Water on well-defined platinum surfaces : an ultra high vacuum and electrochemical study

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Appendix

In this appendix we give explicit expressions for the values of $\left(\frac{d\theta}{dE}\right)_{\theta=\frac{1}{2}}$ in equation (10.8) in the main text. For the adsorption on two-dimensional terraces, we employ the mean-field expression for $\theta(E)$, also known as the Frumkin isotherm:

$$\frac{\theta}{1-\theta} = \exp\left[-\frac{\Delta G_{\mathrm{H}}}{RT}\right]\exp\left[-\frac{FE_{\mathrm{RHE}}}{RT}\right]\exp\left[f\theta\right] \tag{A.1}$$

with

$$f = -\frac{Z\epsilon_{\mathrm{HH}}}{RT} \tag{A.2}$$

where ϵ_{HH} is the nearest-neighbor interaction between two $\mathrm{H_{upd}}$ on the surface, f the Frumkin parameter (which is negative for repulsive interactions and positive for attractive), and $Z = 6$ is the number of neighbors on a (111) surface. From this expression, we obtain:

$$\left(\frac{d\theta}{dE}\right)^{ter}_{\theta=\frac{1}{2}} = -\frac{1}{4-f}\frac{F}{RT}. \tag{A.3}$$

For the adsorption on the one dimensional steps, we use the exact solution derived by Onsager[219]:

$$\frac{\beta-1+2\theta}{\beta+1-2\theta} = \exp\left[-\frac{\Delta G_{\mathrm{H},E_{\mathrm{RHE}}=0}}{RT}\right]\exp\left[-\frac{FE_{\mathrm{RHE}}}{RT}\right]\exp\left[f\theta\right] \tag{A.4}$$

with

$$f = -\frac{\epsilon_{\mathrm{HH}}}{RT} \tag{A.5}$$

and

$$\beta = \exp\left[1-4\theta(1-\theta)(1-e^{f})\right]^{\frac{1}{2}}. \tag{A.6}$$

For the derivative, one obtains:

$$\left(\frac{d\theta}{dE}\right)^{step}_{\theta=\frac{1}{2}} = -\frac{e^{\frac{1}{2}f}}{4}\frac{F}{RT}. \tag{A.7}$$

Bibliography

[1] I. Chorkendorff and J. W. Niemantsverdriet, *Concepts of Modern Catalysis and Kinetics*, Wiley-VCH, 2003.

[2] K. Kleiner, *Nature*, 2006, **441**(7097), 1046–1047.

[3] *IPCC Report: Responding To The Impacts Of Human-Caused Climate Change*, United Nations Environment Programme, 2007.

[4] G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, John Wiley & Sons, Inc., 1994.

[5] K. Honkala, A. Hellman, I. N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C. H. Christensen, and J. K. Norskov, *Science*, 2005, **307**(5709), 555–558.

[6] P. A. Thiel and T. E. Madey, *Surf. Sci. Rep.*, 1987, **7**(6–8), 211–385.

[7] M. A. Henderson, *Surf. Sci. Rep.*, 2002, **46**(1–8), 1–308.

[8] A. Hodgson and S. Haq, *Surf. Sci. Rep.*, 2009, **64**(9), 381–451.

[9] J. L. Gland and V. N. Korchak, *Surf. Sci.*, 1978, **75**(4), 733–750.

[10] A. T. Gee and B. E. Hayden, *J. Chem. Phys.*, 2000, **113**(22), 10333–10343.

[11] J. L. Gland, B. A. Sexton, and G. B. Fisher, *Surf. Sci.*, 1980, **95**(2–3), 587–602.

[12] K. Christmann in *Electrocatalysis*, ed. J. Lipkowski and P. N. Ross; Wiley-VCH, 1998; pp. 1–41.

[13] L. Vattuone, L. Savio, and M. Rocca, *Surf. Sci. Rep.*, 2008, **63**(3), 101–168.

[14] C. Clay, S. Haq, and A. Hodgson, *Phys. Rev. Lett.*, 2004, **92**(4), 046102.

[15] A. Michaelides and P. Hu, *J. Am. Chem. Soc.*, 2001, **123**(18), 4235–4242.

[16] A. Shavorskiy, M. J. Gladys, and G. Held, *Phys. Chem. Chem. Phys.*, 2008, **10**(40), 6150–6159.

[17] J. Harnett, S. Haq, and A. Hodgson, *Surf. Sci.*, 2003, **528**(1–3), 15–19.

