ATOMIC HYDROGEN MASER MEASUREMENTS WITH WALL SURFACES OF CARBON TETRAFLUORIDE

R.F.C. Vessot, E.M. Mattison, E.A. Imbier and Z.C. Zhai

Smithsonian Astrophysical Observatory

Cambridge, Ma. 02138

1. INTRODUCTION

The principal objectives of the SAO cold maser research programs are:

1. To understand the behavior of the atomic hydrogen wall collision process and find better wall coating materials or processes.

2. To develop hydrogen masers of improved stability taking advantage of the following low temperature properties:

a) Lower thermal noise per unit bandwidth (kT). Both the signal-to-noise ratio of the output signal and the intrinsic stability limit vary as $T^{1/2}$

b) Smaller spin exchange cross section for atomic hydrogen. At 4°K this cross section is about 200 times smaller than at room temperature. For a given rate of spin exchange quenching at room temperature we can obtain 200 times greater power output and thus reduce the signal-to-noise in the output signal.

c) Slower speed of the atoms (proportional to $T^{1/2}$), which reduces the wall collision rate.

d) Better mechanical and thermal stability of materials at low temperatures. Superconducting magnetic shields can also be used at sufficiently low temperatures.

The work we report here is aimed principally at understanding more about the interaction of hydrogen atoms with wall coatings of fluorinated ethylene propylene (Dupont Teflon FEP-120 co polymer) and of carbon tetrafluoride (CF_4). The principal measured quantity in these experiments is the "wall shift" of the maser's output frequency. To relate the present data to the study of cold Teflon surfaces made by Michel DeSaintfuscien,[1] we calculated the wall shift per atomic collision from the measured wall frequency shift. As will be seen later, this assumes that the wall surface area is smooth on a molecular scale.

We calculate the average phase shift $\Delta\Phi_g$ per geometrical collision determined from the dimensions of the storage bulb:

$$\Delta\Phi_g(T) = \frac{2\pi\Delta\nu_w(T)}{\nu_c(T)} \tag{1}$$

where ν_c is the rate of atomic collisions with the storage bulb wall and $\Delta\nu_w(T)$ is the frequency shift owing to wall collisions. ν_w is obtained by measuring the maser output frequency ν_{out} and correcting it for second-order Doppler shift, second order magnetic field dependence, and cavity resonator frequency offset pulling as follows:

$$\nu_{out} = \nu_o + \frac{3kT\nu_o}{2mc^2} - 2752H^2 - (f_c - \nu_o)\frac{Q_c}{Q_\ell} + \Delta\nu_w(T) \tag{2}$$

Here ν_o is the unperturbed hyperfine separation frequency of atomic hydrogen,[2] H is the static magnetic field strength in the storage volume, m is the hydrogen atom mass, f_c is the cavity resonance frequency, Q_c is the cavity Q, and Q_ℓ is the atomic line Q.

Each measurement required a determination of the output frequency at several known cavity frequency settings. The output frequency data were fit to a straight line as a function of cavity frequency f_c, and the frequency $\Delta\nu_w$ corresponding to $f_c = \nu_o$ was calculated in order to eliminate the effects of

resonator pulling. From the average velocity of the atoms, $\bar{v} = (8\frac{kT}{\pi m})^{1/2}$, and the geometrical surface-to-volume ratio of the storage volume A_g/V_g, we determine the average collision rate, $\bar{\nu}_c$.

$$\bar{\nu}_c = \frac{\text{average velocity}}{\text{mean free geometrical distance}} = \frac{\bar{v}}{\frac{4V_g}{A_g}} = \frac{1}{\bar{\tau}_c} \tag{3}$$

Following Hardy and Morrow[3] we assume a model for the hydrogen wall surface interaction where some fraction of the wall collisions result in momentary binding of the atom in a potential well characterized by energy E_b. While in the well the atoms have the properties of a two-dimensional gas. The time spent in this state is very much smaller than the mean time between collisions, $\bar{\tau}_c$. The ratio of $\bar{\tau}_s$, the time spent bound to the wall, to $\bar{\tau}_b$, the time between these events, is given by[3]

$$r = \frac{\bar{\tau}_s}{\bar{\tau}_b} = \Lambda \frac{A}{V} e^{E_b/kT} \tag{4}$$

where $\Lambda = \frac{h}{(2\pi mkT)^{1/2}}$ is the thermal de Broglie wavelength.

