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Fermi resonance coupling in the C–H stretching region of methoxide adsorbed on clean Ru(0 0 1): a combined RAIRS and theoretical study

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Abstract

A combined reflection–absorption infrared spectroscopy (RAIRS) and theoretical study on methoxide adsorbed on clean Ru(0 0 1) enabled to interpret the C–H stretching region of the spectrum. The Fermi resonance between the fundamental stretching modes and the overtones of the deformations has been analyzed. Density functional cluster model calculations (DFT) showed that methoxide adsorbs preferentially on hcp threefold cavities, and provided the unperturbed vibrational frequencies. Once corrected by the experimentally determined frequencies, they were used to calculate the Fermi resonance coupling constants by a normal mode model, assuming the local symmetry suggested by the experimental results (C_s). The present approach shows that a reliable description of the experimental C–H stretching region of adsorbed methoxide on Ru(0 0 1) may be obtained.
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1. Introduction

It is known that methanol decomposes as adsorbed methoxide ($CH_3O–$) on clean Ru(0 0 1), when this surface is exposed to a low dose, at low temperature (85–90 K) [1,2]. In general, the data collected by reflection–absorption infrared spectroscopy (RAIRS) enable to infer on the local symmetry of the adsorbate, since in this technique the metal surface selection rule is strictly obeyed. In the case of methoxide, an interpretation of the vibrational data exclusively based on the fundamental modes led to propose a tilted orientation on most metal surfaces [3]. However, the C–H stretching region is strongly influenced by Fermi resonance between the overtones of the methyl deformations ($2 \times \delta CH_3$) and the fundamental symmetric stretching mode ($\nu_s CH_3$), resulting in intensity transfer from the latter to the formers, and repulsion of the states involved [4,5]. More recently, the combination of experimental and theoretical studies [5–8] taking into account the

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Fermi resonance reinforces some previous pro-
posals for an upright configuration on several
metal surfaces, such as Cu(1 1 1) and Ag(1 1 1)
[9,10]. Nevertheless, a tilted orientation has still
been argued for methoxide adsorbed on Ni(1 1 1)
[3], as well as on Ru(0 0 1) [2], suggesting that
lateral interactions, and therefore the coverage,
may be most relevant in the adopted geometry.

In this work, the combination of experimental
RAIRS data with DFT cluster calculations en-
abled to model the Fermi resonance coupling in
the C–H stretching region of methoxide adsorbed
on Ru(0 0 1), providing a better assignment of that
complex spectral region. By this approach, a more
reliable correlation between the infrared data and
the structure/local symmetry of adsorbed meth-
oxide is obtained.

2. Experimental

The experiments were performed in a stainless
steel UHV chamber, operating at a base pressure
of $\sim 10^{-10}$ Torr [11]. The chamber is interfaced to a
Mattson RS1 FTIR spectrometer, equipped with a
narrow band MCT detector (4000–800 cm^{-1}) from
EG&G Judson. In order to detect exclusively the
p-polarised light, a wire grid polariser was placed
before the detector. The Ru(0 0 1) crystal was
cleaned by cycles of argon sputtering and anneal-
ing to 1200 K. The cleanliness was monitored by
LEED and by the RAIR spectrum of CO ad-
sorbed at 100 K and at saturation coverage [12].
The spectra were obtained as a ratio of 1000 co-
added scans for sample and background (clean
surface), at 4 cm^{-1} resolution. The surface was
exposed to methanol (Fluka, 99.8%+) and meth-
anol-d_2 (CHD$_2$OD, Cambridge Isotope Lab,
98%+) by back-filling the chamber. The alcohols
were distilled under vacuum ($\sim 10^{-7}$ Torr) before
use.

3. Computational approach

Adsorption of the methoxide on the Ru(0 0 1)
surface at low coverage has been investigated
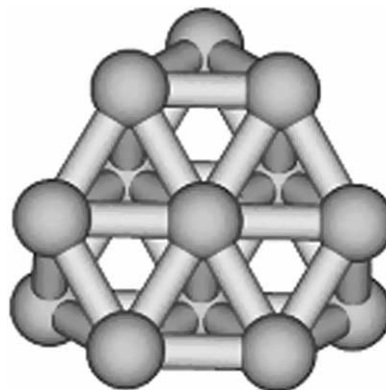within the cluster model approach by density-

