

SPECIAL HYDROGEN MASER WORKSHOP¹

Held on Wednesday, December 5, 1990

Report by

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As part of the 22nd Annual PTTI Meeting, this workshop was held as a discussion forum for hydrogen maser problems, particularly for those related to wall shift and wall relaxation effects. The chairman of the workshop was Jacques Vanier, National Research Council of Canada.

Following are brief summaries of the presentations made by the speakers together with some of the discussion that followed. These summaries were derived from tape recordings of the session and from notes made by Derek Morris.

J. Vanier (National Research Council of Canada)

In his opening remarks, Dr. Vanier stated that the wall effect in hydrogen masers was the main problem under discussion. He asked the speakers to speak frankly about results which they had found. He expressed the hope that frank discussion of the problem would suggest further experiments which might be tried to clarify the problem.

Dr. Vanier presented some data on two masers built at Laval University. The results represented 5 years of experiments, showing the line-Q (extrapolated to zero pressure) varying with time. For a 16.5 cm diameter bulb, the line Q was initially $6-7 \times 10^9$. However, it decreased with time and still had not stabilized after 5 years. A smaller bulb (11.5 cm diameter) showed a less rapid decrease in line-Q with time and the value appeared to stabilize. The reason for the behaviour was not clear.

Possibly there could be contamination from Viton O-rings used, or from silver solder used to braze the palladium leak valve. Both bulbs were coated with FEP-120 Teflon.

C. Audoin (Laboratoire de l'Horloge Atomique, France)

Dr. Audoin gave information on four hydrogen masers constructed at his laboratory. All had bulbs coated with FEP-120 Teflon. No wall shift measurements were made, but measurements of the transverse relaxation time T₂ (proportional to the line-Q) were made. For one maser (built around 1970) which used metal gaskets throughout, T₂ showed a continuous decrease from 515 ms to 320 ms. The maser eventually stopped oscillating, and the bulb was recoated in 1989 with Teflon purchased in 1978. After the recoating, T₂ was measured as 515 ms again, i.e. it returned to its original value.

¹Editors note: This summary was prepared by Dr. Morris from tapes of the workshop and from his notes. Time did not permit proofreading of the text by the various speakers, so if there is a question, please contact the individual speakers directly.

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Later, three smaller masers were built for radioastronomy use. These use some Viton O-rings. The bulbs of these were coated in 1984 with the same batch of Teflon (bought in 1978). The value of T2 decreased more rapidly than for the older maser and the oscillation level decreased. This was particularly true for masers #2 and #3. In 1988 the bulb in maser #2 was recoated with the same batch of Teflon. Afterwards, T2 decreased very rapidly. In the last year or two, this bulb has been recoated, this time with new Teflon. So far, T2 seems to be more stable. For maser #3 it is not certain if T2 has changed further.

Dr. Audoin also mentioned that the masers at his laboratory are shut down for the whole of the month of August each year, with only the vacuum pumps and temperature controls left in operation. When they are set in oscillation again each September the oscillation level is found to be higher initially and then decreases within a few days. In discussion of this effect, it was suggested that contributing causes may be a change in the efficiency of the dissociator after start-up and/or surface absorption of hydrogen on the storage bulb.

H. Schweda (Observatoire Cantonal Neuchatel, Switzerland)

Dr. Schweda presented results for an EFOS hydrogen maser whose storage bulb had a bad coating. The line-Q (extrapolated to zero pressure) decreased from 2.1×10^9 to 1.4×10^9 over 140 days without apparent stabilization of the final value. In addition, the maser output decreased and the frequency (corrected for cavity tuning) showed a non-linear increase with time. The bulb was then recoated with FEP-120 using nominally the same procedure but with better control of parameters, and put back in the same maser with the same hydrogen source. This time the initial line-Q was 2.5×10^9 . It decreased to 2.3×10^9 but had stabilized at this value after 180 days. Attempts are being made to characterize test specimens of Teflon coatings using infrared spectroscopy, electron spin resonance and photoelectron spectroscopy. During discussion on this paper, surprise was expressed that the frequency of the maser increased with time. Several other laboratories have found the frequency decreasing with time. In discussions as to possible causes of a "bad" coating, H.T.M. Wang (Hughes Research Laboratories) mentioned that in one case when a maser had stopped oscillating after two months operation, destructive testing on the bulb showed the presence of titanium on the wall (presumably sputtered from the ion pump).

