

Measuring the Internal Energy Content of Molecules Transported Across the Liquid-Gas Interface

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Abstract. Many details concerning the mechanism associated with the liberation of molecules from a liquid surface remain to be elucidated. We use the liquid microjet technique coupled with laser spectroscopy to measure the rotational and vibrational energy content of benzene spontaneously evaporating from a water-ethanol solution. These measurements provide molecular level insight into the mass and energy transfer processes associated with evaporation.

1. Introduction

While the thermodynamics of evaporation have been understood for over a century [1,2], the molecular-level dynamics of the evaporation process remain ill-defined. Recently, Molecular Dynamics (MD) simulations of evaporation have begun to provide insight into the physics of mass and energy transfer across the liquid-vapor interface in unprecedented detail. Most commonly, simulations of monatomic liquids have made predictions about the translational energy content of the evaporate after it has passed through the interfacial region [3-5]. However, MD simulations have rapidly evolved to the stage that they have begun to describe polyatomic liquid interfaces and have, within a rigid rotator approximation, included predictions of the rotational energy content of the evaporate [6,7]. Further extensions that explore the vibrational energy content of evaporating molecules have yet to be reported.

To date, the only experimental evidence against which to test the validity of predictions made by MD simulations have been measurements of the translational energy distributions of molecules from a liquid microjet ($L\mu\text{J}$) evaporating into a vacuum [8,9]. There remains a critical need to experimentally characterize the nascent internal energy content of the evaporate to provide a much more rigorous test of the predictions made by MD simulations. In tackling this challenge, we have developed an experimental technique to probe the rotational and vibrational energy content of molecules evaporating from a liquid surface. Specifically, we report results for benzene evaporating from aqueous solution into vacuum using the $L\mu\text{J}$ approach coupled with laser spectroscopy.

The mechanism by which molecules leave a liquid surface can be classified as ‘spontaneous’ or ‘stimulated’ [4]. Spontaneous evaporation occurs only 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.

Stimulated evaporation involves vapor-phase molecules above the liquid surface contributing to mass and energy transfer. Experimental studies describing spontaneous evaporation have traditionally been challenging due to the presence of this vapor. Collisions between the emerging molecules and the vapor-phase rapidly equilibrate the nascent energy distributions of the emerging molecules and thereby obscure interrogation of the spontaneous process. The L μ J approach overcomes this complexity by presenting the evaporating liquid surface directly into a vacuum, thus enabling direct interrogation of evaporation in the absence of competing processes.

2. Experiment

We have used a 7.5 μ m radius liquid microjet. All experiments were conducted using 10^{-3} M benzene with ethanol in de-ionized water (25% v/v EtOH in H₂O) as the solvent. The aqueous solution was injected into the vacuum at a flow rate of 0.25 mL/min. Solute benzene molecules that evaporated from the liquid surface were ionized by a collimated and telescoped ultraviolet (UV) laser beam (10 μ J/pulse, 150 μ m radius FWHM) located a fixed distance downstream of the L μ J nozzle aperture and propagating orthogonally to the liquid filament. The UV laser radiation ionized the solute benzene molecules by 1 + 1 resonance-enhanced multiphoton ionization (REMPI) via the $^1B_{2u} \leftarrow ^1A_{1g}$ transition for the first absorption step. The UV laser did not directly irradiate the L μ J, but ionized molecules that had moved a fixed distance away from the liquid filament. Typically, the UV laser was located 300 μ m from the L μ J. Resultant benzene ions were injected into a reflectron time-of-flight (TOF) mass spectrometer. Mass spectra were collected over 50 laser shots at each UV laser wavelength. Typically, 2-4 consecutive wavelength scans were averaged to generate the spectra used for spectral analysis.

The rotational and vibrational energy content of the benzene molecules are reported in terms of rotational and vibrational mode-specific ‘temperatures’. Rotational temperatures in the vibrational ground state of benzene were determined by fitting the experimental 6_0^1 vibronic spectral band contours with ones simulated from known spectroscopic constants and transition line strengths [10-12] using a Levenberg-Marquardt non-linear least squares algorithm [13] and assuming a Boltzmann distribution of internal energies. Measurements of the temperatures of select vibrational modes were made by comparing the integrated intensity ratios of the relevant vibronic hot bands to the 6_0^1 cold band [14].

