ALKALI REACTIONS WITH WALL COATING MATERIALS
USED IN ATOMIC RESONANCE CELLS

J. C. Camparo, R. P. Frueholz, and B. Jaduszliwer

Chemistry and Physics Laboratory
THE AEROSPACE CORPORATION
P. O. Box 92957
Los Angeles, CA 90009

ABSTRACT

In certain atomic frequency standards it is necessary to inhibit the relaxation of atomic polarization induced by collisions between polarized species and the walls of the storage cell. It is well known that the chemisorption of various chlorosilane materials on glass atomic storage vessel walls results in surface coatings which inhibit electronic and nuclear spin relaxation. In the present study the chemical reaction of rubidium, and by analogy other alkali metals, with dichlorodimethylsilane-treated glass surfaces has been studied. We find evidence that rubidium reacts with a freshly prepared coating to produce H_2 and a volatile silicon-containing species. The most reasonable reaction process is postulated to be rubidium reacting with residual silanol groups (Si-OH) found on the surface. As the reaction proceeds these groups would disappear, thus reducing the spin relaxation rate associated with the surface. We believe that this reaction results in the "curing" of wall coatings reported by other investigators. Concurrently, the gaseous reaction products become impurities within the system. The spin relaxation cross section of the silicon containing species is expected to be less than 1×10^{-17} cm^2.

I. INTRODUCTION

In certain atomic frequency standards, it is necessary to inhibit the relaxation of atomic polarization induced by collisions between the polarized species and the walls of the storage cell. One method of reducing the rate of wall relaxation is to place a nonrelaxing coating on the cell walls.[1] In the hydrogen maser, teflon coatings are applied to the storage cell.[2] Wall coatings which inhibit alkali relaxation have also been found. While standards employing wall coated, evacuated cells are currently not in use they should have several attractive features. The rapid motion of the polarized atom throughout the entire storage cell will average inhomogeneities. This will eliminate the "Position Shift Effect", a process felt to produce frequency drift in rubidium gas cell clocks. Additionally the hyperfine transition Q can be extremely high in such a cell leading to a standard with improved frequency stability.

There are two principal types of alkali wall coating materials, paraffins[3] and silane-based coatings.[4] The silane-based coatings contain silicon atoms with hydrocarbon functional groups attached. The relaxation processes associated with silane-based coatings were investigated in a series of experiments by Bouchiat and Brossel.[5] The alkane-type coatings have found use in the determination of basic physical quantities such as g-factor ratios[6] as

well as very practical applications in the area of atomic frequency standards.[7,8] Additionally, various optical pumping experiments have employed silane-type coatings to reduce the wall relaxation of both alkali electronic spin polarization and rare gas nuclear spin polarization.[9,10]

The silane coatings would appear to be particularly attractive for a number of reasons: Bouchiat and Brossel[5] indicate that properly prepared silane coatings display spin polarization relaxation rates quite similar to those of the alkane coatings; the preparation of silane coatings is quite simple, requiring none of the vacuum manipulations associated with the alkane coatings, and, perhaps most importantly they have been found to be stable at temperatures in excess of 350°C. The storage of polarized alkali vapors at elevated temperatures could have a number of practical applications, including use in the production of polarized H⁻ ions.[11] Consequently, with the potentially high utility of silane coatings it is of interest to understand any peculiarities associated with their use in containing alkali vapors. In particular, Zeng et al.[9,10] have found that alkalis appear to react with the silane coatings, resulting in alkali vapor densities far below that expected from simple liquid/vapor equilibrium considerations, and that this depressed density condition continues for several days after alkali introduction. Furthermore, they observed that if cells were cured at 85°C for several days the reduction in vapor pressure tended to decrease. Camparo,[12] in studying the relaxation of Rb^{87} hyperfine polarization in cells with silane coated walls, found that the wall relaxation rates also appeared to decrease after the cell had aged for a number of days.

