Chemical Physics Letters 513 (2011) 1–11

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

FRONTIERS ARTICLE

The dynamics of evaporation from a liquid surface

Olivia J. Maselli [a,1], Jason R. Gascooke [a,b], Warren D. Lawrance [b], Mark A. Buntine [a,c,*]

[a] Department of Chemistry, The University of Adelaide, Adelaide, SA 5005, Australia
[b] School of Chemical and Physical Sciences, The Flinders University of South Australia, G.P.O. Box 2100, Adelaide, SA 5001, Australia
[c] Department of Chemistry, Curtin University, G.P.O. Box U1987, Perth, WA 6845, Australia

ARTICLE INFO

Article history:
Available online 12 June 2011

ABSTRACT

We explore the collisional energy transfer dynamics of benzene molecules spontaneously evaporating from an *in vacuo* water–ethanol liquid beam. We find that rotations are cooled significantly more than the lowest-energy vibrational modes, while the rotational energy distributions are Boltzmann. Within experimental uncertainty, the rotational temperatures of vibrationally-excited evaporating molecules are the same as the ground state. Collision-induced gas phase energy transfer measurements reveal that benzene undergoes fast rotational relaxation, from which we deduce that the rotational temperature measured in the evaporation experiments (200–230 K) is an indication of the translational energy of the evaporate. Conversely, vibrational relaxation of the high frequency mode, ν_6, is very inefficient, suggesting that the ν_6 temperature (260–270 K) is an indication of the liquid surface temperature. Modelling of the relaxation dynamics by both 'temperature gap' and 'Master Equation' approaches indicates that the equivalent of 150–260 hard-sphere collisions occur during the transition from liquid to vacuum.

1. Introduction

The molecular-level dynamics of transport across the liquid–vapour interface are critically important in a range of natural and technological environments, yet they have eluded determination. While one might have expected such a fundamental and ubiquitous process to be well understood in the early 21st century, our knowledge of evaporation at the molecular level is in its infancy. This situation prevails despite the thermodynamics of evaporation having been understood for over a century [1,2]. Developing a comprehensive molecular-level understanding of evaporative mass and energy transfer has a wide-ranging practical importance in, for example, better understanding atmospheric [3,4], chemical [5–9] and technological [10–16] processes.

Inferences about the dynamical processes of surface desorption have been made using various techniques [17] including molecular scattering [18–21] and thermal desorption [22–26]. However, the great variety in the results implies that the nascent distribution of molecular energy is greatly dependent upon the nature of the surface from which the molecules are escaping. Some of the earliest studies involved probing evaporation from solid surfaces. Since the number of evaporating molecules is extremely low, the nascent distributions observed can be assumed to be a result of spontaneous evaporation. Spontaneous evaporation occurs when molecules are liberated from the condensed phase in the absence of external forces; all the energy to leave the surface is supplied either from the bulk phase beneath the evaporating molecule or by the molecule's own internal energy [27].

Though the number of studies is few, the results from observations of spontaneous sublimation from a solid surface of the same material show some striking similarities. Klemperer's 1962 studies on the sublimation of iodine [28] revealed that vibrational temperatures of subliming I_2 were consistent with the bulk temperature. Nesbitt and co-workers [29] found that CO_2 subliming from dry ice displayed Boltzmann distributions amongst the rotational and vibrational modes of the nascent sublimate with temperatures the same as that measured for the bulk. When the temperature of the dry ice film was raised, increasing the likelihood of gas-phase collisions of the sublimate, the rotational distribution cooled to temperatures 0.8 times the measured surface temperature. Similarly, studies of the sublimation of NO from its bulk showed rotational distributions that described the surface temperature of 50 K [30]. Sadtchenko et al. [31] observed that D_2O molecules subliming from an *in vacuo* ice filament displayed a translational energy distribution whose temperature matched that of the bulk. These studies suggest that spontaneous sublimation of molecules from their solid phase produces gas phase molecules thermally equilibrated with the bulk.

In contrast, experiments involving heterogeneous systems – where the thermally-desorbed molecule is different to the material of the surface – show different trends. Both theoretical and experimental studies show significant rotational cooling of molecules

---

[*] Corresponding author at: Department of Chemistry, Curtin University, G.P.O. Box U1987, Perth, WA 6845, Australia.

E-mail address: M.Buntine@curtin.edu.au (M.A. Buntine).

[1] Present address: Department of Hydrologic Sciences, Dessert Research Institute, 2215 Raggio Parkway, Reno, NV 89512, USA.

0009-2614/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2011.06.010

desorbed from solid surfaces [19,32,33]. For example, both Muhlhausen [19] and Cavanagh [22] observed cooler-than-surface-temperature rotational distributions for NO molecules desorbing from Ag(1 1 1) and Ru(0 0 1). In their review of the chemical dynamics of the gas-surface interface, Rettner et al. point out that gas molecules that are trapped and subsequently desorbed from the surface typically display a rotational energy distribution that is Boltzmann with a temperature that is less than the surface [34]. Theoretical calculations by Muhlhausen [19] confirm that the effect is due to strong rotation-to-translation coupling along the desorption coordinate. This occurs due to the presence of an energy barrier along the desorption coordinate, where internal energy must be partitioned into the translational coordinate if the molecule is to escape the surface. The desorption coordinate is typically assigned along the direction normal to the surface since it has been repeatedly shown that the flux of molecules evaporating from a surface, be it liquid or solid, is maximised along the surface normal [17,35–37].

