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Author: J. B. Davidson

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Prepared by the
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830
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INTERIM REPORT

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ACKNOWLEDGEMENTS

FEASIBILITY OF RAMAN SPECTROSCOPY FOR MULTI-SPECIES
DETERMINATION IN FISSION PRODUCT RELEASE STUDIES

I. STATEMENT OF PROBLEM AND OVERALL APPROACH

Laser-Raman Spectroscopy (LRS) is a proposed method for determination of molecular species in a fission product release experiment (Report SAND80-2662).[1] The Sandia (Albuquerque) group have outlined controlled laboratory experiments in which several of the expected vapor species would be examined singly and in combination using a conventional scanning LR excitation and detection system and a high temperature cell. Raman spectra and concentration data from these experiments were to be extrapolated to an actual fuel element vaporization experiment involving high temperature steam to determine the feasibility of doing simultaneous multiwavelength, multispecies recording of spectra as close to the point of fission product release as possible. It was proposed that a wide-range, TV-Echelle spectrograph developed at ORNL might be used for recording the spectra. A series of integrated exposures of the order of 30 s would be recorded on analog video tape for perhaps 1 h. After the experiment, the data at selected intervals could be digitized by and stored in image memory. Spectra could be identified by comparison with previous calibration runs. The evolution of several species it was surmised could be studied at leisure since the whole experiment could be reproduced (spectroscopically) from the tape.

II. SPECIES OF INTEREST

According to SAND80-2662, the main species of interest are listed below with their approximate Raman frequency shifts (Table 1). Data in Angstrom units based on a 4880 A exciting line along with handbook temperatures to give a vapor pressure of 1 torr were added. In discussions and correspondence with the Sandia (Albuquerque) group, it was agreed they would attempt to obtain high temperature spectra for several of the species of primary interest and provide us with concentration and sensitivity (cross-section) data from which we could extrapolate instrumentation requirements for the simultaneous multispecies system which is considered necessary to record as many of the time-varying species as possible. It was believed that the Sandia group could simulate fairly closely (with non-radioactive, single species) the conditions projected for the hot cell experiment with a radioactive fuel element.

While waiting for the Sandia results, we decided to investigate whether our TV-Echelle Spectrograph[2] could be adapted for Raman spectroscopy.

Table 1. Species of interest

Species*	Vapor Pressure 1 mm	Wavelength $\overset{\circ}{A}$	Approximate Raman Frequency Shift	
			$\overset{\circ}{A}$	cm^{-1}
CsH		4677	203	890.7
CsI	738°	4846	33.58	142
H_2	−263.3°C	4019	861	4395
HI	−123°C	4386 Å	494	2390.5
I_2	38.7°C	4829 Å	50.56	214.57
N_2	−226.1°C	4376 Å	50.39	2359.61
O_2	−219°C	4350 Å	349.4	1580.361
OH		4127 Å	752.3	3735.21
Rb_2	297°C	4866 Å	13.60	57.28
Se_2	356°C	4788.6 Å	91.37	391.77
SrI		4838.9	40.85	173.9
Te_2	520°C	4830.9	59.1	251

*Other species are CsOH, Cs_2, CsO, TeO_2 , H_2Te, ZrI_4, RbI and possibly other tellurium compounds. H_2O in the form of high temperature steam will be present. The Raman frequencies of H_2O are 3825.3, 1653.9 and 3935.6 cm^{-1}.

III. RAMAN EXPERIMENTS WITH THE ORNL-TV-ECHELLE SPECTROGRAPH

Although we had no suitable laser for Raman excitation we were able to obtain a pulsed N_2 laser of 50 mW maximum average power at 60 pulses per second. A microscope was adapted with quartz lenses for coupling the scattered light to the spectrograph. Quartz lenses were used to focus the very broad rectangular beam (20 × 40 mm) into the sample.

The Rayleigh line at 3371 A was blocked from the detector by opaque tape. Using this set-up we were able to obtain the strong Raman lines of liquid CC/4, Fig. 1, in 20 - 60 s without wavelength scanning. Both

