Pulsed supersonic expansion of nonvolatile solids

Wolfgang Christen, Stephanie Geggier, Svitlana Grigorenko, and Klaus Rademann
Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin, Germany

(Received 8 June 2004; accepted 2 August 2004; published 3 November 2004)

A compact apparatus for transferring nonvolatile particles into the gas phase and depositing them on a solid surface has been built and tested successfully. As initial experiment, solid caffeine with a vanishingly low vapor pressure has been dissolved in supercritical carbon dioxide, expanded into vacuum using a pulsed, supersonic molecular beam, and detected using a simple residual gas analyzer. © 2004 American Institute of Physics. [DOI: 10.1063/1.1805016]

The transfer of nonvolatile or thermally unstable molecules into the gas phase is of utmost importance for a variety of applications such as analytical mass spectrometry, optical spectroscopy, or the epitaxial growth of thin films. Methods explored so far include laser desorption/ionization or matrix assisted laser desorption/ionization,1–3 electrospray generation,4,5 and the expansion of supercritical solutions into a molecular beam.8–14

In the latter approach the key idea is to dissolve the substance at high pressure, exploiting the supercritical fluid’s solvent power, and precipitate it by expansion. The use of supercritical fluids as solvents offers various advantages:

In laser spectroscopy supersonic gas expansions are of great help because the efficient cooling of the large number of internal degrees of freedom is essential to reduce the large population of excited states.

The experimental challenges of a pulsed supersonic expansion of supercritical solutions are a suitable valve to minimize the gas load and thus pumping requirements, and techniques to avoid clogging or freezing of the nozzle.

In this work we report the expansion of solid caffeine in supercritical CO₂ at temperatures of only 310–315 K, and accompanying detection using a quadrupole mass spectrometer. The high-pressure expansion is accomplished with a widely used, commercially available pulsed valve that has been adapted to the special conditions of high pressures and supercritical fluids. Pumping requirements are modest, allowing a compact setup.

The experimental setup consists of a temperature-controlled high-pressure cell, connected to a differentially pumped vacuum system with an on-axis quadrupole mass spectrometer via a pulsed valve, as depicted in Fig. 1. The pulse valve is a commercially available model (General Valve 9-0500-906) with a conical orifice of 0.5 mm diameter. However, the originally supplied Teflon poppet is not suitable for high pressures and supercritical carbon dioxide and therefore has to be modified with respect to material and geometry.

The nozzle and reservoir can be heated up to 365 K with a thermocox heater. Temperature is controlled using a simple on-off temperature controller with a NiCr–Ni thermocouple, giving an overall temperature homogeneity of ±3 K.

Gaseous CO₂ (57.3 bar vapor pressure at 293 K, 99.995% purity) is passed to the autoclave and the reservoir in which a few milligrams of the solid sample (anhydrous caffeine, <10⁻⁸ mbar vapor pressure at 298 K, >99% purity, Fluka) is placed. Subsequently the autoclave is cooled down using a dewar vessel with liquid nitrogen, condensing CO₂. After closing the valve to the CO₂ gas supply, the autoclave is heated thus increasing the pressure of carbon dioxide up to 200 bar. The pressure is measured using an industrial piezo-resistive stainless steel sensor (BD Sensors DMP333) with 0.35% full scale accuracy.

At elevated temperatures sample molecules can be dissolved in supercritical CO₂ (critical pressure p_c=73.83 bar, critical temperature T_c=304.21 K) and carried to the pulsed valve for injection. Both the solvent and the solute are expanded into vacuum, forming a pulsed supersonic beam of CO₂ clusters and caffeine particles.

The two vacuum chambers are separated by a conical skimmer with a diameter of 5 mm, and pumped by diffusion pumps with 600 ls⁻¹ pumping speed, resulting in a background pressure of 10⁻⁶ mbar. The distance between the skimmer and the ionizer of the residual gas analyzer (Balzers Prisma QMS200) is ≈25 cm.

The mass analyzer is continuously sampling the two masses of CO₂ and C₆H₁₀N₄O₂, and a reference signal (not shown). Figure 2 demonstrates that caffeine and carbon dioxide molecules are ionized and detected in the molecular beam. Due to the late ionization of the molecular beam in the ion source of the quadrupole mass analyzer (by electrons with a kinetic energy of ≈70 eV) the weakly bound molecular clusters fragment, and only individual molecules are measured.

The peak shape of the caffeine signal closely matches the CO₂ signal, as is obvious from the comparison of two different opening times of the pulsed valve.

The ratio of the caffeine and the carbon dioxide ion currents, as derived from the baseline-corrected peak areas in...
Fig. 2, amounts to 5.9±0.9·10\(^{-4}\). Taking into account the different ionization and detection probabilities of caffeine and carbon dioxide in the residual gas analyzer this result compares well with the published solubility of caffeine in supercritical CO\(_2\) of 1.5·10\(^{-5}\) mole fraction at 313 K and 95 bar.\(^{15}\)

Experimen tally, under the chosen experimental conditions neither clogging nor freezing of the valve occurs; it is even possible to deposit visible amounts on a substrate that is brought into the beam, as depicted in Fig. 3.

In summary, using a compact experimental setup permits the transfer of nonvolatile or thermally labile molecules, dissolved in a supercritical fluid, into the gas phase. This way it is possible to deposit visible amounts of the solute onto a solid surface, and to detect it using mass spectrometry.

**ACKNOWLEDGMENTS**

The authors gratefully acknowledge useful discussions with Professor Uzi Even, and the lending of the autoclave by Dr. Horst Hennig. S. G. gratefully acknowledges a scholarship by the German Academic Exchange Service (DAAD).