Fig. 1. Top view of the Ru$_{13}$(7,6) cluster used to model the
(0 0 1) ruthenium surface.

functional theory (DFT). The metallic surface was
represented by a 13-atom cluster with seven atoms
in the top layer and six in the second one, as shown
in Fig. 1. The Ru atoms in this model cluster were
constrained to appropriate hcp lattice positions
taken from the bulk ($a_{Ru} \sim 2.7$ Å). The DFT cal-
culations were performed using the B3LYP [13]
hybrid functional as implemented in the GAUSS-
IAN98 program [14]. Metallic atoms were de-
scribed by the Hay–Wadt [15] relativist effective
core potential and double-zeta basis set for the 16
outer electrons explicitly considered, whereas non-
metallic atoms (O, C and H) were described by the
all-electron 6-31G** basis set.

This simple surface model has certain limita-
tions, particularly for describing properties that
depend on the long-range electronic structure.
However, the cluster approach provides an excel-
lent model to study local properties, such as
adsorbate vibrations, that are less sensitive to
cluster size than binding energies [16]. Thus, the
equilibrium geometry and vibrational frequencies
for methoxide adsorbed at the various Ru(0 0 1)
sites have been obtained using the above described
Ru$_{13}$ cluster (see Fig. 1). It is worth pointing out
that an H atom was deliberately incorporated into
this cluster, placing it as far as possible from
CH$_3$O–, to obtain final singlet closed-shell elec-
tronic states for all adsorbate-cluster systems. This
seems reasonable, since in the present study only
the final adsorbate structures are of interest, the

adsorbed methoxide is produced following dissociation of methanol into the CH_3O- and H radicals, and a closed-shell electronic structure is the natural choice to model an extended surface. Moreover, Ricart et al. [17] have shown that the choice of the electronic state does not largely affect the basic bonding mechanisms.

To begin with, the free optimized adsorbate was placed on the cluster surface model with its oxygen atom pointing toward the high-symmetry surface sites. Partial geometry optimizations, in which the C–H bond lengths were fixed at 1.1042 Å, were then carried out to find the preferred adsorbate site conformations. Harmonic vibrational frequencies for the optimized methoxide and methoxide-d_2 conformations were obtained from the Hessian matrix, and scaled by a factor of 0.9613 as recommended [18]. Adsorption energies were computed as the difference between the total energy of the cluster-adsorbate super-system and the total energies of the cluster plus CH_3O- isolated fragments, and were not corrected for possible basis set superposition errors, since those should not exceed ~ 0.3–0.4 eV in these systems, as checked using the counterpoise technique [19].

The extent of Fermi resonance has been estimated based on a normal mode model, by means of an effective Hamiltonian matrix with the unperturbed modes on the diagonal and the coupling constants as off-diagonal elements [20,21]. To a first approximation, the couplings between the two overtones (the so-called Darling–Dennison coupling constants) and between the overtones and the $\nu_{as}CH_3$ mode were disregarded, since they are expected to be less significant [8,22]. This led to the following symmetric effective Hamiltonian matrix, in which the off-diagonal elements are the coupling constants ω_{12}, ω_{13} and ω_{14} for $\nu_sCH_3/2 \times \delta_sCH_3$, $\nu_sCH_3/2 \times \delta_{as}CH_3(A'')$ and $\nu_sCH_3/2 \times \delta_{as}CH_3(A')$, respectively

$$H = \begin{pmatrix} \upsilon_sCH_3 & \varpi_{12} & \varpi_{13} & \varpi_{14} \\ & 2 \times \delta_sCH_3 & 0 & 0 \\ & & 2 \times \delta_{as}CH_3(A'') & 0 \\ & & & 2 \times \delta_{as}CH_3(A') \end{pmatrix}$$

These constants were allowed to vary (from zero and with steps of 1 cm^{-1}) until finding the

least-square error between the experimental frequencies and the eigenvalues of H [6].

4. Results and discussion

The RAIR spectra (in the range 2600–3100 cm^{-1}), shown in Fig. 2, were recorded upon adsorbing 0.1 L of methanol and methanol-d_2 on clean Ru(0 0 1), at 90 K. At this coverage and temperature, methanol undergoes dehydrogenation, yielding adsorbed methoxide [2].