[18] A. Glebov, A. P. Graham, A. Menzel, and J. P. Toennies, *J. Chem. Phys.*, 1997, **106**(22), 9382–9385.

[19] S. Nie, P. J. Feibelman, N. C. Bartelt, and K. Thürmer, *Phys. Rev. Lett.*, 2010, **105**(2), 026102.

[20] K. Jacobi, K. Bedürftig, Y. Wang, and G. Ertl, *Surf. Sci.*, 2001, **472**(1–2), 9–20.

[21] J. L. Daschbach, B. M. Peden, R. S. Smith, and B. D. Kay, *J. Chem. Phys.*, 2004, **120**(3), 1516–1523.

[22] G. B. Fisher and J. L. Gland, *Surf. Sci.*, 1980, **94**(2-3), 446–455.

[23] X. Su, L. Lianos, Y. R. Shen, and G. A. Somorjai, *Phys. Rev. Lett.*, 1998, **80**(7), 1533–1536.

[24] P. Löfgren, P. Ahlströhm, D. V. Chakarov, J. Lausmaa, and B. Kasemo, *Surf. Sci.*, 1996, **367**(1), L19–L25.

[25] Z. Dohnálek, R. L. Ciolli, G. A. Kimmel, K. P. Stevenson, R. S. Smith, and B. D. Kay, *J. Chem. Phys.*, 1999, **110**(12), 5489–5492.

[26] D. C. Skelton, R. G. Tobin, G. B. Fisher, D. K. Lambert, and C. L. DiMaggio, *J. Phys. Chem. B*, 2000, **104**(3), 548–553.

[27] M. L. Grecea, E. H. G. Backus, B. Riedmüller, A. Eichler, A. W. Kleyn, and M. Bonn, *J. Phys. Chem. B*, 2004, **108**(33), 12575–12582.

[28] M. Morgenstern, T. Michely, and G. Comsa, *Phys. Rev. Lett.*, 1996, **77**(4), 703–706.

[29] H. Ogasawara, J. Yoshinobu, and M. Kawai, *J. Chem. Phys.*, 1999, **111**(15), 7003–7009.

[30] A. C. Luntz, J. Grimblot, and D. E. Fowler, *Phys. Rev. B*, 1989, **39**(17), 12903–12906.

[31] C. T. Campbell, G. Ertl, H. Kuipers, and J. Segner, *Surf. Sci.*, 1981, **107**(1), 220–236.

[32] K. Schwaha and E. Bechtold, *Surf. Sci.*, 1977, **65**(1), 277–286.

[33] D. H. Parker, M. E. Bartram, and B. E. Koel, *Surf. Sci.*, 1989, **217**(3), 489–510.

[34] U. Starke, K. Heinz, N. Materer, A. Wander, M. Michl, R. Döll, M. A. van Hove, and G. A. Somorjai, *J. Vac. Sci. Technol. A*, 1992, **10**(4), 2521–2528.

[35] U. Starke, N. Materer, A. Barbieri, R. Döll, K. Heinz, M. A. van Hove, and G. A. Somorjai, *Surf. Sci.*, 1993, **287/288**(Pt. A), 432–437.

[36] N. Materer, U. Starke, A. Barbieri, R. Döll, K. Heinz, M. A. Van Hove, and G. A. Somorjai, *Surf. Sci.*, 1995, **325**(3), 207–222.

[37] P. J. Feibelman, S. Esch, and T. Michely, *Phys. Rev. Lett.*, 1996, **77**(11), 2257–2260.

[38] K. Mortensen, C. Klink, F. Jensen, F. Besenbacher, and I. Stensgaard, *Surf. Sci.*, 1989, **220**(2–3), L701–L708.

[39] R. B. Getman, Y. Xu, and W. F. Schneider, *J. Phys. Chem. C*, 2008, **112**(26), 9559–9572.

[40] J. L. Gland, *Surf. Sci.*, 1980, **93**(2–3), 487–514.

[41] G. N. Derry and P. N. Ross, *Surf. Sci.*, 1984, **140**(1), 165–180.

[42] G. N. Derry and P. N. Ross, *J. Chem. Phys.*, 1985, **82**(6), 2772–2778.

[43] S. P. Devarajan, J. A. Hinojosa Jr., and J. F. Weaver, *Surf. Sci.*, 2008, **602**(19), 3116–3124.

[44] V. Fiorin, D. Borthwick, and D. A. King, *Surf. Sci.*, 2009, **603**(10–12), 1360–1364.

