# Simple Method for Determining the Vapor Pressure of Materials Using UV-Absorbance Spectroscopy

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S *Supporting Information*

ABSTRACT: Accurate thermodynamic parameters of thin films of materials are crucial in understanding their behavior in the nanometer scale. A new and simple method for determining the vapor pressure and thermodynamic properties of nanometer thick films of materials was developed based on UV-absorbance spectroscopy. Well-characterized benzoic acid was used to calibrate the spectrometer and the experimental conditions. The thermodynamic properties of pentaerythritol tetranitrate (PETN) were determined to validate the use of this new method. The estimated values of the thermodynamic parameters of PETN are in excellent agreement with the values reported using the most widely used Knudsen

effusion method for determining vapor pressure lower than 1 pascal. The elegance of this method is its simplicity. The results indicate that UV-absorbance spectroscopy is a model-free and powerful technique in determining thermodynamic parameters in the nanoscale.
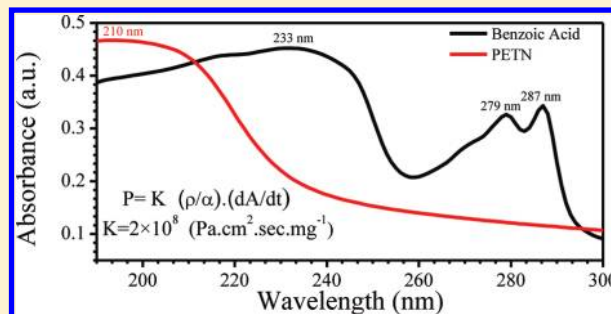
1. INTRODUCTION

Thermogravimetry analysis (TGA) is the most widely used technique in determining thermodynamic parameters in the bulk form of materials and can be calibrated to determine their vapor pressures. TGA often requires a flow of gas through both the balance chamber and the sample to prevent temperature and pressure build-up.[1] Quartz crystal microbalance (QCM) is a more sensitive tool for mass loss in the nanometer scale and has also been used in measuring sublimation rates of materials in the form of noncontinuous thin films.[2,3] However, the uncertainty of the QCM sensitivity to mass loss is about 15−20%. The mass change detectable by both TGA and QCM is on the order of few nanograms whereas some materials mass loss could be on the order of attograms which limits the usefulness of using these techniques. Another technique, atomic force microscopy (AFM), has also been used to determine sublimation rates of nanoislands of materials.[4,5] However, even when operated with special tips in contact mode, the measurement of the volume and surface area of the nanoislands will lack accuracy due to the irregular shape. With the aid of modeling, the vapor pressure of 2,4,6-trinitrotoluene has been estimated with an uncertainty of ∼20% by means of QCM.[2] The use of AFM to determine vapor pressures of materials has not been reported in literature. In addition, the sublimation rates of pentaerythritol tetranitrate (PETN) in the form of nanoislands calculated using AFM are ∼30−40 orders of magnitude larger than those determined by TGA[5] which is caused by the errors induced by evaluating the volume and surface area of the sample. This suggests the inability of AFM to be used to determine/estimate the vapor pressure of low volatile materials, even with better model development.

The majority of volatile organic materials exhibit a signature in the UV region of the electromagnetic spectrum. This fact raises the idea of using UV absorbance spectroscopy in determining the thermodynamic properties of thin films of such species in the nanometer scale. We are primarily interested in thermodynamic properties of explosives. PETN is one of the most commonly used secondary explosives in military and industrial applications.[6] PETN was chosen to facilitate the universality of UV absorbance spectroscopy usage in thermodynamic properties determination since it is a low volatile material exhibiting very low vapor pressure.

Using UV absorbance spectroscopy in determining sublimation rates has the advantage of eliminating the surface area from the rate of mass loss equation. In addition, most importantly, the relatively small scanned area ensures extremely accurate measurements even with the existence of surface roughness, dislocations, and cracks: the surface is relatively smooth within the beam area. The accurate sublimation rates are expected to produce accurate vapor pressures values. In order to validate the use of UV-absorbance spectroscopy in determining vapor pressure, benzoic acid (BA), one of the most characterized and widely used materials for calibration of TGA apparatus, was used as a baseline material to calibrate the UV spectrometer in this study.

In this article, for the first time, we present accurate in situ measurements of thermodynamic parameters including vapor pressure of continuous nanofilms of PETN in air using UV-absorbance spectroscopy. In addition, we present the first

UV-absorbance characterization of solid PETN thin films. Although we are validating the idea of using spectroscopy in determining vapor pressures of materials only in the UV region of the optical spectrum, we believe that this principle is valid throughout the electromagnetic spectrum.

