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Thermal-accommodation measurement of helium on a suspended water droplet

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An innovative method for determining the thermal-accommodation coefficients of gases by means of monitoring the Mie scattering from a single suspended water droplet is described. The heat exchange between the gas molecules and the suspended droplet is analyzed by considering the simultaneous mass- and heat-transfer processes during droplet growth by condensation in a gas–water-vapor environment. Measurements have been carried out for helium with water-vapor-to-helium ratios in the range of 1:0.5 to 1:2.5. The thermal conductivity of this mixture is found to be best represented by its reciprocal average. The thermal-accommodation coefficient of helium on water surfaces is determined to be 0.65 ± 0.05, as compared to unity for water vapor on water surfaces.

I. INTRODUCTION

Among heterogeneous systems, one of the simplest examples of interactions is an elastic collision between a gas molecule and a surface. Within this framework, a molecule ideally makes contact with a surface and rebounds at once with either a loss or a gain of energy. The driving force behind this transfer of energy between the two media is thermal equilibrium, i.e., the temperature difference. For each given pair of an incoming molecule and a host surface, the extent of exchange of energy is usually described by the so-called thermal-accommodation coefficient, α_T,

$$\alpha_T = \frac{T_m - T_0}{T_f - T_0} , \tag{1}$$

where T_0 is the incoming-gas-molecule temperature, T_f is the host-surface temperature, and T_m is the temperature of the leaving molecule.

Extensive measurements of thermal accommodation have been carried out for interactions between gas and solid surfaces. Techniques used in this kind of study generally involve molecular-beam scattering experiments on single-crystal surfaces[1] under ultrahigh-vacuum conditions. The information that the accommodation coefficient carries is extremely useful in the understanding of the role of metals in catalytic reactions, adsorbed gases in the strength and the structure of metals, etc. On the microscopic level, one can also determine the repulsive force constant of the host surface.[2] However, there is a lack of investigations on gas-liquid interface systems. In comparison to the importance that gas-solid interfacial science plays in the study of catalytic reactions, the gas-liquid heterogeneous system represents another important class of interactions in atmospheric chemistry, cloud physics, fossil-fuel combustion, and aerosol science.[3] Among the wide scope of applications of gas-particle interactions, the most interesting and often asked about are the interaction of water surfaces with those gaseous species which are closely related to environmental pollutants.

Recently, there has been an increasing interest in using micrometer-sized spherical particles to study the gas-liquid interfacial science. Mie scattering spectroscopy is one of the state-of-the-art techniques being applied to such research. Chylek *et al.*[4] have demonstrated that the size and the index of refraction of a silicone oil droplet can be deduced with relative error of 5×10^{-5}. This implies that the Mie scattering measurement is capable of detecting size changes as small as only a fraction of a monolayer (a few angstroms). Arnold *et al.*[5] have further illustrated this sensitivity in sizing by calculating the backscattering spectrum of a micrometer-sized water droplet near resonance. They have shown that along the steep slope of a Mie resonance peak, a change of a fraction of an angstom can lead to a significant change in the Mie scattering signal. This principle was later applied successfully in obtaining the infrared spectrum of an aqueous ammonium sulfate solution droplet.[8] Further experimental verification of the sensitivity of the Mie scattering technique can be found in mass-accommodation-coefficient experiments,[7,8] in which the change in size of a single suspended water droplet during condensational growth is monitored as a function of time using Mie resonance spectroscopy.

In this paper we demonstrate an innovative technique for measuring the thermal accommodation of helium on water surfaces. A comparison is then made of the thermal accommodation of helium on different metallic surfaces, which ranges from 0.03 on a clean surface to about 0.5 on gas-covered or oxidized surfaces. An investigation is also carried out to obtain the thermal conductivity of a binary gaseous mixture of water vapor and helium.