The experiments reported in this paper shed light on the chemical reaction of gaseous alkali metals and the silane wall coatings. Through study of hyperfine lineshapes of Rb^{87} atoms contained in cells with silane coated walls, we deduce that a reaction between Rb and the wall coating material does indeed take place. The reaction results in volatile products whose ultimate pressures depend upon the conditions under which the cell was fabricated. Through the use of residual gas analysis (RGA) we have determined that the outgassed reaction products are hydrogen and a silicon-containing species. The experimental procedures and results are discussed in the second section of the paper. While unambiguous identification of the silicon-containing reaction product was not possible, a plausible reaction mechanism and product are presented in the third section.

II. EXPERIMENTAL PROCEDURES AND RESULTS

A. STORAGE CELL FABRICATION

The wall coated resonance cells used in the present study were spherical, typically 6 cm diameter pyrex cells that had a 3 cm long, 0.3 cm inner diameter, pyrex stem attached to one end. The cells were coated with dichlorodimethylsilane using a procedure similar to that of Zeng et al.:[9,10] briefly, a 10% by volume solution of dichlorodimethylsilane in cyclohexane was prepared, inserted into the resonance cells and shaken; the excess was removed; the cells were rinsed twice with pure cyclohexane, and allowed to dry in air overnight. The cells were then attached to a glass vacuum system and baked out at 150°C for

approximately two days at which point the vacuum line's pressure had returned to its nominal value of 5 x 10^{-7} torr. After the bakeout, natural rubidium (72% Rb^{85} and 28% Rb^{87}) was distilled into the cells. For certain cells the Rb was distilled onto the coated cell walls. For other cells care was taken to ensure that no liquid Rb came in contact with the coated surface. In both cases prior to experimentation, the Rb was driven using a mild temperature gradient well into the cell's stem. As the potential for cell outgassing existed, several cells of the same size were fabricated with a second stem containing a barium getter.

Subsequent discussion of alkali/silane coating reactions will be facilitated by briefly describing the process through which dichlorodimethylsilane adheres to the cell walls. When this material chemisorbs to glass a homogeneous siloxane phase is formed on the silica surface by primarily single surface-to-dimethylsilane attachments.[13,14] Essentially, this chemisorption proceeds through multiple steps as illustrated in Fig. 1.[13] In the primary reaction $Si(CH_3)_2Cl_2$ reacts with silanol hydroxl groups on the surface, yielding a condensed siloxane phase. In the secondary reaction step adsorbed water hydrolyzes some of the unreacted chlorines leading to $Si(CH_3)_2ClO-$ and $Si(CH_3)_2(OH)O-$ species in close proximity. With a slight bond angle adjustment these species can then react to form the polymerized structure of Fig. 1b. In addition to the primary silane-glass binding process shown in Fig. 1b, the Si^{29} NMR studies of Sindorf and Maciel[13] indicate that additional attachment structures, shown in Fig. 1c, may also occur. From these diagrams we see that when an alkali atom impinges on the dimethylsiloxane (DMS) surface it would appear to initially interact with the outermost methyl group. One would suppose the relaxation processes to be similar to those occurring when paraffins are used as wall coatings; measurements of Rb isotopic relaxation rates performed by Camparo[12] have demonstrated this supposition to be correct.

B.   RUBIDIUM HYPERFINE LINESHAPE MEASUREMENTS

After fabrication of the storage cells we proceeded to study the Rb^{87} ground state hyperfine transition lineshape. Hyperfine lineshapes can be very dependent upon the environment in which the interrogated atom resides. Specifically, Dicke (or collisional) narrowing in such a transition can result in a lineshape with a spectral width less than the Doppler width,[15,16] and is observed when the atoms are confined to small volumes of space through rapid velocity-changing collisions. In order to observe this phenomenon the atomic mean free path must be less than the wavelength of the atomic resonance under study. Additionally, the phase of the interrogating field must remain constant within the confinement region. A final constraint for observation of the phenomenon requires the confining collisions to be nonperturbing, that is the internal state of the atom must be unchanged by the collisions. In the study of alkali ground state hyperfine transitions, where the transition wavelength is on the order of centimeters, atomic confinement can be obtained through one of two procedures. Collisions with an inert buffer gas are one means of obtaining the required rapid velocity changing collisions, and in this case Lorentzian lineshapes are observed with linewidths being proportional to the atomic mean free path.[15] It is also well known that Dicke narrowed, sub-Doppler linewidths