A. Kirk (Jet Propulsion Laboratory, USA)

Mr. Kirk presented frequency data for six JPL (manufactured by SAO) masers located in different parts of the world as part of the Deep Space Network. Two masers are located at each site, so that one can be tuned against the other. In operation, the masers slowly drift in frequency and the procedure employed is to allow the frequency of a maser to drift until a limit is reached ($+ 5 \times 10^{-13}$). Then the field is checked, the maser is tuned, the line-Q is checked and the synthesizer is calibrated against the NIST time scale. Then the maser cavity is deliberately mistuned to give a maser frequency offset of -5×10^{-13} and the maser is left to run again for about a year before the procedure is repeated. Over the period 1978 to 1990 several masers have shown changes in the synthesizer frequency, indicating that the wall shift is changing. After correcting for the change due to cavity aging, the maser frequencies have all shown a decrease with time. A change of several parts in 10^{12} has occurred for the older VLG-10 masers; the newer VLG-11 units seem to have shown less effect. In one maser a bulb was recoated because the line-Q had deteriorated. The frequency was different by 1×10^{-12} afterwards. In all other cases, the line-Q was stable over the 12 year period.

In many cases, the masers were opened to the atmosphere prior to the tuning measurements in order to replace the ion pump elements. In the future, the maser parameters will be measured before and after replacement of the elements.

E.M. Mattison (Smithsonian Astrophysical Observatory, USA)

Dr. Mattison showed a transparency which replotted the data presented by A. Kirk and showed the frequency decrease of 1 to 2×10^{-15} per day due to wall shift change. He also showed the frequency change due to cavity dimensional changes, as derived from varactor voltage changes required to retune the cavity. The characteristic of this is a decreasing slope with time. All the cavities studied were made of Cervit, and the frequency changes found were consistent with the shrinkage of the actual material of the cavities.

R.F.C. Vessot (Smithsonian Astrophysical Observatory, USA)

Dr. Vessot discussed results obtained on the wall phase shift per collision, $\Delta\phi(T)$, as a function of the inverse of temperature. A change of slope occurs, which is indicative of the change of state of Teflon. In France, Dr. Desaintfuscien obtained data down to a temperature of 77 K. Dr. Vessot's group obtained data to 60 K before maser oscillation stopped. They found that further insight into the process occurring on the wall could be obtained by plotting $-T\Delta\phi(T)$ versus $1/T$. The energy of the interaction of the atom when it resides on the surface could be derived from the plot. The slope was $143.3/T$. When carbon tetrafluoride was frozen on the bulb wall, a lower value of wall shift was found but the data on the plot showed the same slope as before. This indicates that the interaction energy was unchanged but that the surface area was changed by a factor of 3 or 4 compared to that of the Teflon.

The USSR material, Fluorocarbon F-10, has a lower wall shift than FEP-120, perhaps by a factor of 8. This may be due to a better surface area. Experiments with this material over a range of temperature are required in order to clarify this.

D. Morris (National Research Council, Canada)

Dr. Morris presented results showing a decrease in frequency of a hydrogen maser (after correction for cavity tuning) over a period of 10 years as compared with the NRC primary cesium clock CsV. This change in frequency is attributed to a change in wall shift of the bulb. This bulb was coated in 1980 with 4 coats of FEP-120 Teflon which had been purchased in 1965. The total frequency change which occurred in 10 years was 7.2×10^{-12} , or about 2×10^{-15} per day. During the same period the line-Q at operating beam flux showed changes less than 19%. The maser used has many Viton O-rings. It was not run continuously for the whole period, but the cumulative time of oscillation was 7 years. Measurements over periods of 1 to 3 years on four other bulbs, three of which were coated with FEP-120 and one with Teflon 42, have also shown frequency decreases of approximately the same magnitude.

Recently, two new masers have been put into operation. These use metal gaskets throughout. The storage bulbs were coated in 1987 with a batch of FEP-120 purchased in 1985. No wall shift data are available, but one maser has shown a degradation in line-Q of about 30% in one year.

In comments, Dr. F. Walls (NIST) stated that in passive masers he has built they found changes in frequency less than 2×10^{-16} per day. He feels that careful filtering of the FEP-120 dispersion to remove any large particles is important.

