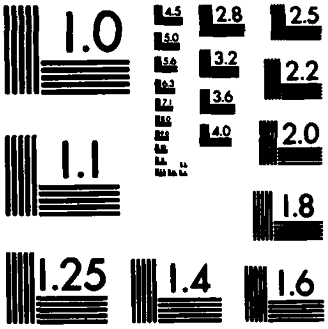
AD-A133 449 INTERACTIONS OF VIBRATIONALLY EXCITED MOLECULES WITH 1/1
SOLID SURFACES(U) CORNELL UNIV ITHACA NY
P L HOUSTON ET AL. 09 SEP 83 ARO-17349.2-CH
UNCLASSIFIED DAAG29-80-K-0020 F/G 7/4 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

ARD 17349.2-CH

AD-A133449

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER

2. GOVT ACCESSION NO. AD-A133449

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)

Interactions of Vibrationally Excited Molecules with Solid Surfaces

Final Report

5. TYPE OF REPORT & PERIOD COVERED

(12)

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)

Paul L. Houston and R. P. Merrill

8. CONTRACT OR GRANT NUMBER(s)

Daag29-80-0020 K

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Cornell University
Ithaca, NY 14853

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS

U. S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27709

12. REPORT DATE

Sept 9, 1983

13. NUMBER OF PAGES

26

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)

Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DTIC
S ELECTE D
OCT 12 1983
A

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Carbon Dioxide, Carbon Monoxide, Silver, Nickel, Tungsten, Energy Transfer, Vibrational Relaxation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

please see continuation sheet...

83 10 12 012

DTIC FILE COPY

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20 Abstract

The interaction of gas-phase molecules with solid surfaces is of importance to heterogeneous catalysis, corrosion, air filtration, pollution control, and chemical deactivation. Our research group has recently obtained some of the first direct measurements of the probability for vibrataional deactivation during gas-solid collisions. A pulsed infrared laser is used to excite CO or CO_2 vibrationally under conditions where the predominant cause of deactivation is due to the gas-surface collision. The probability of relaxation is then monitored by observing the time-dependent decay of infrared fluorescence from the excited molecules. Results for CO_2(001) show that the deactivation probability is 0.22 for collisions with a stainless steel surface, 0.16 for silver, and 0.20 for nickel. The probability for deactivation on the silver surface is invariant with surface temperature in the range from 298 K to 473 K. On the other hand, the probability for deactivation of the (10^01) combination band of CO_2 is 0.72 at room temperature and decreases with increasing temperature. Results for CO(v=2) indicate that the deactivation probability for this molecule on Ag is 0.33 at room temperature and that the probability also decreases significantly with increasing temperature. Finally, thermally averaged accomodation coefficients have been measured for helium and CO_2 on tungsten. For CO_2 the accomodation coefficient is 0.04.

INTERACTIONS OF VIBRATIONALLY EXCITED MOLECULES WITH SOLID SURFACES

P. L. HOUSTON AND R. P. MERRILL

September 8, 1983

U. S. ARMY RESEARCH OFFICE

CONTRACT DAAG29-80-0020

CORNELL UNIVERSITY

Table of Contents

List of Tables, Figures, and Appendices

FINAL REPORT

Interactions of Vibrationally Excited Molecules with Solid Surfaces

P. L. Houston and R. P. Merrill
Department of Chemistry and School of Chemical Engineering
Cornell University
Ithaca, New York 14853

A. Statement of Research Problem

Little is currently known about the manner in which the vibrational modes of gaseous molecules couple with a solid surface during gas-solid collisions. This is a report of some preliminary measurements on the deactivation of vibrationally excited molecules as a result of their collision with a surface. The molecules are excited by absorption of a pulsed laser, while their population is monitored through their infrared fluorescence. The research program includes studies as a function of surface composition over a range of temperatures on a variety of solid surfaces with several gas molecules. Results are given here for the deactivation of $CO_2(00^01)$, $CO_2(10^01)$, and CO(v=2) on silver surfaces from room temperature up to 200°C and for the deactivation of $CO_2(00^01)$ on nickel and stainless steel surfaces at room temperature. In addition, accomodation coefficients at thermal equilibrium have been measured for He and CO_2 on tungsten.

B. Summary of the Most Important Results

1. The Results For Carbon Dioxide (00^01)

A typical fluorescence decay curve obtained from our experimental apparatus is shown in Fig. 1. In this experiment,[1] the surface was silver, the temperature was 298 K and the pressure of carbon dioxide was 10.5 mtorr. The signal (dots) was the result of averaging 5000 laser pulses. The solid line in Fig. 1 is a least squares fit of a single exponential to the data.

The vibrational deactivation probability was monitored as a function of pressure, temperature and surface composition. The pressure dependence of the observed fluorescence decay rate is shown in Fig. 2 for collisions with a stainless steel surface at a temperature of 298 K. Similar results were obtained for deactivation on nickel and silver. In the case of the silver surface, the temperature was varied from 298 to 473 K for a carbon dioxide pressure of 10-15 mtorr. The probability for deactivation on silver was found to be 0.17 ± 0.03 independent of temperature.

In the current experimental apparatus, there is no facility for determining directly the type and amount of impurity adsorbed on the surface, so that it is possible only to speculate about their nature. The adsorption probability of CO and hydrogen, the main components in the residual gas of the vacuum system, has been shown to be vanishingly small on silver at room temperature and above by the use of atomic helium scattering.[2] Carbon dioxide is also known not to be adsorbed on silver.[3] The CO_2 contaminants most likely to adsorb on silver are oxygen and hydrocarbons. The hydrocarbon level was reduced to immeasurable levels by the trapping system. The sticking probability of oxygen on silver is reported to be 3×10^{-3}.[4] A typical experiment in our system required an exposure of about 10 torr-seconds, which would produce only about 1% of an oxygen monolayer. In summary, the silver surface should be relatively clean during the time of our experiment; the greatest contamination possible would be a small fraction of a monolayer of oxygen.

For the experiments on nickel surfaces, since the film was deposited by heating nickel carbonyl at 145°C and since the CO desorption temperature from nickel is 160°C,[5] it is expected that the surfaces should initially be covered with a monolayer of adsorbed CO. As in the silver experiments, oxygen is the contaminant most likely to interact with the surface. Oxygen is known to adsorb dissociatively on nickel but it will not displace CO.[6] Also, adsorbed CO and oxygen atoms are known to react, so any oxygen present on the surface either from oxygen adsorption of CO dissociation should be removed rapidly from the surface. Surface carbon might result from CO dissociation or from the carbonyl decomposition reaction. In summary, the nickel surfaces were most likely covered with at least a monolayer of CO and possibly with some carbon.

The results for the different surfaces and for the temperature ranges of our study are summarized in Table I. The CO_2 is seen to deactivate in 4-5 collisions on either nickel or silver. The deactivation probability is rather independent of temperature.

Table I: CO_2 Deactivation Probabilities

Surface	T (K)	β* (±0.03)	Comments
Ag	298	0.16	Fresh Ag
Ag	298	0.15	7 hrs. old
Ag	298	0.13	1 day old
Ag	473	0.18	1 hr. old
Stainless	298	0.22	
Ni	298	0.20	Fresh Ni

*Corrected for effusion

2. The Results for Carbon Dioxide (10^01)

Carbon Dioxide was excited to its (10^01) level using a pulsed, tunable infrared source generated by the difference frequency between a tunable dye laser and the Nd:YAG fundamental. Relaxation from this level was monitored in a manner similar to that used for the (00^01) level. At room temperature, the probability for deactivation at a silver surface was found to be 0.72. The deactivation probability dropped with increasing temperature as shown in Fig. 3.

3. The Results for Carbon Monoxide (v=2)

CO was excited to its second vibrational level using the same tunable infrared source. Relaxation of this level by collisions with a silver surface was monitored by observation of the $2\rightarrow1$ infrared fluorescence near 5 µm. A deactivation probability of 0.33 was obtained at room temperature, and the probability was found to decrease with increasing temperature, as shown in Fig. 4.