[45] A. Rar and T. Matsushima, *Surf. Sci.*, 1994, **318**(1–2), 89–96.

[46] H. Wang, R. G. Tobin, D. K. Lambert, C. L. DiMaggio, and G. B. Fisher, *Surf. Sci.*, 1997, **372**(1–3), 267–278.

[47] P. Gambardella, Ž. Šljivančanin, B. Hammer, M. Blanc, K. Kuhnke, and K. Kern, *Phys. Rev. Lett.*, 2001, **87**(5), 056103.

[48] Ž. Šljivančanin and B. Hammer, *Surf. Sci.*, 2002, **515**(1), 235–244.

[49] T. Yamanaka, T. Matsushima, S.-I. Tanaka, and M. Kamada, *Surf. Sci.*, 1996, **349**(2), 119–128.

[50] D. V. Heyd, R. J. Scharff, and J. T. Yates Jr., *J. Chem. Phys.*, 1999, **110**(14), 6939–6946.

[51] A. Winkler, X. Guo, H. R. Siddiqui, P. L. Hagans, and J. T. Yates Jr., *Surf. Sci.*, 1988, **201**(3), 419–443.

[52] H. R. Siddiqui, A. Winkler, X. Guo, P. Hagans, and J. T. Yates Jr., *Surf. Sci.*, 1988, **193**(1–2), L17–L23.

[53] M. Sano, Y. Seimiya, Y. Ohno, T. Matsushima, S.-I. Tanaka, and M. Kamada, *Surf. Sci.*, 1999, **421**(3), 386–396.

[54] M. R. McClellan, M. F. Read, and J. L. Gland, *Surf. Sci.*, 1983, **124**(1), 188–208.

[55] K. Christmann, G. Ertl, and T. Pignet, *Surf. Sci.*, 1976, **54**(2), 365–392.

[56] Ş. C. Bădescu, P. Salo, T. Ala-Nissila, S. C. Ying, K. Jacobi, Y. Wang, K. Bedürftig, and G. Ertl, *Phys. Rev. Lett.*, 2002, **88**(13), 136101.

[57] Ş. C. Bădescu, K. Jacobi, Y. Wang, K. Bedürftig, G. Ertl, P. Salo, T. Ala-Nissila, and S. C. Ying, *Phys. Rev. B*, 2003, **68**(20), 205401.

[58] S. L. Bernasek and G. A. Somorjai, *J. Chem. Phys.*, 1975, **62**(8), 3149–3161.

[59] K. Christmann and G. Ertl, *Surf. Sci.*, 1976, **60**(2), 365–384.

[60] M. Salmeron, R. J. Gale, and G. A. Somorjai, *J. Chem. Phys.*, 1977, **67**(11), 5324–5334.

[61] A. M. Baró and H. Ibach, *Surf. Sci.*, 1980, **92**(1), 237–246.

[62] T. H. Lin and G. A. Somorjai, *J. Chem. Phys.*, 1984, **81**(2), 704–709.

[63] A. T. Gee, B. E. Hayden, C. Mormiche, and T. S. Nunney, *J. Chem. Phys.*, 2000, **112**(17), 7660–7668.

[64] D. A. McCormack, R. A. Olsen, and E. J. Baerends, *J. Chem. Phys.*, 2005, **122**(19), 194708.

[65] A. M. Baró, H. Ibach, and H. D. Bruchmann, *Surf. Sci.*, 1979, **88**(2–3), 384–398.

[66] K. E. Lu and R. R. Rye, *Surf. Sci.*, 1974, **45**(2), 677–695.

[67] M. Salmerón, R. J. Gale, and G. A. Somorjai, *J. Chem. Phys.*, 1979, **70**(6), 2807–2818.

[68] J. Ludwig, D. G. Vlachos, A. C. T. van Duin, and W. A. Goddard III, *J. Phys. Chem. B*, 2006, **110**(9), 4274–4282.

[69] R. A. Olsen, S. C. Badescu, S. C. Ying, and E. J. Baerends, *J. Chem. Phys.*, 2004, **120**(24), 11852–11863.

[70] T. Vehviläinen, P. Salo, T. Ala-Nissila, and S. C. Ying, *Phys. Rev. B*, 2009, **80**(3), 035403.

[71] A. A. Koverga, S. Frank, and M. T. M. Koper, *in preparation*.

[72] A. P. Graham, A. Menzel, and J. P. Toennies, *J. Chem. Phys.*, 1999, **111**(4), 1676–1685.

