Supporting Information for the manuscript

Adsorption and Keto-Enol-Tautomerisation of Butanal on Pd(111)

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Chapter 1: Comparative discussion of the assignment of the vibrational bands performed in this study with the assignment previously reported in the literature.

Previously, IR spectra of unperturbed crystalline butanal were reported in the literature[1], as well the vibrational spectra of structurally similar compounds propanal[2-4] and 1-butanol.[5] Generally, there is a good agreement between the assignment of the vibrational bands performed in our study based on the theoretical calculations and the assignment done in the previously published reports mentioned above. It should be noted, however, that the previously reported assignment for butanal[1] is based mainly on the comparison of the measured IR spectra with the IR spectra of structurally similar compounds, which is not always very reliable especially for complex vibrations involving a large number of atoms. In the following, we will provide a short comparative discussion of the assignment previously performed in the literature and the assignment done in this study, which is based on the theoretical calculation.

The band at 2966 cm^{-1} ($\nu_{as}(CH_3)$) was assigned in our study to the assymmetric streching vibraton of the methyl group, which is in a good agreement with the previos reports. [1-5] In contrast, the band at 2940 cm^{-1}, which was assigned to a symmetric stretching vibration of the methylene group (ν_s(-CH_2-$\mathbf{CH_2}$-CH_3)) in our study, was previously assigned to the assymmetric stretching of the methylene group in butanal[1]. Our assignment of the band at 2895 cm^{-1} ($\nu_s(CH_3)$) to the symmetric stretching vibration of the methyl group is in accordance with the assignment performed for in propanal.[2-4] In contrast, Sbrana et al. [1] assign this band to a stretching vibration of a methylene group in solid butanal.

The band at 2869 cm^{-1} (ν_s(OHC-$\mathbf{CH_2}$-CH_2-)) assigned in our study to the symmetric stretching vibration of the methylene group, which is the next methylene group to the aldehyde entity, was previously similarly associated with the symmetric methylene stretching band in butanal[1] and 1-butanol.[5] However, the exact position of the methylene group was not specified in these reports. The band at 2755 cm^{-1} can be assigned to the C–H stretching vibration (ν(CH)) in the aldehyde group based on our theoretical calculations. Previously, Sbrana et al[1] assigned this band in butanal to a Fermi resonance between the CH stretching mode ν(CH) and the overtone of the CH wagging mode at 1390 cm^{-1}. A low-intensity band at 1810 cm^{-1} appears in the experimental IR spectra both obtained in this study and previously reported by Sbrana et al for butanal.[1] However, this mode does not appear in our theoretical calculation, allowing to suggest that this band is most likely related to a mixed mode. In agreement with this hypothesis, Sbrana et al[1] assigned this band to a mixed mode, involving the vibrations at 1118 cm^{-1} (ν(CC)) and 695 cm^{-1} (ρ(CH_2)).

The band at 1715 cm^{-1} (ν(C=O)) lies in the typical range of C=O stretching vibrations (ν(C=O)) in aldehydes[6]: it is experimentally observed at 1730 cm^{-1} for propanal[2, 3] and at 1715 cm^{-1} for butanal.[1] It should be noted that Sbrana et al.[1] assign this band in butanal to a Fermi resonance of the C=O stretching mode at 1715 cm^{-1} and the first overtone of the band at 851 cm^{-1} (ρ(CH_3)). The assignment of the bands at 1466 cm^{-1} (δ_{as}(CH_3) and δ_s(-CH_2-$\mathbf{CH_2}$-CH_3)), 1457 cm^{-1} (δ_{as}(CH_3)) and 1450 cm^{-1} (δ_{as}(CH_3) and δ_s(-CH_2-$\mathbf{CH_2}$-CH_3)) is in perfect agreement with the assignment performed for 1-butanol.[5] Partly agreeing with this assignment, Guirgis et al[3] and Dostert et al[2] assigned their bands 1468 – 1455 cm^{-1} to the assymmetric deformation of the methyl group of propanal. Sbrana et al.[1] complementarily associate the bands found between 1462 cm^{-1} and 1450 cm^{-1} in butanal solely to the deformation of a methylene group. Also the assignment of the band at 1414 cm^{-1} (δ_s(OHC-$\mathbf{CH_2}$-CH_2-)) to the methylene deformation mode done in this study is in agreement with the assignment of this mode in propanal.[2, 3]