can be obtained in storage cells containing no buffer gases, but rather having wall coatings to minimize the relaxation effects of wall collisions on the atomic spin orientation. In these situations, where the atom's spatial confinement results from collisions with the storage vessel's walls, the narrowed lineshape is composed of two components, a Doppler-free central spike whose width is determined by the various relaxation processes occurring within the storage vessel, and a broad underlying pedestal with a width typically found to be approximately equal to the Doppler width.[15,16]

Prior to conducting experiments on the prepared cells, motionally narrowed lineshapes consistent with a bufferless wall coated cell were antici-pated. Somewhat unexpectedly, the observed lineshapes indicated the presence of a buffer gas. The lineshapes of the Rb^{87} (F=1, m_F=0 → F=2, m_F=0) ground state hyperfine transition were observed using optical-microwave double reso-nance with a diode laser serving as the source of optical pumping radi-tion. The experimental apparatus has been described in detail previously.[17,18] For all of the cells that were fabricated the lineshapes displayed widths less than the 9.2 KHz Doppler width. In those where liquid Rb had been allowed to touch the coated surfaces, linewidths of approximately 500 Hz were measured. The measured hyperfine relaxation rate in this cell was 220 Hz, indicating that approximately 300 Hz of the linewidth can be associated with buffer gas induced Dicke narrowing. In cells where care had been exercised to keep liquid Rb from coming into contact with the coated surface, linewidths of approximately 7 KHz were obtained. From the linewidths and the characteristics of Dicke narrowing we knew that an outgassed product was present in both cases. However, the narrower lineshape observed when liquid Rb was allowed to contact the coated surface implied higher outgassed product pressure. Results of calculations presented in Ref. 16 allow an estimation of gas pressures within both types of cells. In the first case the pressure of the outgassed product was estimated to be on the order of 100 mTorr; when liquid Rb was kept off of the coating material, the pressure, as indicated by the transition linewidth, appears to have been approximately 2 mTorr. In cells containing barium getters displaying initial linewidths of 500 Hz, flashing of the getter increased the linewidths to nearly 8 KHz, indicating a significant reduction in the outgassed product's pressure. In cells initially displaying lineshapes with 7 KHz linewidths, getter flashing resulted in the reduction of the linewidths to 5 KHz. While this reduction in linewidth might seem to indicate an increased pressure in the cell after getter flashing, this is not the case. Careful analysis of Dicke narrowing in wall coated cells indicates that in certain cases these cells will display pedestals with widths well below the Doppler width.[18] In these cells the reduction in hyperfine linewidth upon getter flashing shows that the outgassed product's pressure has dropped to the point where a Rb atom's mean free path is greater than the storage cell's dimensions. One then observes the Dicke narrowed lineshape associated with a bufferless storage cell. For our cells that lineshape is dominated by the pedestal with the central spike displaying a negligible amplitude.

It is worth noting that as a consequence of Zeng et al.'s[9,10] observation of reduced alkali vapor density, one would expect the loss rate of alkali atoms to the coating, $(n\tau)^{-1}$, to contribute to the hyperfine resonance linewidth $1/T_2$

(τ is the mean time between wall collisions and n is the mean number of wall collisions before the atom is lost to the coating). One can estimate n by a simple rate equation analysis, which shows that if the reduction of vapor density is less than a factor of ten, which is the case in our experiments, then n > 1000. However, from relaxation rate measurements we performed in cells where the Rb atom's mean free path was greater than the storage cell's dimensions, it was found that $1/T_2$ corresponded to roughly 5 wall collisions. Consequently, though the loss of atoms to a wall coating can contribute to T_2, in the case of the DMS coating under discussion it appears that the contribution is insigificant.