[73] C. Z. Zheng, C. K. Yeung, M. M. T. Loy, and X. Xiao, *Phys. Rev. B*, 2004, **70**(20), 205402.

[74] I. M. N. Groot, K. J. P. Schouten, A. W. Kleyn, and L. B. F. Juurlink, *J. Chem. Phys.*, 2008, **129**(22), 224707.

[75] G. B. Fisher and B. A. Sexton, *Phys. Rev. Lett.*, 1980, **44**(10), 683–686.

[76] T. Schiros, L. Å. Näslund, K. Andersson, J. Gyllenpalm, G. S. Karlberg, M. Odelius, H. Ogasawara, L. G. M. Pettersson, and A. Nilsson, *J. Phys. Chem. C*, 2007, **111**(41), 15003–15012.

[77] J. R. Creighton and J. M. White, *Surf. Sci.*, 1982, **122**(3), L648–L652.

[78] K. Bedürftig, S. Völkening, Y. Wang, J. Wintterlin, K. Jacobi, and G. Ertl, *J. Chem. Phys.*, 1999, **111**(24), 11147–11154.

[79] A. Michaelides and P. Hu, *J. Chem. Phys.*, 2001, **114**(1), 513–519.

[80] G. S. Karlberg, *Phys. Rev. B*, 2006, **74**(15), 153414.

[81] G. Held, C. Clay, S. D. Barrett, S. Haq, and A. Hodgson, *J. Chem. Phys.*, 2005, **123**(6), 064711.

[82] X.-Z. Li, M. I. J. Probert, A. Alavi, and A. Michaelides, *Phys. Rev. Lett.*, 2010, **104**(6), 066102.

[83] G. Zimbitas, M. E. Gallagher, G. R. Darling, and A. Hodgson, *J. Chem. Phys.*, 2008, **128**(7), 074701.

[84] G. S. Karlberg, G. Wahnström, C. Clay, G. Zimbitas, and A. Hodgson, *J. Chem. Phys.*, 2006, **124**(20), 204712.

[85] S. Völkening, K. Bedürftig, K. Jacobi, J. Wintterlin, and G. Ertl, *Phys. Rev. Lett.*, 1999, **83**(13), 2672–2675.

[86] J. Ren and S. Meng, *Phys. Rev. B*, 2008, **77**(5), 054110.

[87] A. Shavorskiy, T. Eralp, M. J. Gladys, and G. Held, *J. Phys. Chem. C*, 2009, **113**(52), 21755–21764.

[88] F. T. Wagner and T. E. Moylan, *Surf. Sci.*, 1988, **206**(1–2), 187–202.

[89] D. Lackey, J. Schott, J. K. Sass, S. I. Woo, and F. T. Wagner, *Chem. Phys. Lett.*, 1991, **184**(4), 277–281.

[90] N. G. Petrik and G. A. Kimmel, *J. Chem. Phys.*, 2004, **121**(8), 3727–3735.

[91] N. Kizhakevariam and E. M. Stuve, *Surf. Sci.*, 1992, **275**(3), 223–236.

[92] Y. Shingaya and M. Ito, *Surf. Sci.*, 1996, **368**(1–3), 318–323.

[93] N. Chen, P. Blowers, and R. I. Masel, *Surf. Sci.*, 1999, **419**(2–3), 150–157.

[94] M. J. Iedema, M. J. Dresser, D. L. Doering, J. B. Rowland, W. P. Hess, A. A. Tsekouras, and J. P. Cowin, *J. Phys. Chem. B*, 1998, **102**(46), 9203–9214.

[95] M. Wakisaka, H. Suzuki, S. Mitsui, H. Uchida, and M. Watanabe, *Langmuir*, 2009, **25**(4), 1897–1900.

[96] J. Clavilier in *Interfacial Electrochemistry: Theory, Principles, and Applications*, ed. A. Wieckowski; Marcel Dekker, New York, 1999; p. 231.

[97] R. Oelgeklaus, J. Rose, and H. Baltruschat, *J. Electroanal. Chem.*, 1994, **376**(1–2), 127–133.

[98] J. H. Barber and B. E. Conway, *J. Electroanal. Chem.*, 1999, **461**(1–2), 80–89.

[99] G. Jerkiewicz, *Prog. Surf. Sci.*, 1998, **57**(2), 137–186.

[100] M. T. M. Koper and J. J. Lukkien, *Surf. Sci.*, 2002, **498**(1–2), 105–115.

[101] G. S. Karlberg, T. F. Jaramillo, E. Skúlason, J. Rossmeisl, T. Bligaard, and J. K. Nørskov, *Phys. Rev. Lett.*, 2007, **99**(12), 126101.