Stokes and anti-Stokes lines were recorded. The total spectral coverage, Stokes and anti-Stokes, was ~100 A, although spectrograph range was much broader -- approximately 6000 A. As may be seen from the table ±1000 A would probably be adequate -- thus casting doubt on the advantages of the Echelle-crossed-dispersion system. The sensitivity of the overall system was disappointing since we felt we should be able to record CCl_4 spectra in realtime or at least in a second or so. The main problem, we believe, is the broad area beam from the N_2 laser which we were unable to concentrate sufficiently in the sample. Lacking a suitable laser we discontinued the TV-Echelle experiment and sought help from G. Begun, of the Chemistry Division, who agreed to look at a sealed CsI sample at temperatures in the 600-800°C range using his conventional Raman spectrometer equipped with a 2 watt Argon laser.
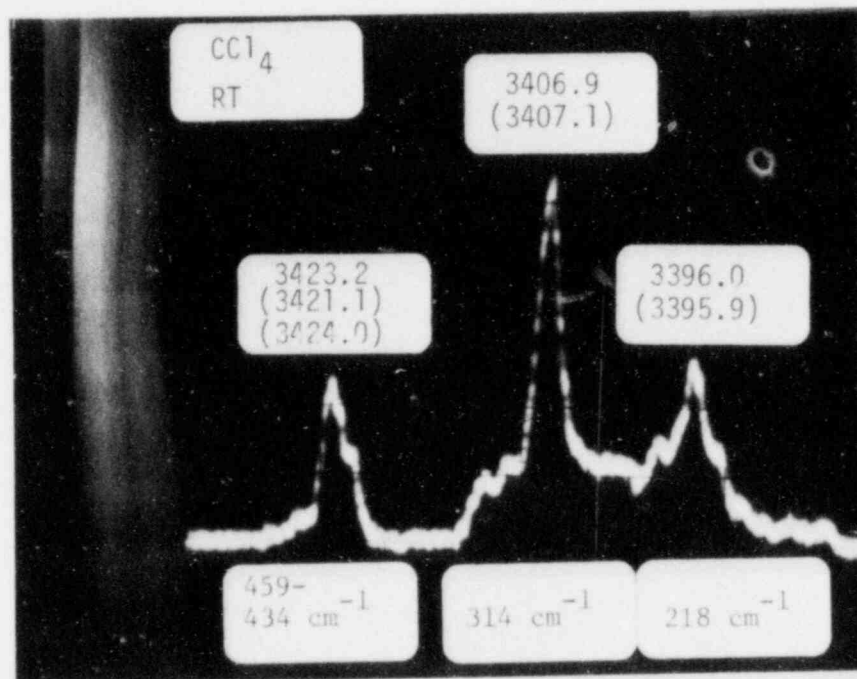
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Fig. 1. Raman (Stokes) lines of CC/4 taken with ORNL TV-Echelle spectrograph using 337.1 mm excitation.

IV.   RAMAN EXPERIMENTS ON CsI AT ORNL

A 6 cm^3 quartz enclosed sample of 5 mg of CsI was run by G. Begun using a furnace and Raman spectrometer in the ORNL Chemistry Division. Inadvertently, the temperature overshot initially and exceeded 900°C. When the temperature was lowered to 650°C no trace of a line assignable to CsI was found. Several I lines in a progression starting at 214 cm^{-1} were observed (Fig. 2). After the run, the quartz cell was found to be devitrified over the region enclosed in the furnace, making further measurements impossible except at one end of the cell which remained clear. Strong I_2 lines were observed from this region when the cell was heated with a heat gun (Fig. 3).

A second sample (containing 15 gm of CsI) was run at several temperatures with care being taken to avoid the high temperatures of the first run. Again no line attributable to CsI was seen and in this case no I_2 lines were seen.

V.   RAMAN EXPERIMENT ON CsI AT ORGDP

We had previously visited the laboratory of Bill McCulla, Enrichment Technology Division, ORGDP, and had seen his Raman system for running high temperature spectra. His system is equipped with a higher power laser than the Chemistry Division system, and has a chopper-lock-in amplifier system which improves sensitivity.[3] He kindly agreed to run a CsI sample for us and using 17 mg was able to obtain strong Raman signals at 880-890°C and later weaker signals at several lower temperatures (Fig. 4). Encouraged by these results we have asked him to run additional samples. Within the next two months, it is believed that sufficient data will be obtained on which to base a decision on the overall feasibility of the hot cell experiment.

VI.   LIGHT COUPLING FROM HOT CELL

An important consideration in the proposed experiment in the hot cell is whether, given adequate signals in a normal, closely coupled, sample to spectrometer system, the cell and spectrograph can be separated by 25 ft (750 cm) without excessive loss. The usual light collection system consists of a fast, f/1-f/2, lens close to the sample which gathers the light and directs it to a second lens whose exit cone matches the entrance f/no of the spectrograph. Since the first lens can be positioned so as to approximately collimate the light, it was believed that a second lens of appropriate input diameter (and f/no appropriate to the spectrometer) could intercept the full beam from the first lens and focus it onto the entrance slit.

