

MID-INFRARED SPECTROSCOPY OF MOLECULAR SPECIES THAT DRIVE SIGNIFICANT ATMOSPHERIC PROCESSES

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Abstract

Small changes in the infrared absorbance observed at levels of concentration in the sub-parts per million (sub-ppm) of atmospherically significant molecular species, such as HCl, SO₂, NO₂ and NH₃, have been quantified as a function of pressure and temperature for the surface reactions of these gases with various materials (e.g. copper, aluminum, stainless steel and teflon). A Nicolet Magna-IR 550 Fourier transform infrared (FT-IR) spectrometer operating in the 400-4000 cm⁻¹ region and fitted with a 10-meter multipass absorption cell and a deuterated triglycine sulfate (DTGS) detector was used for recording the spectra. Tubing materials chosen are typically associated with the hardware of measuring instruments used to collect atmospheric trace gas samples. The degree of adsorption for specific gas-solid interfaces and the kinetic theory of the adsorption process (assuming a mono-layer) enabled the determination of the corresponding rate constants. It is envisioned that the accurate determination of the adsorption coverage parameters and the Langmuir rate constants for the various gas-material combinations will aid in the refinement of precise values for the associated residence time and activation energies and thereby lead to the development of a comprehensive adsorption isotherm model for gas-surface interactions.

Introduction

The absorption features of the trace gas constituents were investigated here with the FT-IR spectrometer by recording the individual rotational-vibrational (ro-vibrational) spectral features of the molecule [1,2], thereby permitting the correct choice of transitions to be made for the different trace species examined at various concentration levels (5 - 100 pm).

The FT-IR spectroscopic technique facilitated the indirect observation [3, 4] of the adsorption effects due to surface interactions of very low concentrations of highly polar molecules, such as HCl, with the interacting surfaces of the measuring apparatus. The adsorption "sticking" effects of the

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HCl noted earlier by Fried et al [3] onto the plumbing and the inner walls of the measuring apparatus provided impetus for this work. The development of accurate reference spectral databases [5] from field measurements using the FT-IR usually requires a continuous gas flow, such as the approach used by NIST. [6] The continuous flow of known concentrations of primary standard gas mixtures through sample cells minimizes biases in the determination of the concentration caused by adsorption of the sample onto the cell walls [7], which in turn minimizes the reported sample concentration loss due to adsorption. A systematic study of the interaction of atmospheric trace gases, such as HCl [8-11], NO₂ [1], NH₃ and SO₂ [12,13], with sheets of various tubing materials that are used for the development of gas handling systems, can aid designs that minimize the effects of adsorption. Atmospheric monitoring [14] of trace gases require improvements on the techniques of correcting the measured concentration by means of fitting Langmuir adsorption isotherm curves to the observed data. Tubing materials of interest, such as stainless steel, teflon, aluminum and copper [15,16] were used to investigate the effects of adsorption.

Theory

The physical adsorption or physisorption process is understood via the concept of an adsorbent or adsorbing surface having a finite number of sites onto which a single molecule (the adsorbate) can stick. The adsorbing surface treated here is a metallic or conducting surface. Physisorption involves a long range weak van der Waals interaction between the molecule and the adsorbing surface. The energy released when a molecule is adsorbed is typically on the order of tens of kJmol⁻¹, which can be taken up as vibrations of the lattice. Figure 1 illustrates the concept of physisorption, based on which the Langmuir adsorption isotherm [17] can be derived. The gas phase molecule may rebound from the surface, where elastically no energy is exchanged in the collision. If the molecule is adsorbed or 'sticks', then the molecule is said to be an adsorbed molecule and is counted as part of the surface coverage.

