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# Energy accommodation coefficients of internally excited molecules

D. R. Anderson, E.-H. Lee,<sup>a)</sup> R. H. Pildes, and S. L. Bernasek

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

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A method for determining partial energy accommodation coefficients is described. Laser radiation is used to excite absorbing molecules in the gas phase, which subsequently strike a solid surface depositing energy. This energy transfer is monitored by observing the temperature rise of the solid. Measurement of this temperature rise as a function of gas pressure is used to determine the vibrational energy accommodation coefficient. This method is applied to the interaction of CH<sub>3</sub>F, SF<sub>6</sub>, methanol, and cyclopropane with a seasoned molybdenum surface. Values of the vibrational energy accommodation coefficient are found to correlate well with the heat of vaporization of the absorbing molecule.

## INTRODUCTION

The transfer of energy between an incident gas molecule and a solid surface is the initial step in every gas-surface interaction. The energy accommodation coefficient (EAC) has traditionally been the quantity used to describe this energy transfer. An EAC is defined as<sup>1</sup>

$$\alpha = \frac{E_i - E_R}{E_i - E_s}, \quad (1)$$

where  $E_i$  is the total energy of the molecule incident on the surface,  $E_R$  is the energy of the reflected molecule, and  $E_s$  would be the energy of the molecule if it had been thermally equilibrated with the surface. In this definition, the molecular energy is partitioned into translational, rotational, and vibrational modes.<sup>2</sup> These modes may be accommodated differently, necessitating the introduction of partial EACs, which are defined as follows:

$$\alpha_i = \frac{E_i^i - E_R^i}{E_i^i - E_s^i}, \quad (2)$$

where the superscript represents the particular mode in question. The relationship of the partial EACs to the total EAC is given by

$$\alpha_{TOT} C_v^{TOT} = \alpha_{trans} (C_v^{trans} + \frac{1}{2}R) + \alpha_{rot} C_v^{rot} + \alpha_{vib} C_v^{vib}, \quad (3)$$

where  $C_v^i$  is the constant volume heat capacity of the respective mode, and the additional  $\frac{1}{2}R$  is the streaming correction to the average energy of molecules striking a surface.<sup>1</sup>

The determination of partial EACs would be quite useful in understanding heterogeneous reaction dynamics. For example, an accurate knowledge of these accommodation coefficients is essential to detailed modeling of laser systems in which wall deactivation is thought to be significant.<sup>3</sup> The solution of problems in aerodynamics also relies on information about the energy accommodation of molecules in the upper atmosphere with aircraft surfaces.<sup>4</sup> There are indications that the course of certain heterogeneously catalyzed reactions<sup>5</sup> is affected by the partitioning of energy among the available molecular modes of the reactant. In each of these cases,

a knowledge of partial energy accommodation coefficients is essential in developing a detailed understanding of the dynamics of the gas surface interaction.

Theoretical and experimental determinations of these quantities have been made in recent years. For the most part, the theoretical calculations have dealt with the determinations of internal EACs for small diatomic molecules, such as H<sub>2</sub>.<sup>6,7</sup> A semiclassical approach was used by Hunter.<sup>8</sup> This approach correlates the internal accommodation coefficients to the adsorption or trapping of molecules on the surface. The most successful experimental technique, thus far, for determining partial EACs has been developed by Rosenblatt *et al.*<sup>9</sup> This technique takes advantage of the increase in the relative translational energy of molecules interacting with a vibrating surface. The results for the partial EACs obtained by this method show that  $\alpha_{trans} \geq \alpha_{rot} > \alpha_{vib}$  for small molecules. For large molecules (i.e., long chain alkanes), the EACs tend to increase toward unity and become more nearly equal.

In this paper, a new method for determining partial EACs is described. Vibrational EACs are determined for SF<sub>6</sub>, CH<sub>3</sub>F, cyclopropane, and methanol on a polycrystalline molybdenum surface. The excitation of vibrational energy levels by infrared laser radiation allows the effects of vibrational energy transfer to be more directly approached. This method is also applicable to work in a UHV system, which would allow a clean surface to be prepared and characterized prior to determination of the vibrational energy accommodation coefficient. The experimental method is described in the next section. A model developed to understand and evaluate the experimental data is discussed in Sec. III. Finally the results and their implications are discussed in Sec. IV.