C. RESIDUAL GAS ANALYSIS STUDIES

As discussed above, the hyperfine lineshape studies indicated the pres-ence of an outgassed product, whose appearance was tied to how intimately liquid Rb came into contact with the DMS wall coating material. To gain some information concerning the identity of the outgassed material, mass spectrometric RGA was performed. After lineshape study a cell was placed into one chamber of a two-chamber, all stainless steel vacuum system with a nominal pressure of 2×10^{-7} torr. The quadrupole mass spectrometer head required for RGA was attached to the second chamber. The chambers were connected by a valve and both were evacuated by a single diffusion pump attached to the chamber with the RGA head. The diffusion pump used a polyphenyl ester oil (Santovac 5) eliminating silicon contamination which could result from a silicon based pump oil. The stem of the storage cell was broken using a small piston attached to a motion feedthrough leading into the first chamber. Prior to opening the cell the valve between the two chambers was closed. Upon breaking the cell's stem the released gas was bled from the first chamber into the second for RGA analysis. The diffusion pump attached to the second chamber was allowed to pump continuously during the RGA analysis. By varying the bleed rate from the first chamber a suitable gas pressure for RGA analysis could be obtained, typically 5×10^{-6} torr.

Mass spectra were obtained over the mass range of 1 to 200 amu using a Leybold-Heraeus, Inc. Quadrex 700 RGA. Spectra of the normal system background gas were compared to those obtained after a cell was opened and the flow configuration was stable. A number of mass peaks in the flow configuration spectra could be attributed to compounds emanating from the DMS coated cell. The principal mass-peaks and the species associated with them were: $2-H_2$, $58-(CH_3)_2Si$, $43-CH_3Si$, $28-Si$, $15-CH_3$, $85/87-Rb$[85,87] (appropriate isotope ratio), and $101/103-ORb$[85,87]. Since it was often the case that some fraction of the indicated peak's amplitude was due to an underlying signal from the system background spectrum, (e.g., mass 28 could be due to Si or N_2) it would be misleading to quantitatively analyze the peak amplitudes However the ratios of the identified peaks to those at adjacent masses increased sufficiently in the flow spectra, compared to background spectra, to give us good confidence that a fragment due to the opened cell was indeed present. Apparently at least two different compounds, hydrogen and a silicon containing species, are reaction products.

Comparison of our spectra to tabulated ones[19] for dichlorodimethylsilane indicated that none of the initial chemical was either present or sufficiently volatile to be detected directly by the RGA. In fact, the complete absence of mass peaks at 63 and 65, corresponding to SiCl fragments weighs against the presence of any chlorosilane compounds.[20] Also, there was no indication of larger silicon containing compounds. The fragmentation pattern of $(CH_3)_6Si_2O$ indicates that the Si-O-Si structure is fairly strong, and had large volatile siloxane species been present they probably would have been detected through observation of a fragment containing this unit. Also the fragmentation pattern of $(CH_3)_3SiOH$ indicates that the SiOH, mass 45, is quite stable. The absence of this mass peak weighs against the parent compound being a silanol. The RGA results are consistent with a reaction product containing a single Si with two methyl substituents. Taken in conjunction with the observation of RbO fragments, the results point to a Rb silanolate $((CH_3)_2XSi(ORb)$ with X unspecified) precursor; volatile alkalitrimethylsilanolates have previously been observed.[21] It is unlikely, though, that a trimethylsilanolate is present in this case, as the $(CH_3)_3Si^+$ fragment is often stable and would be expected to be observed if this silanolate were present. While some form of Rb silanolate appears to be a likely reaction product it is not possible to make an unambiguous identification on the basis of the present mass spectrometric analysis. In the following section possible reaction processes between Rb and the silane coating are briefly discussed.