4. Thermally Averaged Accomodation Coefficients

Two different experimental methods have been proposed to obtain thermal accomodation coefficients: the slip flow "temperature jump" method and the free-molecule flow "low pressure" method. In our apparatus shown in Figs. 5 and 6, the accomodation coefficient α is measured using the "low pressure" method. A 5 mil tungsten wire is placed along the central axis of the inner cylindrical container. The wire is heated by passing electrical current through it, and the electrical resistance of the wire and current flow through wire are monitored. The measured resistance is a direct indication of the wire temperature and the heat flow from the wire is found from the measured current and resistance (i.e., $J = I^2R$). The gas pressure within the annular space between th wire and the inner cylinder is maintained at a sufficiently low value that the mean free path is considerably larger than the gap size. Thus free molecule flow conditions are ensured. The average power loss J per unit area of the heated wire is related to the α by:

$$\alpha = \frac{(2\pi M_g k T_g)^{1/2}}{(C_v + 1/2k)} \cdot \frac{J}{P\Delta T} \qquad (3)$$

where

M_g = molecular weight of sample gas
T_g = wall temperature
ΔT = $T_{wire} - T_g$
P = gas pressure

Figure 6 shows the detail on how the test wire, its electrical connections and the misch-metal getter source are mounted within the cylinder.

The UHV system to which the reaction cell is attached has a titanium sublimation pump and a 110 liter/sec ion pump. Each pump can be separated from the reaction cell by a four inch or one and one-half inch valve, respectively. The system is also equipped with a mass spectrometer for residual gas analysis if necessary and is capable of pressures of 10^{-10} torr and below.

To obtain α for tungsten, the wire (main filament) is flashed to over 2800°C for about two hours, during which time its electrical resistance reaches a stable value. Then the misch-metal evaporator filament is heated to the evaporation temperature in 2-3 Torr of helium which has been processed through charcoal and molecular sieves. This deposits a film of misch-metal getter on the cylinder walls, but the main filament is kept too hot to permit deposition on the test surface.

Before each measurement of α the main filament is flashed briefly (20 sec) and then adjusted to operating temperature. Current and voltage readings are taken every ten minutes until a steady state is achieved. Usually 30 to 40 minutes are required. Radiation losses are made at pressures of 10^{-10} Torr and subtracted from the data for each run. Table II shows α values for helium at gas temperatures of 77°K and 298°K for three different pressures. The values of α are in good agreement with Thomas' data[7] at 77°K and are a bit higher at room temperature. This suggests that our gases are sufficiently clean and demonstrates the suitability of the apparatus.

Accomodation coefficients for CO_2 on tungsten have also been measured. At 77°K values near 0.04 have been measured on tungsten wires giving .01 and less for He. This value is approximately equal to that of Ne reported by Thomas and significantly lower than Thomas' values for Ar or Kr[7], which have adsorption energies and masses more representative of CO_2 than Ne. To our knowledge there are no other measurements of the thermal accomodation coefficients for CO_2. In any case it can be concluded from this that the tungsten surfaces are at least as clean in the CO_2 experiment as they are in the He work. Also, this CO_2 work gives the datum to which vibrationally excited CO_2 accomodation coefficients can be compared in order to evaluate the transfer of vibrational energy from laser excited CO_2 into the metal substrate.

5. Interpretation of Results

The major finding of this research is that the probability for vibrational deactivation at solid surfaces is much larger than might have been expected. The thremally averaged accomodation coefficient for CO_2 on tungsten is only 0.04, while the accomodation of CO and CO_2 vibrational energy on silver is 0.2-0.7. Several theories can be proposed to account for such high probabilities of vibrational relaxation. The transition dipole in the vibrationally excited molecule might interact with the conduction electrons in the metal, the vibrational deactivation might take place by a mechanical interaction with the surface in such a way that the vibrational energy is converted to translation or rotation, or the vibrating molecule might become trapped long enough at the surface to lose its energy either to phonon modes of the surface or by one of the previously mentioned processes. A more complete discussion of these possibilities is provided in Appendix 1, Section IVC.

Table II: Accomodation Coefficient Values for Helium

T	3 mmtorr	10 mmtorr	30 mmtorr
77°K	0.009	.008	.01
298°K	.0173	.0284	.0271

C. List of Publications and Technical Reports

1. J. Misewich, C. N. Plum, G. Blyholder, P. L. Houston, and R. P. Merrill, J. Chem. Phys. 78, 4245 (1983).

2. C. N. Plum, J. A. Misewich, G. Blyholder, R. P. Merrill, and P. L. Houston, "Laser Studies of Vibrational Energy Transfer at Gas-Solid Interfaces," Abstract COLL-109, ACS Meeting, Atlanta, March 29-3, 1981.

3. V. A. Apkarian, R. J. Jamers, P. L. Houston, R. P. Merrill, and J. Misewich, "Interactions of Vibrationally Excited Molecules with Solid Surfaces," Abstrat PHYS-16, ACS Meeting, Washington, August 29, 1983.

4. J. Misewich, P. L. Houston, and R. P. Merrill, "Vibrational Relaxation of $CO_2(10^01)$ and CO(v=2) at Silver Surfaces," manuscript in preparation.

C. Scientific Personnel

Name	Position	Support
R. P. Merrill	Professor	Cornell, ARO
P. L. Houston	Assoc. Prof.	Cornell, ARO
C. Plum	Postdoc	ARO
G. Blyholder	Visiting Prof.	U. Arkansas, ARO
J. Misewich†	Grad Student	ARO
W. Avrin†	Grad Student	ARO
H-S. Shin	Grad Student	Korean Fellowship, ARO

†Ph.D. Expected Fall, 1983.

Bibliography

1. J. Misewich, C. N. Plum, G. Blyholder, P. L. Houston, and R. P. Merrill, J. Chem. Phys. 78, 4245 (1983), included as Appendix I.

