Ortho-Para H_2 Conversion on a Cold Ag(111) Metal Surface

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Electron-energy-loss experiments of H_2 physisorbed on noble metals at low temperature indicate that the ortho-para conversion rate is 2 orders of magnitude faster on a Ag(111) surface than on a Cu(100) one. We suggest a process in which a metal electron is virtually transferred back and forth from a surface band to the molecule antibonding orbital, the ortho-para energy being dissipated by metal (electron-hole) triplet pairs. The ortho-para rates are about 1 min on Ag(111) and 1 h on Cu(100), in agreement with experimental data. This large difference does not characterize Ag and Cu, but is inherent to different surface orientations.

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The electron-energy-loss, high-resolution studies of H_2 adsorbed on Ag surfaces, performed by Avouris, Schmeisser, and Demuth in 1982,[1] were the first observation of rotational excitations of molecules adsorbed on a metal surface. Shortly thereafter, Andersson and Harris[2,3] reached similar resolution with H_2 molecules adsorbed on a Cu(100) surface. Both studies, performed at low temperatures ($T \approx 10$–25 K), displayed unhindered 3D rotational spectra and concluded that there was pure H_2 physisorption. Their conversion patterns were, however, completely opposite. For Ag polycrystalline film and Ag(111) surfaces ortho molecules disappear within the first few minutes of initial exposure. Contradistinctly, on Cu(100) the conversion rate was estimated to be less than 1%/min.[2,4] Clearly, the Ag(111) and Cu(100) ortho-para rates differ by almost 2 orders of magnitude. More recently, fast conversion rates were also observed on graphite[5] and at the surface of H_2 bubbles precipitated in oxygen-free copper.[6] The fast rates observed on clean metal surfaces together with the experimental proof of pure physisorption contradict the mental picture, acquired more than half a century ago, that ortho-para conversion can only proceed either through dissociation or under the catalytic influence of magnetic impurities. The experiment of Avouris, Schmeisser, and Demuth[1] establishes, to the author's knowledge, the primary observation of ortho-para H_2 conversion performed on (i) a single crystal, (ii) a metal without chemisorption, and (iii) a nonmagnetic catalyst. The only theoretical attempt to model ortho-para H_2 conversion on a clean metal surface failed since the best among the investigated processes leads to a conversion time of the order of 20 h.[7]

The purpose of this Letter is to suggest an alternate and efficient process and to show that apparent contradictions might be reconciled on a simple basis. This process can be described as the hyperfine-Coulomb excitation of metal electron-hole triplet pairs which carry away the ortho-para rotational energy as well as the nuclear angular momenta. The metal is thus left in a magnetic excited state in contrast to previous mechanisms which rely on an initial magnetic ground state. The most efficient channel is found to be the virtual charge transfer of a metal electron to the molecule. As this process is much stronger when the metal electron occupies a surface state, we attribute the fast rate observed by Avouris, Schmeisser, and Demuth[1] to the well-known Ag(111) surface state and suggest that the different magnitudes reported do not characterize intrinsic differences between Ag and Cu, but are related to particular choices of surface orientations.

We consider a H_2 molecule physisorbed on a metal surface, at low temperature, a distance d away. The two H_2 electrons occupy the $\sigma_g(1s)$ spin orbitals, denoted in the following by g (and $\bar{g}$, a bar on the top of the spin orbital will indicate 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, $|S_i\rangle = |g\bar{g} \ldots k\bar{k} \ldots|$, which represents its initial and spin-singlet 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 electron-hole (e-h) pair states. We denote by $^3[k\chi]$ one of the triplet magnetic substates, $m=1,0,-1$, $|k\chi|$, $|k\bar{\chi}+\bar{k}\chi|/\sqrt{2}$, $|\bar{k}\bar{\chi}|$, and by $|T_f\rangle = |g\bar{g} \ldots {}^3[k\chi] \ldots|$ the final state of the electron system after excitation of the corresponding e-h pair. The molecule and metal electron states $g, k, \ldots$ are not orthogonal and the electrons are coupled through the Coulomb interaction $\sum_{\alpha\beta}(1/r_{\alpha\beta})$, denoted C in the following. The nuclear system is described by a set of ortho (L odd, $I=1$) and para (L even, $I=0$) states, where as usual $\mathbf{L}$ and $\mathbf{I}$ denote the rotational and nuclear-spin angular momenta of the H_2 molecule. At low temperature, only the transition $L=1 \rightarrow L=0$ is effective. The electron and nuclear systems are assumed to interact via a hyperfine contact interaction whose antisymmetric part (in the proton coordinates) is

$$Y=\zeta\sum_{\alpha}\mathbf{i}\cdot\mathbf{s}(\alpha)\{(a\alpha)-(b\alpha)\}\ , \tag{1}$$

where $p=a,b$ denote the two H_2 protons of nuclear-spin difference $\mathbf{i}=\mathbf{I}(a)-\mathbf{I}(b)$, α is any metal or molecule electron of spin $\mathbf{s}(\alpha)$ and position $\mathbf{r}(\alpha)$, while $(p\alpha)$ is the Dirac operator $\delta(\mathbf{r}_\alpha-\mathbf{r}_p)$ and ζ the contact strength ($\zeta\approx 3.4\times 10^{-7}$ a.u.).