## III. POTENTIAL INTERACTIONS BETWEEN RUBIDIUM AND THE SILANE WALL COATING

The exposure of silicon containing compounds to alkali metals is a procedure often used in organosilylmetallic synthesis.[22] Study of the reactions which have been observed to proceed can shed some light into what may be occurring within the silane coated cells. It is important to note, though, that many previously analyzed reactions proceed in anhydrous solvents such as ether $((C_2H_5)_2O)$ or tetrahydrofuran $((CH_2)_4O)$. The ability of these reactions to proceed in a solventless environment has often not been demonstrated. Consequently the processes discussed should be considered as illustrative of reactions which might take place and not definitive statements.

As a starting point, it is reasonable to expect that alkalis do not react with the principal form of the surface coating, structure (iii) in Fig. 1. Should this reaction occur the entire coating would be susceptible to attack, nullifying its value as a nonrelaxing surface; the coating, however, is observed to maintain its value as a nonrelaxing surface even after significant outgassing. Consequently, reactions which occur are probably between Rb and minority forms of the surface covering, such as structures (iv) and (v), or isolated silanols not close enough to a chlorosilane group to have undergone the second polymerization reaction shown in Fig. 1b. After reviewing the chemical literature the SiOH containing species would appear most labile under alkali attack. In the presence of an alkali metal trimethylsilanol reacts to form the silanolate with the evolution of molecular hydrogen.[21] A similar reaction in the wall coated cell,

$$-O(CH_3)_2SiOH + Rb \rightarrow 1/2\ H_2 + -O(CH_3)_2Si(ORb), \tag{1}$$
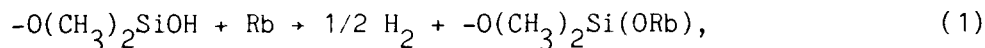
where $-O$ indicates attachment to a silicon atom in the glass lattice, could explain the origin of molecular hydrogen observed in the RGA, as well as providing a precursor for the hypothesized, volatile Rb silanolate compound. In reaction (1) the silicon containing product will be referred to as the "silanolate intermediate."

To obtain a gas phase silicon-containing compound a reaction must take place which disrupts the Si-O-Si structure which binds the wall coatings to the glass. The ability of an alkali to cleave these bonds is highly dependent on the silicon substituents.[22] Hexamethyldisiloxane ($(CH_3)_3SiOSi(CH_3)_3$) is unaffected by alkali metals, and the similarity of structure (iii) in Fig. 1 to hexamethyldisiloxane is evident. Consequently, a corresponding lack of reactivity in the presence of an alkali metal could explain the general stability of the wall coating and a similiar inertness of structure (iv) in Fig. 1. In contrast, the silanolate intermediate just discussed may be significantly more reactive with respect to alkali attack. A potential reaction resulting in a Rb disilanolate is described by reaction (2).

$$-O(CH_3)_2Si(ORb) + 2Rb \rightarrow -Rb + (CH_3)_2Si(ORb)_2 \tag{2}$$
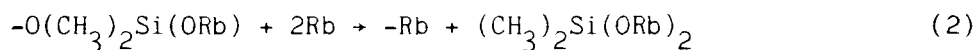
This process is consistent with the reactions other siloxanes, such as 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane, undergo.[22] The volatile silanolate is then hypothesized to be Rb dimethyldisilanolate ($(CH_3)_2Si(ORb)_2$), to be abbreviated as RbDDS. The outlined reaction scheme yields products, H_2 and RbDDs, whose expected mass spectra would be consistent with the present RGA. The extent to which these reactions can occur is of course dependent on the amount of unreacted silanol substituents on the glass surface prior to introduction of the alkali metal. Sindorf and Maciel[13] indicate unreacted silanols may comprise up to approximately 20% of the total surface coating silane. This is an appreciable fraction and could lead to the considerable outgassing observed. It is also apparent from the present studies that the rapidity with which the reactions proceed, and potentially the degree to which all surface silanols are consumed, depends on the concentration of Rb at the cell surface. Should liquid Rb be present the reaction would be expected to proceed more rapidly and to a higher degree of completion; this is consistent with our observations. To emphasize the conjectural nature of this reaction sequence we should point out that in our review of the literature we could not find previous mention of RbDDS. The definitive verification of this sequence of reactions would require additional studies. Of particular value should be Si^{29} NMR studies of the form performed by Sindorf and Maciel which could monitor silanol concentrations on the glass surface before and after alkali exposure.