To test the spectral simulation algorithm, and to provide a benchmark against which the L μ J evaporation spectra can be interpreted, we recorded and analyzed the room-temperature REMPI spectrum of benzene in a static cell. The cell is equipped with a pair of 1 cm² electrodes separated by a distance of 1 cm and biased with a potential difference of 90 V. This spectrum was recorded at a pressure of 0.45 Torr by passing the resulting photocurrent from each electrode through a differential amplifier.

3. Results and Discussion

Measured rotational contours of the 6_0^1 vibronic band of benzene at room temperature and after evaporating from the L μ J are shown in Figure 1. The L μ J spectrum in Figure 1(b) was recorded with the UV laser set at a distance of 300 μ m from the centre of the liquid filament and 1 mm downstream of the nozzle orifice. Comparison with the room temperature spectrum (Figure 1(a)) shows that the evaporation contour is significantly truncated at lower transition energies, revealing a considerably colder rotational energy distribution than found at room temperature. Overlaid on each spectrum is the best-fit spectral simulation. The simulated spectral contours, displayed as dashed lines in Figure 1, are convoluted with a Gaussian of 0.3 cm⁻¹ (FWHM) to account for the laser bandwidth. Simulation of the gas cell spectrum in Figure 1(a) yields a best-fit rotational temperature of 295 \pm 6 K, where the uncertainty represents 1 standard error. This illustrates the accuracy of the rotational temperatures that can be extracted. The average of fitting nine spectra equivalent to that presented in Figure 1(b) yields a rotational temperature for the benzene evaporate of 206 \pm 4 K.

Extended spectra of benzene recorded at room temperature in the low pressure gas cell and under L μ J evaporation conditions are presented in Figure 2. Here, several additional vibronic bands are labeled according to the assignments of Stephenson *et al* [15]. The multi-peaked band between 38,515 cm⁻¹ and 38,535 cm⁻¹ is assigned to overlapping 6_1^2 and $6_1^0 11_0^2$ transitions. Although the peaks in this band involve mixed vibronic transitions, the initial vibrational level prior to laser excitation always

includes 6_1 , so the change in the band's integrated intensity under evaporation conditions relative to the equilibrated room-temperature gas cell allows us to determine the degree of cooling for the ν_6 vibrational mode. Such analysis yields a ν_6 vibrational temperature of 256 ± 11 K following evaporation.

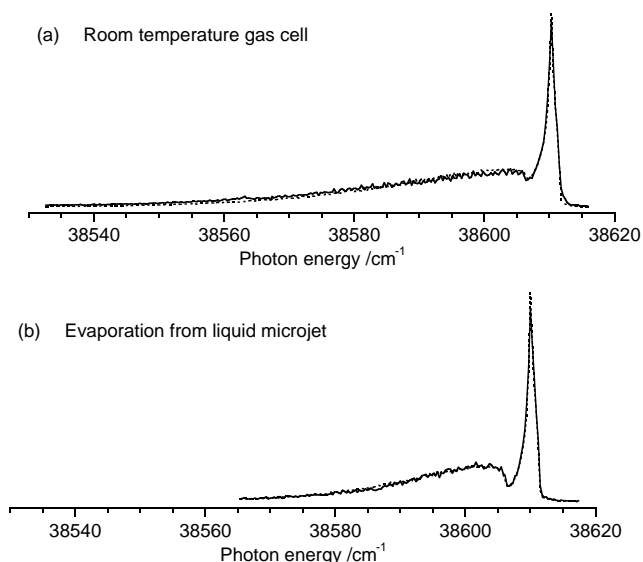


Figure 1 1+1 Resonance-Enhanced MultiPhoton Ionization (REMPI) spectra of the 6_0^1 vibronic transition of benzene. **(a)** under room-temperature gas cell conditions. **(b)** evaporated from the surface of a $\text{H}_2\text{O}/\text{EtOH}$ liquid microjet. Overlaid on each spectrum is a dashed line representing the best-fit spectral simulation for the 6_0^1 transition, assuming a Boltzmann distribution of rotational states.