2 R. Sau and R.P. Merrill, Surf. Sci. 34, 268 (1973).

3 A.W. Czanderna, J. Colloid and Interf. Sci. 22, 482 (1966).

4. M. Bowker, M.A. Barteau and R.J. Madix, Surf. Sci. 92, 528 (1980).

5. W. Erley and H. Wagner, Surf. Sci. 74, 333 (1978).

6. M. Oku and C. R. Bundle, J. Vac. Sci. Technol. 20, 532 (1982).

7. L. B. Thomas, in Fifth Symposium, Rarefied Gas Dynamics, Academic Press (1967), p. 155.

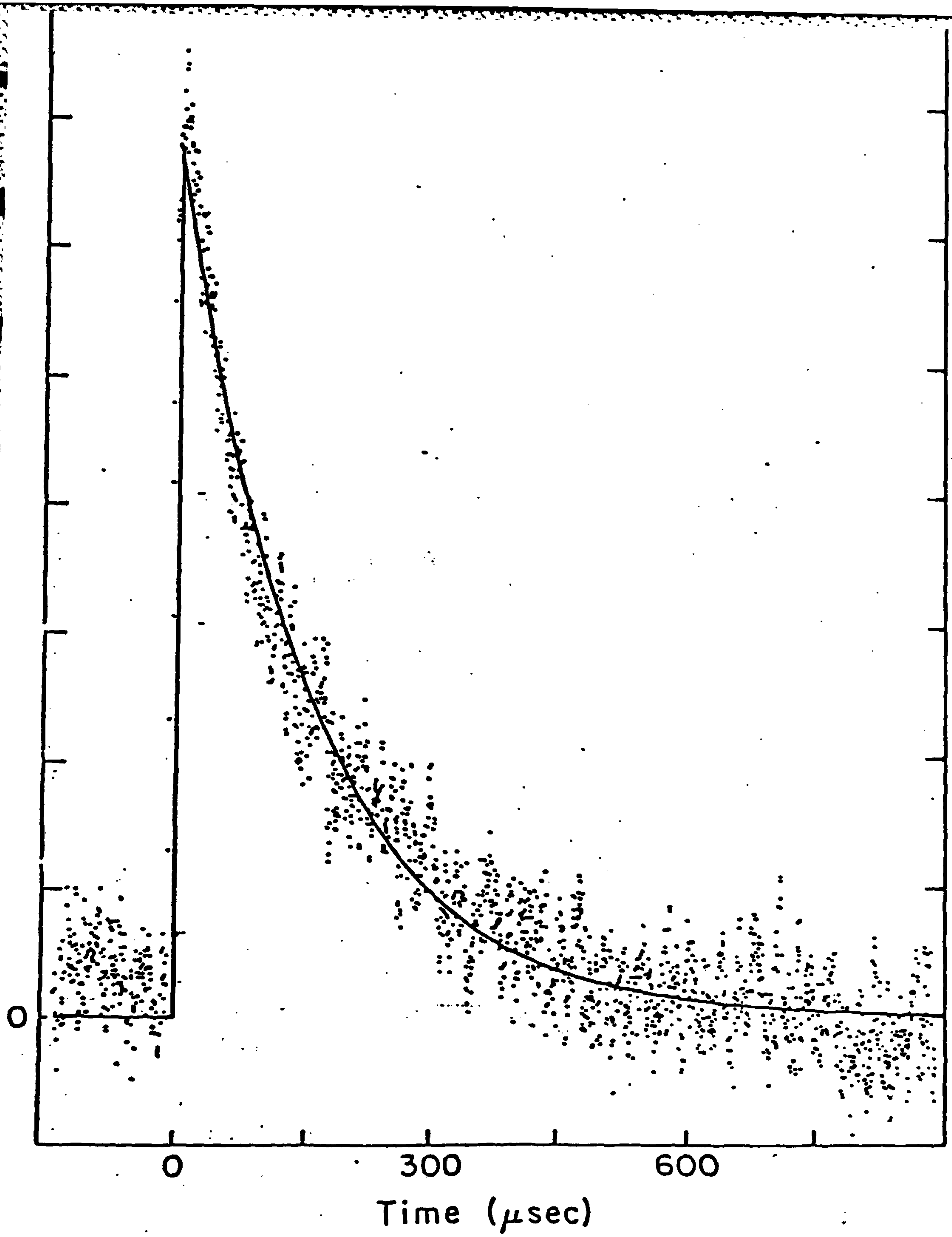


Figure 1. Typical Fluorescence Signal for CO_2 deactivation on Silver Surfaces.