We investigate the two-step process along the following path: One metal electron k (below the Fermi level E_F) being virtually transferred to the hydrogen molecule in an ionic state is returned to the metal in a state χ (above E_F). The "surface-complex" intermediate state is composed of the ionized metal, left with a hole and denoted ${}^2M_v{}^+$, and of the $H_2{}^-$-ion ${}^2\Sigma_u^+$ ground state. ${}^2\Sigma_u^+$ is known to be a resonance in the gas phase (the antibonding state being located ≈ 2.3 eV above the vacuum level). It is, however, shifted downwards at a metal surface by the image-charge potential by an amount of about 1.15 eV, and we shall assume in the following that for the adsorbed molecule it is nearly a bound state. The surface complex is coupled to the initial and final states by the Coulomb interaction C which performs the molecule rotational transition and by the hyperfine contact Y which induces the nuclear transition. Two channels are open for the ortho-para conversion according to the surface-complex spin manifold. If the Coulomb interaction operates first, the virtual excited state remains a singlet:

$$|S_v\rangle={}^1[{}^2\Sigma_u\times{}^2M_v{}^+]=|g\bar{g}\ldots(k\bar{u}-\bar{k}u)/\sqrt{2}\ldots|\ ,$$

where u denotes the molecule antibonding orbital. In contrast, if the hyperfine contact operates first, it induces a singlet-triplet transition to the triplet intermediate:

$$|T_v\rangle={}^3[{}^2\Sigma_u\times{}^2M_v{}^+]=|g\bar{g}\ldots{}^3[ku]\ldots|\ ,$$

with similar notation as for T_f. The conversion rate, relative to this "Coulomb-contact" mechanism, is then obtained from the second-order probability:

$$P_{\rm op}=(2\pi/\hbar\Delta^2)\sum_{k,\chi,o}|\langle T_f,p|Y|S_v\rangle\langle S_v|C|S_i,o\rangle+\langle T_f,p|C|T_v\rangle\langle T_v|Y|S_i,o\rangle|^2\delta(\varepsilon_\chi-\varepsilon_k-\varepsilon_{\rm op})\ . \tag{2}$$

The summation is performed over the electron states k,χ and the set "o" of nuclear ortho substates (the summation over the intermediate substates being implicit). $\varepsilon_{\rm op}$ is the ortho-para energy and

$$\Delta=E_i-E_v=E({}^1\Sigma_g^+)-E({}^2\Sigma_u^+)-\Phi\ ,$$

where Φ is the metal work function. The hyperfine matrix elements, in the singlet channel, are simply worked out:

$$\langle T_f m_s,L=I=0|Y|S_v,L=0,I=1,m_I\rangle=-\zeta u(a)\chi(I)\delta_{m_I,m_s}\ , \tag{3}$$

where the wave functions u and χ are calculated, respectively, at the molecule proton a and the center I. The matrix elements of the Coulomb interactions among the $2N+2$ electrons might be reduced and expressed in terms of two electron ones:

$$\langle S_v,L=0|C|S_i,L=1,m\rangle=2\sqrt{2}\langle kg|c|u_m g\rangle\ , \tag{4}$$

where u_m is the rotational average $\langle 0|u|1,m\rangle$. In this expression we have neglected the exchange contribution $\langle kg|c|gu\rangle$, which remains small as the molecule orbitals g and u are orthogonal, and matrix elements of the form $\langle k'k|c|k'u\rangle$, which measure the tunneling of the molecule electrons inside the metal (these terms contribute weakly since the molecular orbital is strongly localized). A similar expression is obtained in the triplet channel by interchanging the electron χ and the hole k.