Since an atom does not bind to the wall on each impact, the time $\bar{\tau}_b$ may involve many collisions. The probability of binding per collision is represented by the fraction $\alpha = \frac{\bar{\tau}_c}{\bar{\tau}_b}$. During a binding collision the phase of the hyperfine interaction is retarded an amount

$$\Delta\phi = 2\pi\bar{\tau}_s\Delta_s$$

where Δ_s is the frequency change of the atom while in the bound state. The wall collision frequency shift is

$$\Delta\nu_w = \frac{\nu_c\alpha}{2\pi}\Delta\phi = \frac{h}{(2\pi mkT)^{1/2}}\frac{A}{V}\, e^{E_b/kT}\Delta_s \tag{5}$$

and the average phase shift per collision is

$$\Delta\Phi_g(T) = \frac{V_g}{A_g}\frac{A}{V}\frac{2\pi h}{kT}e^{E_b/kT}\Delta_s \qquad (6)$$

We note in this expression that A/V is the actual area to volume ratio and A_g/V_g is the geometrically determined area to volume ratio. A is the effective surface area of the storage region coating, which may be microscopically rough, while A_g is the area of the storage region assuming perfectly smooth walls. Because the surface roughness has negligible effect on the storage volume, for practical purposes $V = V_g$.

2. EXPERIMENTAL PROCEDURE

The cryostat shown in Fig. 1 was equipped with a TE_{111}-mode cavity[4] whose interior surface was coated with FEP-120 Teflon and that had a Teflon FEP septum 0.25 mm thick. The atomic hydrogen source is cooled by contact with the copper shroud, and operates at about 80°K. Liquid helium admitted via a control valve into the sample holder cools the cavity.

The maser was operated in the range of 78°K to 50°K with the bare Teflon surface. After completing the data runs for bare Teflon, the system was stabilized at about 60°K and gaseous CF_4 was beamed toward the cavity entrance aperture by a nozzle located in the shadow of one of the pole tips of the hexapole magnet. The system pressure rose to about 10^{-3} torr and was kept there for about 4 minutes by the flow of CF_4.

The wallshift was measured and the coating process was repeated a second and third time. No further shift in frequency was observed. We conclude that we had completely and thoroughly coated the surface using this procedure.

3. EXPERIMENTAL RESULTS

Figure 2 shows the average phase shift per collision based on the geometrical surface to volume ratio of the storage volume. For Teflon we include the entire data set of 1983 and 1984 and the data point at 77.4K made by DeSaintfuscien in 1976.[1] The carbon tetrafluoride data were obtained within 30 minutes of the time of injection of CF_4. The system was then cooled at a rate of 5°K per hour to 52°K, was allowed to equilibrate at 52°K for about 40 minutes, and was then again cooled at 5°K per hour until the cavity reached 45°K. We paused for equilibration for 20 minutes before cooling steadily to 33.6°K at a rate of about 4°K per hour. Frequency measurements were made with the continuously oscillating maser. Measurements at each temperature were made for three or more cavity frequency settings. Each data set was made within a two-minute time interval to minimize errors owing to the constant slow cooling of the cavity.

We found that the temperature gradient between the sample holder and the cavity caused magnetic quenching, probably due to thermoelectric currents. To keep the maser oscillating the field coil current was raised to produce a magnetic field as high as 27×10^{3} gauss. The usual field setting was 12.8×10^{-3} gauss; when gradients were small, data were successfully taken at 2×10^{-3} gauss.

The plot of $-T\Delta\Phi_g(T)$ vs 1000/T shown in Fig. 3 was calculated from measurements taken between noon and 7 P.M. on October 15, 1984. The straight line is a least squares fit to $-T\Delta\Phi_g(T) = 0.42\times10^{-3}e^{154.6/T}$. Measurements made at 43°K, 44°K and 46°K on October 16 fell into the spread of the October 16 data set. Measurements made on October 17 at 53°K and 55°K and on October 18 at 60°K lie well below expected values. We can perhaps conclude that at the higher

temperatures the CF_4 surface sublimes away. The jagged edges and prominences of this surface would disappear first, leaving a progressively smoother surface until all of the CF_4 had been pumped away. This behavior upon warming the CF_4 surfaces has been observed on at least three previous occasions. To date, we have not been able to find reliable values of the CF_4 vapor pressure for temperatures below its melting point of 89°K. From the pressure behavior observed when we warm up the system, we believe that the vapor pressure is significant, perhaps on the order of 10^{-5} torr, at temperatures around 60°K and that at higher temperatures the surface is sufficiently volatile to change its structure significantly in an interval of several days.

We have recalculated $-T\Delta\Phi_g(T)$ vs 1000/T using DeSaintfuscien's data, our 1983 and 1984 Teflon data, and the October 15 data of Fig. 3. The results are plotted in Fig. 4.

From this plot we conclude that the interaction energy of atomic hydrogen on carbon tetrafluoride is 154.6°K, and that of FEP-120 Teflon is 143.4°K. These differ by only about 8 percent, and lead us to the conclusion that the surface interaction of hydrogen colliding with a fluorine atom bound to carbon does not significantly depend on the internal carbon structure. However, we observe a significant difference between the magnitudes of the phase shift per collision for Teflon and CF_4. There is about three times less phase shift per collision for frozen-in-place CF_4 than for Teflon.