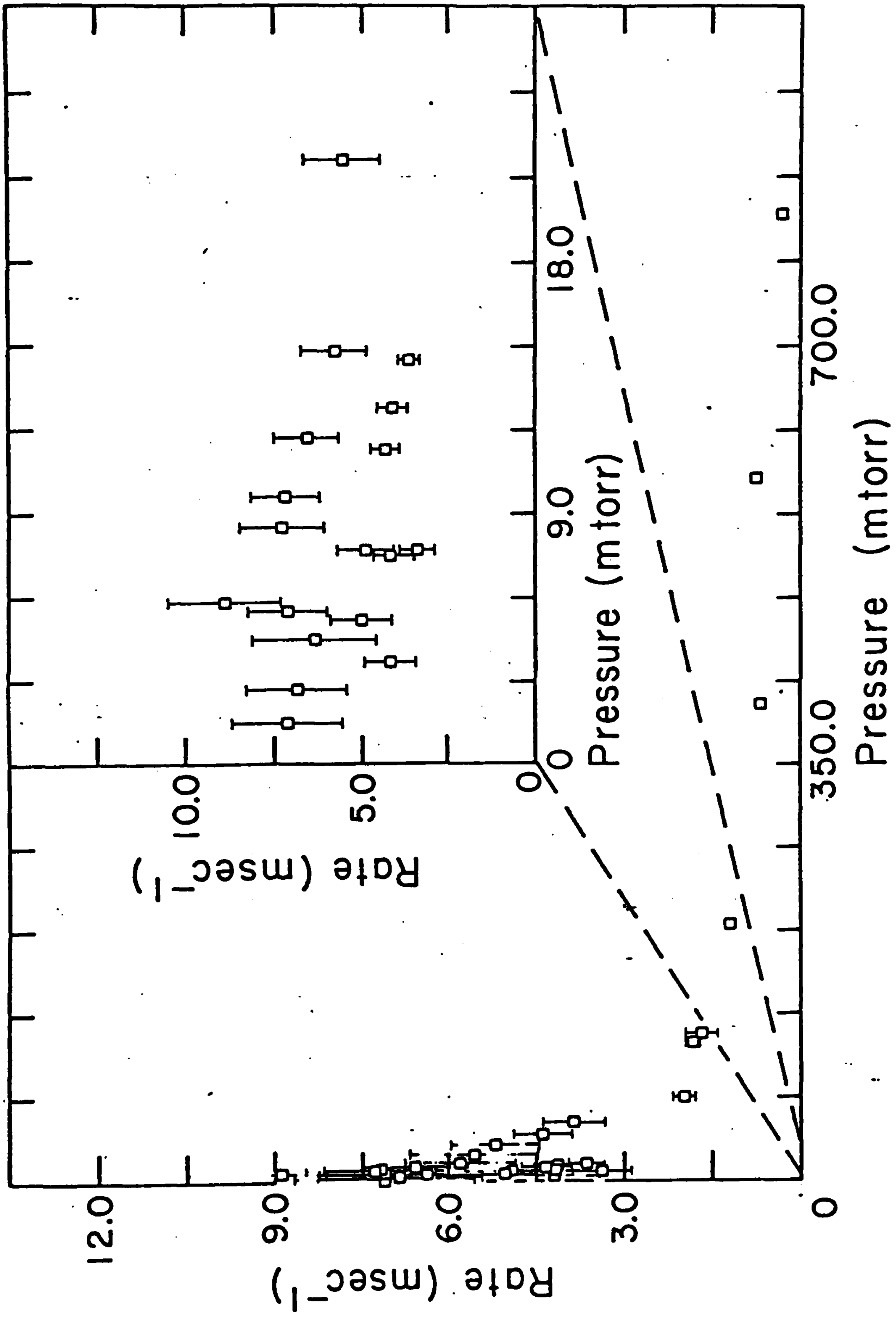


Figure 2. Pressure Dependence of Fluorescence Deactivation Rate

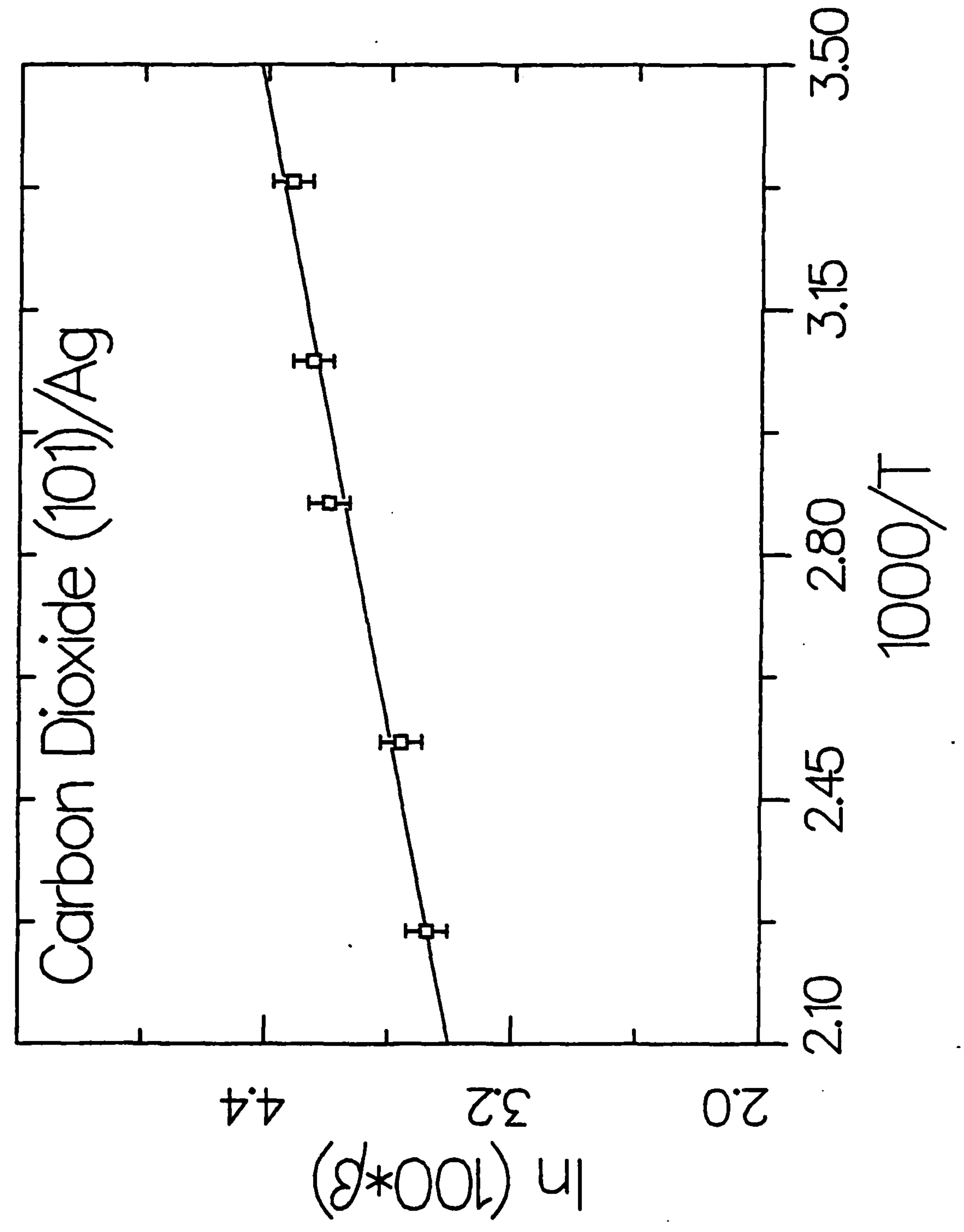


Figure 3. Temperature dependence of the deactivation probability for $CO_2(101)$ on silver.

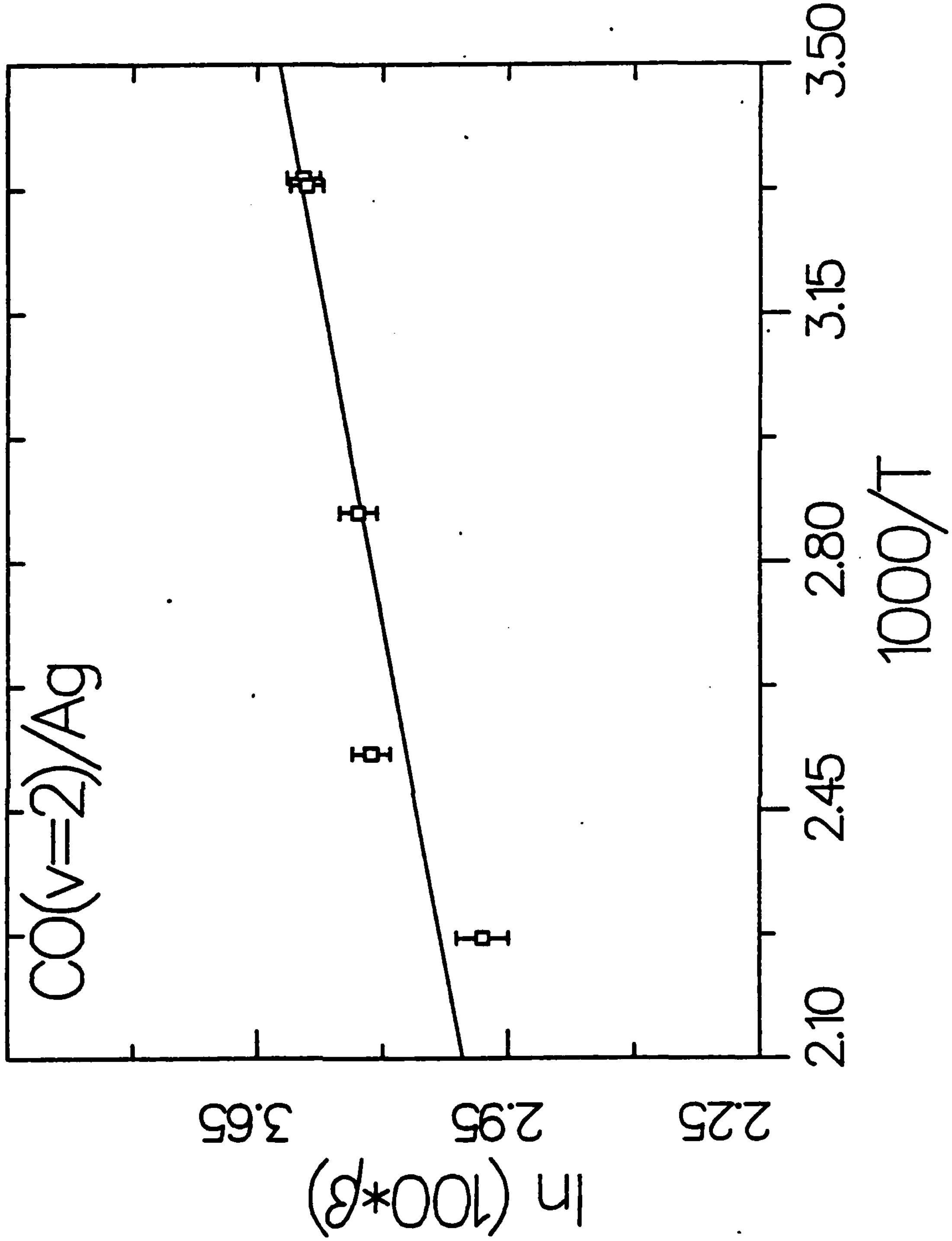


Figure 4. Temperature dependence of the deactivation probability for CO(v=2) on silver.