Figure 5 shows the results from a test in which two lenses and a point light source were set up to approximate the separation conditions
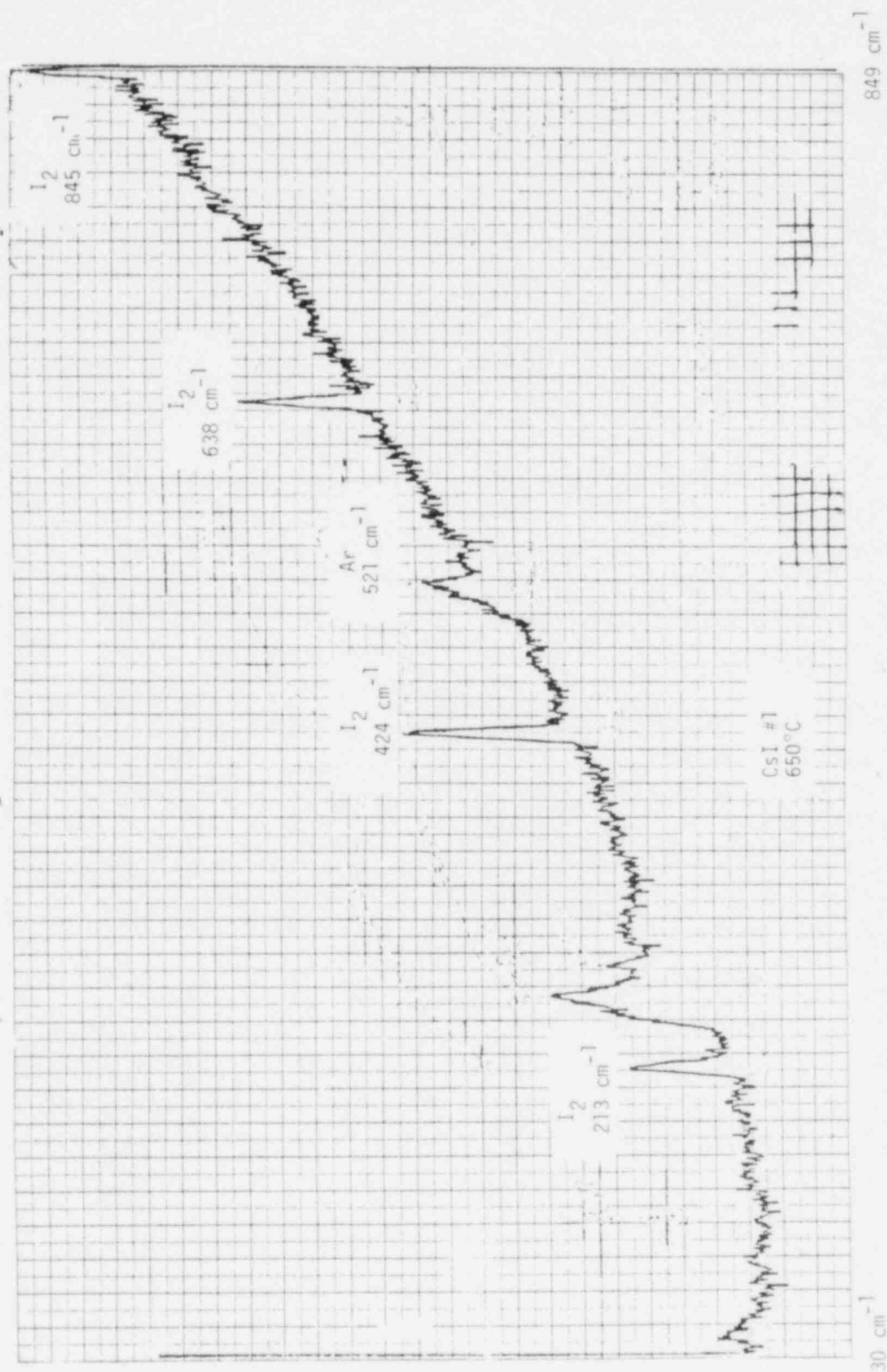
Fig. 2. CsI run after initial heating to 950°C (Courtesy G. Begun).

Fig. 3. I_2 spectrum from CsI sample after 950°C exposure, cooling to room temperature and warming (Courtesy G. Begun).

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Fig. 4. Raman spectrum of CsI (preliminary data) Courtesy -
W. H. McCulla, ORGDP.