IV. DISCUSSION

The reaction sequence discussed in the preceding section is not only consistent with the experimental data of the present study, but also can explain observations of prior investigations. Both the initial reaction of Rb with the

residual silanols on the glass surface, as well as formation of the volatile RbDDs, consume atomic Rb. Thus, while these reactions are proceeding one would expect the vapor density of atomic Rb in a wall coated cell to be depressed below that expected from liquid/vapor equilibrium considerations. This is consistent with the observations of Zeng et al.[9,10] Also, observations of reductions in wall relaxation rates (i.e., cell curing) after Rb exposure can be explained on the basis of two different effects. First, the outgassed product will act as a buffer gas reducing the number of wall collisions per unit time compared to an evacuated cell. In unpublished experiments Happer has observed, though, that the cell curing is observed even in cells containing many torr of buffer gas. The relatively small contribution of the outgassed product to total cell pressure in these cases could not then explain the observed reduction in wall relaxation rate. Consequently the reaction sequence must also modify the relaxation properties of the surface itself.

To better understand how the discussed reaction sequence can modify the relaxation properties of the wall coating material we visualize the bulk glass as covered by a siloxane canopy, akin to the foliage canopy covering a rain forest. The outermost "branches" of the glass surface's canopy are the hydrogen atoms attached to the carbons of the methyl groups. The studies of Bouchiat and Brossel[5] and Camparo[12] show that paraffins and silane coatings relax nuclear and electronic polarization through the same mechanisms. Consequently, the outermost hydrogen and carbon atoms play the greatest roles in the wall relaxation process. Silicon atoms in the siloxane coating are of only secondary importance. Interspersed among the canopy's methyl groups are hydroxyl groups. McNeal[23] demonstrated that molecules with permanent dipole moments can be highly depolarizing. Specifically he found that dimethylether, a polar molecule, had a depolarization cross section of 3×10^{-18} cm^2, compared to 8×10^{-24} cm^2 for nonpolar methane. On the basis of simple elec-tronegativity considerations one would expect the SiOH, silanol units on the coating material to also have permanent dipole moments. These hydroxyl substituents are then sites for strong electronic and nuclear depolarization.

The reaction scheme we have outlined results in the eventual removal of hydroxyl groups from the surface coating canopy. However, after the removal of the RbDDs product one might expect a patch of bulk glass to become visible to an impinging alkali atom. Herzberg and Erwin[24] found though, that glass surfaces treated with dichlorodimethylsilane can develope greater than monolayer coating coverages. Consequently, the surface canopy could be dense enough that even after the removal of isolated RbDDs molecules, rearrangements of the canopy would still provide effective coverage of the surface. Furthermore, with regard to the volatile RbDDs product, it is quite possible that it too has a permanent dipole moment, and is thus depolarizing. However, since gas phase collision interaction times are typically orders of magnitude smaller than atom/surface interaction times, the net effect of producing a volatile RbDDs product would be a reduction in the influence of permanent dipole moment species on alkali spin relaxation. Thus, within this postulated reaction sequence, experimental observations of a gradual curing or aging of the silane wall coatings, resulting in reduced wall relaxation rates, can be explained.