From Equation 6 we see that the terms that govern this shift are the actual surface area and the hyperfine frequency shift of the hydrogen atom while in the bound state, Δ_s. Calculations of the hyperfine shift[5] have been given with reasonable agreement with experiments using the assumption that the inter-atomic hyperfine shift is proportional to the interaction potential. When the

hyperfine shift is calculated for collisions with an aggregate of atoms, such as a Teflon molecule, the actual structure of the surface must be modeled in the same way. This micro model of the collision process where hydrogen is considered to interact with, say, 10 fluorine atoms bound to a carbon core must be contrasted with a macro model where the surface is irregular on a much greater scale involving, say, tens of millions of atoms. The situation involving the latter scale can be represented in terms of surface area-to-volume and related to free molecular flow collision processes. In either case it is a question of the actual physical configuration of the fluorine atoms encountered by the impinging hydrogen atom.

We must remember that our plots of log $[T\Delta\Phi_g(T)]$ vs T^{-1} are normalized to a collision rate estimated from geometrical surface and volume. We have used equation 6 to show the connection between DeSaintfuscien's data and ours; we see from this equation that, in principle, $\Delta\Phi_g(t)$ is independent of A/V.

A more realistic way to plot the data is to use equation 5, plotting $\log[T^{3/2}\Delta\nu_w]$ vs T^{-1}. This has the same slope as the $T\Delta\Phi_g(T)$ data, and the prefactor contains A/V and Δ_s.

We conclude from the close agreement between DeSaintfuscien's data and ours that the FEP-120 Teflon dispersion has produced a fairly reproducible surface in these two applications.

From the similarity in the experimental terms shown in the FEP-120 and CF_4 data plotted in Figure 4, we see that the energy of interaction is very similar for these two surfaces. The question of the three-fold to four fold disparity in the wall shift remains.

Fluorine, the most electronegative of all elements, forms extremely stable carbon compounds (fluorocarbons) whose molecular attraction (as well as repulsion) are entirely governed by fluorine. The long chains of the CF_2 (tetrafluor-ethylene) homopolymer (TFE Teflon) or the shorter branched chains of the FEP co-polymer (fluorinated ethylene-propylene) have substantially similar structure in that they can be either crystalline or largely amorphous, depending on their condition after melting, i.e. whether slowly annealed or quenched. There are substantial differences in wallshift between these two physical states[6,5,7], and these differences have been associated with the surface structure. The crystalline surface has the larger wallshift owing to the growth of platelets that produce a rougher surface on a macroscopic scale and to microscopic textural effects of the platelets when pictured as a stack of cordwood where the Teflon chains (logs) of various lengths protrude from the sides of the generally well organized stack.

The homopolymer is obtained in the form of a water dispersion of particles about 0.22 micro meters average diameter stabilized with a soap-like substance to prevent coagulation. The co-polymer has 0.1 micro meter sized particles and is also available in a water dispersion. These dispersions are cast on the surface to be coated, the water evaporated, and the particles sintered or melted together to form a film. The homopolymer has a high viscosity of about 10^{11} poises in the melted state. Its consistency is "more like a frame than a liquid".[5] The co-polymer has melt viscosity of about 10^6 poises and flows more easily. In 1978, the surface of thin films, say 0.002 inches in thickness, were found to be porous from tests made at the U.S. Naval Research Laboratory using electron scattering and low energy electron diffraction techniques.[8] This has led us to increase the coating thickness of our films from about 1 milligram per cm^3 to well over 3 milligrams per cm^3 by applying successive coatings of the

Dupont FEP-120 co-polymer. Whether or not the density of the films has been improved is open to question. What has probably happened under these multiply coated conditions is that we have piled up more and more platelets but still have a porous and, to the hydrogen atom, macroscopically rough surface.

The threefold decrease in apparent surface area by freezing CF_4 probably results from the smoothing of the Teflon surface by a build-up of CF_4 "frost" on the interior of the storage chamber. That this "frosted" CF_4 surface itself is not as smooth as it could be is strongly evidenced by the further reduction in wallshift when the surface is warmed to 60°K. Here we envision a further smoothing of the surface either by melting, or more probably, by sublimation where the pointed peaks are first to go, leaving a smoother surface that lasts as long as there is CF_4 available.

The fact that the Teflon surface is porous and that the collision rate apparently can be reduced by a factor of as much as four times leads us to reconsider the present status of wall coatings created by fusing granules of Teflon applied from a water dispersion. This is a difficult process to control and has a great deal of variability.

