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A SHORT DISCUSSION OF UV/VIS ABSORPTION BY OTHER SPECIES

A. L. SCHMELTEKOPF

I WILL DISCUSS THE SPECTROMETERS WE HAVE BUILT USING THE RETICON RL1024S DIODE ARRAY CHIPS. THESE CHIPS HAVE DIODES THAT ARE 24 MICRONS WIDE AND 2.5 MM HIGH. THIS GIVES A VERY GOOD ASPECT RATIO FOR USE AS THE EXIT SLIT OF A SPECTOMETER. EACH DIODE HAS 2 PICOFARADS OF CAPACITANCE AND IS CHARGED TO 5 VOLTS THAT MEANS THAT EACH DIODE HAS IN ACCESS OF 64 MILLION ELECTRONS STORED ON IT WHEN IT IS READY TO BE EXPOSED TO LIGHT. THUS SINCE THE DIODES HAVE 30 TO 85 PERCENT QUANTUM EFFICIENCY (AROUND 80 THROUGHOUT THE VISIABLE) WE CAN SAY THAT EACH DIODE IS CAPIABLE OF INTEGRATING 64 MILLION PHOTONS. THUS THE NOISE ON EACH DIODE DUE TO SHOT NOISE ALONE IS 8000 PHOTONS YIELDING A BEST SIGNAL TO NOISE FOR A DIODE OF 8000 WITH A SINGLE INTEGRATION. WE OFTEN INTEGRATE FOR 64 CYCLES AND THUS WE COMMONLY HAVE A SIGNAL TO NOISE OF 64000 PER DIODE.

THE SPECTROMETERS WE HAVE BEEN USING ARE 26 CM CROSSED ASYMETRIC CZERNY-TURNERS THAT HAVE 0.05 NM/DIODE DISPERSION IN 3RD ORDER AND 0.075 NM/DIODE DISPERSION IN THE 2ND ORDER. THE SPECTROMETERS HAVE BEEN DESIGNED TO BE USED FOR NO2 FROM 400 TO 450 NM IN THE 3RD ORDER AND FOR NO3 FROM 600 TO 675 NM IN 2ND ORDER. WE HAVE A CAREFULLY SELECTED SET OF FILTERS TO SEPERATE THE 2ND AND 3RD ORDERS SO THAT, BY CHANGING FILTERS UNDER COMPUTER CONTROL, ONE CAN LOOK AT NO2 OR NO3. BY CAREFULLY LOOKING AT THE BAND WIDTHS OF NO2 AND NO3 WE HAVE SELECTED THE ENTRANCE SLIT WIDTH TO BE 250 MICRONS THUS (TAKING INTO ACCOUNT THE ASYMETRY OF THE SPECTROMETER) CORRESPONDING TO A RESOLUTION OF 12 DIODES OR 0.6 NM IN THE 3RD ORDER AND 0.9 NM IN 2ND ORDER

WE HAVE USED THESE SYSTEMS TO LOOK AT NO2 USING THE SUN, THE SKY AND THE MOON AS LIGHT SOURCES AND HAVE LOOKED AT NO3 USING THE MOON AS THE LIGHT SOURCE. FROM ANY OF THESE SOURCES YOU CAN GET A LITTLE INFORMATION ABOUT THE ALTITUDE OF THE ABSORBING LAYER BUT ONLY IN A GROSS SENSE. HOWEVER, WE CAN GET VERY HIGH SENSITIVITY. IT IS EASY TO RESOLVE 0.01% ABSORPTION IN THAT CASE YOU CAN SEE 3.0(14)/CM**2 FOR NO2 AND 6.0(12)/CM**2 FOR NO3. THIS SENSITIVITY IS VERY EASY TO OBTAIN EVEN IF YOU DO NOT HAVE A VERY GOOD KNOWLEDGE OF THE OTHER SPECIES IN YOUR SPECTRAL RANGE. IF YOU HAVE A GOOD QUALITY FRONHOFFER SPECTRUM OF THE SUN WITH NO, OR LITTLE, INTERVENING ATMOSPHERE AND AN UNDERSTAND THE RING EFFECT THEN IF THE ATMOSPHERE IS NOT TOO WET YOU CAN DO NO2 ABOUT 50 TIMES BETTER THAN STATED ABOVE (TO ABOUT 6.0(12)/CM**2). TO IMPROVE NO3 SENSITIVITY YOU NEED TO KNOW SEVERAL OTHER THINGS AS WELL; YOU NEED TO KNOW THE CROSSECTIONS FOR H2O, O2 AND O4. THEN YOU COULD GET DOWN TO ABOUT 2.0(11)/CM**2. THIS LOOKS TO BE MUCH BETTER THAN THE SIGNAL TO NOISE THAT WAS STATED ABOVE, BUT YOU GAIN FROM TWO SOURCES; YOU HAVE DONE AN AVERAGING TO FORM AND EFFECTIVE EXIT SLIT AND YOU USE ALL THE DIODES IN THE SPECTRUM IN A LEAST-SQUARES ROUTINE TO FIT THE SPECTRUM. THE AMOUNT YOU GAIN FROM THE LEAST-SQUARES DEPENDS ON THE SPECTRAL SIGINATURE OF THE GAS OF INTREST (LOTS OF WIGGLES; BIG GAIN, FEW WIGGLES; SMALL GAIN).

