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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:

$$\frac{\theta}{1-\theta} = \exp\left[-\frac{\Delta G_H}{RT}\right] \exp\left[-\frac{FE_{RHE}}{RT}\right] \exp[f\theta] \quad (\text{A.1})$$

with

$$f = -\frac{Z\epsilon_{HH}}{RT} \quad (\text{A.2})$$

where ϵ_{HH} is the nearest-neighbor interaction between two 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:

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

For the adsorption on the one dimensional steps, we use the exact solution derived by Onsager²¹⁹:

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

with

$$f = -\frac{\epsilon_{HH}}{RT} \quad (\text{A.5})$$

and

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

For the derivative, one obtains:

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

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. Nørskov, *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] Ș. 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] Ș. 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. Bădescu, 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. Krahle-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. Nørskov, *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.

BIBLIOGRAPHY

- [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.

BIBLIOGRAPHY

- [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. Rodriguez, 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.