In the spectrum of CHD_2O-, the observation of a pair of bands, at 2957 and 2918 cm^{-1}, assigned to the νCH mode (in plane A' in C_s, and A in C_1,
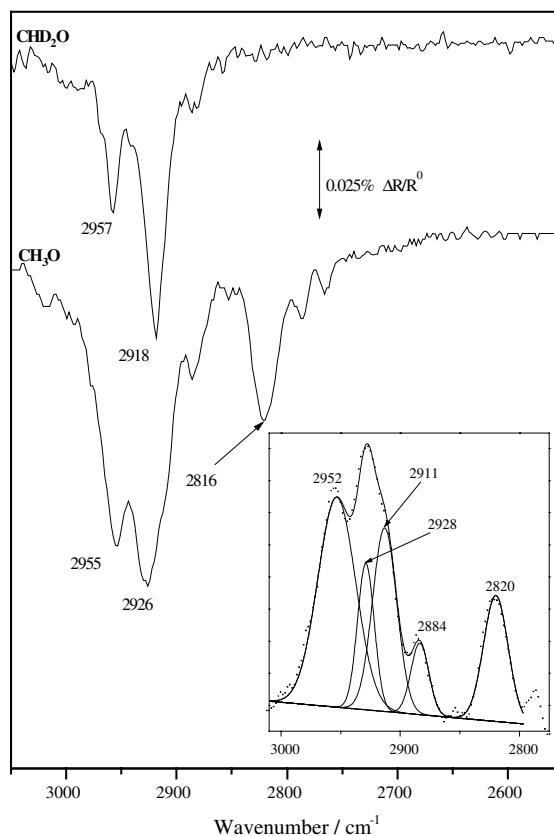

Fig. 2. RAIR spectra (region between 2600 and 3100 cm^{-1}) of methoxide and methoxide-d_2 adsorbed on clean Ru(0 0 1), at 90 K, after an exposure of 0.1 L. *Inset*: deconvolution of the CH stretching region of the CH_3O-spectrum.

Table 1
Calculated properties and adsorption energy (E_{ads}) of CH_3O– on the different sites of Ru(0 0 1)

Parameter	hcp	top	bridge	fcc
E_{ads}/eV	2.32	1.88	1.86	1.64
d(O–Ru)/Å	1.59	2.05	1.75	1.76
ang(C–O–Surf)/°	177	116	133	173
Order of stability	1	2	3	4

Vibrational modes at the hcp site	
Assignment	Wavenumber/cm^{-1}
$\delta_s CH_3(A')$	1413
$\delta_{as} CH_3(A'')$	1435
$\delta_{as} CH_3(A')$	1444
$\nu_s CH_3(A')$	2828
$\nu_{as} CH_3(A'')$	2895
$\nu_{as} CH_3(A')$	2898

respectively [23]), is indicative of two non-equivalent C–H coordinates, confirming that this species is adsorbed in a tilted configuration, although still containing a symmetry plane (C_s) [5]. Taking this local symmetry into account, the three bands at 2820, 2926 and 2955 cm^{-1} in the CH_3O-spectrum were assigned to the $\nu_s CH_3$, $2 \times \delta_s CH_3/2 \times \delta_{as} CH_3$ and $\nu_{as} CH_3$ modes, respectively [2]. The observation of the latter can only occur for C_s symmetry.

This interpretation is supported by the results of the DFT cluster calculations. In fact, inspection of Table 1 shows that radical methoxide adsorbs preferentially on threefold hcp hollow sites, adopting a slightly tilted orientation, as shown in Fig. 3. The computed frequencies for these sites also confirm the likelihood of a Fermi resonance in the vibrational spectra, since the antisymmetric and symmetric methyl overtones are very close in

Fig. 3. Top and side and views of the optimized methoxide adsorbed on the hcp site of the Ru$_{13}$(7,6) cluster.

energy to the stretching fundamentals. To further check these results, additional test calculations were performed with two cluster models that preserve the hcp and fcc threefold symmetry, namely a Ru$_{13}$ [6,7] cluster to model the hcp adsorption site (the inverted Ru$_{13}$ cluster, i.e., with six Ru atoms in the top surface layer and seven in the second one) and a Ru$_9$ [6,3] cluster to model the fcc site (with six Ru atoms in the top surface layer and three in the second one). Such calculations resorted to a similar strategy and the same electronic structure method as described previously. The attained results confirmed that the titled C_s optimal geometry adopted by the adsorbed CH_3O– was not an artefact of the present calculations, since identical geometric parameters were obtained for this species (e.g., Ru$_{13}$ [6,7]: ang(C–O–Surf) = 177°; Ru$_9$ [6,3]: ang(C–O–Surf) = 172°).