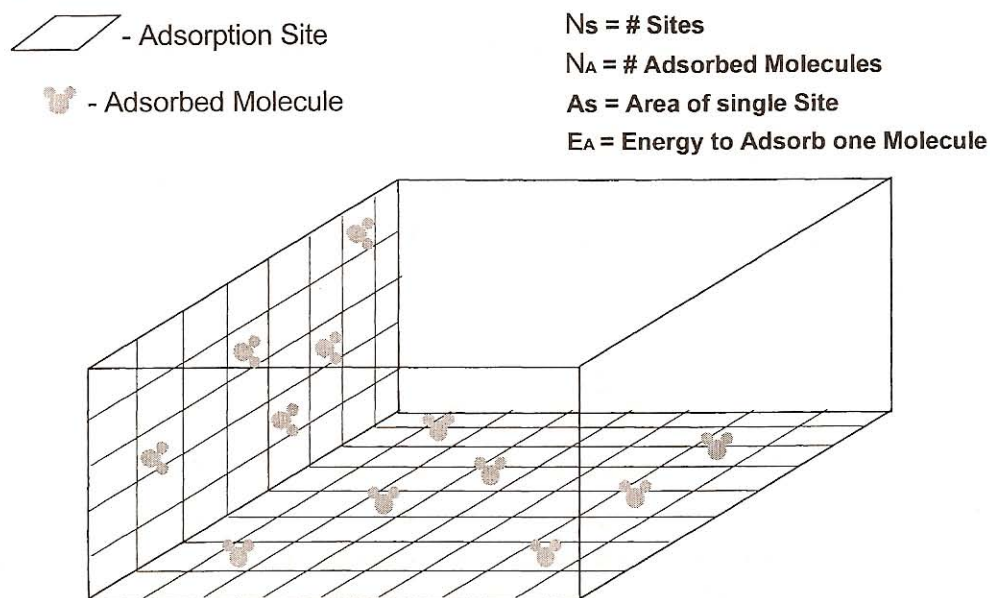


Fig. 1. Physical Adsorption { Physisorption } of Molecules onto Adsorption Sites

The coverage θ is defined as the ratio of the number of adsorption sites occupied divided

by the total number of available sites. The coverage value has the range $0 \leq \theta \leq 1$. For the adsorption, the rate of change for a surface coverage is directly proportional to the number of unoccupied sites or proportional to $(1 - \theta)$. Thus, the adsorption rate equation may be written as

$$\frac{d\theta}{dt} = K_a p(1 - \theta) \quad (1)$$

where K_a is the Langmuir adsorption rate constant [18] and P is the partial pressure of the adsorbing molecule in the gas phase. The reverse of the adsorption process is the desorption and may be define by the rate equation written as

$$\frac{d\theta}{dt} = K_d \theta \quad (2)$$

The equations (1) and (2) may be written in a more convenient form using the concentration C for the gas phase in units of molecules per cm^3 , respectively:

$$\frac{d\theta}{dt} = \frac{K_a c}{N_{AD\max}} (1 - \theta) \quad (3)$$

$$\text{and} \quad \frac{d\theta}{dt} = \frac{K_d}{N_{AD\max}} \theta \quad (4)$$

where $N_{AD\max}$ is the maximum number of adsorbed molecules on the surface. The combined adsorption and desorption effects [15,18] may then be expressed as

$$\frac{d\theta}{dt} = \frac{K_a c}{N_{AD\max}} (1 - \theta) - \frac{K_d}{N_{AD\max}} \theta \quad (5)$$

At static equilibrium, the effect of the adsorption and desorption rates cancel, and

$$\frac{K_a c}{N_{AD\max}} (1 - \theta) = \frac{K_d}{N_{AD\max}} \theta \quad (6)$$

$$\text{Integrating (5)} \quad \theta = \frac{K_a c}{K_a c + K_d} \left(1 - e^{-\frac{K_a c + K_d}{N_{AD\max}} t}\right) \quad (7)$$

At equilibrium [15, 19, 20],

$$\theta_\infty = \frac{K_a c}{K_a c + K_d} = \frac{c}{c + \kappa} \quad (8)$$

This is Langmuir isotherm at equilibrium (as $t \rightarrow \infty$). The constant $\kappa = K_d / K_a$ is proportional to $\exp[\frac{\Delta G}{k_B T}]$, where ΔG is the free energy of adsorption at infinite dilution [21, 22]. Also, from other equilibrium considerations, the Langmuir isotherms may be derived considering dissociative (the adsorbed molecule constituent atoms dissociate at the adsorbing surface) as well as non-dissociative processes. The dissociative reaction is strongly dependent on the temperature and therefore on the kinetics activation energy E_a . The coverage, illustrated in Figure 2, may be

written as

$$\theta = \frac{bP}{1 + bP} = B(T) \quad (9)$$

where P is the partial pressure of the gas phase and b is a constant of coverage and is dependent on the strength of the gas-surface interaction, if enthalpy of adsorption is independent of the coverage, and is given by

