

Prominence of Terahertz Acoustic Surface Plasmon excitation in Gas-Surface interaction with Metals

G. Bracco^{1,2#}, L. Vattuone^{1,2#}, M. Smerieri², G. Carraro^{1,2}, L. Savio², G. Paolini¹, G. Benedek^{3,4}, P. M. Echenique⁴, M. Rocca^{1,2*}

#contributed equally to the work

¹ *Dipartimento di Fisica, Università di Genova; Via Dodecaneso 33, 16146 Genova, Italy
Corresponding author M.Rocca; Rocca@fisica.unige.it*

² *IMEM-CNR Unità di Genova; Via Dodecaneso 33, 16146 Genova, Italy*

³ *Dipartimento di Scienza dei Materiali, Università di Milano Bicocca; Via R. Cozzi 55,
20125 Milano, Italy*

⁴ *DIPC, Paseo Manuel de Lardizabal 4, Donostia 20018, Spain*

Understanding the dynamics of gas-surface interaction has been at the focus of research for the last decades. One reason for this interest is the modelling of the energy transfer to solid surfaces which dictates the drag force on aerospace shuttles. For telecommunication satellites orbiting the Earth typically below 600 km, this process represents the main source of orbital perturbation [1-3]. Another main application is heterogeneous catalysis, since the rate of the processes is often limited by the energy accommodation of the gas phase reactants [4]. In both cases, the interaction of gases up to mild hyperthermal kinetic energies (0.1 to 1 eV) with metal surfaces is of pivotal importance.

The classical understanding of gas-surface dynamics based on direct collisions with the surface atoms is that the excess kinetic energy of the colliding particles is transferred to the vibrational degrees of freedom of the target [5,6]. This process was demonstrated to dominate, e.g., for H₂ dissociation on Cu(111) [7] and Ru(0001) [8], methane on Ni(100) [9], and water on Ni(111) [10]. Energy transfer to the electronic degrees of freedom (electron hole (*e-h*) pair excitations) was observed only for much higher energies: impact energies of several eV for H [11] and HCl [12] scattering off Au(111), and high vibrational excitation for NO dissociation on Au(111) [13]. In all these cases, as well as in the interpretation of friction phenomena,¹⁶ only *e-h* pair generation was considered.

Here we show that this picture does not hold for metal surfaces supporting acoustic surface plasmons [14-16]. Such loss, dressed with a vibronic structure, is shown to make up a prominent energy transfer route down to the terahertz region for Ne atoms scattering off Cu(111) and is expected to dominate for most metals [17]. This mechanism determines, e.g., the drag force acting on telecommunication satellites which are typically gold plated to reduce

overheating by sunshine. The electronic excitations can be unambiguously discerned from the vibrational ones under mild hyperthermal impact conditions.

- [1] Sundén, B.; Fu J. *Heat Transfer in Aerospace Applications*. Elsevier: **2017**.
- [2] Josyula, E.; Burt, J. Review of Rarefied Gas Effects in Hypersonic Applications. YTC Document RTO-EN-AVT-194, **2011**, pp. 40.
- [3] Livadiotti, S.; Crisp, N.H.; Roberts, P.C.E.; Worrall, S.D.; Oiko, V.T.A.; Edmondson, S.; Haigh, S.J.; Huyton, C.; Smith, K.L.; Sinpetru, L.A.; *et al.* A review of gas-surface interaction models for orbital aerodynamics applications. *Progress in Aerospace Sciences* **2020**, *119*, 100675.
- [4] Wodtke, A.M. Electronically non-adiabatic influences in surface chemistry and dynamics. *Chem. Soc. Rev.* **2016**, *45*, 3641-3657.
- [5] Alducin, M.; Diez Muino, R.; Inaki Juaristi, J. Nonadiabatic Effects in Gas-Surface Dynamics. In *Handbook of Surface Science*; Rocca, M.; Rahman, T.S.; Vattuone, L. Eds; Springer: **2020**; Chap. 28, pp 937- 973.
- [6] Auerbach, D.J.; Tully, J.C.; Wodtke, A.M. Chemical dynamics from the gas-phase to surfaces. *Nat. Sci.* **2021**, *1*:e10005. <https://doi.org/10.1002/ntls.10005>
- [7] Diaz, C.; Pijper, E.; Olsen, R.A.; Busnengo, H.F.; Auerbach, D.J.; Kroes, G.J. Chemically Accurate Simulation of a Prototypical Surface Reaction: H₂ Dissociation on Cu(111). *Science* **2009**, *326*, 832-834.
- [8] Nieto, P.; Pijper, E.; Barredo, D.; Laurent, G.; Olsen, R.A.; Baerends, E.J.; Kroes, G.J.; Farias, D. Reactive and Nonreactive Scattering of H₂ from a Metal Surface is Electronically Adiabatic. *Science* **2006**, *312*, 86.
- [9] Yoder, B.L.; Bisson, R.; Beck, R.D. Steric Effects in the Chemisorption of Vibrationally Excited Methane on Ni(100). *Science* **2010**, *329*, 553.
- [10] Hundt, P.M.; Jiang, B.; Van Reijzen, M.E.; Guo, H.; Beck, R.D. Vibrationally Promoted Dissociation of Water on Ni(111). *Science* **2014**, *344*, 504.
- [11] Bünermann, O. et al., Electron-hole pair excitation determines the mechanism of hydrogen atom adsorption. *Science* **2015**, *350*, 1346.
- [12] Ran, Q.; Matsiev, D.; Auerbach, D.J.; Wodtke, A.M. Observation of a Change of Vibrational Excitation Mechanism with Surface Temperature: HCl Collisions with Au(111). *Phys. Rev. Lett.* **2007** *98*, 237601.
- [13] Nahler, N.H.; White, J.D.; LaRue, J.; Auerbach, D.J.; Wodtke, A.M. Inverse Velocity Dependence of Vibrationally Promoted Electron Emission from a Metal Surface. *Science* **2008**, *321*, 1191.
- [14] Diaconescu, B. et al., Low-energy acoustic plasmons at metal surfaces. *Nature* **2007**, *448*, 57.
- [15] Pohl, K. et al., M. Acoustic surface plasmon on Cu(111). *Europhys. Lett.* **2010**, *90*, 57006.
- [16] Pischel, J.; Welsch, E.; Skibbe, O.; Pucci, A. Acoustic Surface Plasmon on Cu(111) as an Excitation in the Mid-Infrared Range. *J. Phys. Chem. C* **2013**, *117*, 26964-26968.
- [17] G. Bracco et al., Prominence of acoustic surface plasmons in hyperthermal gas energy transfer to metal surfaces, *J. Phys. Chem. Lett.* **12**, 9894-9898 (2021).