[102] M. T. M. Koper, J. J. Lukkien, N. P. Lebedeva, J. M. Feliu, and R. A. van Santen, *Surf. Sci.*, 2001, **478**, L339–L344.

[103] G. Attard and C. Barnes, *Surfaces*, Oxford Science Publications, 1998.

[104] D. A. King, *Surf. Sci.*, 1975, **47**(1), 384–402.

[105] A. M. de Jong and J. W. Niemantsverdriet, *Surf. Sci.*, 1990, **233**(3), 355–365.

[106] W. P. Ellis and R. L. Schwoebel, *Surf. Sci.*, 1968, **11**(1), 82–98.

[107] M. Henzler, *Surf. Sci.*, 1970, **19**(1), 159–171.

[108] M. A. van Hove and G. A. Somorjai, *Surf. Sci.*, 1980, **92**(2–3), 489–518.

[109] J. W. Niemantsverdriet, *Spectroscopy in Catalysis*, Wiley, 1993.

[110] P. W. Atkins, *Physical Chemistry*, Oxford University Press, 6th ed., 1998.

[111] H. G. Jenniskens, A. Bot, P. W. F. Dorlandt, W. van Essenberg, E. van Haas, and A. W. Kleyn, *Meas. Sci. Technol.*, 1997, **8**(11), 1313–1322.

[112] B. Riedmüller, F. Giskes, D. Glastra van Loon, P. Lassing, and A. W. Kleyn, *Meas. Sci. Technol.*, 2002, **13**(2), 141–149.

[113] J. T. Yates, Jr., *Experimental Innovations in Surface Science*, Springer-Verlag New York, Inc., 1998.

[114] A. J. Bard and L. R. Faulkner, *Electrochemical methods: fundamentals and applications*, Wiley-Interscience, 2nd ed., 2004.

[115] E. Barsoukov and J. R. Macdonald, *Impedance spectroscopy: theory, experiment, and applications*, Wiley-Interscience, 2nd ed., 2005.

[116] M. E. Orazem and B. Tribollet, *Electrochemical impedance spectroscopy*, The Electrochemical Society series, John Wiley & Sons, Inc., 2008.

[117] N. R. Avery, *Chem. Phys. Lett.*, 1983, **96**(3), 371–373.

[118] G. Zimbitas, S. Haq, and A. Hodgson, *J. Chem. Phys.*, 2005, **123**(17), 174701.

[119] G. Zimbitas and A. Hodgson, *Chem. Phys. Lett.*, 2006, **417**(1–3), 1–5.

[120] G. A. Kimmel, N. G. Petrik, Z. Dohnálek, and B. D. Kay, *J. Chem. Phys.*, 2006, **125**(4), 044713.

[121] D. M. Collins and W. E. Spicer, *Surf. Sci.*, 1977, **69**(1), 85–113.

[122] J.-Y. Kim and J. Lee, *J. Chem. Phys.*, 2000, **113**(7), 2856–2865.

[123] S. Ferrer and H. P. Bonzel, *Surf. Sci.*, 1982, **119**(2–3), 234–250.

[124] A. Picolin, C. Busse, A. Redinger, M. Morgenstern, and T. Michely, *J. Phys. Chem. C*, 2009, **113**(2), 691–697.

[125] R. Smoluchowski, *Phys. Rev.*, 1941, **60**(9), 661–674.

[126] L. L. Kesmodel and L. M. Falicov, *Solid State Commun.*, 1975, **16**(10–11), 1201–1204.

[127] K. Besocke, B. Krahl-Urban, and H. Wagner, *Surf. Sci.*, 1977, **68**, 39–46.

[128] M. Morgenstern, J. Müller, T. Michely, and G. Comsa, *Z. Phys. Chem.*, 1997, **198**(1–2), S43–72.

[129] M. T. M. Koper, S. C. S. Lai, and E. Herrero in *Fuel Cell Catalysis: A Surface Science Approach*, ed. M. T. M. Koper; John Wiley & Sons, Hoboken, 2009; pp. 159–207.

[130] F. Abild-Pedersen, J. Greeley, F. Studt, J. Rossmeisl, T. R. Munter, P. G. Moses, E. Skúlason, T. Bligaard, and J. K. Norskov, *Phys. Rev. Lett.*, 2007, **99**(1), 016105.

[131] N. M. Marković and P. N. Ross, *Surf. Sci. Rep.*, 2002, **45**(4–6), 117– 229.