V. CONCLUSIONS AND SUMMARY

This study has shown that a reaction occurs when Rb, and potentially other alkali metals, is exposed to a silane wall coating. Volatile products including H_2 and a silicon containing species are produced, and the degree to which the reaction proceeds is found to be dependent on the amount of Rb to which the wall coating is exposed. A reaction sequence was suggested which could result in the reduction of wall coating relaxation rates as it proceeds; a consequence of the reaction that is consistent with the cell curing observations made by previous investigators. While the suggested reactions may tend to improve the coating's properties, it is important to be aware that trace impurities are being introduced into the system. On the basis of measured relaxation rates and estimated outgassing pressures, we estimate that the electron spin relaxation cross section of the silicon containing species must be less than 1×10^{-17} cm^2, which is a depolarization cross section that is consistent with either polar or nonpolar species.[25] In gas cell atomic standards, the presence of the impurity species can, as a result of altered Dicke-narrowing, decrease the hyperfine transition Q. This would degrade the frequency stability of a standard using such a cell. Consequently, for standard use, care must be taken to insure the curing process is completed prior to final sealing of such an evacuated wall coated cell.

REFERENCES

1. W. Happer, Rev. Mod. Phys. 44, 169 (1972).

2. D. Kleppner, H. M. Goldenberg and N. F. Ramsey, Phys. Rev. 126, 603 (1962).

3. H. G. Robinson, E. S. Ensberg and H. G. Dehmelt, Bull Am. Phys. Soc. 3, 9 (1958).

4. C. O. Alley, in Advances in Quantum Electronics, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 120.

5. M. A. Bouchiat and J. Brossel, Phys. Rev. 147, 41 (1966).

6. C. W. White, W. M. Hughes, G. S. Hayne, and H. G. Robinson 174, 23 (1968).

7. A. Risley, S. Jarvis, Jr. and J. Vanier, J. Appl. Phys. 51, 4571 (1980).

8. H. G. Robinson and C. E. Johnson, Appl. Phys. Lett. 40, 771 (1982).

9. X. Zeng, Z. Wu, T. Call, E. Miron, D. Schreiber and W. Happer, Phys. Rev. A 31, 260 (1985).

10. X. Zeng, E. Miron, W. A. Van Wijngaarden, D. Schreiber and W. Happer, Phys. Lett. 94A, 191 (1983).

11. D. R. Swenson and L. W. Anderson, Nucl. Instrum. & Methods B12, 157 (1985).

12. J. C. Camparo, J. Chem. Phys. 86, 1533 (1987).

13. D. W. Sindorf and G. E. Maciel, J. Am. Chem. Soc. 105, 3767 (1983).

14. W. J. Herzberg, J. E. Martin and T. Vermeulen, J. Colloid Interface Sci. 33, 164 (1970).

15. R. H. Dicke, Phys. Rev. 89, 472 (1953).

16. R. P. Frueholz and C. H. Volk, J. Phys. B: At. Mol. Phys. 18, 4055 (1985); also see references cited therein.

17. J. C. Camparo and R. P. Frueholz, Phys. Rev. A 30, 803 (1984).

18. R. P. Frueholz and J. C. Camparo, to Phys. Rev. A. to be published.

19. Eight Peak Index of Mass Spectra, second edition, Volume I, Table I (Mass Spectrometry Data Center, AWRE, Aldermaston, Reading, UK, 1974).

20. C. A. Hirt, Anal. Chem. 33, 1786 (1961).

21. V. H. Schmidbaur, J. A. Perez-Garcia and H. S. Arnold, Z. Anorg. Allgem. Chem. **328**, 105 (1964).

22. H. Gilman and H. J. S. Winkler, in <u>Organometallic Chemistry</u>, edited by H. Zeiss (Reinhold, New York, 1960), pp. 270-345.