The importance of wall coatings is crucial to the hydrogen maser storage technique, where the linewidth of the oscillator is limited by the wall relaxation process. Remarkably little has been done to improve wall coatings since the invention of the maser by Kleppner, Goldenberg and Ramsey in 1969. With support from the Office of Naval Research included as a small part of a contract with the U.S. Naval Research Laboratory (N00014-71-A-0110-0003) an attempt was made in 1975-1976 by our group at SAO to obtain bulbs coated with Teflon polymerized in place using C_2F_4 monomer gas. The technique was developed by the Laboratoire Suisse de Recherches Hologeres (L.S.R.H.), Neuchatel,

Switzerland in 1975 and patented in the U.S.A., France, Japan and Germany. SAO engaged the L.S.R.H. to coat two quartz bulbs with a film of 1000Å to 3000Å thickness made from polymerized C_2F_4, using ultraviolet surface photo polymerization. This was to be done along with samples of glass and KB_r for analyses by pyrolysis to determine molecular weight, and other measurements to determine molecular structure and film thickness.

One bulb was received and tested in December 1975. Samples tested at L.S.R.H. by infrared spectroscopy showed proper Teflon polymer lines. The high temperature pyrolysis test showed no deterioration over 3½ hours at 220°C, indicating satisfactory molecular weight. As part of the contract, a complete report of the coating process from L.S.R.H. was received. Tests run at SAO on the bulbs initially showed excellent line Q results, but in less than a week the coating had failed.

While the maser was oscillating we measured the wallshift and found it to be in the range of normal values for P.T.F.E. Teflon. However, in a few days the line Q diminished steadily from a relatively high value of 1.5×10^9 to well below 1×10^9. We took the maser apart to examine the bulb and found that its surface had deteriorated and was very easily wetted, and that a loose powder appeared on the surface of the water drop we had introduced. We concluded that the film on the bulbs was not the same as on the test samples. L.S.R.H. agreed to recoat the bulbs after testing their system with other bulbs. This work was not done and we were forced to conclude our contract with L.S.R.H. in August of 1977.

To the best of our knowledge, no further work on Teflon-like coatings for hydrogen masers has been done since this date. The present results with frozen CF_4 suggest that another attempt at polymerizing C_2F_4 in place would be

worthwhile. The prospect of a possible fourfold improvement in storage time and developing a controllable means of coating hydrogen maser bulbs is a strong motivation for this renewed effort.

5. ACKNOWLEDGEMENTS

We are happy to acknowledge the excellent work by Mr. Richard Nicoll and Mr. Donald Graveline in the design and construction of much of the experimental apparatus. We are grateful to Prof. Isaac F. Silvera and Dr. Herman Godfried for their many helpful discussions. This work was supported by the Office of Naval Research under Contract N00014-77-0777.

REFERENCES

1. DeSaintfuscien, M., "Etude des effects de paroi dans le maser a hydrogene," Thesis presented at the University of Paris XI Centre d'Orsay, 6 Nov. 1975.

2. Hellwig et.al., "Measurement of the Unperturbed Hydrogen Hyperfine Transition Frequency", IEEE Transactions on Instrumentation and Measurement, Vol. IM-19, No. 4., November 1970. Pp. 200-209.

3. Hardy, W.N., and M. Morrow, "Prospects for Low Temperature Hydrogen Masers Using Liquid Helium Coated Walls", Journal de Physique - C8 Vol. 42, December 1981. Pp. 171-179.