[132] N. P. Lebedeva, A. Rodes, J. M. Feliu, M. T. M. Koper, and R. A. van Santen, *J. Phys. Chem. B*, 2002, **106**(38), 9863–9872.

[133] G. García and M. T. M. Koper, *Phys. Chem. Chem. Phys.*, 2009, **11**(48), 11437–11446.

[134] K. M. Ogle and J. M. White, *Surf. Sci.*, 1984, **139**(1), 43–62.

[135] G. E. Mitchell, S. Akhter, and J. M. White, *Surf. Sci.*, 1986, **166**(2–3), 283–300.

[136] L. K. Verheij and M. B. Hugenschmidt, *Surf. Sci.*, 1998, **416**(1–2), 37–58.

[137] M. Nagasaka, H. Kondoh, K. Amemiya, A. Nambu, I. Nakai, T. Shimada, and T. Ohta, *J. Chem. Phys.*, 2003, **119**(17), 9233–9241.

[138] C. Sachs, M. Hildebrand, S. Völkening, J. Wintterlin, and G. Ertl, *Science*, 2001, **293**, 1635–1638.

[139] C. Sachs, M. Hildebrand, S. Völkening, J. Wintterlin, and G. Ertl, *J. Chem. Phys.*, 2002, **116**(13), 5759–5773.

[140] S. C. S. Lai, N. P. Lebedeva, T. H. M. Housmans, and M. T. M. Koper, *Top. Catal.*, 2007, **46**, 320–333.

[141] G. Held, L. B. Jones, E. A. Seddon, and D. A. King, *J. Phys. Chem. B*, 2005, **109**(13), 6159–6163.

[142] D. Chandler, *Nature*, 2005, **437**(7059), 640–647.

[143] W. Chen, A. Y. Fadeev, M. C. Hsieh, D. Öner, J. Youngblood, and T. J. McCarthy, *Langmuir*, 1999, **15**(10), 3395–3399.

[144] X. Yu, Z. Wang, Y. Jiang, and X. Zhang, *Langmuir*, 2006, **22**(10), 4483–4486.

[145] H.-J. Wang, X.-K. Xi, A. Kleinhammes, and Y. Wu, *Science*, 2008, **322**(5898), 80–83.

[146] R. S. Smith, C. Huang, E. K. L. Wong, and B. D. Kay, *Surf. Sci.*, 1996, **367**(1), L13–L18.

[147] R. S. Smith, C. Huang, E. K. L. Wong, and B. D. Kay, *Phys. Rev. Lett.*, 1997, **79**(5), 909–912.

[148] W. Barthlott and C. Neinhuis, *Planta*, 1997, **202**(1), 1–8.

[149] R. Blossey, *Nat. Mater.*, 2003, **2**(5), 301–306.

[150] E. H. G. Backus, M. L. Grecea, A. W. Kleyn, and M. Bonn, *Phys. Rev. Lett.*, 2004, **92**(23), 236101.

[151] B. Rowland and J. P. Devlin, *J. Chem. Phys.*, 1991, **94**(1), 812–813.

[152] V. Buch and J. P. Devlin, *J. Chem. Phys.*, 1991, **94**(5), 4091–4092.

[153] J. Shan, J. F. M. Aarts, A. W. Kleyn, and L. B. F. Juurlink, *Phys. Chem. Chem. Phys.*, 2008, **10**(16), 2227–2232.

[154] M. W. Urban, *Vibrational spectroscopy of molecules and macromolecules on surfaces*, Wiley-Interscience: New York, 1993.

[155] J. Shan, J. F. M. Aarts, A. W. Kleyn, and L. B. F. Juurlink, *Phys. Chem. Chem. Phys.*, 2008, **10**(32), 4994–5003.

[156] R. S. Smith, Z. Dohnálek, G. A. Kimmel, K. P. Stevenson, and B. D. Kay, *Chem. Phys.*, 2000, **258**(2–3), 291–305.

[157] B. A. Sexton, *Surf. Sci.*, 1980, **94**(2–3), 435–445.

[158] E. Langenbach, A. Spitzer, and H. Lüth, *Surf. Sci.*, 1984, **147**(2), 179–190.

[159] A. L. Glebov, A. P. Graham, and A. Menzel, *Surf. Sci.*, 1999, **427–428**, 22–26.

[160] M. Nakamura, Y. Shingaya, and M. Ito, *Chem. Phys. Lett.*, 1999, **309**(1–2), 123–128.