## EXPERIMENTAL METHOD

In this experimental method, laser radiation is used to excite a molecule internally. The molecule travels to a solid surface and deposits a portion of its energy. The fraction deposited is the EAC. The energy deposited in the solid is monitored as a temperature change. The total energy available to be transferred is determined by gas phase energy transfer considerations.

<sup>a)</sup>Present address, Monsanto Company, P. O. Box 8, St. Peters, MO 63376.

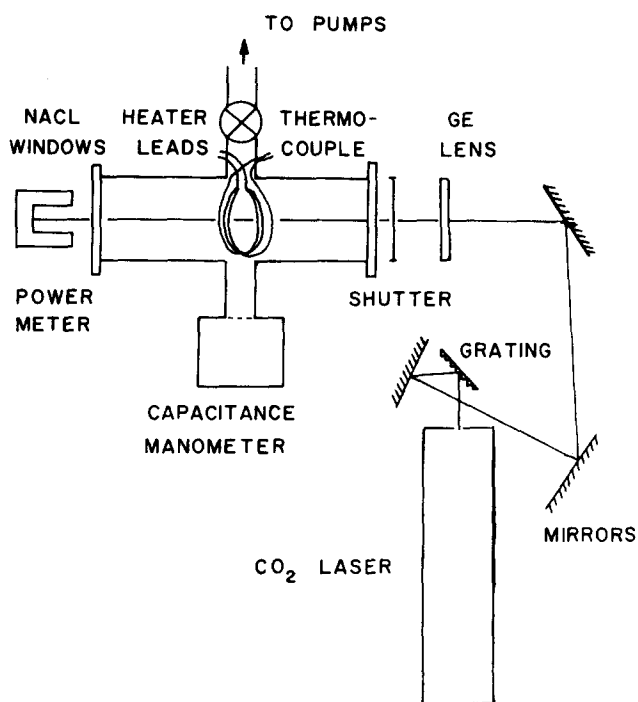


FIG. 1. Schematic diagram of experimental apparatus.

The experimental apparatus includes a gas handling system, a line-tunable cw CO<sub>2</sub> laser and the necessary electronics, and is illustrated in Fig. 1. The glass test chamber is fitted with NaCl windows at each end. The test cell could be evacuated to  $<10^{-5}$  Torr by means of a mechanical and oil diffusion pumping system. The leak rate was determined to be  $<2$  mT/h. The pressure could be determined by one of two capacitance manometers.

A polycrystalline molybdenum ribbon ( $7.6 \times 0.35 \times 0.002$ ) cm is used as the solid surface. It is supported by two electrical leads, such that it forms a circle which is centered on the cell axis. The electrical leads allow the filament to be heated and the thermoconductivity from the filament to be determined. The temperature of the filament is monitored by a chromel-constantan thermocouple and recorded by a strip-chart recorder.

A cw CO<sub>2</sub> laser (Coherent model 40) fitted with a Littrow-mounted grating which allows the laser to be tuned to the desired transition, is used to excite the molecule of interest. The power is monitored after the beam exits the test cell and enables the absorption coefficient of the gas to be determined. The 1 cm diameter beam is focused into the test cell by using a germanium lens (focal length—25 cm) with the focal point at the center of the metal filament.

The gases employed are SF<sub>6</sub>, CH<sub>3</sub>F, cyclopropane, and CH<sub>3</sub>OH. The gases were obtained from Matheson or Scientific Gas Products with a minimum purity of 99%. The methanol was spectral grade. The important properties of these materials are tabulated in Table I.

The experimental procedure involves the fixing of the laser's power and transition with the test cell evacuated. The test gas is used to purge the system several times

TABLE I. Pertinent properties of adsorbates used in this work.<sup>a</sup>

	SF <sub>6</sub>	CH <sub>3</sub> F	CH <sub>3</sub> OH	Cyclopropane
Excited by	P(20)	P(20)	P(18)	P(14)
CO <sub>2</sub> transitions	10.6 $\mu$	9.6 $\mu$	9.6 $\mu$	9.6 $\mu$
$K_{V-T}$ (s <sup>-1</sup> Torr <sup>-1</sup> )	8200	590	6900	8000
Purity (%)	99.99	99.0	99.5	99.0
Molecular weight (gm/mole)	146	34	32	42
$D$ (cm <sup>2</sup> Torr/s)	27.7	82.0	...	...