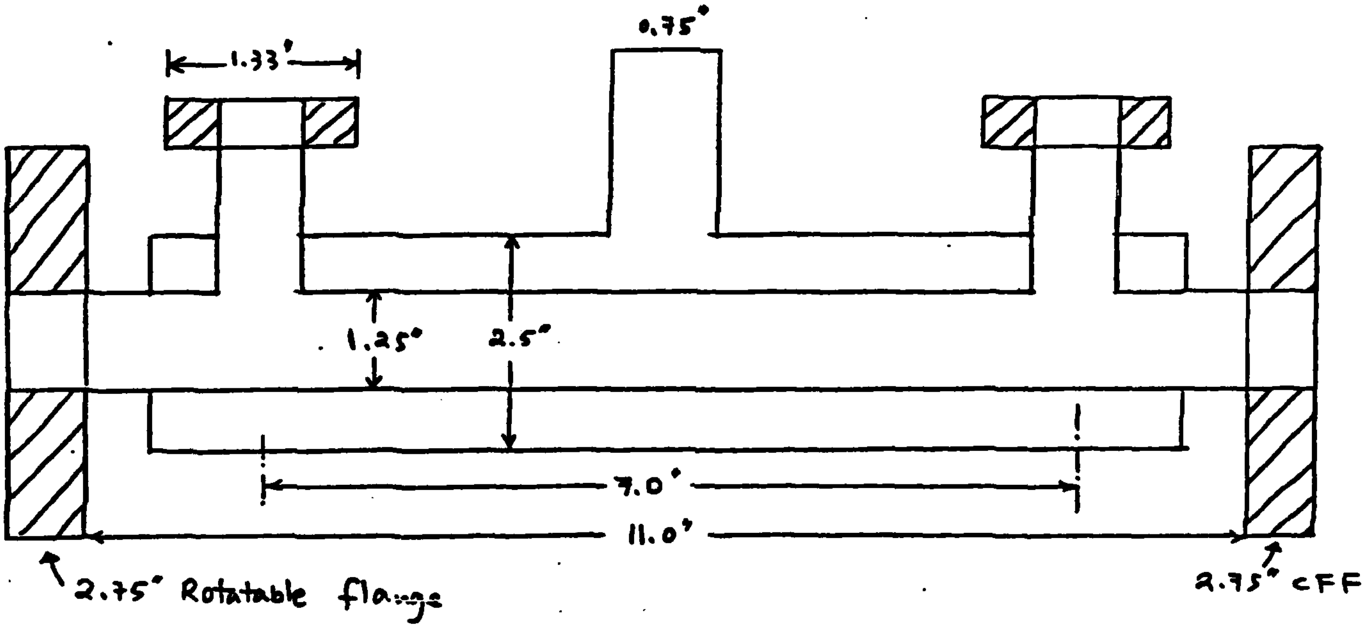


Figure 5. Schematic Diagram of Reaction Cell

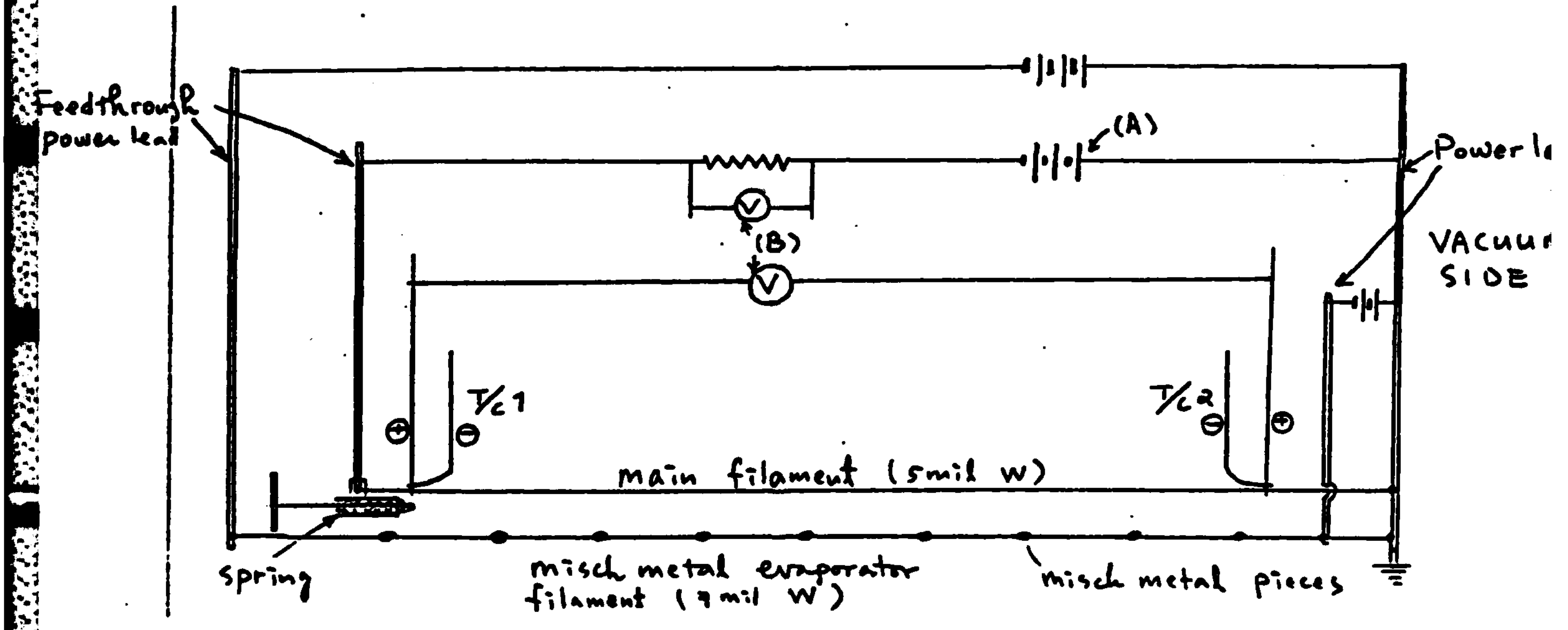


Figure 6. Electrical connections for reaction cell
(A) Kepco ATE 15-25 power supply
(B) LEEDS-Northrup K-3 Potentiometer

Vibrational relaxation during gas–surface collisions

J. Misewich, C. N. Plum,[a] G. Blyholder,[b] and P. L. Houston[c]

Department of Chemistry, Cornell University, Ithaca, New York 14853

R. P. Merrill

School of Chemical Engineering, Cornell University, Ithaca, New York 14853

(Received 13 August 1982; accepted 15 October 1982)

The probability for deactivation of $CO_2(001)$ has been found to be 0.22 for collisions with a stainless steel surface, 0.16 for silver, and 0.20 for nickel. The probability for deactivation on the silver surface was invariant with surface temperature in the range from 298 to 473 K. A pulsed CO_2 laser was used to excite the CO_2, while the population of vibrationally excited molecules was monitored by observing their infrared fluorescence at 4.3 μm.

I. INTRODUCTION

Little is currently known about the manner in which the vibrational modes of gaseous molecules couple with a solid surface during gas–solid collisions. This is a report of some preliminary measurements on the deactivation of vibrationally excited molecules as a result of their collision with a surface. The molecules are excited by absorption of a pulsed laser, while their population is monitored through their infrared fluorescence. The research program includes studies as a function of surface composition over a range of temperatures on a variety of solid surfaces with several gas molecules. Results are given in this paper for the deactivation of $CO_2(001)$ on silver surfaces from room temperature up to 200 °C and on stainless steel and nickel surfaces at room temperature.

Laser techniques are increasingly being used to study the dynamics of gas–solid interactions. Recent studies have applied lasers to investigate the accommodation of rotational energy in collisions of NO with Ag(111)[1,2] and Pt(111),[3] and of CO[4] and HF[5] with LiF (001). In addition, the dynamics of NO desorption from Ru (001),[6] OH desorption from Pt,[7] and NH desorption from Pt and Fe[8] have been investigated. In all of these studies the laser has been used to detect the final states which result from the gas–surface encounter. By contrast, in the investigation reported here the laser is used to prepare the initial state of the reactant. Carbon dioxide is excited to the (001) level by absorption of radiation from a pulsed CO_2 laser. Its vibrational relaxation on collision with metal surfaces is monitored by observing the decay of infrared fluorescence.

The surface deactivation probability for $CO_2(001)$ has been measured previously to be 0.18–0.40 on Pyrex.[9–11] and has been found not to depend on variations in surface composition ranging from Pyrex to brass, Mylar, or Teflon.[11] The absence of a dependence on surface composition was likely due to contaminants, since no attempt to prepare the surface under clean conditions was made. In the current study the surface deactivation probability was found to be 0.22 for stainless steel, 0.16 for silver, and 0.20 for nickel. Varying the surface temperature over the range from 298 to 473 K produced no observable effect on the silver deactivation probability.

II. EXPERIMENTAL

A specially designed experimental cell for our studies is illustrated in Fig. 1. It is attached to an ultra high vacuum system pumped by an ion pump and a titanium sublimation pump with a base pressure of 8×10^{-11} Torr. The 10.6 μm output of a pulsed CO_2 laser is focused through an aperture in a gold coated mirror located inside the cell. The laser radiation passes down the center line of the cylinder and excites carbon dioxide molecules from the (100) level to the (001) level. The population of $CO_2(001)$ is monitored by collecting 4.3 μm fluorescence arising from the $(001)\rightarrow(000)$ transition. Parallel rays are reflected by the gold coated mirror, collected with an $f/1$ CaF_2 lens, and detected by a 4 K mercury doped germanium semiconductor element. The fluorescence signal is then digitized using a Biomation 805 transient recorder and fed to an LSI-11 computer for signal averaging to enhance the signal-to-noise ratio. The data are fit to a single exponential decay using an iterative least squares fitting technique. A schematic diagram of the experimental apparatus is shown in Fig. 2.