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POINT
SOURCE

L_1 =100mm,f/2.3

MIRROR

DETECTOR

L_2 =76mm,f/1.25

A

2.1m

2.3m

B

2.4m

MIRROR

C

D

Fig. 5. SOURCE-DETECTOR DISTANCE METERS

INTENSITY

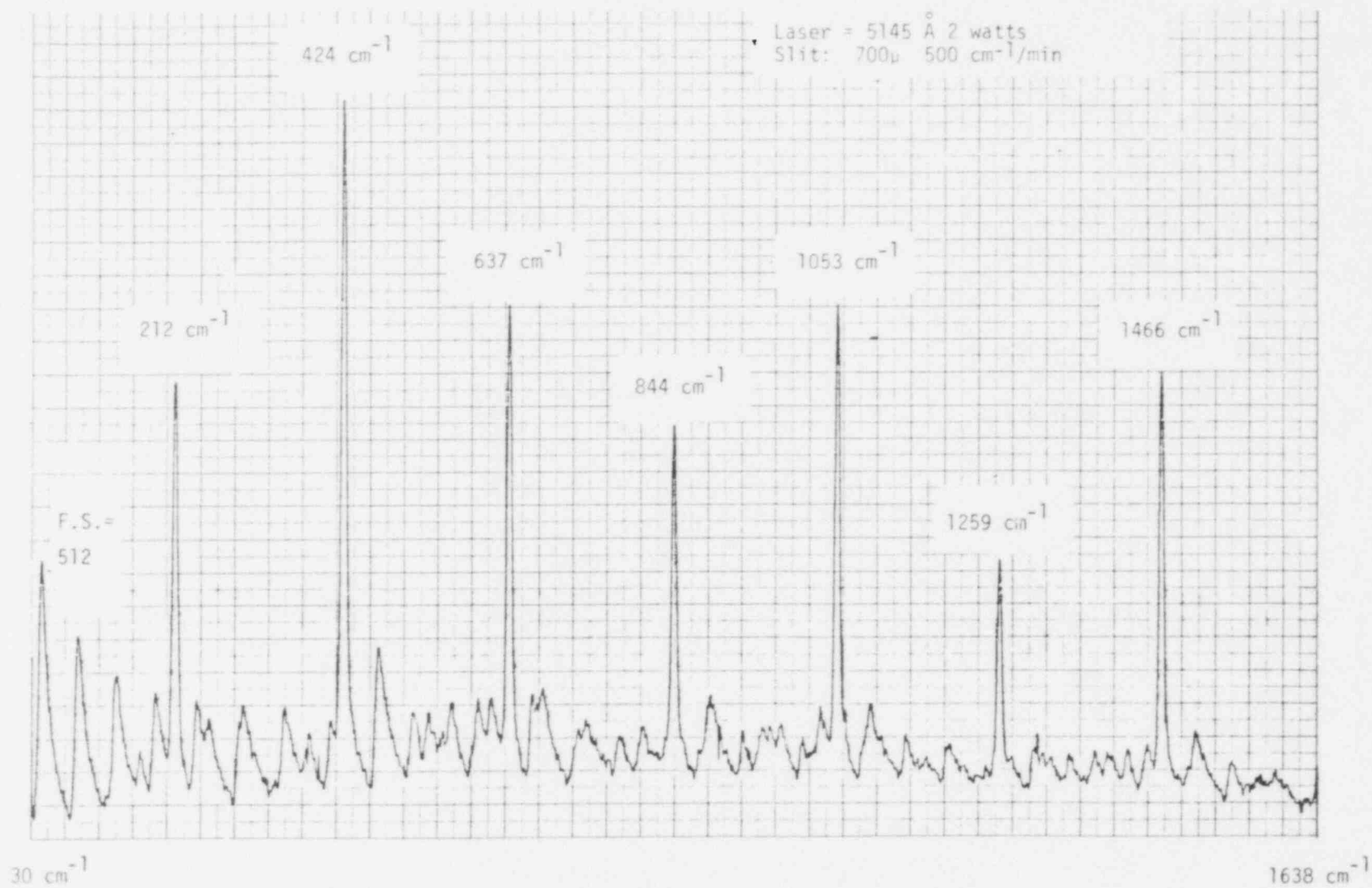