23. R. J. McNeal, J. Chem. Phys. **37**, 2726 (1962); **40**, 1089 (1964).

24. W. J. Herzberg and W. R. Erwin, J. Colloid Interface Sci. **30**, 172 (1970).

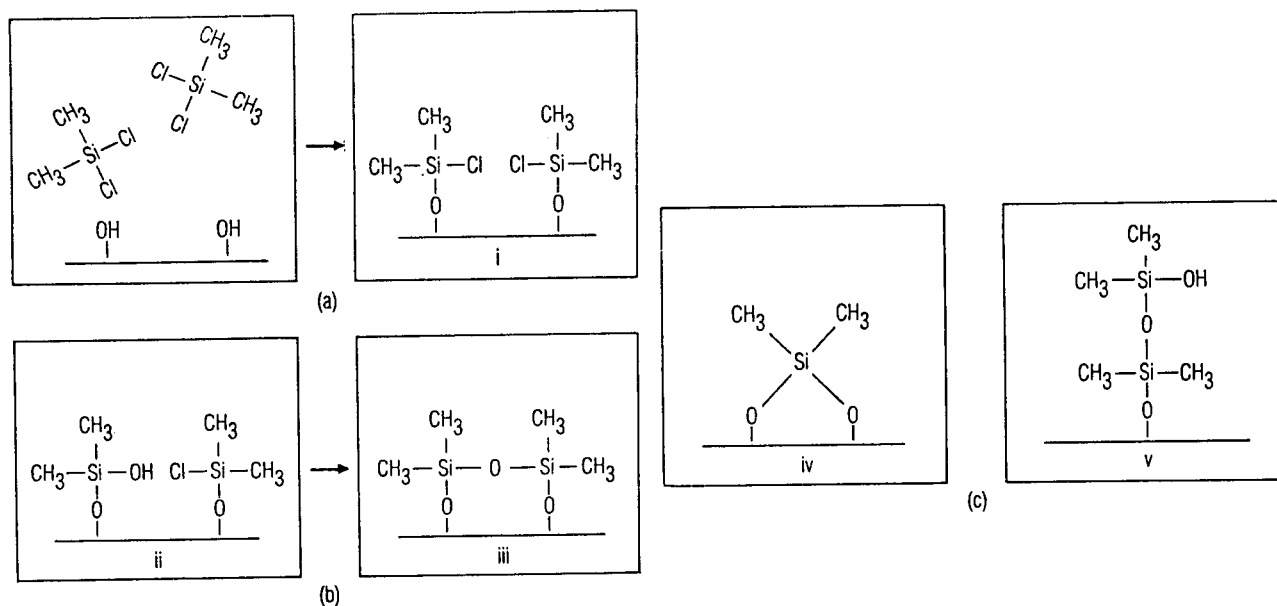25. R. J. McNeal, R. A. Bernheim, R. Bersohn and M. Dorfman, J. Chem. Phys. **40**, 1678 (1964).

Figure 1. Schematic representation of the reaction steps for the chemisorption of dichlorodimethylsilane to glass. In Fig. 1a, $Si(CH_3)_2Cl_2$ reacts with OH groups on the surface yielding HCl and a condensed siloxane molecule $Si(CH_3)_2ClO-$. Subsequent reaction of this siloxane molecule with adsorbed water leads to situations as depicted in 1b. In Fig. 1b adsorbed water has hydrolyzed some of the unreacted chlorines, leading to $Si(CH_3)_2ClO-$ and $Si(CH_3)_2(OH)O-$ species in close proximity. With a slight bond angle adjustment these neighboring species can react to form HCl and the polymerized dimer $O[Si(CH_3)_2(O-)]_2$. In Fig. 1c surface coating structures that occur with a lower frequency are shown.

QUESTIONS AND ANSWERS

Jacques Vanier, National Research Council: I have a problem with your last conclusion. I disagree completely. If you remove the products, you will not have any buffer gas. Then you will have a relaxation time that will be so short that it will be equivalent to one transversal of the bulb. The atom will die. I don't think that your coating will help.

Mr. Frueholtz: According to the results, which will be published in the paper, the coating is fairly good. Additionally, We have done some relaxation studies using the coating and we know that we can get five bounces off the surface. This is not as good as a paraffin coating, but we have not optimized the coating procedure. The point that should be made is that this coating looks very similar to paraffin in that, when an impinging atom what it sees is primarily the same thing.

Mr. Vanier: My experience is that by using this coating, you lose a milligram of rubidium which gets swallowed by the wall.

Mr. Frueholtz: We get somewhat different results then.