From now on, we restrict ourselves to metal electron states which belong to a surface band in the close vicinity of the Fermi level. As the ortho-para energy is very small, $\varepsilon_{\rm op}\approx 14.7$ meV, the electron and hole are described by similar wave functions, which vary negligibly with energy. Then, bringing together (1)–(4) and performing the summation over the electron- and nuclear-spin states, we obtain the conversion rate

$$P_{\rm op}\approx(2^2 3^3\pi\zeta^2/\hbar)|\chi(I)\langle kg|c|u_0 g\rangle|^2 N_s^2(\varepsilon_F)\varepsilon_{\rm op}/\Delta^2\ , \tag{5}$$

where $\varepsilon_{\rm op}\ll\varepsilon_F$ has been used, the average over k (parallel to the surface) is implicit, and $N_s(\varepsilon_F)$ is the metal surface density of states at the Fermi energy. Note that, as the surface band has an axial symmetry, we have only retained the $L=1$, $m=0\rightarrow L=0$, ortho-para transition which gives the largest contribution. The Ag(111) surface band is located in the L gap where the nearly-free-electron-like sp bands are split at the Brillouin-zone boundary. It has been observed by angular-resolved UV photoemission in all noble-metal (111) faces.[8,9] As the d bands are relatively far (≈ 3.7 eV below[10,11]), this surface band is known to be fairly well reproduced within the nearly-free two-band model.[12,13] With the data given in Fig. 1 we obtain, at the Fermi energy,

$$\Psi_s(r)=e^{ik\rho}\psi(z),\quad k\simeq 0.074\ , \tag{6}$$

$$\psi(z<z_0)\simeq 0.077e^{-0.0446z}\cos(0.7z-0.23)\ , \tag{7}$$

$$\psi(z>z_0)\simeq 0.088e^{0.56z}\ . \tag{8}$$

All numbers are given in atomic units (as well as in the following unless otherwise specified) and the wave functions Ψ_s have been normalized to a unit-surface-cell area. This model uses a simple rectangular surface po-

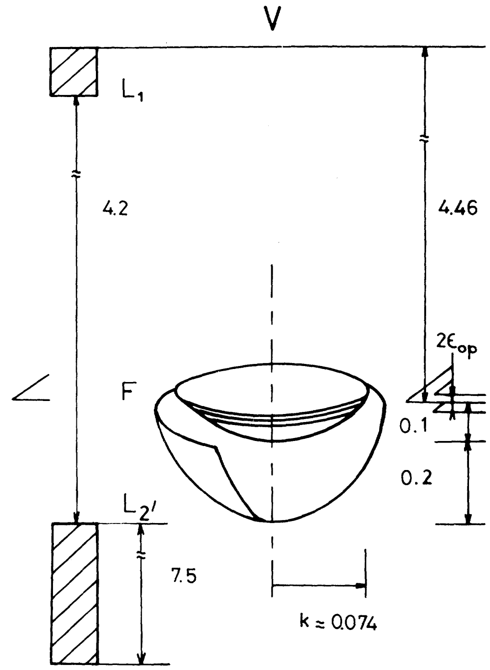

FIG. 1. Representation of the energy surface band dispersion around the center $\bar{\Gamma}$ of the two-dimensional Brillouin zone (inside the projected bulk one). It intersects the Fermi level at $k \approx 0.074$ a.u. Intersections with the planes $\varepsilon_F \pm \varepsilon_{op}$ are also drawn ($\varepsilon_{op} \approx 14.7$ meV). The surface and conduction bands, the $L_{2'}L_1$ *sp* gap, and the metal work function are taken from Refs. 9–11 and 14 (all energies are given in eV).

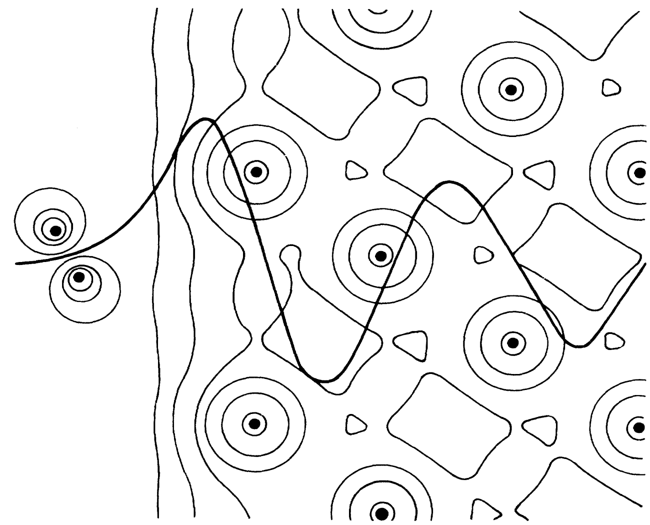

FIG. 2. Representation of the surface-state wave function $\psi(z)$, given by (7) and (8), in a plane perpendicular to the surface, together with the charge-density contours of Ag (extrapolated from Ref. 15) and of H_2 (in its antibonding intermediate state). The origin of z is set at the jellium edge (1.18 Å above the uppermost layer of ions) and the matching plane lies at $z_0 = 0.36$ Å outside the jellium background.