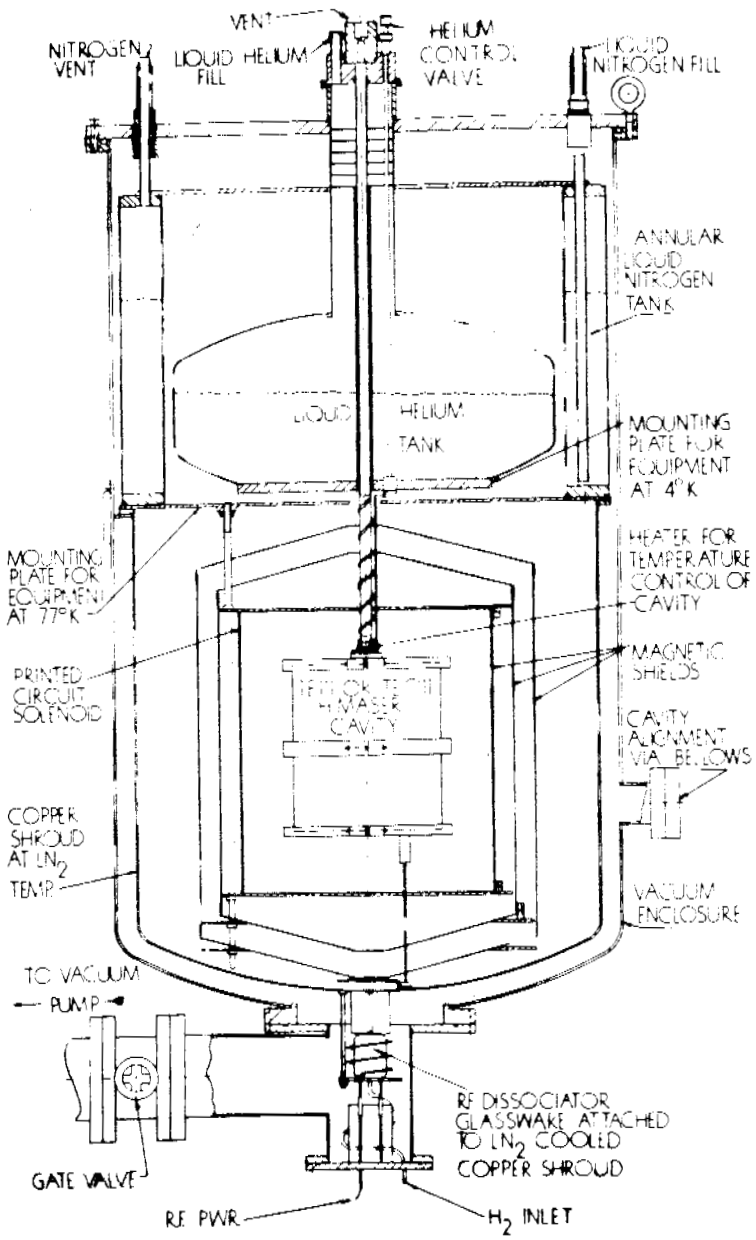
4. Mattison, E.M., M.W. Levine, and R.F.C. Vessot, "New TE_{111}-mode hydrogen maser," Proc. 8th Annual P.T.T.I., Nov. 30 - Dec. 2, 1976. U.S. Naval Research Laboratory, Washington, D.C., pp. 355-367.

5. Zitzewitz, P.W., "Surface Collision Frequency Shifts in the Atomic Hydrogen Maser," PhD Thesis, Harvard University, March 1970.

6. Vessot, R.F.C. and M.L. Levine, "Studies of Hydrogen Maser Wallshift for High Molecular Weight Polytetrafluoroethylene." Proc. 24th Annual Symposium on Frequency Control, USAERADCOM, Ft. Monmouth, NJ, April 27-29, 1970.

7. Zitzewitz, P.W, E.E. Uzgeris, and N.F. Ramsey, "Wallshift of FEP Teflon in the Hydrogen Maser", Rev. Sci. Instr. 41 (1970)