$$b = e^{\frac{E_a^{des} - E_a^{ads}}{RT}} \quad (10)$$

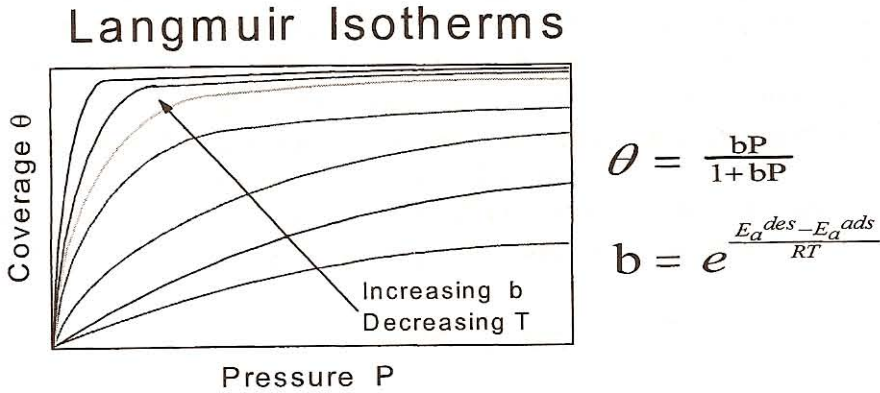


Fig. 2. Coverage based on Langmuir Isotherms

It must be pointed out that the coverage of the adsorption surfaces described here is restricted to one of a mono-layer or a single layer of adsorbed molecules (ca. 10^{15} - 10^{16} molecule/cm²), since the concentrations of the gas mixtures studied here are in the low ppm range. In order to obtain good spectral scans, the FT-IR system had to be purged regularly, so as to prevent the over contamination of the surface walls of the absorption cell and the inner connecting tubing links.

The coverage on the inner surface of the tubing of area $A = 2\pi rl$ is

$$\theta = \frac{V_A(c - c')}{\sigma_{MAX} 2\pi rl} \quad (11)$$

where σ_{MAX} is the molecular surface density in units of molecules per cm². The number of molecules lost to the adsorption process is $V_A(c - c')$, which was determined directly from absorption spectroscopy using the FT-IR. Equating the two expressions, (7) and (11), for θ , we have

$$\frac{K_a c}{K_a c + K_d} \left(1 - e^{-\left(\frac{K_a c + K_d}{N_{ADMAX}}\right)t}\right) \approx \frac{K_a c}{K_a c + K_d} \left[1 - \left(1 - \frac{K_a c + K_d}{N_{ADMAX}} t + \dots\right)\right] \approx \frac{V_A(c - c')}{\sigma_{MAX} 2\pi rl} \quad (12)$$

which yields

$$\frac{K_a c}{N_{ADMAX}} t \approx \frac{V_A(c - c')}{\sigma_{MAX} 2\pi rl} = \frac{V_A(c - c')}{N_{ADMAX}} \quad (13)$$

wherefrom the value of cK_a with units $\left(\frac{\text{molecules}}{\text{cm}^2 \text{ sec}}\right)$, the same units as K_d , is determined as

$$cK_a \approx \left(\frac{V_A(c - c')}{\sigma_{MAX} 2\pi rl}\right) \frac{N_{ADMAX}}{t} \quad (14)$$

From $\sigma_{MAX} = \frac{N_{ADMAX}}{2\pi r l}$, it follows that $cK_a = \frac{V_A(c - c')}{t}$. (15)

The time t that is required for the number of adsorbed molecules on the surface of area $A = 2\pi r l$ of the metal tubing to increase from zero to the value $N_{AD} = V_A(c - c')$, as the volume V_A is filled with gas of concentration c' . The value $N_{AD} \rightarrow N_{ADMAX}$ and $c' \rightarrow c$, as $t \rightarrow \infty$.

Experimental

Accurate measurements of the absorption spectra were performed using the FT-IR spectrometer and associated accessories. Figure 3 shows the experimental layout of the Nicolet Magna-IR 550 FT-IR spectrometer. The resolution of the FT-IR instrument was varied from 0.25 cm^{-1} to 32 cm^{-1} as deemed appropriate for the measurements. In addition to a deuterated triglycine sulfate (DTGS) detector at room temperature, a Mercury Cadmium Telluride (MCT) liquid nitrogen cooled detector permitted measurements in the range 10 - 500 ppm, requiring fewer than 64 scans (10 minutes) [23, 24]. The detectivity D^* for the MCT-A detector used here is on the order of $10^{11} \text{ cmHz}^{0.5}/\text{W}$. [23]. KBr windows were used throughout for high transparency in the mid-IR region.