<sup>a</sup>References 10–17.

and finally introduced at the desired pressure. The temperature rise of the filament is monitored as the laser radiation passes through the cell, until a steady-state is achieved. The bulk temperature rise of the gas in the cell is determined by monitoring the pressure rise due to an increase in the translational energy of the molecules. This pressure rise is converted to a corresponding temperature rise by the ideal gas law. This procedure is repeated for other pressures ranging from  $10^{-3}$  to 1 Torr. A typical plot of temperature rise versus pressure is shown in Fig. 2.

## EXPERIMENTAL MODEL

In order to obtain the desired quantities (i.e., EACs), it is necessary to develop an experimental model which will allow one to determine the total energy available for transfer at the surface. This model must take into consideration the effects of cooling by ground state molecules, variations in the laser intensity as the beam passes through the cell, cell geometry effects, and the redistribution of vibrational energy into translational and rotational energy modes due to collisions in the gas phase.

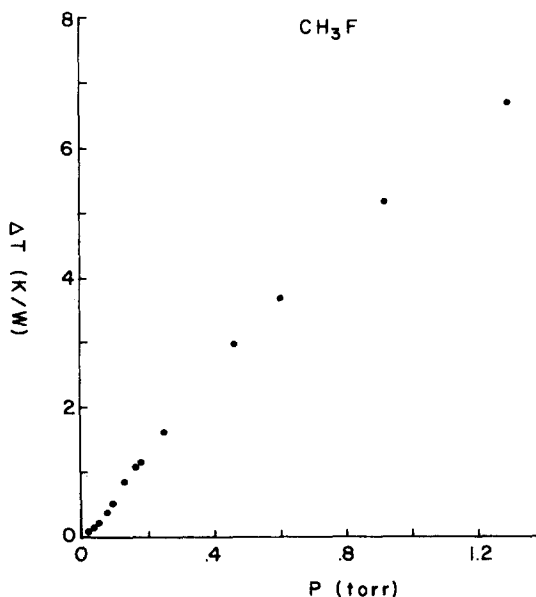


FIG. 2. Experimentally observed temperature rise of surface vs pressure.

The obvious starting point for such a model is

$$\frac{dQ}{dt} = C_p \frac{dT}{dt}, \quad (4)$$

where  $dQ/dt$  represents the net energy flux to the filament,  $C_p$  is the heat capacity of the filament, and  $dT/dt$  is the temperature change with respect to time. Since the data are collected under steady-state conditions:

$$\frac{dT}{dt} = 0. \quad (5)$$

This implies that the heat flux into the filament is equal to the heat flux out. The heat flux out is simply represented by the losses due to conduction through the leads, radiation, and conduction through the gas. The overall rate of heat loss is given by

$$\frac{dQ_{out}}{dt} = (K_{COND}^{(1)} + K_{RAD} + K_{COND}^{(g)})\Delta T \approx K_{TOT}\Delta T, \quad (6)$$

where the  $K$ 's represent the thermoconductivity coefficients for the individual loss mechanisms.  $K_{TOT}$  is measured experimentally.

The rate of heat input to the filament can be attributed to vibrationally or vibrationally, rotationally, and translationally excited molecules. It is impossible to separate the rotationally excited molecules from those which are translationally excited. The general approach to the modeling is to determine the number of molecules excited per second, the probability that an excited molecule will strike the filament and the probability that the molecule will be vibrationally excited.

The number of molecules excited per second is

$$\frac{dN_{EX}}{dt} = \frac{I_0}{h\nu} (1 - e^{-\sigma p L}), \quad (7)$$

where  $I_0$  is the incident laser power,  $\sigma$  is the measured absorption coefficient,  $p$  is the gas pressure,  $\nu$  is the frequency of the absorbed photon, and  $L$  is the path length of the cell. In this same vein, the number of molecules excited per unit distance per second is

$$\frac{d}{dX} \left( \frac{dN_{EX}}{dt} \right) = \frac{I_0}{h\nu} \sigma p e^{-\sigma p X}, \quad (8)$$

where  $X$  is the distance along the cell length.