For the experiments on silver, a tungsten filament wrapped with silver is mounted in the apparatus so that it is slightly off center but parallel to the walls of the cylinder. By heating the filament electrically, silver can be rapidly evaporated onto the walls of the cylinder. During evaporation the maximum pressure recorded in the UHV system is 7×10^{-8} Torr. The deactivation measurements were completed immediately after deposition of the film.

---

[a] Present address: Department of Chemistry, University of California, Riverside, California 92521.

[b] Permanent address: Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701.

[c] Camille and Henry Dreyfus Teacher-Scholar.

0021-9606/83/064245-05$02.10

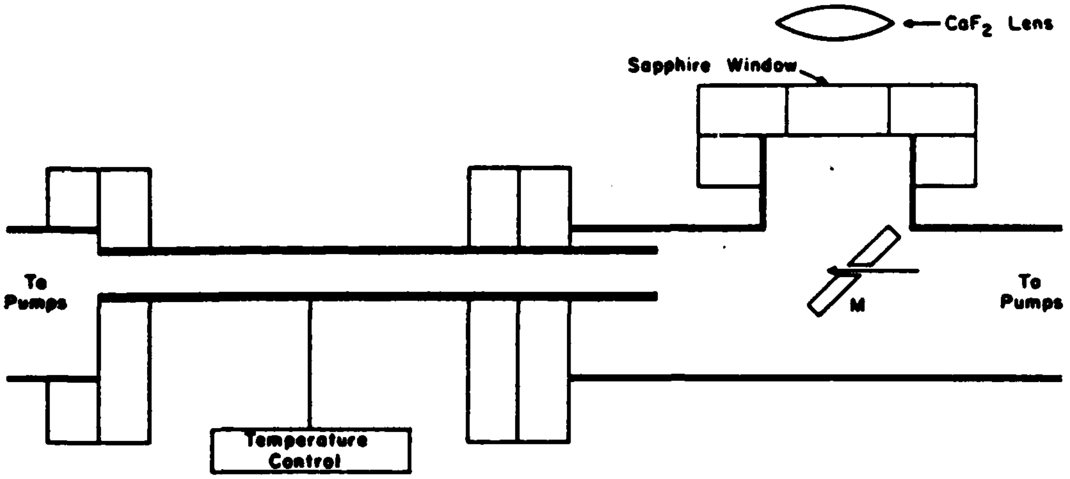


FIG. 1. Detail of experimental cell used for studies of vibrational relaxation during gas–solid collisions.

For the experiments with nickel, the nickel film was deposited over the internal surface of the cylinder by heating 300 Torr of $Ni(CO)_4$ to 145 °C.

III. RESULTS

Figure 3 displays a typical fluorescence decay curve obtained from our apparatus. For this experiment the surface was silver, the temperature was 298 K, and the pressure of CO_2 was 10.5 mTorr. The signal (dots) was the result of averaging 5000 laser shots, while the solid line is a fit to the signal of a single exponential decay.

Experiments were performed for a variety of pressures, surfaces, and temperatures. On the stainless steel surface at 298 K, for example, the variation of the rate constant with CO_2 pressure is shown in Fig. 4. Similar results were obtained for nickel and silver.

In the case of the silver surface, the temperature was varied from 298 to 473 K for a CO_2 pressure of 10–15 mTorr. The probability of deactivation was found to be 0.17 ± 0.03, independent of temperature.

IV. DISCUSSION

A. Signal analysis

There are four possible causes for decay of the 4.3 μm fluorescence signal: radiative decay of the (001) vibrational level, gas-phase intermolecular collisional energy transfer from the (001) level, effusion of the excited molecules out of the cylindrical cell, and relaxation as a result of gas–solid collision. The radiative decay rate of $0.42\ \mathrm{ms}^{-1}$[12] is much smaller than the observed decay rate (see Fig. 4), so that this channel can be neglected. The energy transfer out of the (001) level as a

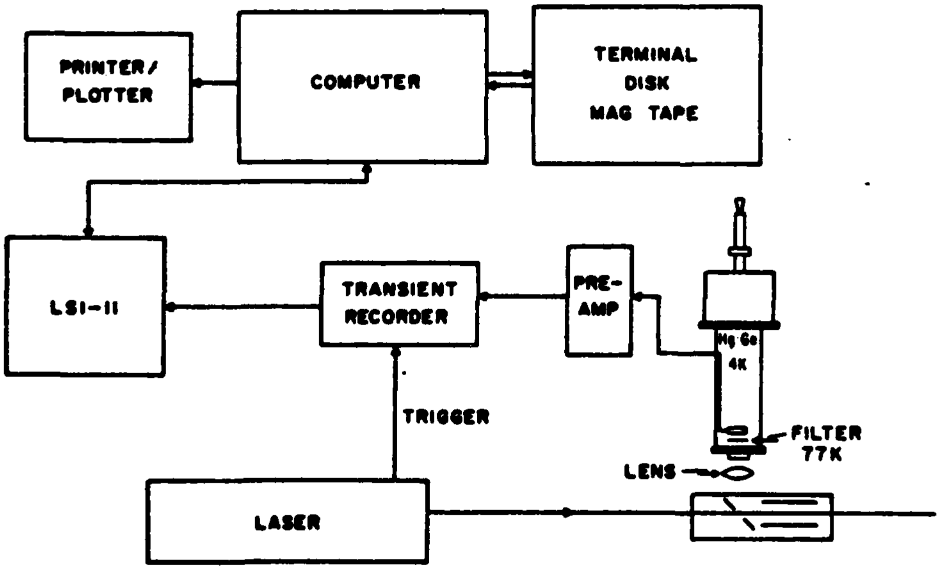


FIG. 2. Schematic diagram of the experimental apparatus.

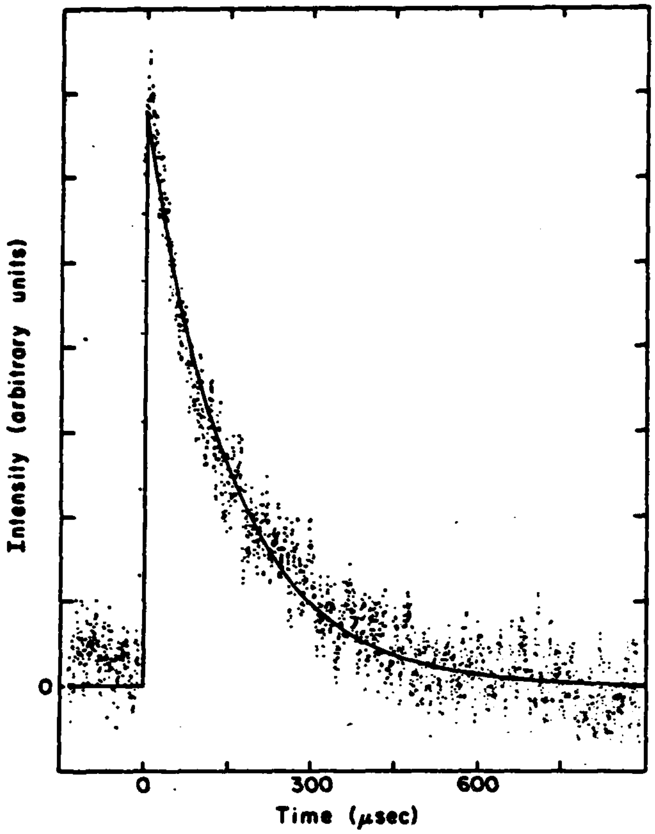


FIG. 3. Fluorescence decay curve obtained for 10.5 mTorr of CO_2 and a silver surface at 298 K. The signal is the average of 5000 laser pulses.

result of encounters with other CO_2 molecules is known to be inefficient, requiring on the order of 25 000 gas phase collisions.[13] For pressures below 20 mTorr the deactivation rate due to self-collisions is less than 0.007 ms^{-1} and is, therefore, negligible in comparison to the observed decay rate. The effusion rate of excited CO_2 out of the cell can be calculated to be 1.35 ms^{-1}. Although this rate is not negligible in comparison to the observed decay rate, the correction due to effusion is still quite small. Therefore, the predominant energy transfer channel for relaxation from the (001) level is by the gas–surface interaction.