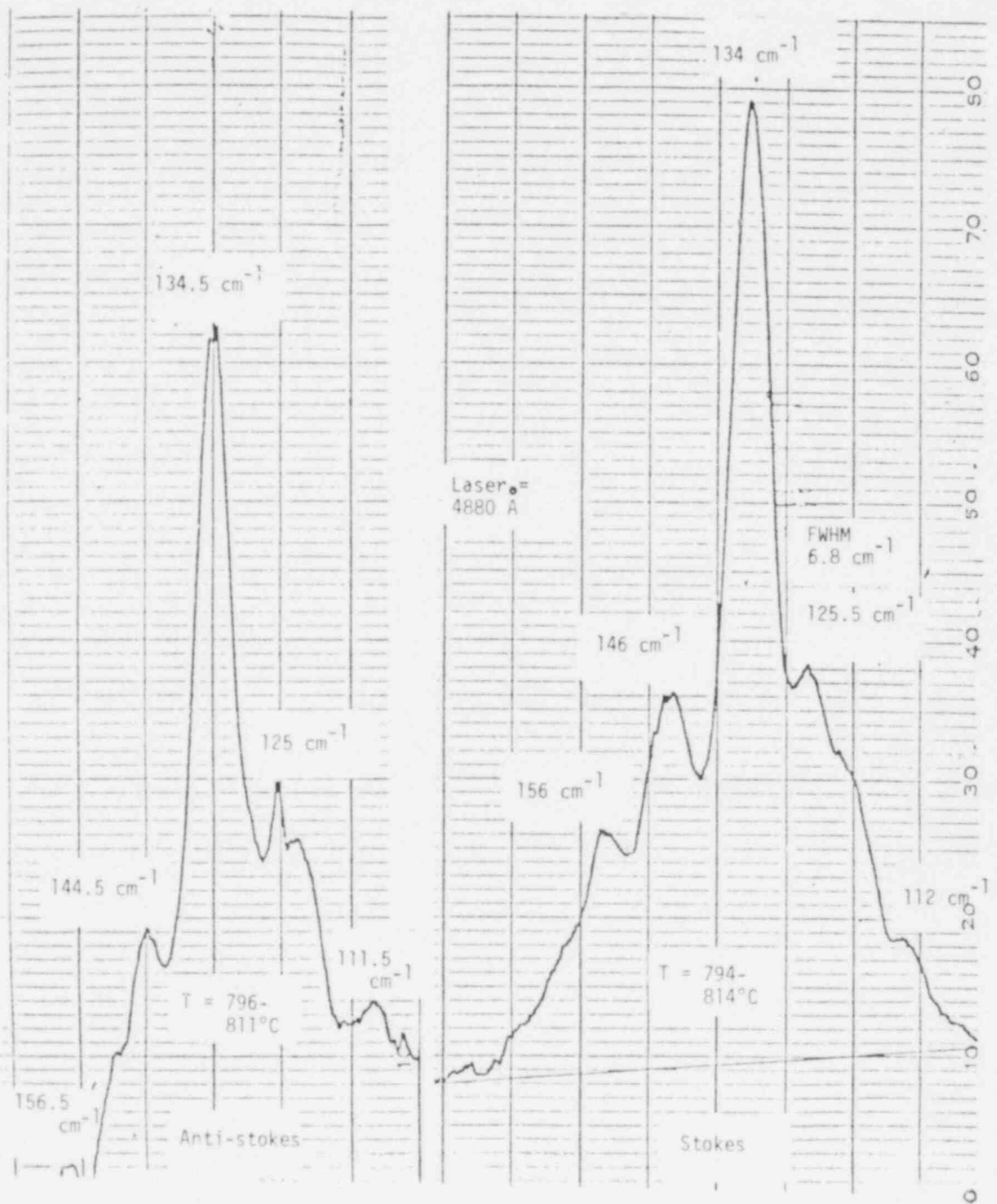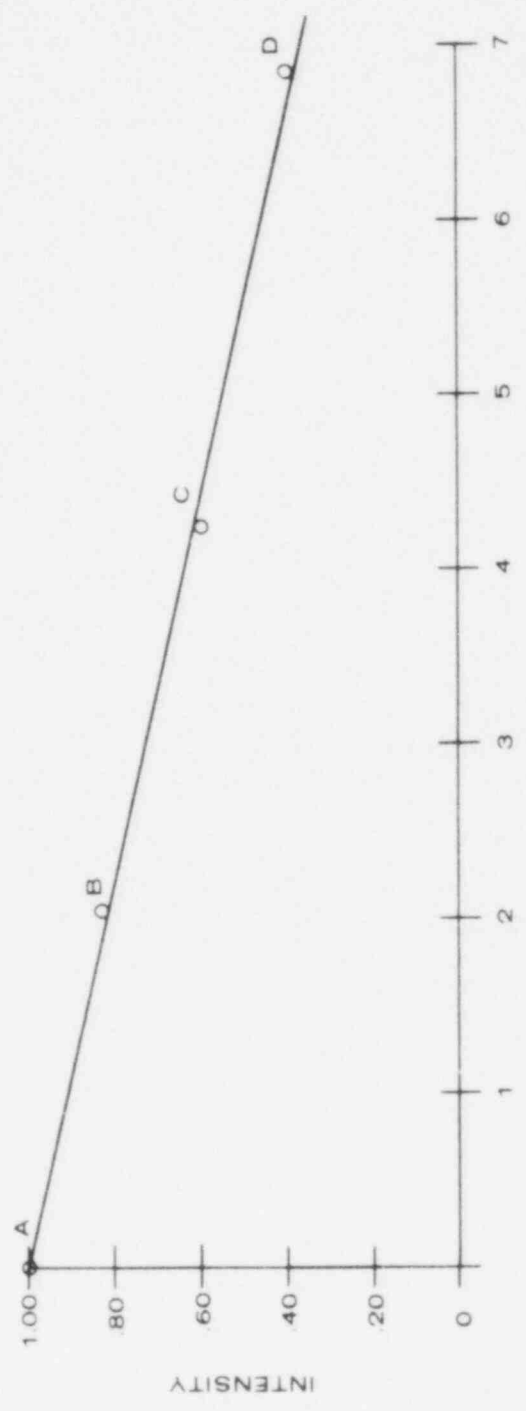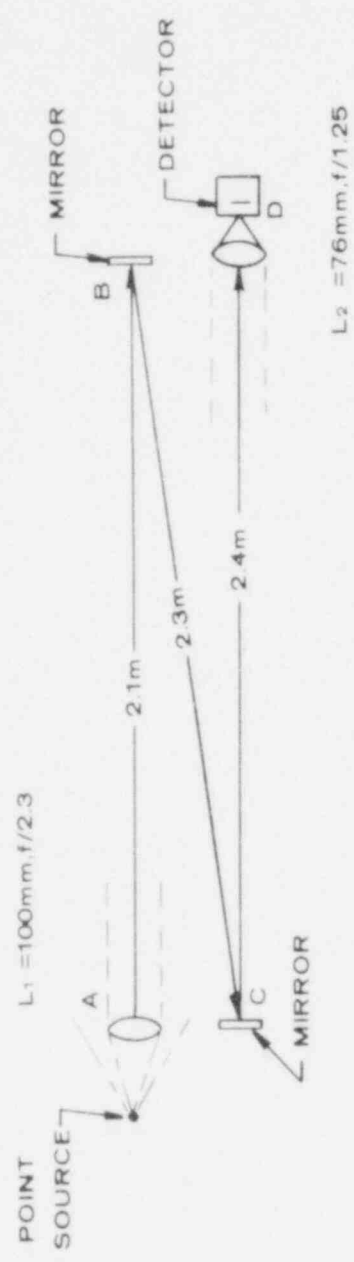described above. The results indicate that the Raman signals can be directed out of the hot cell using lenses and mirrors without excessive loss.