The probability that the excited molecule will strike the surface is treated by assuming that the laser beam is a one-dimensional source along the cell axis. The probability is then the ratio of exposed molybdenum ribbon surface area to the surface area of a sphere with a radius equal to the distance between that point on the axis and the ribbon. This can be represented as

$$\bar{P}(X) = \frac{A}{4\pi(\sqrt{(X-B)^2 + C^2})^2} = \frac{A}{4\pi Y^2}, \quad (9)$$

where  $A$  is the exposed area of the filament,  $B$  is the distance between the entrance window and the filament,  $C$  is the radius of the filament, and  $Y$  is the distance between the excited molecule and the filament.

The third consideration involves the separation of vibrationally excited molecules from those which are translationally excited. The vibrationally excited mole-

cules are deactivated collisionally, therefore it is necessary to take into account the number of collisions the excited molecule experiences. Also, at pressure greater than  $10^{-2}$  Torr, diffusion plays a role in the molecular motion. By using data from gas phase energy transfer measurements it is possible to write an expression for the probability that a molecule is vibrationally deactivated:

$$\bar{P}_D(X, p) = \left[ \frac{K_{V-T} p}{Z} \right] \left[ Z \cdot \frac{Y^2}{2D} \right], \quad (10)$$

where  $K_{V-T}$  is the energy transfer rate,  $Z$  is the collision frequency, and  $D$  is the diffusion coefficient. The first term in the equation is the probability of deactivation per collision and the second is the number of collisions the molecule undergoes traveling to the filament. This expression can be simplified somewhat by separating out the pressure dependence of the diffusion coefficient to yield the following expression, where  $K_1$  combines  $K_{V-T}$  and the pressure independent diffusion coefficient:

$$\bar{P}_D(X, p) = K_1 Y^2 p^2. \quad (11)$$

In order to keep this probability bounded, an exponential form was chosen:

$$\bar{P}_D(X, p) = 1 - \exp(-K_1 Y^2 p^2). \quad (12)$$

The more relevant value is the probability of a molecule not being vibrationally deactivated. It is given by

$$\bar{P}_{ND}(X, p) = \exp(-K_1 Y^2 p^2). \quad (13)$$

By taking these three things into consideration it is now possible to arrive at an expression which defines the number of vibrationally excited molecules striking the filament per second. This value is given by

$$\bar{N}_v = \frac{I_0}{h\nu} \int_0^L \sigma p e^{-\sigma p X} \cdot \exp(-K_1 Y^2 p^2) \cdot \frac{A}{4\pi Y^2} \cdot dX. \quad (14)$$

A similar expression can be determined for the number of translationally excited molecules:

$$\bar{N}_T = \frac{I_0}{h\nu} \int_0^L \sigma p e^{-\sigma p X} \cdot [1 - \exp(-K_1 Y^2 p^2)] \cdot \frac{A}{4\pi Y^2} dX. \quad (15)$$

These integrals can be evaluated numerically by using experimentally determined quantities or values obtained from the literature. As an example, one finds that the number of vibrationally excited molecules should peak at approximately 100  $\mu$  for  $\text{CH}_3\text{F}$ .

An expression for the rate of heat input to the filament can be obtained assuming that all the energy put into the molecule is available for transfer at the surface:

$$\frac{dQ_{in}}{dt} = h\nu (\alpha_T \bar{N}_T + \alpha_V \bar{N}_V). \quad (16)$$

The contribution due to rotationally excited molecules is included in the translational term. The temperature rise of the filament can then be determined by equating the heat flux terms:

$$K_{TOT}\Delta T = h\nu (\alpha_T \bar{N}_T + \alpha_V \bar{N}_V). \quad (17)$$

Several points should be noted. First, this model assumes that molecular motion plays an important role