8. Folen, Dr. V., "U.S. Naval Research Laboratory, Washington, DC, Private Communications.



S.A.O. COLD MASER
FIGURE 1

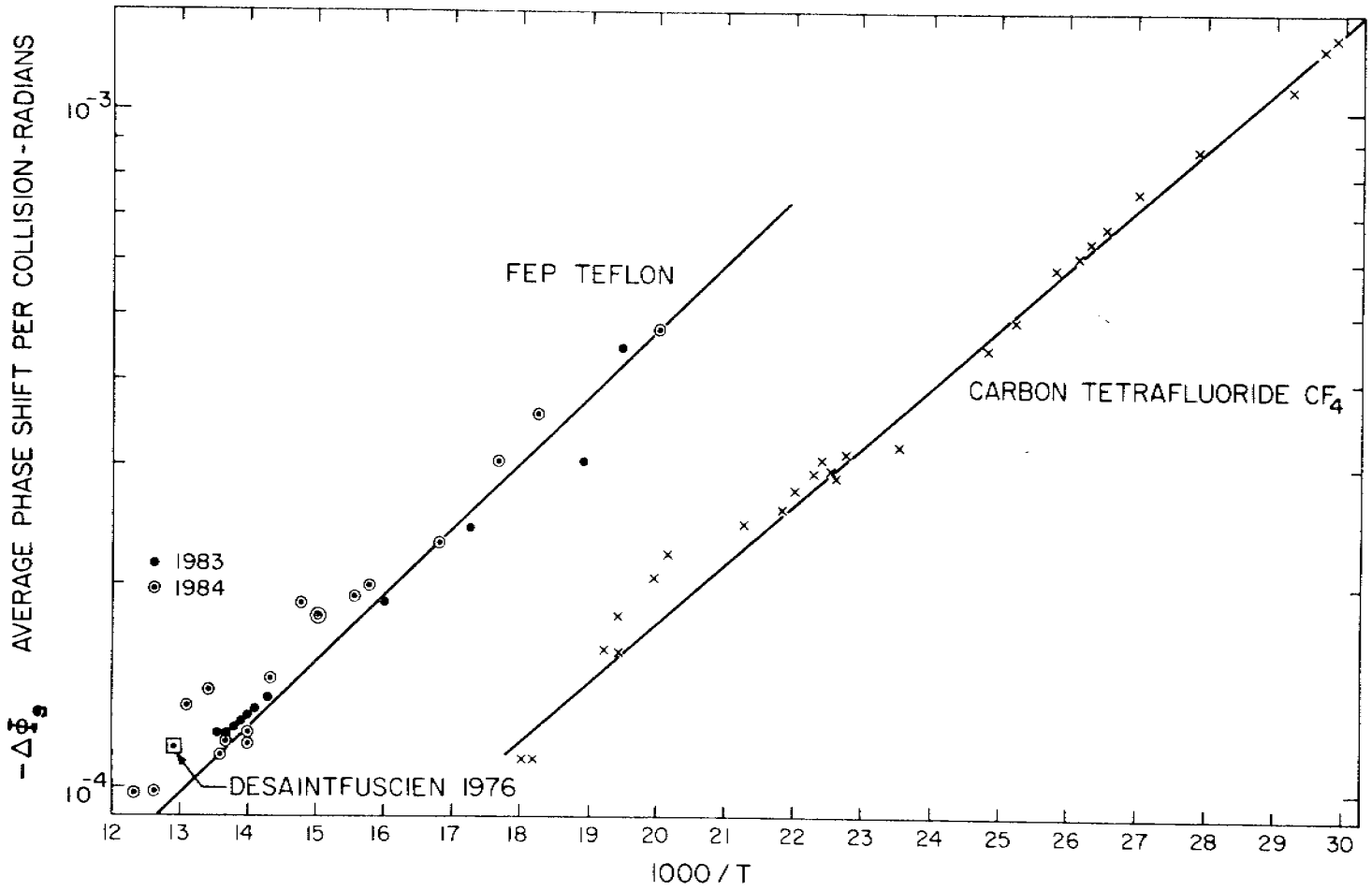

$-\Delta\bar{\Phi}_g$ AVERAGE PHASE SHIFT PER COLLISION - RADIANS
10^{-3}
10^{-4}
FEP TEFLON
CARBON TETRAFLUORIDE CF_4
1983
1984
DESAINTFUSCIEN 1976
12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
1000 / T