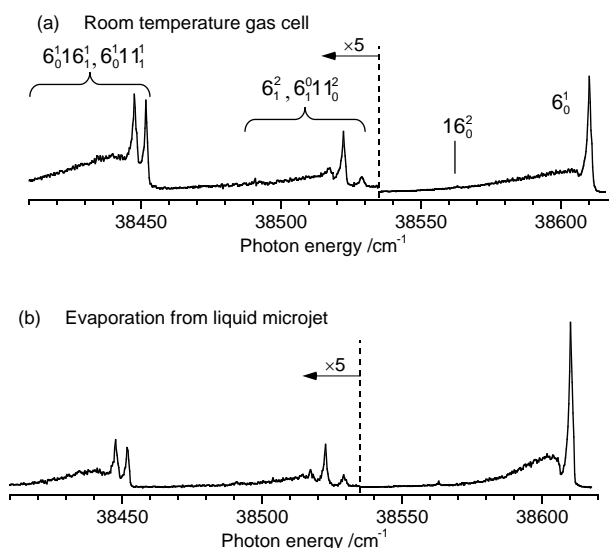


Figure 2 Extended 1+1 REMPI spectra of benzene to lower photon energy of the 6_0^1 vibronic transition. **(a)** under room-temperature gas cell conditions. **(b)** evaporated from the surface of a $\text{H}_2\text{O}/\text{EtOH}$ liquid microjet. Intensities to lower photon energy of the dashed vertical line in each spectrum have been multiplied by a factor of five. Vibronic transitions discussed in the text are labeled. Vibrational temperatures are determined by the ratio of integrated band intensities for each hot band relative to that of the 6_0^1 transition.

To lower transition energy, the series of peaks around $38,450 \text{ cm}^{-1}$ are assigned to the $6_0^1 16_1^1$ and $6_0^1 11_1^1$ vibronic transitions. Analysis of this band to determine vibrational temperatures is less straightforward because the overlapping transitions arise from molecules initially populating both ν_{11} and ν_{16} in the ground electronic state. However, the vibrational energies of ν_{11} and ν_{16} are 674 cm^{-1}

and 399 cm^{-1} , respectively [16,17], so assuming a Boltzmann distribution at the gas-cell temperature of 295 K as well as equal electronic transition probabilities, the population ratio between ν_{11} and ν_{16} is 0.13. As such, 87% of the intensity from this band, at least in the upper trace of Figure 2, arises from ground electronic state population in the lower-energy ν_{16} level. We therefore conclude that the contribution of ν_{11} to the spectral profile is minimal. Assuming an identical ratio of vibrational populations under evaporation conditions yields a ν_{16} vibrational temperature of 229 ± 12 K. Because of its lower frequency, ν_{16} is expected to relax faster than ν_{11} so this temperature should be viewed as an upper limit [16,17].

It is important to ascertain that the measured temperatures represent the final values, *i.e.* collisional cooling is complete prior to laser ionization of the benzene evaporate. This was verified by measuring spectra at the larger distance of 1200 μm from the $L_{\mu}\text{J}$. Within experimental error there is no change in either the rotational or vibrational temperatures in moving from 300 to 1200 μm away from the liquid filament, indicating that the experiment probes the quantum state distributions of benzene after vapor-phase collisional energy transfer is complete.

The important results to emerge from this study are that (i) the rotational and vibrational temperatures are different, and (ii) the temperatures of ν_6 and ν_{16} are different. This is only possible if there have been insufficient collisions to establish equilibrium between the rotational and various vibrational degrees of freedom. The data allow for a comprehensive assessment of the number of collisions undergone by a molecule as it passes from the condensed phase, and thereby insight into the dynamics occurring at the liquid-vapor interface. This analysis is reported elsewhere [18].

We have directly measured the rotational and mode-specific vibrational energy content of benzene that has spontaneously evaporated into the vacuum from an aqueous liquid microjet. The rotational and ν_6 and ν_{16} vibrational temperatures of benzene are all different, pointing to non-equilibrated collisional energy transfer occurring within the liquid-vapor interphase region.

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