II. EXPERIMENTAL

A schematic diagram of the experimental setup is shown in Fig. 1. The particle-containment apparatus (front view) consists of two end-cap electrodes formed from stainless-steel mesh sandwiching a central stainless-steel ring electrode. Machined Teflon spacers are used as insulator between the electrodes. This particle contain-

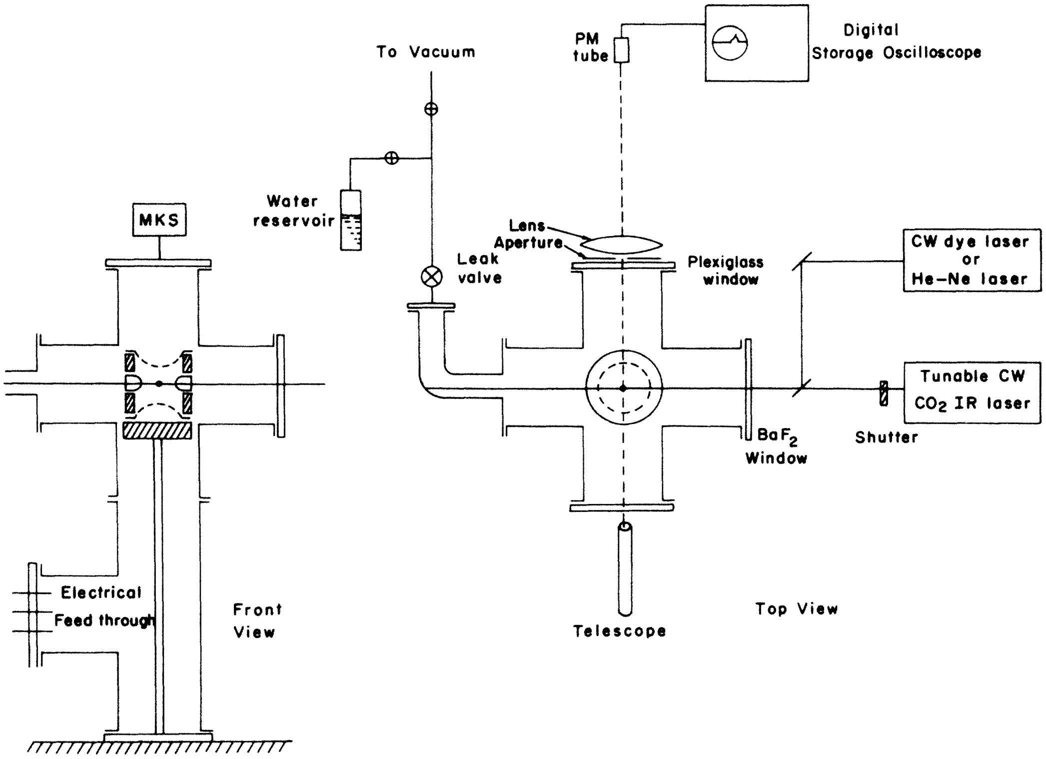

FIG. 1. Schematic diagram of the experimental setup.

ment trap is mounted and centered in a stainless-steel six-way cross. Salt particles from a plunger-driven nozzle are introduced at the top port of the chamber. After a particle is caught, its size is first roughly estimated by the "spring-point voltage" technique.[9] The port is closed with a vacuum flange equipped with a capacitance manometer (MKS 145 AH-100) to monitor the chamber pressure and the system is slowly evacuated through a leak valve. When the chamber has achieved a base pressure below 10^{-5} Torr, the vacuum system is closed off. Subsequently, water vapor is admitted gradually into the chamber until the suspended particle deliquesces. The size of the saline-solution droplet is governed by its ambient temperature and water-vapor partial pressure. This particle levitation chamber is kept at room temperature and is monitored continuously by means of a calibrated chromel-alumel thermocouple. During the course of the experiment, the variation of the ambient temperature is within a few tenths of a degree. Since the time scale of the actual measurement is on the order of a few seconds, the temperature can be considered as constant for all practical purposes.