WE HAVE A YEARS WORTH OF ZENITH SKY DATA FOR NO2 TAKEN AT FRITZ PEAK IN 1985 AND A YEARS WORTH OF NO3 DATA TAKEN AT FRITZ PEAK USING THE MOON AS A LIGHT SOURCE BY JOHN NOXON IN 1984. THE NO2 DATA IS BEING REDUCED AND NOXON HAD REDUCED SOME OF HIS NO3 DATA BY HAND. HOPEFULLY THAT DATA REDUCTION WILL BE COMPLETED SOMEDAY.

WE ORIGINALY DESIGNED THESE SPECTROMETERS TO BE CONTROLLED BY A HOME BUILT COMPUTER WHICH IS TOO SMALL TO ADEQUATLY CONTROL THE SPECTROMETER AND DIODE ARRAY. THE DIODE ARRAY ELECTRONICS IS SLIGHTLY NOISIER THAN WE WOULD LIKE AND IS NOT AS FLEXIBLE AS WE WOULD LIKE. AS A RESULT WE ARE NOW REDESIGNING THE ELECTRONICS TO WORK WITH A NEW COMPUTER AND WE HOPE TO HAVE

THAT COMPLETED BY THE END OF THE YEAR. WE PLAN TO USE THE SYSTEMS MOSTLY TO DO TROPOSPHERIC MEASURMENTS OF NO2, NO3, H2O, O4 (TO GET AT TEMPERATURE), OH, SO2, O3 AND A NUMBER OR OTHER SPECIES. THIS SYSTEM WILL USE A RETRO REFLECTOR 10 KM ACROSS A VALLEY FROM FRITZ PEAK AND USE EITHER A QUARTZ IODINE OR HIGH PRESSURE XENON LIGHT SOURCE. IN THE RESIDUALS OF THE DATA THAT WE HAVE TAKEN TO DATE THERE ARE A NUMBER OF SPECTRAL FEATURES THAT WE HAVE NOT BEEN ABLE TO IDENTIFY AND SOME OF THEM HAVE VERY INTRESTING DIURNAL CHARACTERISTICS. WE HOPE TO BE ABLE TO MEASURE SOME OF THE CROSSECTIONS THAT WE NEED IN THE LAB AND THEN USE THEM TO REDUCE OUR RESIDUALS. I BELIEVE THAT IF SHOT NOISE WERE THE ONLY NOISE SOURCE THAT WE WOULD EASILY BE ABLE TO HAVE 1(6) AS AN EFFECTIVE SIGNAL TO NOISE. THESE DIODE ARRAYS WORK FROM BELOW 250 NM TO 1100 NM, THEY HAVE A HIGHER QUANTUM EFFICIENCY THAN ANY PHOTOMULTIPLIER AND THE HAVE THE MULTIPLEX ADVANTAGE OF TAKING ALL OF THE SPECTRUM AT ONCE, FOR THOSE REASONS I BELIEVE THAT THEY WILL BE INCREASINGLY USED IN ATMOSPHERIC ABSORPTION MEASUREMENTS. THE ONLY DISADVANTAGE IS THE FACT THAT YOU CANNOT MAKE AN AMPLIFIER THAT HAS A NOISE LEVEL BELOW 450 ELECTRONS (BECAUSE OF THE VIDIO LINE CAPACITANCE ON THIS ARRAY) AND THUS A DIODE ARRAY ONLY EXIBITS ITS SUPERIORITY OVER THE PHOTOMULTIPLIER FOR LARGE SIGNALS.