2. EXPERIMENTAL METHODS

ACS reagent grade crystalline benzoic acid was obtained from Sigma-Aldrich (St. Louis, MO) and used without further purification. Pentaerythritol tetranitrate (PETN) powder of high purity was supplied by Lawrence Livermore National Laboratory and used without further purification. A stock solution of 0.4 M of benzoic acid and 0.2 M of PETN in acetone were used to prepare continuous thin films on quartz substrates by spin coating (single wafer spin processor, Laurell technologies corp., North Wales, PA) 20 μL of each material solution at 3000 rpm for 1 min. The quartz substrates were cleaned using acetone and deionized water before films were deposited. Concentrations below 0.2 M were not used since they were found to form noncontinuous films.

The thickness and roughness of the thin films were determined by PSIA XE Atomic force microscope (AFM) (Santa Clara, CA) in contact mode with a silicon cantilever (Nanosensor pointprobes, nominal spring constant 5.0 N/m). Absorbance spectra of thin films of benzoic acid and PETN were recorded in situ at different temperatures using a Lambda 1050 UV/vis/ NIR (Perkin-Elmer, U.K.) spectrometer at 0.5 nm resolution and 2 nm slit width with quartz as reference. The spectrometer is equipped with a temperature controller allowing for in situ temperature-dependent absorbance measurements with an accuracy of 0.05 °C for both sample and reference. All absorbance spectra were collected within 1 h of preparation. The effect of the surface energy between quartz and thin films is negligible, since it is in the range of a few nanometers.

3. RESULTS AND DISCUSSION

3.1. Benzoic Acid. The benzoic acid (ρ = 1.27 g/cm^3) films are continuous with faceted morphology as observed by both optical spectroscopy and atomic force microscopy. The thickness of benzoic acid films obtained by spin coating was determined to be ~320 nm with relatively high rms roughness of ~40 nm using AFM.

For a thin film of a material with surface area S and thickness l, the sublimation rate per unit area of an arbitrary material could be written in the form[7]

$$\frac{dm}{S\,dt} = \frac{\rho}{\alpha}\frac{dA}{dt} = f\exp\left(-\frac{E_a}{k_B T}\right) \qquad (1)$$

where ρ is the density of the material, α is the absorbance coefficient at a single wavelength, f is the frequency factor, E_a is the activation energy of sublimation, k_B is Boltzmann's constant, and dA/dt is the rate of absorbance change. Thus, in using UV spectroscopy to determine sublimation rates, the sublimation rate is given by $(\rho\,dA)/(\alpha\,dt)$, and a plot of $\ln[(\rho/\alpha)(dA/dt)]$ versus the inverse of temperature in Kelvin yields a straight line following the Arrhenius equation with a slope of $-E_a/k_B$.

The room temperature absorbance spectrum of benzoic acid, in the form of nanofilms, exhibits three absorbance peaks in the UV region. The locations of the three peaks were determined from the second derivatives of its spectra to be centered at 233,
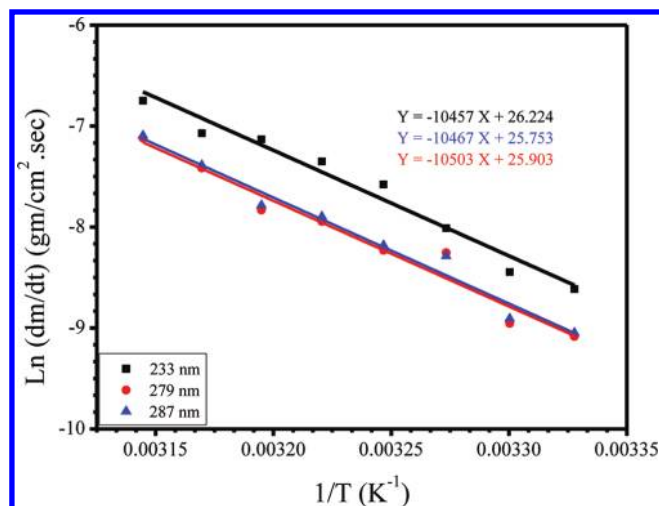

Figure 1. log the rate of mass loss versus the inverse of absolute temperature monitored at 233, 279, and 287 nm absorbance peaks of benzoic acid.