VII. SIMULTANEOUS MULTIWAVELENGTH RECORDING OF RAMAN SPECTRA

In the usual Raman system, the spectrum is scanned across an exit slit onto a photomultiplier tube which is usually cooled and operated in the "photon counting" mode. Scanning speed depends upon frequency range to be covered, signal strength, S/N required and speed with which data are required, for example, in an experiment involving transient species. Commercial systems have scanning rates of approximately 1 cm^{-1}/min – 2000 cm^{-1}/min. Typically, runs last tens of minutes.

The idea of recording the whole Raman spectrum (or a considerable fraction of it) at one time is not new. The original Raman spectra in the 1920s were recorded photographically. In 1967 Bridoux used an image intensifier to decrease the film exposure time ~1000 X. In 1968, Delhaye[4] used a vidicon detector following an image intensifier. He recorded a spectrum from dilute solution of azabenzene (M/100) in 1 ms using a HeNe laser of 160 mW power. He observed the decomposition of NOCl by the appearance of a doublet due to Cl_2 using a single 0.5 ms flash from a ruby laser.

A notable advance was made by Savage and Maker[5] who demonstrated a multichannel photon counting detector system using a high gain image intensifer, isocon camera tube and a multichannel analyzer to record extremely weak hyper-Raman spectra. A pulsed laser was used, and in order to reduce background, the intensifier was gated to accept signals in 250 resolution elements only during the laser pulse. Signals as low as one photo-event per resolution element per 10 laser flashes were recorded. Similar sensitivities were reported by Boksenburg Burgess in a system designed for astronomical spectroscopy.[6] Thus, it is clear that multiwavelength sensitivity using TV-intensifier techniques can equal the sensitivity of the conventional photomultiplier tube and like the photomultiplier approaches that of the ideal detector, i.e., one which would register every incident photon.

A more recent study is that of Freeman, et al.[7] They compared conventional (scanning) Raman techniques with multichannel techniques using silicon intensified target vidicon detector. In similar sets of conditions (exact comparison was not possible with their apparatus) they achieved a 1000 X increase in speed of spectrum collection over a 250 cm^{-1} band.

In a very pertinent paper, Chao[8] has described application of multichannel low-level signal averaging and detector gating to picosecond, laser generated Raman spectra.

As an alternative to TV image tubes, H. Surbeck et al.[9] has reported the use of diode arrays in Raman spectroscopy. Noise per diode equivalent to ~1000 incident photons was demonstrated with a cooled intensified array.

Although many other references to multichannel detection could be given, the above are considered representative and are directly pertinent to Raman spectroscopy. Information on commercially available detectors

which closely approach the ideal sensitivity mentioned above, are given in Appendix E.

The ORNL-TV Echelle Spectrograph, although not developed for Raman work, has many times the spectral coverage of the above reported systems while at the same time maintaining excellent resolution. The price paid for simultaneous wide spectral coverage is typically a proportionate loss in resolution (See Appendix for data on SPEX - TRIPLE MATE showing resolution versus coverage). As stated earlier, the extreme coverage of the TV-Echelle system may not be required for Raman spectra. The sensitivity of our system can certainly be brought to the ultimate "photon counting" level by the addition of another intensifier. The excellent integrating property of the S.E.C. vidicon allows integration times of minutes. Alternatively, at extremely low levels single photoelectrons could be detected and stored in memory as single events. Gating of the detector in synchrony with a pulsed laser as in the system of Maker and Savage can be used to reduce background from thermally generated electrons and non-laser generated straylight. Television tape recordings of the spectra as they are accumulated still appears a useful approach. This applies not only to the TV-Echelle system, where we have demonstrated it in emission spectroscopy but also in other (commercial) optical multichannel analyzer systems (see Appendix E) which use camera tubes and standard TV scanning rates. Spectra from systems using linear diode arrays can be stored directly in computer memory for later analysis.

CONCLUSION

The feasibility of using Raman spectroscopy to elucidate several species in a fission product release experiment has not yet been determined. Experiments underway at ORGDP with W. H. McCulla with one- and two-species samples will provide more information on which to make a judgement. Extrapolation from the static single or double sample experiments to the flowing, multispecies steam environment in the hot cell will be tentative at best. As for the instrumentation, our experiments, numerous reports in the literature and the commercially available components all indicate that the problems of transient multiwavelength detection and recording of the Raman spectra are tractable, if reasonably strong signals are obtained with a conventional single wavelength Raman system.

Assuming successfully recorded spectra, the identification and quantitation of multiple species under non-equilibrium conditions which may involve concentration and temperature dependent dissociation and recombination would seem to present formidable tasks for the spectroscopist and chemist. Closer simulation of the hot cell experiment with regard to number of species, concentrations and temperatures will be required to assure the likely success of the actual experiment. A multi-wavelength detection and recording system coupled to the ORGDP equipment could further improve the simulation.

One approach to storing spectra obtained from the linear (one-dimensional) detectors would be to use a digital image memory such as in

the ORNL-TV Echelle system to store up to 512 spectra of 512 resolution elements each. At a rate of one spectrum per minute, the time course of the experiment for approximately 1 h could be stored and displayed totally or in part.

REFERENCES

1. J. C. Cummings, et al., "Status Report on the Fission-Product Research Program," SAND80-2662 (NUREG/CR-1820) 1980.

2. J. B. Davidson and A. L. Case, " A Digital TV-Echelle Spectrograph for Simultaneous Multielement Analysis Using Micro-computer Control," ORNL/TM-7260, Dec. 1980.

3. W. H. McCulla, "The Polytopicity of Ionic Ternary Compounds," UCC-ND Report K/ET-833, 1981.

4. M. Delhaye, "Rapid Scanning Raman Spectroscopy," App. Opt. 7 2195-2199 (1968).

5. C. M. Savage and P. D. Maker, "Multichannel Photon-Counting Spectrographic Detection System," App. Opt. 10 965-9681 (1971).

6. A. Boksenburg, "An Image Photon Counting System for Optical Astronomy," Astronomical Use of Television Type Image Sensors, NASA SD-256, 77-84 (1970).

7. J. J. Freeman, et al., "Raman Spectroscopy with High Sensivitity," App. Spect. 35, 196-202 (1981).

8. J. L. Chao, "Application of the Optical Multichannel Analyzer for Low Light Level Signal Averaging and Two-Dimensional Mode Detection of Picosecond Laser-Generated Raman Spectra," App. Spect. 35, 281-289 (1981).