FIGURE 2

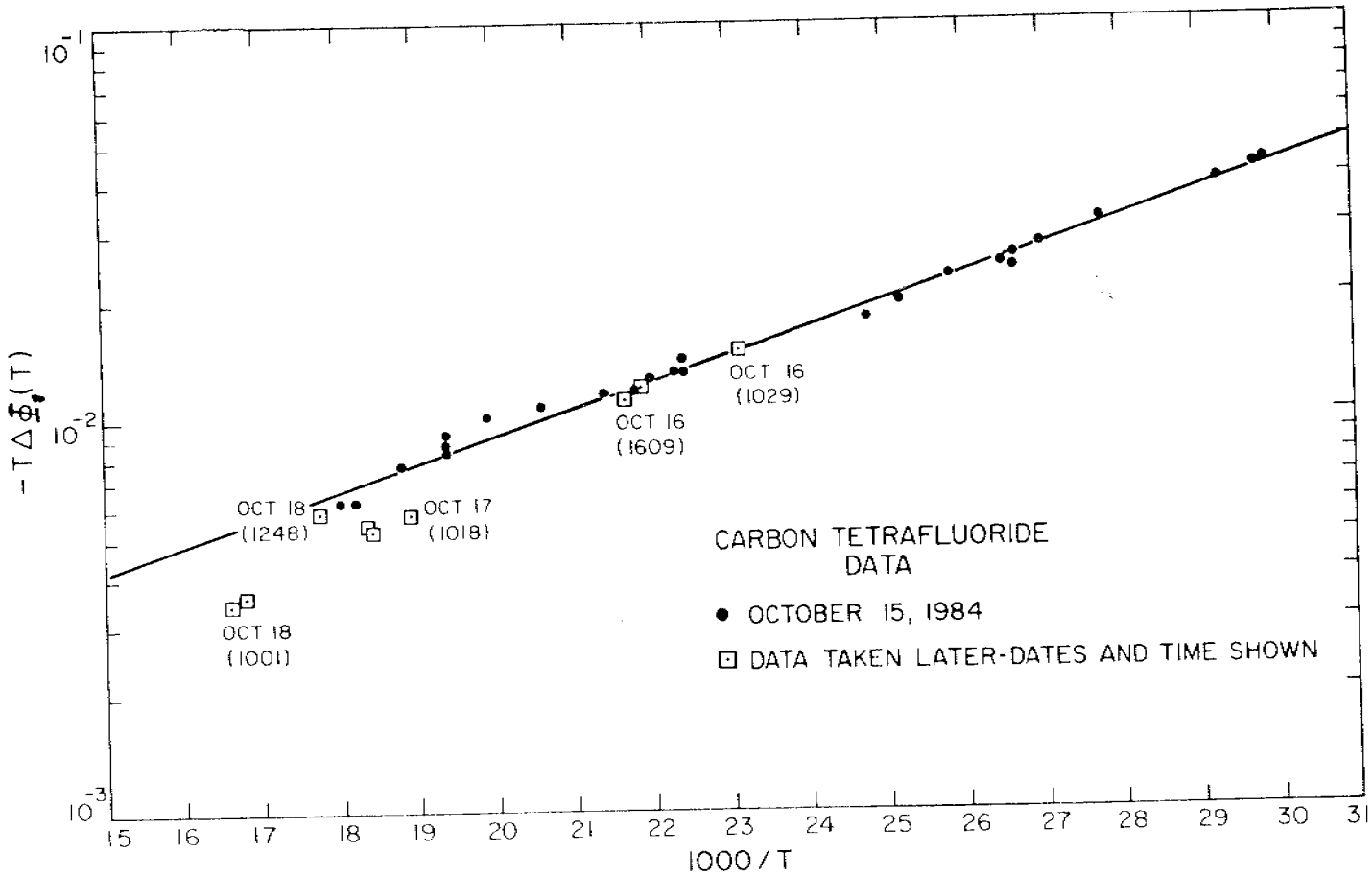

10^{-1}
10^{-2}
10^{-3}
$-T\Delta\Phi(T)$
15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
1000 / T
OCT 18 (1248)
OCT 17 (1018)
OCT 16 (1609)
OCT 16 (1029)
OCT 18 (1001)
CARBON TETRAFLUORIDE DATA
● OCTOBER 15, 1984
⊡ DATA TAKEN LATER-DATES AND TIME SHOWN

