matrix elements, summing over the metal states and inserting in the two-step transition probability we obtain the conversion rate

$$P_{o \rightarrow p}(uO) = 115 \Theta^2 \Psi^4(I) N_s^2(\varepsilon_F) \varepsilon_{op} / \hbar \Delta^2 \quad (20)$$

expressed in au and where Δ is the energy excitation of the u -state which lies in the close vicinity of the vacuum level: $\Delta \approx 4.6$ eV. It is worth noticing that although the reaction takes place in two virtual steps, the above transition probability remains a first-order one in the sense of time-dependent perturbation theory. The rate (20) is, as the preceding one (10), proportional to the number of band states involved in the conversion process: $N_s^2(\varepsilon_F) \varepsilon_{op}$ which may also be related to the population of emitted (E-H) pairs. Contrary to (10) which varies slowly with distance, (20) is proportional to the fourth power of the band tail at the molecular centre $\sim e^{-4\gamma_v d}$ and is thus very sensitive to the metal molecule distance d which lies within the range: 4.3–4.7 b [9]. Inserting the numerical values leads to a conversion time of the order of 30 min. This figure is too long for the Ag(111) rate which has been measured to be shorter than 2 min [2]. It agrees however with the ones observed on a Cu(100) surface [3] and other Cu catalysts [10]. Whereas the Ag(111) surface band has been found very efficient in contact processes (where the molecule angular momenta are dissipated by the electron spins), it is unable to transfer large electron momenta in view of its very small k_{\parallel} components. By contrast, numerous bulk bands of large k_{\parallel} cross the Fermi level in Cu(100) thin films [11] and could provide large momentum transfers which strengthen the rate (20).

4. Concluding remarks

A precise characterization of the different conversion processes on noble metals catalysts would give interesting information on the surface electron distribution, position and dispersion of the surface and bulk bands at the Fermi level as well as on the adsorption well minimum. For (111) surfaces, the noble metals (111) surface state seems to give rise to the faster conversion rates through the Coulomb–Contact mechanism [4]. For (100) surfaces, the (100) surface state located in the vicinity of the \bar{X} point is too weak, being characterized by a small effective mass ≈ 0.067 [12]. The observed rate might thus

be attributed to bulk bands and the above described Coulomb-Orbital UO process agrees with the experimental feature. It would be of interest also to perform experiments on (110) surfaces where a strong surface band has been observed near the \bar{Y} point [13].

Summarizing, the fast conversion rates observed at low temperatures on noble metals surfaces open a new branch in O-P H₂ conversion history by contradicting the picture developed over more than half a century, that O-P conversion can only proceed through dissociation or under the catalytic influence of magnetic impurities. Quite recently [4], we have shown that semi-magnetic processes are able to give rise to fast rates on noble metals by emitting magnetic electron-hole pairs through the crystal. We report here a possible non-magnetic mechanism, based on a momentum transfer from the molecule to the metal. The momentum transfer to the electron-hole pairs is found to be strongly enhanced by a Coulomb-induced virtual charge transfer.

References

- [1] Wigner E P 1933 *Z. Phys. Chem. Abt* **23** 28
- [2] Avouris Ph, Schmeisser D and Demuth J E 1982 *Phys. Rev. Lett.* **48** 199
- [3] Andersson S and Harris J 1982 *Phys. Rev. Lett.* **48** 545
- [4] Ilisca E 1991 *Phys. Rev. Lett.* **66** 667
- [5] Yucel S 1989 *Phys. Rev. B* **39** 3104
- [6] Edmonds A R 1974 *Angular Momentum in Quantum Mechanics* (Princeton, NJ: Princeton University Press)
- [7] Heimann P, Neddermeyer H and Roloff H F 1977 *J. Phys. C: Solid State Phys.* **10** L17
- [8] Dose V 1985 *Surf. Sci. Rep.* **5** 337
- [9] Liebsch A and Harris J 1983 *Surf. Sci.* **130** L349
- [10] Kolac M, Neganov B S, Sahling A and Sahling S 1986 *J. Low Temp. Phys.* **63** 459
- [11] Smith J R, Gay J G and Arlinghaus F J 1980 *Phys. Rev. B* **21** 2201
- [12] Kevan S D 1983 *Phys. Rev. B* **28** 2268
- [13] Heimann P, Hermanson J, Miosga H and Neddermeyer H 1979 *Surf. Sci.* **85** 263