[161] R. Lewis and R. Gomer, *Surf. Sci.*, 1969, **17**(2), 333–345.

[162] E. G. Seebauer and L. D. Schmidt, *Chem. Phys. Lett.*, 1986, **123**(1–2), 129–133.

[163] K. Umezawa, T. Ito, M. Asada, S. Nakanishi, P. Ding, W. A. Lanford, and B. Hjörvarsson, *Surf. Sci.*, 1997, **387**(1–3), 320 –327.

[164] K. Fukutani, A. Itoh, M. Wilde, and M. Matsumoto, *Phys. Rev. Lett.*, 2002, **88**(11), 116101.

[165] R. A. Olsen, G. J. Kroes, and E. J. Baerends, *J. Chem. Phys.*, 1999, **111**(24), 11155–11163.

[166] G. Papoian, J. K. Nørskov, and R. Hoffmann, *J. Am. Chem. Soc.*, 2000, **122**(17), 4129–4144.

[167] K. Nobuhara, H. Kasai, H. Nakanishi, and A. Okiji, *Surf. Sci.*, 2002, **507-510**, 82–86.

[168] M. J. T. C. van der Niet, C. Badan, M. T. M. Koper, and L. B. F. Juurlink, *in preparation*.

[169] S. Morin, H. Dumont, and B. E. Conway, *J. Electroanal. Chem.*, 1996, **412**(1–2), 39–52.

[170] N. M. Marković, N. S. Marinković, and R. R. Adžić, *J. Electroanal. Chem.*, 1988, **241**(1–2), 309–328.

[171] J. Clavilier, A. Rodes, K. El Achi, and M. A. Zamakhchari, *J. Chim. Phys.*, 1991, **88**, 1291–1337.

[172] I. M. Tidswell, N. M. Markovic, and P. N. Ross, *J. Electroanal. Chem.*, 1994, **376**(1–2), 119–126.

[173] E. Sibert, R. Faure, and R. Durand, *J. Electroanal. Chem.*, 2001, **515**(1–2), 71–81.

[174] T. Pajkossy and D. M. Kolb, *Electrochim. Acta*, 2001, **46**(20–21), 3063–3071.

[175] B. E. Conway and B. V. Tilak, *Electrochim. Acta*, 2002, **47**(22–23), 3571–3594.

[176] K. Domke, E. Herrero, A. Rodes, and J. M. Feliu, *J. Electroanal. Chem.*, 2003, **552**, 115–128.

[177] D. Strmcnik, T. D, D. van der Vliet, V. Stamenkovic, and N. Marković, *Electrochem. Commun.*, 2008, **10**, 1602–1605.

[178] Z. Kerner, T. Pajkossy, L. A. Kibler, and D. M. Kolb, *Electrochem. Commun.*, 2002, **4**(10), 787–789.

[179] T. Langkau and H. Baltruschat, *Electrochim. Acta*, 1998, **44**(6–7), 909–918.

[180] H. Kita, S. Ye, A. Aramata, and N. Furuya, *J. Electroanal. Chem.*, 1990, **295**(1–2), 317–331.

[181] N. S. Marinković, N. M. Marković, and R. R. Adžić, *J. Electroanal. Chem.*, 1992, **330**(1–2), 433–452.

[182] V. D. Jović, R. Parsons, and B. M. Jovic, *J. Electroanal. Chem.*, 1992, **339**(1–2), 327–337.

[183] M. T. M. Koper and J. J. Lukkien, *J. Electroanal. Chem.*, 2000, **485**(2), 161–165.

[184] A. Gray-Weale and J. K. Beattie, *Phys. Chem. Chem. Phys.*, 2009, **11**(46), 10994–11005.

[185] J. K. Beattie, A. M. Djerdjev, and G. G. Warr, *Faraday Discuss.*, 2009, **141**, 31–39.

[186] V. Buch, T. Tarbuck, G. L. Richmond, H. Groenzin, I. Li, and M. J. Schultz, *J. Chem. Phys.*, 2007, **127**(20), 204710.

[187] R. Vácha, V. Buch, A. Milet, J. P. Devlin, and P. Jungwirth, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4736–3737.

[188] G. A. Kimmel, N. G. Petrik, Z. Dohnálek, and B. D. Kay, *Phys. Rev. Lett.*, 2005, **95**(16), 166102.

[189] O. Pecina and W. Schmickler, *Chem. Phys.*, 1998, **228**(1–3), 265–277.