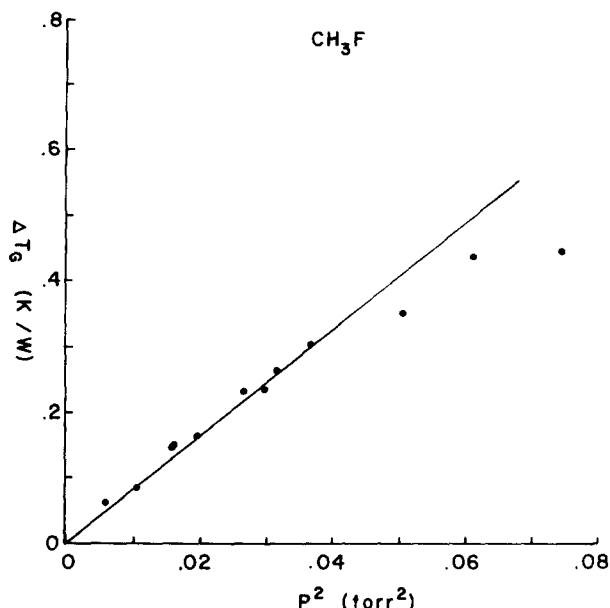


FIG. 3. Experimentally obtained temperature rise of gas vs pressure squared.

in the process even at high pressures (i.e.,  $p > 200 \mu$ ). At the higher pressures bulk thermoconductivity should become more important. Second, one must consider the effect of the cell wall on the rate of deactivation. These points are considered below.

The bulk temperature rise of the gas should be proportional to the number of translationally excited molecules created per second, excluding geometry effects. For sufficiently low pressures the expression becomes

$$\Delta T_G \approx \bar{N}_T h\nu \approx (I_0 \sigma p L) \left( K_1 p^2 \frac{A}{4\pi} \right) \approx \beta p^3, \quad (18)$$

where  $\beta$  is a constant. This implies that the bulk temperature rise is proportional to the pressure cubed. Figure 3 illustrates the behavior observed.  $\Delta T_G$  appears to be proportional to  $p^2$  instead of  $p^3$  as expected.

This type of behavior can be explained if one considers the effects of wall deactivation of the vibrationally excited molecules. This can be treated as follows. The number of vibrationally excited molecules being created per second is equal to the number of molecules being deactivated per second by the wall or by transfer of energy to translational modes:

$$\frac{dN_{EX}}{dt} = \frac{dN_{DEAC}}{dt} = \frac{dN_{DEAC}^V}{dt} + \frac{dN_{DEAC}^T}{dt}. \quad (19)$$

The number of molecules excited per second is found in Eq. (7). From the kinetic theory of gases the number of molecules deactivated by the wall is given by

$$\frac{dN_{DEAC}^V}{dt} = \frac{1}{4} n^* \bar{c} A \alpha'_V, \quad (20)$$

where  $n^*$  is the density of excited molecules,  $\bar{c}$  is the velocity,  $A$  is surface area of the cell, and  $\alpha'_V$  is the EAC for the cell wall. The deactivation rate for the transfer of energy to translational modes is given by

$$\frac{dN_{DEAC}^T}{dt} = n^* Z \bar{P}_D V, \quad (21)$$

where  $Z$  is the collision frequency of the molecules,  $\bar{P}_D$  is the probability of deactivation per collision, and  $V$  is the volume of the cell. This term is also proportional to the bulk temperature rise in the gas. If the pressure dependency of the collision frequency is considered the equation becomes

$$\frac{dN_{DEAC}^T}{dt} = n^* Z' \bar{P}_D V, \quad (22)$$

making the proper substitutions one arrives at an expression for  $\Delta T_G$ :

$$\Delta T_G \approx \frac{(I_0/h\nu)(1 - e^{-\sigma p L})Z' p \bar{P}_D V}{\frac{1}{2} \bar{c} A \alpha'_V + Z' p \bar{P}_D V}. \quad (23)$$

At low pressure this expression can be simplified to

$$\Delta T_G \approx \frac{K_2 p^2}{1 + K_3 p}, \quad (24)$$

where  $K_2$  and  $K_3$  are constants. This expression yields results equivalent to those shown in Fig. 3. The original derivation of the pressure cubed dependence, however, is a valid result. For thermal lensing studies the temperature of the gas along the laser beam yields this pressure cubed dependence.<sup>18</sup>