Theorists modelling collision-free molecular evaporation from the condensed phase typically describe the translational velocity distribution of escaping molecules as a half-range or modified Maxwellian distribution. Backward scattered molecules are not found in the vapour phase [38–40] since the surface escape requirement is to have a velocity along the surface normal. The presence of molecular collisions above the surface distort the nascent distributions toward a floating Maxwellian with a translational temperature cooler than the surface and with a net translational velocity away from it [36,41–46]. References to the substantial body of research performed on the translational velocities of desorbed molecules can be found in reviews such as those by Comsa [17] and Rettner [34].

In general, determining the translational, rotational and vibrational distributions of nascent molecules liberated from an equilibrated liquid surface can be confounded by the presence of a jacket of vapour molecules that sits above the surface, blurring the boundary between the isotropic liquid and vapour phases. The properties of energy transfer through this interface have been studied extensively by Molecular Dynamics (MD) and other theoretical methods [27,39,47–62]. In a recent review of simulations describing this interface, Garrett and co-workers [47] highlight the general conclusions that (i) the density transition from bulk liquid to water vapour occurs over a laterally-averaged distance of 0.3–0.6 nm, that is, over molecular length scales, and (ii) the interface is rough over these molecular length scales.

Garrett's simulations suggest that localised regions of the liquid–vapour interface are molecularly sharp, but as a whole, the interface appears as a rough outer layer consisting of molecules in direct contact with one another penetrating into the vacuum. X-ray scattering studies have measured liquid water surface roughness values that are in good agreement with the predictions from these MD simulations [63]. In general, the high vapour pressure of liquids enhances surface roughness and widens interface thickness; adding complexity to the evaporation processes. Interestingly, in the case of liquid sodium, which has a particularly low volatility, an experimental study of spontaneous emission of Na_2 from its bulk liquid surface [35,37] revealed rotational and vibrational temperatures the same as the bulk phase.

In summary, the investigations discussed above indicate that sublimation of molecules from homogenous solid surfaces liberates molecules with nascent rotational and vibrational temperatures equilibrated with the surface. A similar situation occurs following evaporation from homogenous liquid surfaces for molecules having very low volatilities. Sublimation from heterogeneous solid surfaces and from liquid surfaces where sample volatility is not particularly low is more complex, and results in varying amounts of translational, rotational and vibrational cooling. This variation in the extent of cooling suggests that collisional energy transfer dynamics play a crucial role during the phase transition process, especially under conditions where the interfacial boundary is less well defined (on a molecular scale). In this Letter we explore the rotational and translational energy content of benzene molecules evaporating from an aqueous liquid surface and use the results to comment on the number of collisions experienced by a benzene molecule as it undergoes a transition from the condensed to the vapour phase.

Collision-induced energy transfer that can occur between an evaporating molecule and the vapour phase prevents us from learning about the spontaneous mass transfer process since molecular collisions redistribute the evaporate's nascent internal energy. The presence of vapour-phase collisions can tend to focus the molecular flux along the surface normal [17,24,35–37,40,43,44], remove molecular anisotropy [29,39], equilibrate the internal molecular degrees of freedom [42,43] and reduce the net evaporation flux by forcing some molecules to return back to the surface [27]. While temperature constraints on the bulk system can be used to control the number of vapour-phase collisions a molecule experiences as it escapes from a liquid surface, placing geometric constraints on the surface itself can allow for the study of spontaneous emission from more volatile liquids. An *in vacuo* cylindrical filament of water, for example, is able to satisfy the Knudsen condition for obtaining collision-free molecular flow from the liquid surface if the diameter of the filament is less than the estimated mean free path of the evaporating molecules [64–66].

Faubel et al. were able to use *in vacuo* liquid filaments, which we term 'liquid microjets' (LμJs), to determine translational velocity distributions of nascent, volatile liquids such as water [67] and carboxylic acids [68]. Using 5-μm diameter LμJs of pure water, it was found that translational velocities could be fitted with a floating Maxwellian distribution. The net bulk velocity was thought to be a result of only a few gas-phase collisions converting the internal energy of the evaporating molecules into translational energy away from the bulk. For water LμJs of 25-μm radius or greater, the velocity distribution observed was significantly narrower, which Faubel et al. concluded was due to significant translational cooling from collisions within the interface [68].

Augmenting the experimental studies, Molecular Dynamics (MD) simulations of evaporation have begun to provide insight into the mass and energy transfer across the liquid–vapour interface in unprecedented detail. Simulations have rapidly evolved to the stage where they are able to describe polyatomic liquid interfaces and have, within a rigid rotor approximation, included predictions of the rotational energy content of the evaporate [39,41]. Further extensions that explore the vibrational energy content of evaporating molecules have yet to be reported.

This contribution builds upon the body of experimental research discussed above by quantifying the rotational and vibrational energy distributions of molecules spontaneously evaporating from an *in vacuo* LμJ. Specifically, we report the energy distributions for benzene molecules that have spontaneously evaporated from the surface of a 15-μm diameter aqueous LμJ and interpret the results in terms of collisional energy transfer. The robustness of the conclusions drawn from this study is underpinned by the use of two distinct (and unrelated) models to describe the collisional energy transfer dynamics. Both models yield, semi-quantitatively, the same conclusions.

Benzene was chosen as the candidate with which to determine the internal energy distribution of molecules liberated from LμJ because its spectroscopy is well characterised [69–72]. The shape and intensity of a molecule's rovibrational absorption contour is indicative of the temperature of the molecule's rotational and vibrational motion, respectively. Temperature itself is essentially a description of the distribution of molecular energy within a