As mentioned above, the Fermi analysis of the C–H stretching region was performed considering the coupling between the symmetric stretching and the deformation modes. Only the latter can be determined experimentally, although they are too weak to be detected by our RAIR system at such low coverage [2]. Therefore, the wavenumber obtained for $\delta_s CH_3$ (1435 cm^{-1}), by Hrbek et al. using EELS [1], was used. The unperturbed $\delta_{as} CH_3$ and $\nu_s CH_3$ modes were estimated as by Ásmundsson et al. [6]

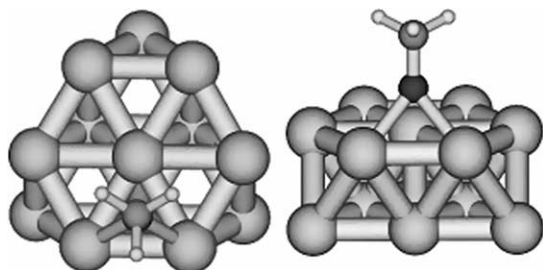$$\delta_{as}CH_3 = [\delta_{as}CH_3(calc)/\delta_s CH_3(calc)]$$
$$\times \delta_s CH_3(exp) \qquad (1)$$

$$\nu_s CH_3 = [\nu CH(CHD_2O, exp)/\nu CH(CHD_2O, calc)]$$
$$\times \nu_s CH_3(calc). \qquad (2)$$

The measured and calculated frequencies determined for the νCH mode in CHD_2O were 2918 and 2875 cm^{-1}, respectively. The remaining values were taken from those calculated by DFT for the preferential hcp adsorption site (see Table 1).

The perturbed experimental frequencies were obtained by deconvolution of the CH_3O-spectrum, the best adjustment (with $\chi^2 = 1.8 \times 10^{-11}$ and $\rho = 0.998$) being achieved with five gaussians, as shown in the inset of Fig. 2. The bands at 2820, 2884, 2911, 2928 and 2952 cm^{-1} are assigned to the $\nu_s CH_3$, $2 \times [\delta_s CH_3(A')]$, $2 \times [\delta_{as}CH_3(A'')]$, $2 \times [\delta_{as}CH_3(A')]$, and $\nu_{as}CH_3$ modes, respectively. The experimental and estimated data applied are summarised in Table 2, including the resulting best-fit coupling constants and the perturbed frequencies obtained upon diagonalization of the H matrix. An estimate of the relative band intensities can also be determined from the amount of the methyl symmetric stretch in the corresponding eigenvectors of the diagonalized matrix; the square of these coefficients are given as percentages in Table 2.

As can be seen, the calculated perturbed frequencies differ less than 7 cm^{-1} from the experimental values with a mean squared deviation of only 0.8 cm^{-1}. The absolute values of the Fermi resonance coupling constants compare also well with those obtained for the free methanol molecule [24].

Nonetheless, the calculated band intensities do not reproduce the experimental ones, although the two more intense are the same: $\nu_s CH_3$ and $2 \times \delta_{as}CH_3(A'')$. This problem may arise from some applied simplifications, such as not including other modes in the H matrix (for instance $\nu_{as}CH_3$). So far, the results obtained by including this mode were not satisfactory, most probably due to the difference between the experimental maximum (at 2952 cm^{-1}) and the theoretical unperturbed value predicted by the DFT cluster calculations (~ 2895 cm^{-1}). An alternative way that remains is to include the Fermi resonance coupling on an ab initio level as well.

5. Conclusions

The combination of DFT cluster calculations and Fermi resonance analysis enables a successful qualitative description of the C–H stretching region of methoxide adsorbed on Ru(0 0 1), whenever the effective coverage induces a tilted geometry, and therefore C_s local symmetry. In this

Table 2
Experimental and unperturbed data used in the Fermi resonance analysis

Experimental values		Unperturbed values	Mode
Wavenumber/cm^{-1}	Intensity (%)	Wavenumber/cm^{-1}	
2928	21	2933	**4:** $2 \times \delta_{as}CH_3(A')$
2911	40	2894	**3:** $2 \times \delta_{as}CH_3(A'')$
2884	12	2870	**2:** $2 \times \delta_s CH_3(A')$
2820	27	2870	**1:** $\nu_s CH_3$