279, and 287 nm with absorbance coefficient of 47813, 24818, and 25697 cm^{-1}, respectively. This is in agreement with the reported data for benzoic acid in various solvents, where these peaks are red-shifted and centered at 228, 273, and 280 nm, respectively.[8,9] To obtain an accurate/average value of α and ensure a homogeneous film thickness, the absorbance coefficients of the absorbance peaks of benzoic acid were determined by recording the absorbance spectra at five different spots on three different films. In addition, no significant change in absorbance was observed in quickly raising the temperature of the films within the temperature range in this study indicating that the values of the absorbance coefficients of the three peaks are temperature-independent.

The time-dependent change in absorbance spectra of a benzoic acid thin film were recorded isothermally at temperatures between 27.5 and 45 °C in a 2.5 °C steps. The change in absorbance spectra was monitored at the three observed absorbance peaks. However, it was observed that the entire region between 233 and 190 nm in the absorbance spectra is decreased by the same value. The same behavior was observed between 279 and 287 nm but with a slower decrease rate which is expected due to the relatively smaller absorbance coefficients at this region. It is obvious that the absorbance systematically decreases consistently with time for all temperatures used in this study indicating a homogeneous temperature-dependent thickness decrease due to sublimation of benzoic acid molecules from the thin film.

The time-dependence decrease of the absorbance monitored at the three absorbance peaks is linear for all temperatures with very good R values. The slopes of the straight lines were used to calculate the rate of mass loss/sublimation rate at each temperature using eq 1. The logarithm of the sublimation rates of benzoic acid at different temperatures are plotted versus the inverse of the absolute temperature.

As shown in Figure 1, a plot of the log of the rate of mass loss monitored at 233, 279, and 287 nm absorbance peaks, at different temperatures, versus $1/T$ yields straight lines, from which the activation energy of sublimation was calculated to be 86.9, 87.0, and 87.3 kJ/mol for the 233, 279, and 287 nm peaks, respectively. These values are in excellent agreement with the mean value of the activation energy of sublimation of benzoic acid that has been

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Table 1. Sublimation Rates of Benzoic Acid Determined Using UV-Absorbance Spectroscopy by Monitoring Change in Absorbance at 233, 279, and 287 nm Peaks along with Those Reported in the Literature Using Different Techniques

	sub. rate (ng/cm^2 s)					
T (K)	233 nm	279 nm	287 nm	Oxley[13]	Xie[14]	Ribeiro[12]
318.0	35.4	41.2	41.3	22.9	11.4	28.7
315.5	27.3	31.8	31.8	19.0	8.2	22.0
313.0	20.9	24.4	24.4	15.7	5.9	16.9
310.5	15.9	18.6	18.6	13.0	4.3	12.9
308.0	12.2	14.2	14.1	10.7	3.1	9.8
305.5	9.2	10.7	10.7	8.75	2.2	7.4
303.0	6.9	8.1	8.1	7.15	1.5	5.5
300.5	5.2	6.1	6.0	5.83	1.1	4.2

Figure 2. Plot of vapor pressure of benzoic acid monitored at 233 nm absorbance peak versus ν to determine the k value of the UV spectrometer and its evaporation constant (α).

reported in literature (84.0−95.5 kcal/mol).[10−14] However, two extreme values of 62 and 107 kcal/mol have been reported by Oxley et al. who used rising-temperature TGA technique[12] and Xie et al.[14] using TGA-FTIR apparatus, respectively. Our value is in excellent agreement with the activation energy values reported by Zielenkiewicz et al.[10] and Ribeiro da Silva et al.[11] using gas saturation and torsion effusion methods, respectively. The sublimation rates of benzoic acid measured in this study are also in excellent agreement with those reported in literature using Knudsen effusion method.[12,14] The values of sublimation rates calculated using the best fit to our data along with those found in literature are tabulated in Table 1. It is clear that our results are in excellent agreement with the values reported using the most accurate and widely used Knudsen effusion technique in measuring thermodynamic parameters of materials. This indicates the high accuracy of this new simple technique in calculating thermodynamic parameters of materials.

Starting from Langmuir equation for free evaporation/sublimation, the vapor pressure of any volatile material can be determined.[15] Using a standard material of a well-characterized vapor pressure, a calibration procedure could be used to estimate the vapor pressure of other materials to a good accuracy.[16] For vapor pressure determination, the Langmuir equation is usually written in the form[17]

$$P = k\nu, \text{ where } \nu = \frac{1}{S}\frac{dm}{dt}\sqrt{\frac{T}{M}} \text{ and } k = \frac{\sqrt{2\pi R}}{\alpha} \qquad (2)$$

where $(1/S)(dm/dt)$ (kg s^{-1} m^{-2}) is the rate of mass loss per unit area, T is the absolute temperature (K), M is the molecular weight (kg mol^{-1}), R is the universal gas constant (J K^{-1}), and α is the unitless instrument-dependent evaporation constant.