The probe laser used in the Mie scattering measurement is a Coherent CR-699, tunable ring dye laser. The probe-laser beam is perpendicularly polarized with respect to the scattering plane. The front port of the particle cell is fitted with a sight-glass flange to view and align the suspended particle with a telescope. The back port is covered by a $\frac{1}{2}$-inch-thick Plexiglas flange. The detection optics is made up of a fixed-diameter aperture (15 mm), a 40-mm asymmetric planoconvex lens, and a photomultiplier (PM). The lens is positioned halfway between the PM tube and the particle so that it gives unity magnification. In addition, a vertical 0.2-mm slit is placed at the collective lens to select the acceptance angle. The total angle is about 0.5°. In front of the PM tube, a 2-mm diameter orifice further reduces the noise due to background scattering (spurious scattering from chamber walls and particle trap). The size of the droplet is measured by scanning the dye laser between 6150 and 5600 Å. The photomultiplier signal is processed by a phase-sensitive lock-in amplifier, digitized, and recorded on an IBM PC-XT computer. The obtained Mie spectrum is then analyzed to yield the size and the index of refraction of the suspended droplet. Based on the thermodynamic data of Hamer and Wu[10] for aqueous NaCl solutions, the dry-particle mass is deduced subsequently.

For the condensational growth measurement, an additional infrared laser (Molectron IR-250) is aligned to overlap with the probe laser at a germanium beam splitter and enters the chamber through a BaF_2 window. The droplet is irradiated momentarily so that it is slightly heated to cause its size to reduce by about 5% by evaporation. When the heating laser beam is blocked off, the suspended droplet is quickly grown back to its original preheating size by water-vapor condensation. The condensational growth is driven by vapor-liquid equilibrium.[8] As the temperature of the droplet returns to that of the environment, chemical equilibrium causes water vapor to condense onto the droplet so that the chemical activity of the solution droplet will maintain at a constant value. In this study, it is found that a few hundred milliwatts of infrared laser power is sufficient to produce a droplet size change corresponding to several Mie resonance peaks necessary for analysis purposes. Typically, about 15 Torr of water is admitted to the single-particle chamber initially. High-purity (99.9999%) helium is then admitted to form a gaseous mixture with water vapor for the condensational growth measurement.

III. RESULTS AND DISCUSSION

The scattering of monochromatic light by a dielectric sphere has been well studied. The most widely used solution to this problem is the far-field solution obtained by Mie in 1908.[11] For a nonabsorbing dielectric sphere, the intensity of the scattered light can be expressed in terms of the partial-wave amplitudes, $|a_n|^2$ and $|b_n|^2$,

$$Q_{sc} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2) , \tag{2}$$

where $x = 2\pi r/\lambda$ is the size parameter; r and λ are the radius of the particle and the scattering light wavelength, respectively. Since both $|a_n|$'s and $|b_n|$'s have singularities over discrete values of x at a given scattering angle, the scattering intensity will show resonance peaks at these singularities. This is best illustrated by examining the experimental result as shown in Fig. 2(a). This spectrum, obtained by monitoring the Mie scattering intensity from a saline droplet as a function of the excitation-laser wavelength, agrees exactly with a calculated spectrum [Fig. 2(b)] for an 8.148-μm radius particle with refractive index $m = 1.395$. The precision of our measurement is limited by the stability of the water pressure inside the particle levitation cell. Some irregular intensities displayed in the spectrum are due entirely to the dye-laser intensity variations. The bandwidth of the dye laser is about 1 GHz. Based on this measured spectrum, the size and the refractive index of the droplet can be determined[4] with better than 99.95% accuracy.

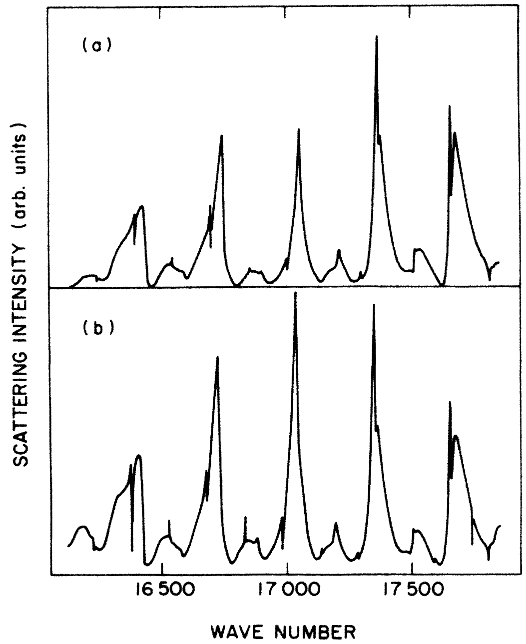

FIG. 2. (a) Observed Mie scattering spectrum of a saline-solution droplet. (b) Calculated Mie spectrum for an 8.148-μm droplet with its index of refraction $= 1.395$ and scattering angle $= 92.1°$.