FIGURE 3

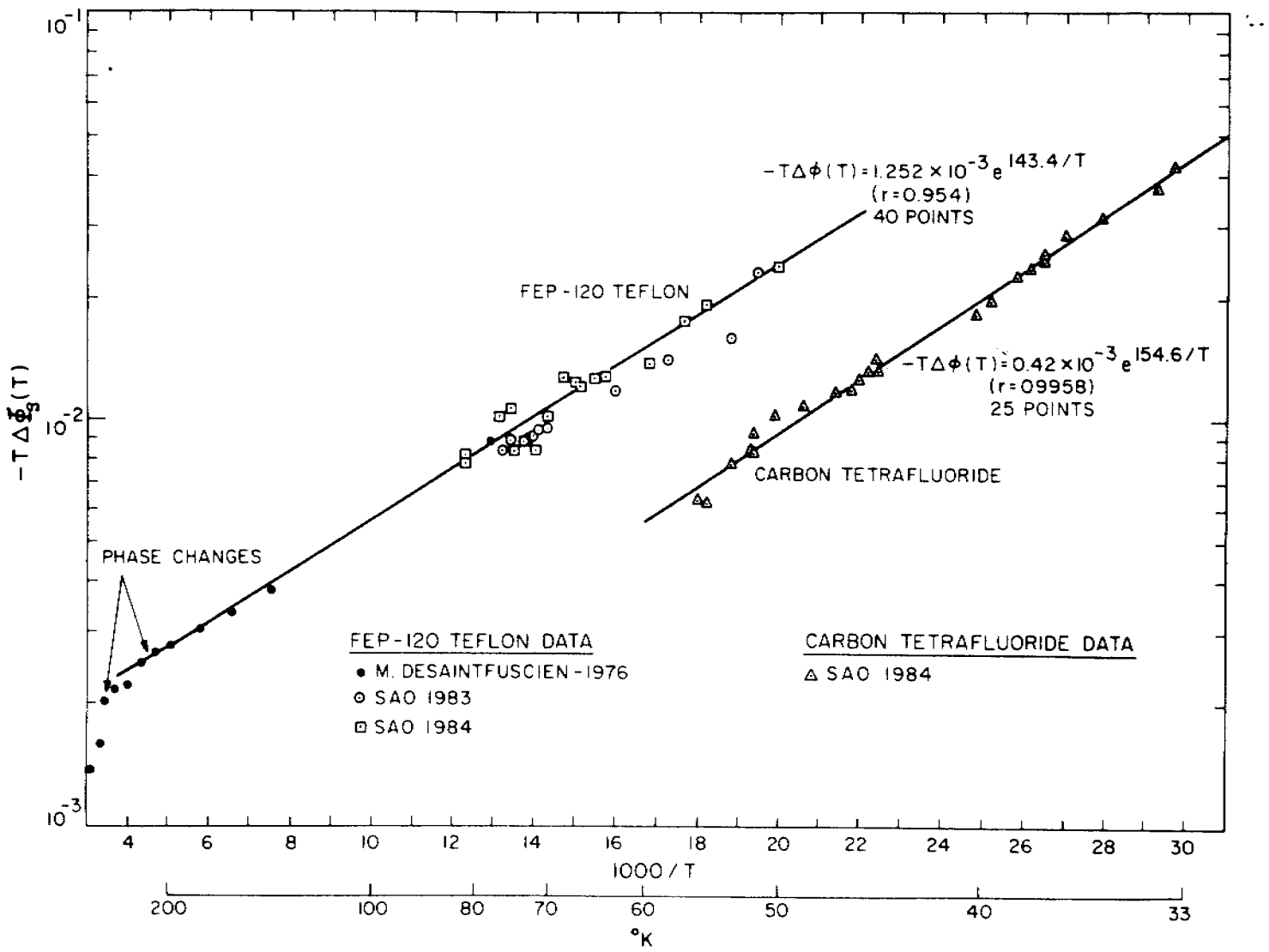

$-T\Delta\phi(T) = 1.252 \times 10^{-3} e^{143.4/T}$
(r = 0.954)
40 POINTS
FEP-120 TEFLON
$-T\Delta\phi(T) = 0.42 \times 10^{-3} e^{154.6/T}$
(r = 09958)
25 POINTS
CARBON TETRAFLUORIDE
PHASE CHANGES
FEP-120 TEFLON DATA
• M. DESAINTFUSCIEN-1976
⊙ SAO 1983
⊡ SAO 1984
CARBON TETRAFLUORIDE DATA
△ SAO 1984
$-T\Delta\phi_s(T)$
10^{-1}
10^{-2}
10^{-3}
4 6 8 10 12 14 16 18 20 22 24 26 28 30
1000 / T
200 100 80 70 60 50 40 33
°K

FIGURE 4

QUESTIONS AND ANSWERS

SAMUEL WARD, JET PROPULSION LABORATORY: Are you ready to make a commitment as to which of these two things is causing the pulling?

MR. MATTISON: I think that both things are going on. In the beginning of the life of the maser when you have just assembled it, the joints between the end plates and the cylinders of the cavity tend to grow together. After a while that stops, or slows down, and what you see is the shrinkage of the bulk material.

MR. WARD: My second question is: We returned a VLG-10 to you, serial number 6, last year for service, and when it came back to us -- we have had it on-line for a year now -- there has been no measurable drift. What happened?

MR. MATTISON: I am glad to hear it. I don't know what happened, but if the cavity was not disassembled, I would expect it to drift very little. The answer is that I am happy to hear it, but I can't give you a reason right off.

MICHEL TETU, LAVAL UNIVERSITY: Have you considered, as a possible influence on the change in tuning of a maser, the change in the characteristic of the tuning of the varactor with time as a possible source?

MR. MATTISON: No, but it's a possibility.

VICTOR REINHARDT, HUGHES AIRCRAFT COMPANY: This is a question really for the questioner. Have you observed that phenomenon?

MR. TETU: No, I haven't.

ALBERT KIRK, JET PROPULSION LABORATORY: What was the actual net difference in daily drift between what you measured against NBS, I guess, and what you determined by cavity tuning? I notice that they don't exactly agree. What was that disagreement?

MR. MATTISON: My rcollection is that the drift measured by cavity tuning was on the order of four in the fifteens per day, and the observed drift rate was, approximately, comparable. The difference would be a couple of parts in the fifteens per day, but the cavity tuning measured rate was an estimate, you can see the change in the slope of the curve. I can't say exactly to what extent they disagree.

MR. KIRK: Would you say that virtually all of the drift is due to the cavity, or is there a possibility that one or two parts per day drift is due to something other than the cavity?

MR. MATTISON: I think that most of it seems to be consistent with the cavity frequency change. I would expect some change in the wall properties, some long term change in the wall shift, but that doesn't show up because you can't separate the two.

MR. McCOUBREY: This initial drift, the relatively rapid drift, does it take place when the masers are first assembled? Does it start when the masers are first assemble, or when they are first turned on?

MR. MATTISON: You can't observe it until you turn them on.

MR. McCOUBREY: But they appear to start when the operation first began at the Naval Observatory, from the data you showed us.

MR. MATTISON: Those masers were built several months before that, and we had tracked that drift prior to the installation at the Observatory. We had observed it in several masers also; you have a drift that starts fairly large, and decreases over time, from the time that they are assembled.

MR. McCOUBREY: If you turn them off for a while, and then turn them back on, you would not expect to see that initial drift again?

MR. MATTISON: The drift would not go back to the original value.