The experiments were carried out in a pressure regime where the mean free path was on the order of the cell diameter. Simple kinetic theory was used to extract the surface deactivation probability from the fluorescence decay rate. As shown in the Appendix, the surface deactivation probability is given by

$$\beta = 1 - \exp(-kd/c) , \qquad (1)$$

where k is the experimentally observed decay rate, d is the cell diameter (1.0 cm), and c is the two-dimensional average velocity. The surface deactivation probabilities obtained in this work are listed in Table I.

B. The nature of the surfaces

One can only speculate about the cleanness of the surface. It has been shown conclusively using atomic helium scattering[14] that the adsorption probability of CO and H_2, the main components in the residual gas of the vacuum system, are vanishingly small on silver at room temperature and above. Likewise, CO_2 is known not to be adsorbed on silver. The CO_2 is "five nines pure" with ppm quantities of N_2, O_2, CO_2, H_2, and hydrocarbon. The contaminants in the CO_2 most likely to adsorb are the hydrocarbons and oxygen. The sticking probability of O_2 on silver is reported to be 3×10^{-3}.[15] Typical experiments require exposures of only about 10 Torr s, which would produce only about 1% of an oxygen monolayer. The hydrocarbon contamination is reduced to immeasurable levels by passing the CO_2 over a molecular sieve and activated charcoal traps.

TABLE I. Deactivation probabilities for CO_2 (001).

Surface	T (K)	β^a (±0.03)	Comments
Ag	298	0.16	Fresh Ag
Ag	298	0.15	7 h old
Ag	298	0.13	1 day old
Ag	473	0.18	1 h old
Stainless	298	0.22	
Ni	298	0.20	Fresh Ni

[a] Corrected for effusion.

For the experiments with nickel, since the film was deposited by heating $Ni(CO)_4$ at 145 °C, and since the CO desorption temperature from nickel is 160 °C,[16] it is expected that the surfaces should be initially covered with a monolayer of adsorbed CO. Our experiments were carried out with ~10^{-7} Torr s of O_2. It is known that O_2 will not displace CO from nickel and that when it does adsorb it does so dissociatively.[17] Also, adsorbed CO and oxygen atoms are known to react. Thus, any oxygen present on the surface either from oxygen adsorption or CO dissociation should be removed rapidly from the surface. Surface carbon might result from CO dissociation or from the carbonyl decomposition reaction. Therefore, the nickel surfaces were most likely covered with at least a monolayer of CO and possibly with some carbon.

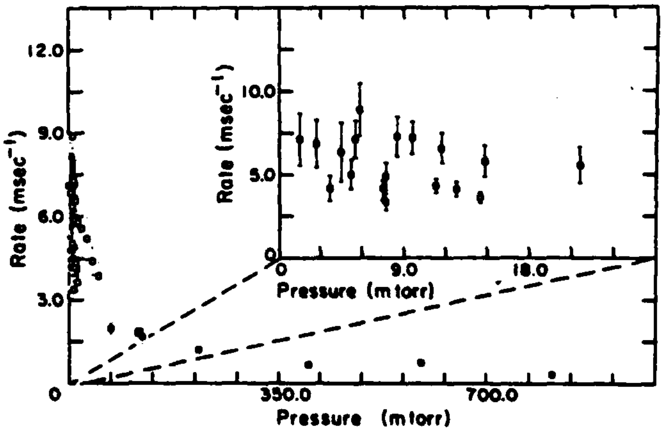


FIG. 4. CO_2 fluorescence decay rate as a function of pressure for collisions with stainless steel at 298 K.

C. The mechanism of vibrational relaxation

Several theoretical papers concerning the relaxation of vibrationally excited molecules above metal surfaces have appeared recently in the literature. In this section we give a brief reveiw of the proposed mechanisms with a comparison, where possible, to our experimental results.

Two papers have suggested mechanisms of vibrational relaxation based on energy transfer to electronic motions in the solid. Both papers consider the transfer of energy to individual metal electrons. The neglect of collective effects such as the excitation of surface plasmons is justified because surface plasma frequencies are much higher than molecular vibrational frequencies. For example, the Ag plasmon is at 0.35 μm, whereas the wavelength of CO_2 radiation is 4.3 μm.

Persson and Persson[18] have calculated the rate at which energy transfer from a CO molecule adsorbed on a copper surface excites electron-hole pairs in the solid. The lifetime of 10^{-11} s indicates that this might be an efficient deactivation channel, even for molecules colliding with the surface.

Brus[19] has suggested that coupling between the oscillating dipole of the vibrationally excited molecule and the metal conduction electrons might lead to efficient energy transfer. The decay rate of the dipole in the presence of the metal is given by[21]

$$k_d = C(\lambda, \epsilon) k_r / r^3 \, , \tag{2}$$

where r is the distance from the surface, k_r is the radiative decay rate in the absence of the metal, and $C(\lambda, \epsilon)$ is a constant which depends on the wavelength of radiation and on the dielectric constant of the metal. In order to see whether this mechanism might be responsible for the relaxation of $CO_2(001)$, we have integrated Eq. (2) over a straight-line trajectory $r = b + c|t|$, where b is the distance of closest approach to the metal:

$$\int_{-\infty}^{+\infty} k_d(r)\, dt = \int_{-\infty}^{+\infty} \frac{C(\lambda, \epsilon) k_r}{(b + c|t|)^3}\, dt = \frac{C(\lambda, \epsilon) k_r}{c b^2} = \beta \, . \tag{3}$$

Evaluation of C and k_r for CO_2 and Ag and use of $b = 1$ Å gives $\beta = 0.011$. Thus, this model predicts a much smaller deactivation probability than is observed in our experiments. However, it should be noted that the simple collision trajectory used above neglects the possibility of carbon dioxide trapping on the metal. Such trapping could greatly increase the deactivation probability.

Trapping probabilities have been estimated from angular scattering distributions for the rare gases on several surfaces by calculating the fraction of the scattered atoms which are diffusely emitted from the surface.[20] Angular scattering for CO_2 from Ag(111) has more recently been reported.[21] Both in-plane and out-of-plane angular distributions were measured, so that more accurate estimates of the fraction trapped should be possible than in the earlier work on rare gases. From the CO_2 data it can be estimated that the fraction tapped is ~ 0.15. Since it is unlikely that the silver surfaces (deposited by evaporation) used in our work are atomically smooth, the actual trapping probability should be higher. If each CO_2 molecule suffers on the average two collisions, then the overall trapping probability would be 0.28.

Empirically, the fraction trapped for rare gases is determined by the ratio of the incident kinetic energy of the gas to the well depth of the gas-surface potential. The well depth of CO_2 on silver is reported to be 6200 cal/mol.[21] From a correlation of the well depths with gas-phase Lennard-Jones parameters[22] the well depth is estimated to be 5800 cal/mol. The analogous rare gas atom would be Xe/Ag(111), which has a well depth of 6100 cal/mol.[20] The trapping probability for Xe/Ag(111) was found to be 0.42, somewhat larger than that estimated for CO_2. Kr/Ag(111) has a well depth of 1400 cal/mol and a trapping probability of 0.20.

From these results it is clear that the trapping probability for CO_2 on silver can easily be of the same order of magnitude as the vibrational relaxation probabilities we have measured. An additional question, however, is whether the residence times in the trapped state are long enough to result in complete vibrational relaxation before the CO_2 molecules are readmitted. Calculations of such residence times have been made for the rare gases on tungsten surfaces.[22] At room temperature the residence time for Xe is greater than 23 cycles. This is likely to be adequate for complete relaxation of the intramolecular vibration for those molecules of CO_2 which are trapped. Since heats of adsorption vary little from substrate to substrate, this trapping mechanism may provide an explanation for why the β values are so similar on a variety of surfaces.