[190] M. Osawa, M. Tsushima, H. Mogami, G. Samjeské, and A. Yamakata, *J. Phys. Chem. C*, 2008, **112**(11), 4248–4256.

[191] V. Climent, R. Gómez, J. M. Orts, A. Aldaz, and J. M. Feliu in *The Electrochemical Society Proceedings: The Electrochemical Double Layer*, Vol. 97–17; Pennington, NJ, 1997; pp. 222–237.

[192] V. Climent, N. García-Araez, E. Herrero, and J. Feliu, *Russ. J. Electrochem.*, 2006, **42**(11), 1145–1160.

[193] N. Garcia-Araez, V. Climent, E. Herrero, J. M. Feliu, and J. Lipkowski, *Electrochim. Acta*, 2006, **51**(18), 3787–3793.

[194] N. Garcia-Araez, J. J. Lukkien, M. T. M. Koper, and J. M. Feliu, *J. Electroanal. Chem.*, 2006, **588**(1), 1–14.

[195] N. M. Marković, H. A. Gasteiger, and P. N. Ross, *J. Phys. Chem.*, 1996, **100**(16), 6715–6721.

[196] ed. M. T. M. Koper, *Fuel Cell Catalysis: A Surface Science Approach*, John Wiley & Sons, Hoboken, 2009.

[197] J. Clavilier, R. Faure, G. Guinet, and R. Durand, *J. Electroanal. Chem.*, 1980, **107**(1), 205–209.

[198] J. Clavilier, *J. Electroanal. Chem.*, 1980, **107**(1), 211–216.

[199] J. Clavilier, R. Durand, G. Guinet, and R. Faure, *J. Electroanal. Chem.*, 1981, **127**(1–3), 281–287.

[200] J. Clavilier, D. Armand, and B. L. Wu, *J. Electroanal. Chem.*, 1982, **135**(1), 159–166.

[201] J. Clavilier and D. Armand, *J. Electroanal. Chem.*, 1986, **199**(1), 187–200.

[202] J. Clavilier, D. Armand, S. G. Sun, and M. Petit, *J. Electroanal. Chem.*, 1986, **205**(1–2), 267–277.

[203] D. Armand and M. L. Rosinberg, *J. Electroanal. Chem.*, 1991, **302**(1–2), 191–206.

[204] M. T. M. Koper, *Faraday Discuss.*, 2008, **140**, 11–24.

[205] R. J. Nichols and A. Bewick, *J. Electroanal. Chem.*, 1988, **243**(2), 445–453.

[206] K. Al Jaaf-Golze, D. M. Kolb, and D. Scherson, *J. Electroanal. Chem.*, 1986, **200**(1–2), 353–362.

[207] P. Vassilev, M. T. M. Koper, and R. A. van Santen, *Chem. Phys. Lett.*, 2002, **359**(3–4), 337–342.

[208] A. Berná, V. Climent, and J. M. Feliu, *Electrochem. Commun.*, 2007, **9**(4), 2789–2794.

[209] J. Clavilier, K. El Achi, and A. Rodes, *J. Electroanal. Chem.*, 1989, **272**(1-2), 253–261.

[210] J. Clavilier, K. El Achi, and A. Rodes, *Chem. Phys.*, 1990, **141**(1), 1–14.

[211] A. Rodes, K. El Achi, M. A. Zamakhchari, and J. Clavilier, *J. Electroanal. Chem.*, 1990, **284**(1), 245–253.

[212] R. Gisbert, G. García, and M. T. M. Koper, *Electrochim. Acta, in press*, 2010, DOI: 10.1016/j.electacta.2010.04.009.

[213] C. Stoffelsma, P. Rodriquez, G. García, N. Garcia-Araez, D. Strmcnik, N. Marković, and M. T. M. Koper, *submitted*, 2010.

[214] J. R. Creighton and J. M. White, *Surf. Sci.*, 1984, **139**(1), 43–62.

[215] G. S. Karlberg, F. E. Olsson, M. Persson, and G. Wahnström, *J. Chem. Phys.*, 2003, **119**(9), 4865–4872.

[216] A. N. Frumkin and O. A. Petrii, *Electrochim. Acta*, 1975, **20**(5), 347–359.

[217] V. A. Marichev, *Electrochim. Acta*, 2008, **53**(27), 7952–7960.

[218] M. Alsabet, M. Grden, and G. Jerkiewicz, *J. Electroanal. Chem.*, 2006, **589**(1), 120–127.

[219] T. L. Hill, *An Introduction to Statistical Thermodynamics*, Addison-Wesley, 1960.