9. H. Surbeck et al.,"The Direct Recording of Raman Spectra with Solid State Detectors," Opt. Comm. 38, 57-60 (1981).

APPENDIX A

A DIGITAL TV-ECHELLE SPECTROGRAPH FOR SIMULTANEOUS MULTIELEMENTAL ANALYSIS USING MICROCOMPUTER CONTROL

A digital TV-Echelle spectrograph with microcomputer control has been developed for simultaneous multielemental analysis (Fig. A1). The optical system is a commercially available unit originally equipped for film and photomultiplier (single element) readout. The film port was adapted for the intensifier camera. The camera output is digitized and stored in a microcomputer-controlled, $512 \times 512 \times 12$ bit memory and image processor. Multiple spectra over the range of 200-800 nm are recorded in a single exposure. Spectra lasting from nanoseconds to seconds are digitized and stored in 0.033 s and displayed on a TV monitor. An inexpensive microcomputer controls the exposure, reads and displays the intensity of predetermined spectral lines, and calculates wavelengths of unknown lines. The digital addresses of unknown lines are determined by superimposing a cursor on the TV display. The microcomputer also writes into memory wavelength fiducial marks for alignment of the TV camera.

Wavelength determination of ± 0.02 nm can be made and resolution of 0.05 nm FWHM at 260 nm has been measured. A sensitivity improvement of 100 X at 546 nm was demonstrated in a comparison with a standard DC-operated photomultiplier at room temperature using integration on the camera tube target. Rapid qualitative comparison of two stored spectra can be done by "blink testing" at one comparison per second.
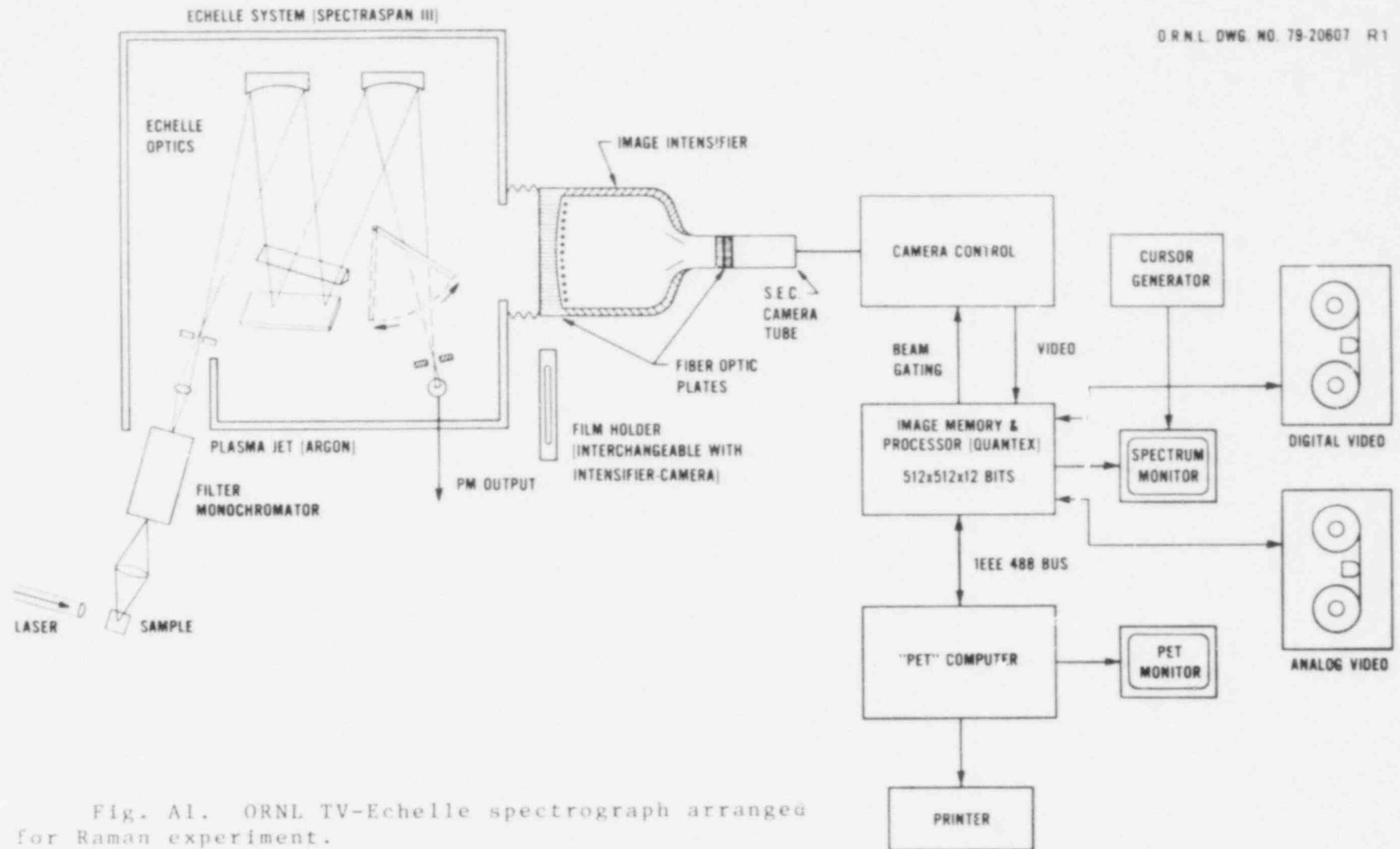
Fig. A1. ORNL TV-Echelle spectrograph arranged for Raman experiment.