To solve the mass- and heat-transfer processes in the present experiment, we use the coupled rate equations shown as follows:[12]

$$\frac{dW}{dt} = 4\pi r D \beta_m \frac{M_W}{RT}(P_\infty - P) , \tag{3}$$

$$C_T W \frac{dT}{dt} = L \frac{dW}{dt} - 4\pi r k_m \beta_T (T - T_\infty) , \tag{4}$$

where

$$\beta_m = \frac{r}{r + \frac{D}{\alpha_M}\sqrt{2\pi M_W/RT}} , \tag{5}$$

$$\beta_T = \frac{r}{r + k_m/(l_1 + l_2)} , \tag{6}$$

$$l_i = \frac{\alpha_{Ti} P_i (C_{vi} + R/2)}{\sqrt{2\pi M_i R T}} , \tag{7}$$

where α_M is the mass-accommodation (or condensation) coefficient, r is the droplet radius, W is the droplet mass, M_W is the molecular weight of water, R is the gas-law constant, P_∞ is the system pressure at temperature T_∞ as measured, P is the droplet vapor pressure at the interface temperature T, C_T is the heat capacity of the droplet, C_{vi} is the heat capacity of gas i, L is the latent heat of water, k_m is the thermal conductivity of the gaseous mixture, and α_T is the thermal-accommodation coefficient. For the present binary mixture of helium and water the following form for the conductivity is used:

$$1/k_m = \frac{y_1}{k_1} + \frac{y_2}{k_2} . \tag{8}$$

When the vapor pressure of water is parametrized as a linear function of W and T, the solution to the coupled differential equations above can be written in the following form:[8]

$$\begin{bmatrix} W(t) \\ T(t) \end{bmatrix} = a_1 e^{\lambda_1 t} \begin{bmatrix} x_{11} \\ x_{12} \end{bmatrix} + a_2 e^{\lambda_2 t} \begin{bmatrix} x_{21} \\ x_{22} \end{bmatrix} + \begin{bmatrix} W_p \\ T_p \end{bmatrix} . \tag{9}$$

Both the mass and thermal condensation coefficients of water have recently been investigated by several groups.[8,13] The accepted values are $\alpha_T = 1$ and $\alpha_M = 1$ for water vapor.

After the size of the dry salt is determined from the observed spectrum (Fig. 2), the laser is fixed at a chosen wavelength for the condensation growth measurement. The choice of the fixed wavelength is based on the identification of an appropriate resonance peak. The growth spectrum for a saline droplet in a water-helium environment is shown in Fig. 3(a). For evaluation purposes, a Mie spectrum for a growing saline droplet is calculated at this same scattering wavelength, so that the size of the droplet can be readily identified. The occurrence of many prominent Mie resonance features fa-

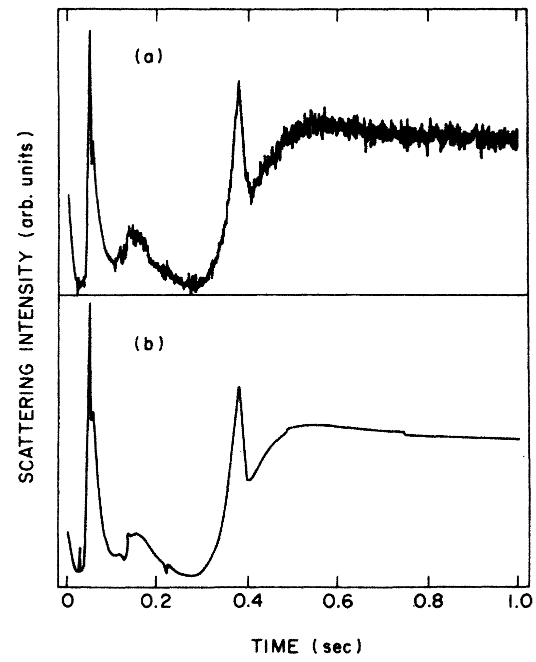

FIG. 3. (a) Growth spectrum for a saline droplet in a mixture of 14.9-Torr water vapor and 35.5-Torr helium; the scattering wavelength is 17751 cm^{-1}. (b) Simulated growth spectrum for the same particle described above with the thermal-accommodation coefficient of helium on water being 0.65.

cilitates the analysis of the growth curve which is recorded on a digital oscilloscope. In Fig. 3(b) a calculated spectrum of the growing droplet is shown for comparison purposes.