The sublimation rates calculated using the change in absorbance of the 279 and 287 nm peaks are relatively larger (20% higher) than those calculated using the 233 nm absorbance peak. These less accurate values are expected since the absorbance coefficients of these two peaks are smaller than that of the 233 nm peak. Thus, the sublimation rate calculated using the change in absorbance of the 233 nm peak was used in calibrating the UV spectrometer. The most recent benzoic acid vapor pressure data reported by both Ribeiro da Silva et al.[12] and Monte et al.[18] were used to calibrate the UV spectrometer since it was collected in a temperature range similar to or partially within our studied temperature range (37.5−45 °C). These pressure values in pascal
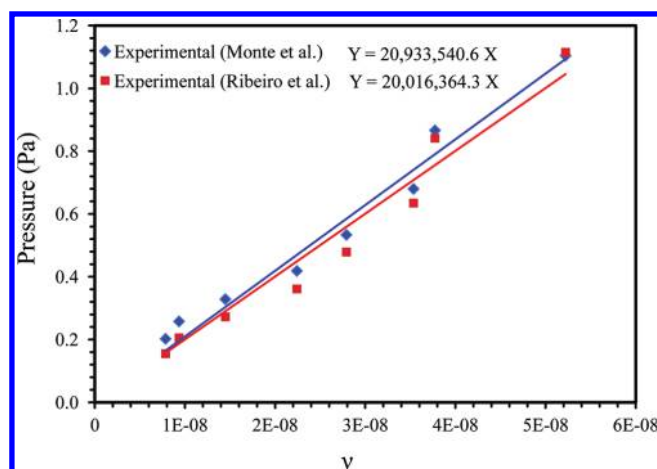
were plotted versus our experimental ν values in the same temperature range used in our study. As shown in Figure 2, using the ν values calculated by monitoring the 333 nm absorbance peak, the plots are linear. The slopes of the straight lines (k) were used to calculate the evaporation constant (α) of the UV spectrometer and were found to be 3.45 × 10^{-4} using Monte et al.[18] pressure values and 3.61 × 10^{-4} using those of Ribeiro da Silva et al.[12] It is of interest that the three absorbance peaks of benzoic acid produce similar values of energy of activation and sublimation rates which allows for use of a single wavelength for determination of thermodynamic parameters.

3.2. PETN. PETN (ρ = 1.76 g/cm^3) Films are continuous. The thickness and the rms surface roughness of the PETN films were determined using AFM operated in contact mode to be ∼100 and ∼3 nm, respectively, with excellent reproducibility. PETN, like other explosives, does not absorb in the visible region of the spectrum. The PETN absorbance spectrum exhibits a single broad absorbance peak in the UV region centered at 210 nm, with an absorbance coefficient of 53 340 cm^{-1}, as indicated by the second derivative of its spectrum. The location of the peak does not change with increasing the temperature. However, a broadening in the peak was evidenced with increasing temperature. This broadening could be due to crystallization which is usually observed at temperatures close to the melting point (142 °C for PETN) when organic molecules are rearranged in a more organized solid matrix (crystalline structure).

The isothermal time-dependent changes in the absorbance spectra of PETN were monitored at different temperatures between 70 and 90 °C at 5.0 °C steps. Spectra were recorded every two minutes. It was observed that the absorbance decreases consistently with time for all temperatures used in this study indicating a systematic temperature-dependent thickness decrease due to sublimation of PETN molecules.