The second observation is that the temperature rise of the ribbon due to vibrationally excited molecules can be separated from the temperature rise due to translationally excited molecules. Since at high pressure,  $\Delta T_G$  is proportional to the temperature rise of the ribbon due to translationally excited molecules, the following expression can be realized:

$$\Delta T_V = \Delta T - \gamma \Delta T_G, \quad (25)$$

where  $\Delta T_V$  is the temperature rise due to vibrational

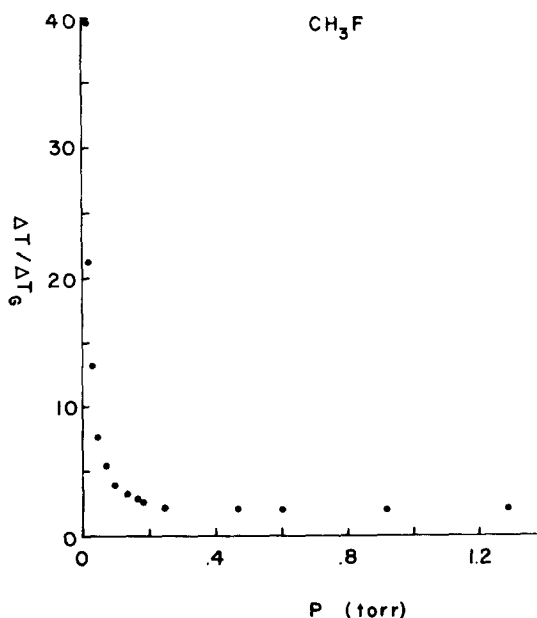


FIG. 4.  $\Delta T/\Delta T_G$  vs pressure.  $\gamma$  is obtained from constant value of  $\Delta T/\Delta T_G$  at high pressure.

energy transfer and  $\gamma$  is a constant obtained from the plot of  $\Delta T/\Delta T_0$  versus pressure as shown in Fig. 4.

A third observation is that at low pressures the expression for determining  $\alpha_v$  can be greatly simplified in light of the preceding observations:

$$K_{TOT}\Delta T_v = \alpha_v I_0 \sigma p L \bar{P}, \quad (26)$$

where  $\bar{P}$  is the geometry factor. Figure 5 illustrates the data obtained for  $\text{CH}_3\text{F}$ . The slope of the low pressure portion of this plot allows one to directly extract  $\alpha_v$ , since  $I_0$ ,  $\sigma$ ,  $p$ ,  $L$ , and  $\bar{P}$  are all known. Vibrational EACs for the molecules used in this study obtained in this manner are listed in Table II.

## DISCUSSION

Rosenblatt has suggested a correlation between partial EACs and the heat of vaporization of the adsorbing gas.<sup>20</sup> As the heat of vaporization increases, the residence time of the adsorbate on the surface increases. This results in partial EACs which increase with increasing heat of vaporization. The vibrational EACs obtained in this study also follow this correlation.

This correlation suggests that under the conditions of the present study, and in Rosenblatt's work, the metallic substrate-adsorbate interaction has little to do with the collisional accommodation of energy with the surface. The adsorbate-adsorbate interaction, as evidenced by the adsorbate heat of vaporization appears to be the factor determining energy accommodation under these conditions. This seems reasonable, since in this work as well as in Rosenblatt's, no effort was made to ensure interaction between the adsorbate and a clean metallic substrate. Under the conditions of this work, the energy accommodation is likely to be trapping dominated.

Extension of this work to include clean, characterized

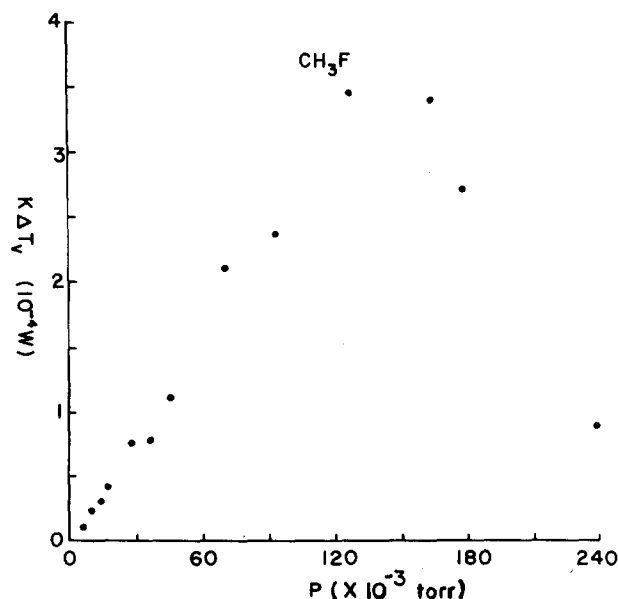


FIG. 5.  $K\Delta T_v$  vs pressure.  $\alpha_v$  is obtained from the low pressure slope of this plot.