The fitting of each growth curve involves the identification of the droplet size at specific times and subsequent evaluation of α_T for helium by Eq. (7). In most cases, a total of about ten droplet-size values are used to evaluate the growth curve. The α_T for each mixture of water vapor and helium is deduced by means of least-square analysis. Figure 4 illustrates the droplet-growth spectra in several helium mixtures, using $\alpha_T = 0.65 \pm 0.05$ as the best fit.

Several models were used to calculate the conductivity of the binary mixture of helium and water. These include models[14] such as the Brokaw model for nonpolar mixtures, the Lindsay and Bromley model for general mixtures, as well as the more common approaches such as the linear mole-fraction average and the reciprocal average. Although these models claim to yield results with better than 90% accuracy, we found that only the reciprocal average gives a good enough fit over the range of helium pressure which we used throughout this investigation. Various models represent different deviations of the thermal conductivity from the ideal linear combination of the mole-fraction average. Reciprocal average indicates a large negative deviation, whereas models such as the Brokaw model gives an intermediate value between linear and reciprocal combination.

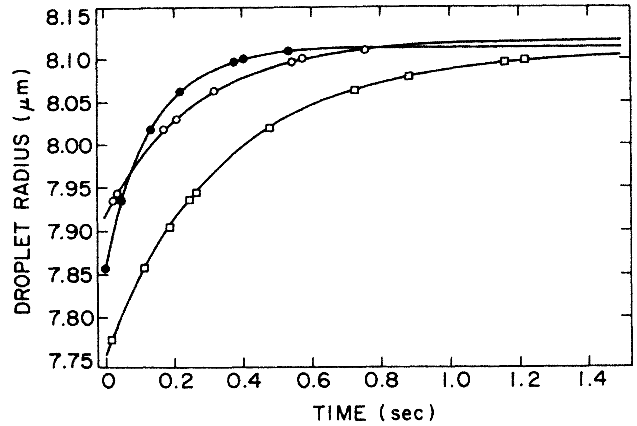

FIG. 4. Illustration of the growth spectra for a saline solution droplet under various mixtures of helium and water vapor. —— indicates calculated spectra and the symbols show different helium and water-vapor mixtures: □, 14.9-Torr water; ○, 14.9-Torr water plus 7.2-Torr helium; ●, 14.9-Torr water plus 35.5-Torr helium.

The thermal-accommodation coefficient on a water surface for several common gases such as nitrogen, oxygen, and water are known to be unity.[13] However, the α_T for helium ranges from 0.03 on a clean platinum surface to 0.53 on an oxidized tungsten surface. Table I gives a summary of the thermal-accommodation coefficients for these gases on various surfaces. Similarly, the α_T of helium on a gas-covered platinum surface was found to be relatively high as well, i.e., $\alpha_T = 0.42$. All these indicate that on the "nonideal" surfaces, the α_T for helium would be in the neighborhood of 0.5. The present experiment can be viewed as a confirmation of α_T for helium on "soft" surfaces which involve mostly inelastic collisions.

IV. CONCLUSION

We have demonstrated that optical Mie scattering spectroscopy on a single suspended particle can be used to study the energy exchange between gases and liquid surfaces. Present experimental results show that the conductivity of the binary mixture of water vapor and heli-

TABLE I. Thermal-accommodation coefficients.

Gas	Substrate surface	α_T
H_2O	Water droplet	1
N_2	Water droplet	1
N_2	Clean W	0.35
He	Water droplet	0.65 ± 0.05
He	Clean W	0.02–0.06
He	Gas-covered W	0.19
He	Oxidized W	0.53
He	Clean Pt	0.03
He	Gas-covered Pt	0.42

um can be described by their reciprocal average. The thermal-accommodation coefficient of helium on a water surface is determined to be 0.65±0.05, which is significantly lower than that of the common diatomic gases such as nitrogen and oxygen. The thermal accommodation coefficients for these gases and water vapor are equal to unity.

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