A plot of absorbance versus time indicates that the time-dependence decrease of the absorbance is linear for all temperatures used in this study. The slopes of the resulting straight lines were used to calculate the rate of mass loss/sublimation rate at each temperature. The logarithm of the sublimation rates at different temperatures are plotted versus the inverse of temperature in Kelvin as shown in Figure 3.
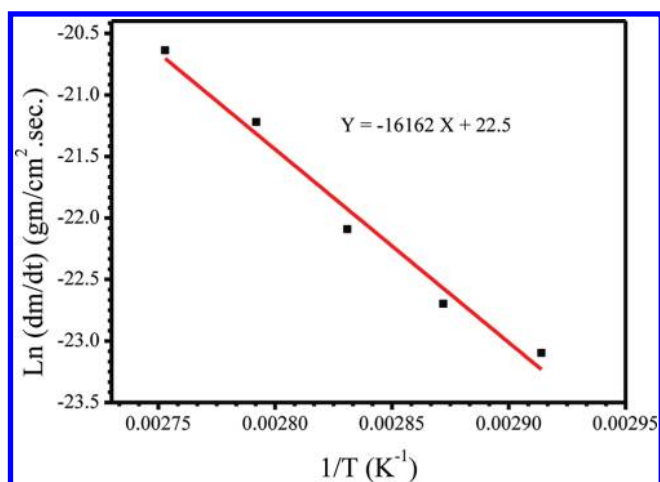
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Figure 3. log the rate of mass loss versus the inverse of absolute temperature monitored at 210 nm absorbance peak of PETN.
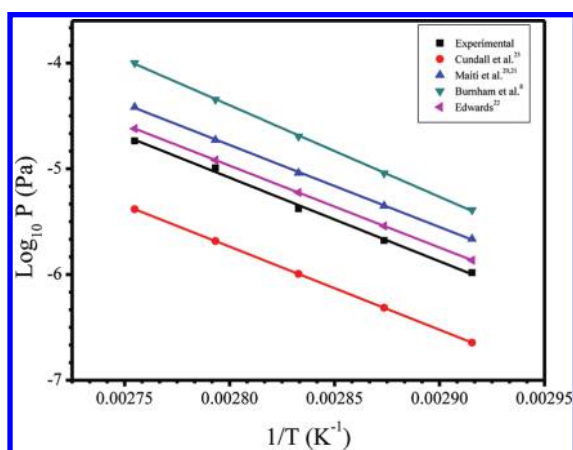

Figure 4. Experimental vapor pressure values of PETN calculated using UV-absorbance spectroscopy along with those reported in literature.

As shown in Figure 3, a plot of the log of the rate of mass loss, at different temperatures, versus $1/T$ yields a straight line, from which the activation energy of sublimation was calculated to be 134.4 ± 4 kJ/mol. This is in excellent agreement with the reported values for single crystals of PETN ($E_a = 134.5$ kJ/mol)[5] and microcrystals of PETN ($E_a = 127.5$ and 137.5 kJ/mol)[4,5,19] using thermogravimetric analysis (TGA) and atomic force microscopy AFM, respectively. The values of the sublimation rates of PETN calculated using UV-absorbance spectroscopy are two times larger than those calculated in the nanometer scale using TGA.[5] This indicates that UV-absorbance is a more accurate method in determining sublimation rates in the nanometer scale than AFM technique which produced sublimation rates of 300−400 times larger than those determined using TGA[5] in the same study. As expected, our relatively larger sublimation rates are a result of the decrease in surface area during the course of the measurement which is always assumed to be constant throughout the TGA experiment which is not the case since sublimation of PETN is expected to take place from all the facets of the crystal.

The k value, corresponding to Monte et al.[18] vapor pressure values, calculated from Figure 2 was used to calculate the vapor pressures of PETN at the different temperatures used in this study. There are few available theoretical and experimental reports on PETN vapor pressure.[8,20−23] These data are summarized in Figure 4. along with our experimental results. This figure indicates that our calculated vapor pressure values of PETN are close to the mean value of those reported by different methods. In addition, our results are in an excellent agreement with the calculated vapor pressure values of PETN reported by Edwards, who used the Knudsen effusion method.[22] It is clear that the data obtained for PETN using UV-absorbance spectroscopy is in good agreement with those reported in literature. This indicates the accuracy and high potential for use of UV-absorbance spectroscopy in determining thermodynamic properties of solid materials in the nanometer scale. In addition we show that UV-absorbance spectroscopy is a more reliable technique than both QCM and AFM in determining such physical parameters in the nanometer scale. However, this method is limited to materials with a signature in the UV region of the electromagnetic spectrum and continuous films.

4. CONCLUSIONS

In this article we demonstrate the successful use of UV absorbance spectroscopy in determining the vapor pressure of thin films of materials that absorb in the UV region of the electromagnetic spectrum. Once the instrument is calibrated and a calibration chart is developed, the vapor pressure of UV absorbers could be accurately determined in the nanometer scale. PETN was studied as an example of such materials of interest. With development of sophisticated software, optical characterization of UV absorbers will allow for the use of a single wavelength to determine their thermodynamic properties in minutes.

ASSOCIATED CONTENT

S **Supporting Information.** The isothermal time-dependent spectra of BA and PETN as well as plots of the absorbance versus time monitored at the absorbance peaks of the two materials are provided. These plots allow for the calculation of the rate of absorbance decrease which is related to the sublimation rates at different temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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