The excitation of surface phonons is another possible channel for the deactivation of vibrationally excited molecules. However, the molecular vibrational frequencies are typically much higher than surface Debye frequencies. As an example, the vibrational energy of carbon dioxide as measured from the ground state is 2349 cm^{-1}, while the surface Debye frequency for silver corresponds to 107 cm^{-1}.[23] Thus, the transfer of a large fraction of the molecular vibrational energy into surface phonons would require a high-order multiphonon process. It seems unlikely that such a process would be efficient, although the phonons might be expected to couple with the translational energy of the incident molecules and to assist in the vibrational energy transfer.

A final mechanism by which vibrational energy might be lost from $CO_2(001)$ is vibration-to-rotation energy transfer, for example,

$$CO_2(001, J = 20) + M \rightarrow CO_2(100, J = 52) + M + \Delta E \simeq 50\ cm^{-1} . \tag{4}$$

Recent calculations by Gerber *et al.*[24] and by Bawagan *et al.*[25] indicate that such large changes in rotational quantum number might be quite common in the vibrational deactivation of excited at molecules surfaces. Indeed, for the relaxation of H_2, D_2, T_2, HD, N_2, O_2, Cl_2, and I_2 on smooth, phononless surfaces it has been found that rotation is the dominant receiving mode for the energy released in vibrational relaxation at surfaces.[24,25]

V. CONCLUSION

The vibrational relaxation of $CO_2(001)$ on silver, nickel, and stainless steel surfaces has been found to require only 4–5 collisions. Although it is difficult to single out a particular mechanism for the relaxation, it is likely that trapping and vibration-to-rotation energy transfer are important. The laser excitation/infrared fluorescence technique for measuring the probability of deactivation in gas-surface collisions has been shown to be direct and useful.

Continuing work in our laboratory is aimed at extending this study to other molecules and surfaces. Also, the work with bulk gas samples and polycrystalline surfaces is a precursor to work involving the excitation of molecular beams and the use of single crystal surfaces. Other questions to be answered include what fraction of the energy lost is transferred to the surface, and how the rest of the energy is partitioned in the molecule leaving the surface.

ACKNOWLEDGMENTS

This work has been supported by the Army Research Office under Grant 17349-C and by the Standard Oil Company of Ohio. We are also grateful for an unrestricted grant from the Mobil Foundation which was used during the course of the studies described here.

APPENDIX: RELATIONSHIP OF DECAY RATE TO DEACTIVATION PROBABILITY

In this appendix we derive the relationship between the concentration of vibrationally excited molecules $[A(t)]$ and the surface deactivation probability β for conditions such that the mean free path of the excited molecules is much greater than the diameter of the cylinder in which they are contained. If $A(t)$ gives the number of excited molecules at any time, then

$$A(t)=A(0)(1-\beta)^{N(t)}\,, \tag{A1}$$

where $N(t)$ is the number of collisions occurring during time t, and β is the probability that a molecule will be deactivated on a collision with the surface.

An approximate solution for $N(t)$ may be obtained by assuming specular reflection and an average radial velocity c. Under this approximation, $N(t)$ is given for $t \gg (d/2)/c$ by

$$N(t)=1+\left(t-\frac{d/2}{c}\right)\frac{c}{d}\ . \tag{A2}$$

The first term (unity) accounts for the first collision of each excited molecule with the surface. This collision occurs in a time equal to $(d/2)/c$, since the molecule originates at the center of the cylinder and travels outward at a velocity c. During the remaining time $t-(d/2)/c$, the excited molecule traverses the cylinder c/d times per second. Rearrangement of Eq. (A2) gives

$$N(t)=\tfrac{1}{2}+tc/d\ . \tag{A3}$$

Substitution of Eq. (A3) into Eq. (A1) gives the result

$$A(t)=A(0)(1-\beta)^{1/2}(1-\beta)^{tc/d}\ . \tag{A4}$$

Finally, since $a^y=\exp(y\ln a)$, we obtain

$$A(t)=A(0)\exp\{(\tfrac{1}{2}+tc/d)\cdot\ln(1-\beta)\}\,, \tag{A5}$$

or

$$A(t)=\text{constant}\cdot\exp\{(tc/d)\ln(1-\beta)\}\ . \tag{A6}$$

The experimentally observed rate constant k is defined by $A(t)=\text{constant}\cdot\exp(-kt)$, so that

$$k=-(c/d)\cdot\ln(1-\beta)\ . \tag{A7}$$

Rearrangement of Eq. (A7) gives Eq. (1) of the text.

It should be noted that the average two-dimensional velocity c is obtained from the distribution

$$dN/N_0=(m/kT)\exp\{-mc^2/2kT\}c\,dc \tag{A8}$$

and is equal to $(\pi kT/2m)^{1/2}$.

[1] G. M. McClelland, G. D. Kubiak, H. G. Rennagel, and R. N. Zare, Phys. Rev. Lett. 46, 831 (1981).

[2] A. W. Kleyn, A. C. Luntz, and D. J. Auerbach, Phys. Rev. Lett. 47, 1169 (1981); A. C. Luntz, A. W. Kleyn, and D. J. Auerbach, J. Chem. Phys. 76, 737 (1982).

[3] F. Frenkel, J. Hager, W. Krieger, H. Walther, C. T. Campbell, G. Ertl, H. Kuipers, and J. Segner, Phys. Rev. Lett. 46, 152 (1981).

[4] J. W. Hepburn, F. J. Northrup, G. L. Olgram, J. C. Polanyi, and J. M. Williamson, Chem. Phys. Lett. 85, 127 (1982).

[5] D. Ettinger, K. Honma, M. Keil, and J. C. Polanyi, Chem. Phys. Lett. 87, 413 (1982).

[6] R. R. Cavanaugh and D. S. King, Phys. Rev. Lett. 47, 1829 (1981); J. Chem. Phys. 76, 5634 (1982).

[7] D. E. Tevault, L. D. Talley, and M. C. Lin, J. Chem. Phys. 72, 3314 (1980).

[8] G. S. Selwyn, G. T. Fujimoto, and M. C. Lin, J. Phys. Chem. 86, 760 (1982).

[9] R. Abouf and F. Legay, J. Chim. Phys. 63, 1393 (1966).

[10] M. Margottin-Maclou, L. Auditi, H. Gueguen, and L. Doyenette, C. R. Acad. Sci. Paris 271, 563 (1970); M. Margottin-Maclou, L. Doyenette, and L. Henry, Appl. Opt. 10, 1768 (1971).

[11] M. Kovacs, P. R. Rao, and A. Javan, J. Chem. Phys. 10, ? 3339 (1968).

[12] P. F. Eggers and B. L. Crawford, J. Chem. Phys. 19, 1554 (1951).

[13] C. B. Moore, R. E. Wood, B. Hu, and J. T. Yardley, J. Chem. Phys. 46, 4222 (1967).

[14] R. Sau and R. P. Merrill, Surf. Sci. 34, 268 (1973).

[15] M. Bowker, M. A. Barteau, and R. J. Madix, Surf. Sci. 92, 528 (1980).

[16] W. Erley and H. Wagner, Surf. Sci. 74, 333 (1978).

[17] M. Oku and C. R. Bundle, J. Vac. Sci. Technol. 20, 532 (1982).

[18] B. N. J. Persson and M. Persson, Surf. Sci. 97, 609 (1980).

[19] L. E. Brus, J. Chem. Phys. 73, 940 (1980).

[20] A. C. Stoll, D. L. Smith, and R. P. Merrill, J. Chem. Phys. 54, 163 (1971); W. H. Weinberg and R. P. Merrill, *ibid.* 56, 2881 (1972); R. Sau and R. P. Merrill, Surf. Sci. 32, 317 (1972).

[21] H. Asada, Jpn. J. Appl. Phys. 20, 527 (1981).

[22] W. H. Weinberg and R. P. Merrill, J. Vac. Sci. Technol. 10, 411 (1973).

[23] E. R. Jones, J. T. McKinney, and M. B. Webb, Phys. Rev. 151, 476 (1966).

[24] R. B. Gerber, L. H. Beard, and D. J. Kouri, J. Chem. Phys. 74, 4709 (1981).

[25] A. O. Bawagan, L. H. Beard, R. B. Gerber, and D. J. Kouri, Chem. Phys. Lett. 84, 359 (1981).

FIL