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Review

Energy transfer and chemical dynamics at solid surfaces: The special role of charge transfer

Alec M. Wodtke [a,*], Daniel Matsiev [a], Daniel J. Auerbach [b]

[a] *Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA*
[b] *Gas Reaction Technologies, 861 Ward Drive, Santa Barbara, CA 93111, USA*

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This article is dedicated to the memory of my mother, Dana Wodtke.

Abstract

Molecular energy transfer processes at solid surfaces are profoundly important, influencing trapping, desorption, diffusion, and reactivity; in short, all of the elementary steps needed for surface chemistry to take place. In this paper we review recent progress in our understanding of energy transfer at surfaces with a particular emphasis on those phenomena, which are peculiar to solids with delocalized electronic structure, e.g. *electronically nonadiabatic* energy transfer. This area of study represents an area requiring significant extensions of our theoretical understanding, which is largely based on density functional theory. This review provides an overview of some of the experimental and theoretical tools presently being used in this field and a description of several illustrative examples of work that have helped to shape our understanding.

Keywords: Energy transfer; Surface science; Chemical dynamics; Electronic nonadiabaticity; Born–Oppenheimer breakdown

Contents

* Corresponding author. Tel.: +1 805 893 8085; fax: +1 805 893 4120.
E-mail address: wodtke@chem.ucsb.edu (A.M. Wodtke).

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"...Motion is the very essence of what has hitherto been called matter." – Lord Kelvin

1. Background and history including previous reviews

In championing the "dynamic theory of heat" being researched by Joule in 1872, William Thomson (Lord Kelvin – Fig. 1) admitted that prior to 1847: "I did not...know that motion is the very essence of what has hitherto been called matter". Joule's work on the mechanical equivalent of heat and the scientific movement he belonged to radically changed our view of the interconnected scientific concepts of heat [1], energy and motion [2], from a material theory concerning the flow of a hypothetical "caloric" fluid to a dynamical view subject to the laws of mechanics. With the acceptance of descriptions of heat as 'jiggling atoms', one may find the rumblings of notions that are now at the heart of the field that would eventually become known as *molecular energy transfer*.

Indeed, we may trace back the origins of this field even further. While Thomson's blessing of the dynamic theory of heat in the second half of the 19th century was a crucial step in its acceptance by the general scientific community – he was knighted in 1866 and was to become president of the influential Royal Society in 1890 – it was the Dutch-born mathematician Daniel Bernoulli more than 100 years prior (Fig. 2), who clearly formulated an early version of the kinetic theory of gases, and laid down the idea of heat in terms of the motion of atoms [3]. Essential to his contributions, was an analytic derivation of Boyle's empirical law (at constant T, $PV = \text{const.}$) based on the insight that pressure on a surface is produced by the collisions of molecules against the walls of its container. This may be the first and is certainly one of the most profoundly important instances of scientific analysis of the interactions of atoms and molecules at solid surfaces, the topic of this review.