FT-IR Spectrometer

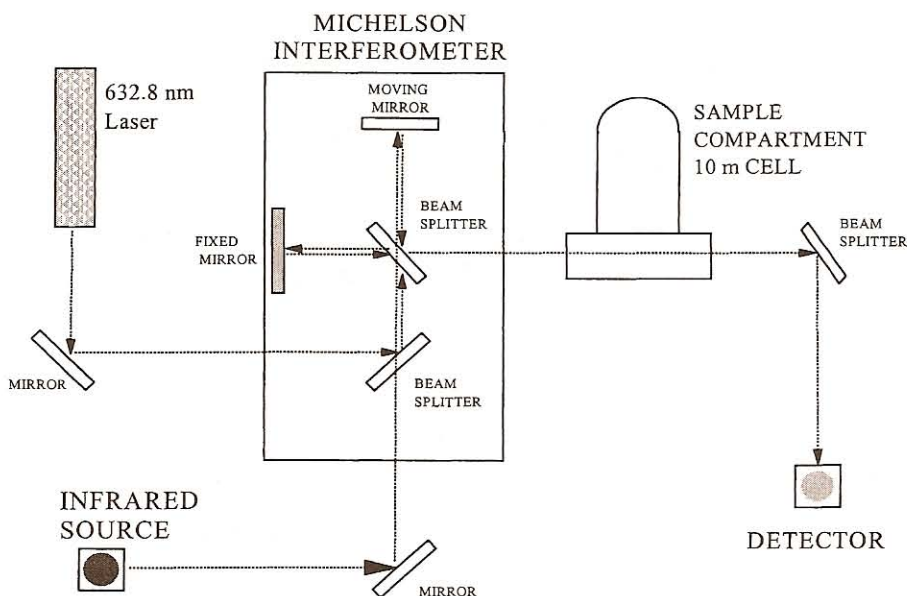


Fig. 3. The Nicolet Magna 550 FT-IR Spectrometer Experimental Arrangement

Results and Discussion

For illustrative purposes, we will choose the interaction of gaseous NH_3 on aluminum. Aluminum sheets with total surface area of 1300 cm^2 were exposed to 760 Torr of the gas concentration of NH_3 in N_2 . The absorbance as a function of time was recorded using the FT-IR instrument by taking snapshots of the absorbance at the fundamental line $\nu_2(a_1) = 967.31 \text{ cm}^{-1}$. The results for the spectroscopic data scan for the NH_3 - Aluminum adsorption reaction are given

in Table 1 and plotted in Figure 4. The time varying concentration corresponding to the absorbance is calculated from $\ln\left(\frac{I}{I_0}\right) = -\sigma c N_0 l$ and the absorption cross-section obtained was $\sigma_\nu = 2.203 \cdot 10^{-19} \pm 1.661 \cdot 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$.

Table 1. NH₃ - Aluminum Desiccator Interaction Measurement at 100 ppm NH₃ in N₂

NH ₃ - Aluminum Interface Desiccator				
Ps(Torr) = 760	Initial concentration	c(ppm) = 100	Reaction Volume	V(cm ³) = 7500
Pa(Torr) = 30	Res(cm ⁻¹) = 0.5	T(°C) = 5	Surface Area	A(cm ²) = 1300
Time (min)	Time (sec)	Absorbance at $\nu_2(a_1) = 967.31 \text{ cm}^{-1}$	Number Adsorbed/cm ² (calculated)	Instantaneous Concentration (ppm)
2.0	120	0.0187	0.00	100.0
16.0	960	0.0110	5.89(14)e+15	58.8
29.0	1740	0.0091	7.34(17)e+15	48.7
43.0	2580	0.0081	8.11(19)e+15	43.3
125.0	7500	0.0051	1.04(2)e+16	27.3
204.0	12240	0.0042	1.11(3)e+16	22.5