The experimentally measured band at 1393 cm^{-1} involvs three modes – δ_s(CH_3), δ_s(OHC-$\mathbf{CH_2}$-CH_2-) and δ(CH)) – according to our theoretical results. For solid propanal, Guirgis et al.[3] observed two bands at similar frequencies (1394 and 1392 cm^{-1}), which were assigned to the symmetric deformation mode of the methyl group, partly corresponding to our assignment (δ_s(CH_3)). Our assignment of the wagging mode at 1368 cm^{-1} (ω(CH_2)) is in good agreement with the data reported for butanal[1] and 1-butanol[5]. The CH_2 wagging modes in propanal were reported to be shifted by nearly 30 cm^{-1} to 1343 cm^{-1} [3] and 1340 cm^{-1} [4] compared to butanal. The second wagging mode appears in our study at a lower wavenumber at 1284 cm^{-1} (ω(CH_2)). Previously, several bands in this range were reported for structurally similar compounds, e.g at

1285 cm^{-1} and 1280 cm^{-1} for butanal[1], at 1261 $cm^{-1.3}$ and 1254 $cm^{-1.4}$ for propanal. The latter bands were previously assigned to twisting modes of the methylene group in butanal[1] and propanal.[3, 4]

The bands apearing in the range 1120 – 854 cm^{-1} are assigned in our study to different types of sceletal stretching vibrations (ν(CCC)). The experimentally detected vibrational modes are almost identical to those previously reported for butanal[1] and propanal. [3, 4]. The higher frequency mode observed at 1118 cm^{-1} for solid butanal[1] and 1138 cm^{-1} for gaseous propanal[4] were also assinged by the authors to the CC stretching bond. Similarly, the vibrational mode at 1035 cm^{-1} (ν(CCC)) identified in our study was also assigned by Sbrana et al.[1] to a CC stretching mode in butanal. The modes at 958 cm^{-1} (ν(CCC)) and 854 cm^{-1} (ν(CCC)) were peviously also associated with skeletal stretching vibrations in the literature for propanal[3] (861 cm^{-1}), 1-butanol[5] (961 cm^{-1} and 953 cm^{-1}). On contrary, the vibrational modes in this frequency range were assigned to the rocking vibrations of the methyl group at 958 cm^{-1} and 854 cm^{-1} in butanal[1] and at 848 cm^{-1} in propanal[4].

Chapter 2: Comment on the adsorption configuration of the proposed complex D2 (Fugure 8)

It should be kept in mind that the structure of the molecular species adsorbed on the surface can be strongly distorted as compared to the gas phase, e.g. the bonds, lying in one plane in the unperturbed gas phase molecule, can become inclined with respect to each other (i.e. lying not in the same plane anymore) when the molecule is interacting with the underlying metal. In the case of both $\eta_2(C,O)$ and $\eta_1(O)$ configurations, the vibrational bands can be observed experimentally, which implies that the related bonds are (at least slightly) inclined with respect to the surface plane. Indeed, in the opposite case, i.e. if both bonds were oriented perfectly parallel to the surface, the vibrational bands would have a zero intensity due to MSSR (see the main text of the manuscript). The same logic applies also for the C-O single bond of enol species, which must be also inclined with respect to the surface plane. Thus, in the proposed D2 dimer shown in Figure 8 of the main manuscript, the bond C-OH in enol and the bond C=O in ketone must be both inclined with respect to the surface plane. The hydrogen bonding in this complex can be realized if e.g. the OH group of the enol species and the aldehyde H (**H**-C=O) are both lifted above the surface at a certain inclination angle. In this case they can be situated in the spacial vicinity and realize the hydrogen bonding between the aldehyde H of ketone and O atom of enol.

References

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