tential barrier which locates the "matching" plane at $z_0 = 0.36$ Å outside the jellium background, while a Coulomb image potential reduces this distance to 0.07 Å.[13] The relative insensitivity of this state to the shape of the surface potential barrier has suggested the appellation of "crystal derived." The surface-state wave function $\psi(z)$ is represented in Fig. 2, in a plane perpendicular to the surface. The Ag(111) surface band dispersion has been measured by inverse photoemission, below[16] ($m_s \approx 0.7m$) and above[17] ($m_s^* \approx m$) the Fermi level. We shall therefore assume an average effective mass of $m_s^* \approx 0.8m$ in the close vicinity of the Fermi energy which leads to a surface density of states of 0.12 state/(surface ion) eV. Inserting the surface-state wave function (6) and accurate Hartree-Fock bonding and antibonding molecular orbitals[18,19] into the Coulomb integral, $U_0 = \langle kg|c|u_0 g\rangle$, we obtain $U_0 \approx 21.7e^{-0.56d}$ eV, where d is the distance between the molecule center and the metal jellium edge ($U_0 \approx 1.74$ eV at $d = 4.5$). The conversion time is then calculated from (5) to be (in s)

$$\tau_{op} = P_{op}^{-1} = 1.9\times 10^{-3} e^{4\gamma d}, \qquad (9)$$

where γ measures the surface-state decay outside the metal ($\gamma = 0.56$ in our model).

The conversion rate being proportional to the fourth power of the surface-state wave function at the molecule center, it varies sharply with the distance d. This distance is not precisely known, although the H_2-Ag(111) potential modeled to interpret diffraction-beam experiments seems to locate the well minimum around 4.5 a.u.[19,20] At this distance $\tau_{op} \approx 54$ s (for $d = 4.3$ it drops to 34 s, whereas at $d = 4.7$ it increases to 70 s). These figures agree fairly well with experimental data although the experiment was not designed to measure the conversion rate. In view of the sharp distance dependence of the rate, its precise measurement would locate the well minimum with high accuracy and test different models of the surface potential (a small change in the distance d of 0.1 a.u. induces a relative variation of 22% in the rate).

These estimates are obtained for a surface state located very near $\bar{\Gamma}$ ($k \approx 0$). Around $\bar{\Gamma}$ we may expand the Coulomb integral U_0 (4) in powers of k/λ, where λ is the molecular attenuation length ($\lambda \approx 1.2$), and obtain $U_0(k) = U_0(0)(1 - 30k^2/\lambda^2 \cdots)$. Thus for a mode traveling along the surface plane ($k \neq 0$), U_0 appears to be strongly reduced. The Ag(111) bulk band, for instance, which crosses ε_F a little further on ($k \approx 0.095$) and with a smaller effective mass ($m^*/m \approx 0.37$) than the surface one, leads to a conversion rate 6 times smaller than the surface-state contribution (assuming similar attenuation and amplitude). For a (100) surface the decrease is even stronger. The only surface state detected at ε_F is located near $\bar{X}$,[21] giving an almost vanishing contribution to U_0.

The closest (to $\bar{\Gamma}$) bulk band crosses ε_F at $k \approx 0.17$,[22] which decreases U_0 by more than 60%. As the corresponding $N(\varepsilon_F)$ of the bulk band is also smaller, the conversion rate is about 2 orders of magnitude smaller for a (100) surface than for a (111) surface. Therefore, the astonishing difference noticed in the observed rates[1,2] is not essentially related to the choice of Cu or Ag but to particular surface orientations and their corresponding surface states. Cu and Ag (111) faces should give similar conversion rates, as well as Cu and Ag (100) ones. Moreover, other surfaces such as (110) and low-index faces of all noble metals might be valuably investigated.

From a theoretical point of view, it appears that Yucel's model[7] was too crude for three main reasons: (1) The metal surface states although mentioned were not explicitly considered, (2) the molecular electronic degrees of freedom were omitted, and (3) only one-step processes were investigated. In contrast, our suggested mechanism relies on a two-step process where the metal electrons are virtually transferred back and forth from the metal surface band to a molecular antibonding excited state. It is 3 orders of magnitude more effective.

In summary, we have considered a new process to interpret ortho-para H_2 conversion on a cold metal surface which gives surprisingly good agreement with experimental data. Additional experiments would give very precise information on surface potentials and metal surface states. Ortho molecules might be viewed as sinks of nuclear momenta and energy which decay at metal surfaces through *e-h* triplet pair excitation. In contrast to the usual belief, the displayed mechanism shows that the catalyst does not need to be magnetic to induce ortho-para H_2 conversion.

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