TABLE II. Vibrational energy accommodation coefficients obtained in this work.

	$\alpha_v (\pm 0.1)$	$\Delta H_v$ (kcal/mole) <sup>a</sup>
$\text{CH}_3\text{F}$	0.49	4.2
Cyclopropane	0.53	4.8
$\text{SF}_6$	0.61	5.6
$\text{CH}_3\text{OH}$	0.81	8.6

<sup>a</sup>Reference 19.

substrates is certainly possible with this technique, using a UHV cell, and standard surface characterization tools. Such measurements are currently underway in our laboratory. In principle, the technique is applicable to any adsorbate which can be excited by absorption of laser photons. A wide range of gas-surface vibrational energy accommodation coefficients could be obtained in this way.

A new method for determining vibrational EACs has been presented in this paper, using laser excitation of molecules in the gas phase, followed by direct measurement of energy deposited in a surface to obtain the vibrational EAC. This method has been applied to the interaction of  $\text{SF}_6$ ,  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{OH}$ , and cyclopropane with an uncharacterized polycrystalline molybdenum surface. Values of  $\alpha_v$  obtained increase with increasing heat of vaporization of the adsorbate, and are in reasonably good agreement with the measurements of Rosenblatt and coworkers, using the vibrating surface method.

## ACKNOWLEDGMENT

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- <sup>1</sup>F. O. Goodman and H. Y. Wachman, *Dynamics of Gas-Surface Scattering* (Academic, New York, 1976).
- <sup>2</sup>F. O. Goodman, *Prog. Surf. Sci.* **5**, 261 (1975).
- <sup>3</sup>K. G. Anlauf, D. S. Horne, R. G. Macdonald, J. C. Polanyi, and K. B. Woodall, *J. Chem. Phys.* **57**, 1561 (1972).
- <sup>4</sup>B. E. Halpern and D. E. Rosner, *J. Chem. Soc. Faraday Trans. 1* **74**, 1883 (1978).
- <sup>5</sup>R. Herman and R. J. Rubin, *J. Chem. Phys.* **29**, 591 (1958).
- <sup>6</sup>P. Feuer, *J. Chem. Phys.* **39**, 1311 (1963).
- <sup>7</sup>A. A. Pyarnpuu, *Soviet Phys. Tech. Phys.* **12**, 1397 (1968).
- <sup>8</sup>T. F. Hunter, *J. Chem. Phys.* **51**, 2641 (1969).
- <sup>9</sup>C. Draper and G. Rosenblatt, *J. Chem. Phys.* **69**, 1465 (1978).
- <sup>10</sup>J. I. Steinfeld, I. Burak, D. G. Sutton, and A. V. Nowak, *J. Chem. Phys.* **52**, 5421 (1970).
- <sup>11</sup>C. L. O'Connor, *J. Acoust. Soc. Am.* **26**, 361 (1954).
- <sup>12</sup>G. T. Fujimoto and E. Weitz, *Chem. Phys.* **27**, 65 (1978).
- <sup>13</sup>E. Weitz and G. Flynn, *J. Chem. Phys.* **56**, 6060 (1972).
- <sup>14</sup>G. A. Miller and R. D. Bernstein, *J. Phys. Chem.* **63**, 710 (1959).
- <sup>15</sup>F. R. Grabner and G. Flynn, *J. Chem. Phys.* **60**, 398 (1974).
- <sup>16</sup>R. A. Ruehrwein and T. M. Powell, *J. Am. Chem. Soc.* **68**, 1063 (1946).
- <sup>17</sup>T. Batuecas, *J. Chim. Phys.* **29**, 269 (1932).
- <sup>18</sup>W. H. Thomason, D. C. Elbers, and J. D. Macomber, *J. Appl. Phys.* **49**, 5382 (1978).
- <sup>19</sup>*Handbook of Chemistry*, edited by N. A. Lange (McGraw-Hill, New York, 1969).
- <sup>20</sup>G. Rosenblatt, *Acc. Chem. Res.* **14**, 42 (1981).