H.E. Peters (Sigma Tau Standards Corporation, USA)

Mr. Peters stated that a number of design features of their masers were different to those built in other laboratories. For example, they use metal cavities, non-spherical storage bulbs, and cavity frequency switching servos. In addition they coat their bulbs differently; only one coat is used and the firing temperature is different. He showed results obtained at the U.S. Naval Observatory with Sigma Tau maser NAV-2 from one month after it was delivered in November 1989 up to August 1990. The frequency of this maser showed a slope of $+ 3.2 \times 10^{-15}$ per day initially versus TAI. This has decreased to $+ 9.4 \times 10^{-16}$ per day more recently. The increase in frequency with time is typical of all their masers. A second set of results was presented for 4 other masers over 90 days. All showed a drift of $+ 2 \times 10^{-15}$ per day relative to TAI. Mr. Peters said that it is conceivable that frequency changes might be due to a drift in the electronics but it is unlikely that, in this case, all the 24 masers that they have built would show a frequency change in the same direction. Therefore, he feels that either the wall shift is changing with time or the ratio of the hydrogen and cesium hyperfine frequencies is changing with time, which would imply that the fundamental constants are changing.

J. Ponsonby (University of Manchester, UK)

Dr. Ponsonby drew attention to a form of Teflon, designated Teflon AF, which dissolves in perfluorinated solvents. According to an article cited (Electronic Product Design, Vol. 11, No. 10, p. 22, October 1990) defect-free layers as thin as $0.2 \mu\text{m}$ can be put on using this material and can be removed with an appropriate solvent.

In discussion, Dr. R. Vessot (SAO) said that they had purchased some of this material and had used it to coat glass slides. It has a higher specific gravity than FEP-120. It was found to stick to glass only if the surface had been roughened by sandblasting. He felt that it would be worthwhile to try Teflon AF in hydrogen masers.

J.J. Suter (Johns Hopkins University, Applied Physics Laboratory, USA)

Dr. Suter described experiments to determine if exposure of a storage bulb coated with Teflon to nuclear radiation affected the line-Q. In one maser the bulb was recoated and the line-Q was measured. Then the bulb was removed and was irradiated in air by a commercial company with 10 krad of 1.25 MeV photons from a gamma ray source. After irradiation the bulb was put back in the maser, and it was found that the line-Q had increased by between 6% and 15%. He emphasized that this was based on just one experiment. They are planning to repeat this experiment on another hydrogen maser under more carefully controlled conditions.

They also have an ongoing program examining irradiated Teflon samples on quartz slides, using microscopy. He showed results obtained using an X-ray topography technique on such a slide before and after irradiation. The X-rays were focussed on a part of the slide where some lamellae of the Teflon could be seen. The measurements indicate that the density of the layer is decreased by the irradiation. He feels that a change in polymerization of the Teflon is occurring on irradiation, but he had expected

the line-Q to decrease rather than increase.

A.A.Uljanov ("QUARTZ" Research and Production Association, USSR)

Dr. Uljanov gave some details of the "QUARTZ" company. This company specializes in the development of measuring devices and medical instrumentation. It consists of a scientific institute, two laboratories and five production plants, and employs a total of 20,000 people. Dr. Uljanov is director of the company and director of the institute. The company produces frequency standards based on rubidium, cesium and hydrogen. The company has 15 years experience with hydrogen masers, and has produced the system used in the State Standard of Time and Frequency in the USSR.

N.A. Demidov ("QUARTZ" Research and Production Association, USSR)

Dr. Demidov stated that the stability of the wall shift in a hydrogen maser depends on the material used (they have used Fluorocarbon F-10 recently), on the method of application, and also on the level of residual gas in the storage bulb. He gave information on a poor coating. The bulb was operated at a temperature of 50°C, and the maser showed a large change in frequency with time at first. This is believed to be due to outgassing of the coating. The bulb was then operated at 37°C and the frequency change then diminished. Thereafter, the temperature of the bulb was raised to 50°C without removing it from the maser, and the stability of the wall shift improved. In their masers they use a three-section vacuum system. By improving the technology of their masers they have lowered the drift in wall shift. As described in the paper by N.B. Koshelyaevsky of VNIIFTRI given on December 4, the drift in wall shift of their masers was about 1×10^{-16} per day. No data are available for the latest masers but the results are expected to be about the same as this. Dr. Demidov feels that higher bulb operating temperatures tend to give rise to greater frequency drifts. Therefore, they are planning to put a CHI-75 maser in a refrigerator at VNIIFTRI to reduce the bulb temperature to 20°C. In addition to an increase in the stability of the resonator by this means, a reduction in wall shift drift should occur.