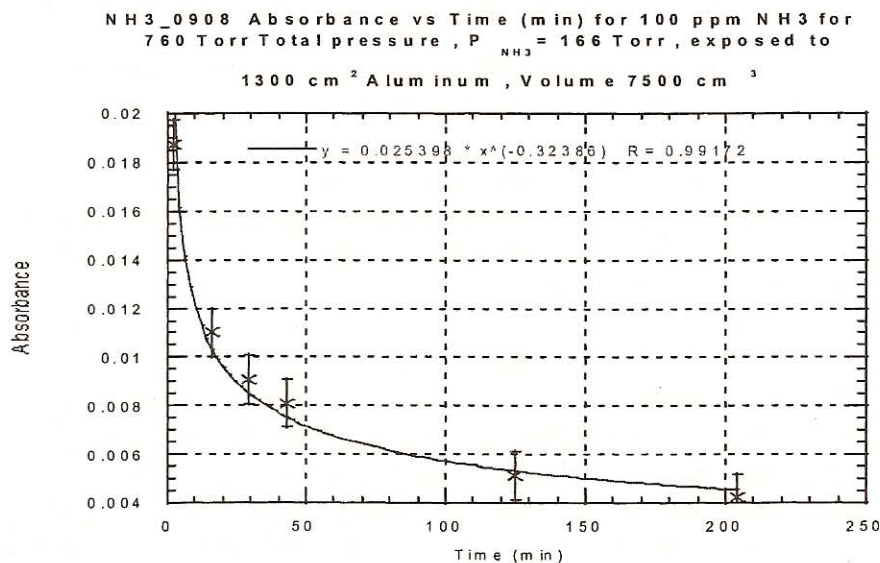


Fig. 4. Instantaneous Absorbance for Desiccator Samples @ 100 ppm for NH₃ - Aluminum Interface Reaction (Table 1)

The relative error for $\Delta N_{adsorbed}$ was determined from the uncertainties $\Delta T = 1 \text{ }^\circ\text{C}$, $\Delta P = 1 \text{ Torr}$, $\Delta P_a = 1 \text{ Torr}$, $\Delta L = 1 \text{ cm}$, $\Delta \sigma_\nu = 1.661 \cdot 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$, $\Delta V = 10 \text{ cm}^3$ and $\Delta A = 1 \text{ cm}^2$, whereby

$$N_{Error} = \Delta N \sqrt{\left(\frac{1}{300}\right)^2 + \left(\frac{5}{760}\right)^2 + \left(\frac{1}{50}\right)^2 + \left(\frac{1}{1000}\right)^2 + \left(\frac{1.66e-21}{2.203e-1}\right)^2 + \left(\frac{10}{7500}\right)^2 + \left(\frac{1}{1300}\right)^2} = 0.0237 \cdot \Delta N. \quad (16)$$

A plot of the instantaneous concentration vs time is shown in Fig. 5.

The first-order rate constant K (molecules/cm²/sec) for NH₃ are extractable from the plot(s) of Number of Adsorbed NH₃ Molecules / cm² adsorbed onto aluminum as function of Time (sec).

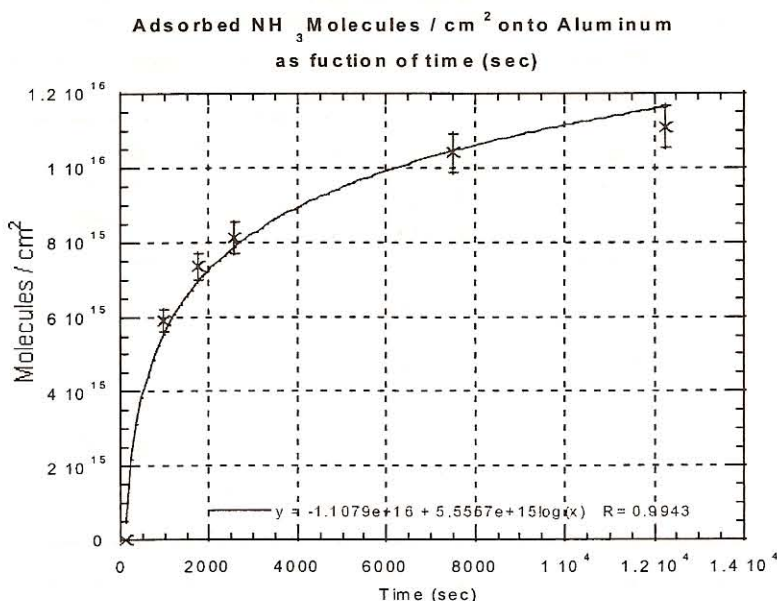


Fig. 5. Number of Adsorbed NH₃ Molecules / cm² as function of Time (sec).

Acknowledgments

The lead author (PM) would like to acknowledge the financial support provided by Howard University's Fund for Academic Excellence Grants Program and the Center for the Study of Terrestrial and Extraterrestrial Atmospheres.

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