Calculated values			
Wavenumber/cm^{-1}	Intensity (%)	Coupling constants	Mode
2934	3	$|\omega_{14}| = 5$	**4:** $2 \times \delta_{as}CH_3(A')$
2918	42	$|\omega_{13}| = 16$	**3:** $2 \times \delta_{as}CH_3(A'')$
2890	4	$|\omega_{12}| = 42$	**2:** $2 \times \delta_s CH_3(A')$
2825	51		**1:** $\nu_s CH_3$

Calculated wavenumbers, intensities and coupling constants $|\omega_{ij}|$, giving the best fit to experiment.

study, it was taken into account the coupling between the symmetric stretching mode and the overtones of the deformation methyl modes, yielding coupling constants of 42, 16 and 5 cm^{-1} for $\nu_s CH_3 / 2 \times \delta_s CH_3$, $\nu_s CH_3 / 2 \times \delta_{as} CH_3 (A'')$ and $\nu_s CH_3 / 2 \times \delta_{as} CH_3 (A')$, respectively. They led to theoretical wavenumbers in accord with the experimental values to within 7 cm^{-1} or better. The modelling of the intensity redistribution is not so satisfactory. This may be due either to neglecting other anharmonic resonances or combination modes that are significant in the C-H stretching region, or to a coverage dependence of the unperturbed and experimental frequencies. The improvement of the present analysis will be the focus of future work, both by attempting to decrease the experimental coverage and by including the effect of lateral interactions in the theoretical calculations.

References

[1] J. Hrbek, R.A. dePaola, F.M. Hoffmann, J. Chem. Phys. 81 (1984) 2818.

[2] R.B. Barros, A.R. Garcia, L.M. Ilharco, Phys. Chem. B 105 (2001) 11186.

[3] R. Zenobi, J. Xu, J.T. Yates, B.N.J. Persson, A.I. Volokitin, Chem. Phys. Lett. 208 (1993) 414.

[4] E. Fermi, Z. Phys. 71 (1931) 250.

[5] P. Uvdal, A.D. MacKerell Jr., C.M. Friend, Phys. Rev. B 50 (1994) 12258.

[6] R. Ásmundsson, P. Uvdal, J. Chem. Phys. 112 (2000) 366.

[7] K. Mudalige, S. Warren, M. Trenary, J. Phys. Chem. B 104 (2000) 2448.

[8] M.P. Andersson, P. Uvdal, A.D. MacKerell Jr., J. Phys. Chem. B 106 (2002) 5200.

[9] M.A. Chesters, E.M. McCash, Spectrochim. Acta 43A (1987) 1625.

[10] W.S. Sim, P. Gardner, D.A. King, J. Phys. Chem. 99 (1995) 16002.

[11] L.M. Ilharco, A.R. Garcia, J.L. Silva, Surf. Sci. 371 (1997) 289.

[12] H. Pfnür, D. Menzel, F.M. Hoffmann, A. Ortega, A.M. Bradshaw, Surf. Sci. 93 (1980) 431.

[13] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[14] M.J. Frisch et al., Inc., Gaussian 98, Revision A.11.2, Pittsburgh PA, 2001.

[15] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270.

[16] P.S. Bagus, F. Illas, in: P.V. Schleyer, N.L. Allinger, T. Clark, J. Gasteiger, P.A. Kollman, H.F. Schaefer III, P.R. Schreiner (Eds.), Encyclopedia of Computational Chemistry, 4, Wiley, Chichester, UK, 1998, p. 2870.

[17] J.M. Ricart, J. Rubio, F. Illas, P.S. Bagus, Surf. Sci. 304 (1994) 335.

[18] P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502.

[19] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.

[20] J.P. Champion, A.G. Robiette, I.M. Mills, G. Graner, J. Mol. Spectrosc. 96 (1982) 422.

[21] E.B. Wilson, J.C. Decius, P.C. Cross, Molecular Vibrations, Dover, New York, 1980.

[22] W. Schneider, W. Thiel, Chem. Phys. 159 (1992) 49.

[23] A. Serrellach, R. Meyer, Hs.H. Gunthard, J. Mol. Spectrosc. 52 (1974) 94.

[24] L. Halonen, J. Chem. Phys. 106 (1997) 7931.