There were a number of questions regarding the F-10 coating material (made in Leningrad), which apparently has a smaller wall shift than FEP-120. Dr. Demidov said that the material is in the form of a suspension in water with additional surfactants. Three layers are usually used on a storage bulb. The coating procedure is as follows: - a small amount of the suspension is placed in the bulb and the material is dried on the wall using a stream of dry nitrogen. The bulb is then baked at 120 - 140°C. A second coat is then applied in the same way, and, if possible, a third coat is applied. If the third coat cannot be put on successfully the coatings have to be removed and the complete procedure repeated. If the firing temperature is raised to 260°C after the first coat, it is not possible for a second coat to adhere. The average time to coat a bulb is from 3 to 7 days. Several patents have been obtained for the coating procedure.

He mentioned that in addition to the maser with a flexible storage bulb which he described in a paper on December 4 they are now working on an improved design of flexible storage bulb maser.

H.T.M. Wang (Hughes Research Laboratories, USA)

Dr. Wang discussed some results which, although not directly connected with the wall shift problem, were relevant to masers with Viton O-rings. In 1983 they built a small maser which used some O-rings, and was pumped by a getter pump and a small ion pump. The output frequency of the maser

was stable. When the ion pump was switched off the maser continued to oscillate but the frequency drifted. There was no detectable vacuum leak. However, when a residual gas analyzer was put on the system it was found that, with the ion pump off, the partial pressure of argon after five weeks rose to three times that of the hydrogen. This was attributed to argon permeation of the Viton seals. It was thought that this might be responsible for the frequency change that was found. Therefore, they have used metal gaskets on later masers.

Dr. Vessot (SAO) said that they had observed similar affects. For that reason, when they built a lightweight maser which had some O-rings, they baked it at 100°C for 3 weeks to outgas it, and used a small ion pump in addition to the sorption cartridge. Residual gas analysis showed that the argon contamination was greatly reduced. He does not feel that argon is causing wall shift problems. Contamination by hydrocarbons is a more likely cause. Both speakers agreed that it is desirable to use metal gaskets throughout the maser.

G.M.R. Winkler (U.S. Naval Observatory)

Dr. Winkler described the performance of 12 hydrogen masers (6 made by Sigma Tau Standards Corporation and 6 by the Smithsonian Astrophysical Observatory) in use at USNO. All of these masers have exhibited constant frequency drift rates. The masers are in five locations which are up to 200 m from the central monitoring location. Phase measurements between them are made at 100 s intervals, with a resolution of 5 ps. He discussed the possible effect of impurity atoms not only on the storage bulb wall but also on the dissociator. Impurities in the discharge may cause variations in the hydrogen flux which can cause output frequency variations, if the cavity is slightly detuned.

Nevertheless, under optimum conditions at USNO they have been able to reproduce the variations of an unknown maser oscillator over a period of 95 days within 1 ns with respect to the mean of the group. He stressed that any change in maser environment causes instability. He has found that, after an interruption, the subsequent re-establishment of various servos may cause changes which can last for a week.

Further discussion

Dr. L. Maleki (JPL) referred to a suggestion by Prof. Norman Ramsey that diamond films might make a good storage bulb coating material if the technology could be worked out, and asked if anyone knew if such films had been made. Dr. H.T.M. Wang (Hughes Research Laboratories) said that experiments were being carried out for the production of diamond films on substrates for integrated electronics. Dr. R. Vessot (SAO) said that he understood that there was a process available by which diamond films could be put on flat plates. So far, such films have not been tried on bulbs. He feels that perhaps a more promising material to try is Fomblin oil. This is a stable perfluorinated oil which Prof. Ramsey has used for storing polarized neutrons.

Closing remarks

In his concluding remarks Dr. J. Vanier said that, although there are still many unanswered questions regarding the wall shift problem in hydrogen masers, he felt that the presentations and discussion had been valuable in pointing out further avenues for exploration.