APPENDIX B

MULTIPHOTON IONIZATION AND MICROWAVE SPECTROSCOPY

In addition to several variations of Raman spectroscopy such as resonance Raman and coherent anti-Stokes, there are two other techniques which might be considered for the species identification. The first of these is multiphoton ionization of selected species followed by synchronous detection of the ionization produced. Discussion with R. N. Compton, HASR Division, and literature checks[*] have confirmed that a monitor for I_2 could easily be built (Fig. B1). Simultaneous monitoring of several species would require separate lasers (and suitable energy levels). The excited volumes and the pick-up probes could be separated spatially along the vapor stream as well as in time by programming the lasers.
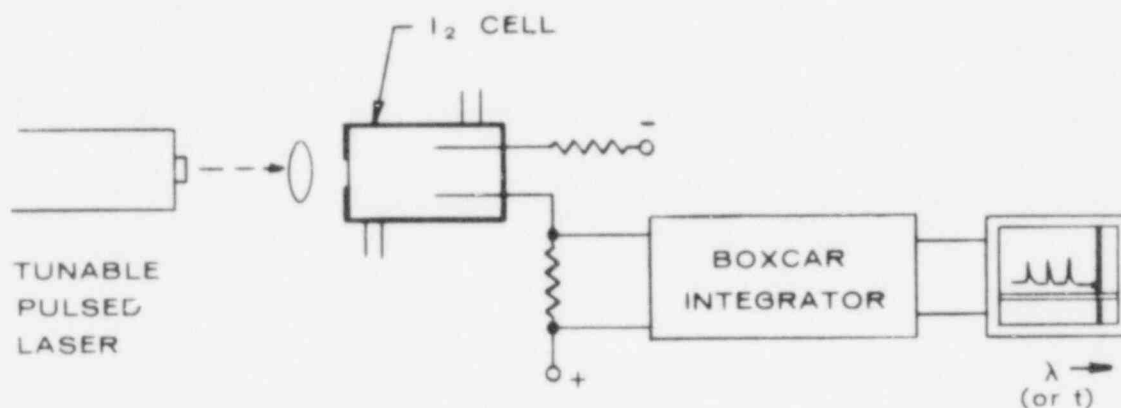
ORNL-DWG-82-13944

Fig. B1. Multiphoton Ionization Monitor for I_2 (After Petty, Tai and Dalby)

[*]G. Petty, et al., "Nonlinear Resonant Photoionization in Molecular Iodine," Phys. Rev. Lett. 34, 1207-1209 (1975).

A second possibility is microwave spectroscopy. Absorption spectroscopy of alkali halides was done in the 1950s.[*] An absorption cell (wave guide) could be heated to approximately 1000°C. A separate electrode (Stark plate) was used to modulate the microwave absorption for increased detection sensitivity.[†] Honig, et al.[‡] reported data from spectra of LiI, NaI, KI, RbI and CsI among others. Three CsI transitions were observed at about 640°C. Mays described the high temperature cells at Harvard and Duke. The Duke arrangement is noteworthy in that windows were eliminated, since the vapor was injected between sending and receiving pyramidal horns.

It seems likely that with modern microwave techniques and components[**] this method could be improved and could be useful under the severely corrosive conditions of the hot cell experiments where optical windows may not stand up. Swept-frequency techniques would be necessary if several species are to be measured.

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[*]J. Sheridan, "Recent Advances in Microwave Spectroscopy," Adv. in Infrared and Raman Spect., 5, 276-321 (1978), B. Leskovar and W. F. Kolbe, "Detection and Measurement of Air Pollutants and Constituents by Millimeter-Wave Spectroscopy," IEEE Trans. Nuc. Sci. Vol. NS-26, 780-790 (1979).

[†]J. M. Mays, "Spectroscopic Measurements on High-Boiling, Reactive, and Unstable Molecules," Amm. NY Acad. Sci. 55, Article 5, 789-799 (1952).

[‡]M. L. Stitch, et al., "High Temperature Microwave Spectrometer," Rev. Sci. Instr. 25, 759-764 (1954).

[**]A. Honig, et al., "Microwave Spectra of the Alkali Halides," Phys. Rev. 96, 629-642 (1954).

APPENDIX C

RAMAN SPECTROSCOPY OF CONDENSED SAMPLES

In the actual experiment, the vapor species will condense on a layer of platinum lining the thermal gradient tube for analysis by gamma-ray spectroscopy and other analytical techniques. If an auxiliary sample illuminator system were set up outside, small samples of platinum (a few mm^2) could be studied using the same laser Raman setup for the transient experiment and possibly providing further insight into the vapor chemistry without disturbing the material on the surface.* Both SPEX and ISA make solid sample attachments which could be used.

If the small samples are too hot to handle, the surface Raman could, in principle, be done inside the hot cell.

Even more detailed information on the spatial distribution of the various (Raman active) species could be obtained by scanning the specimens with a Raman microscope. Such an attachment can be purchased for commercial Raman systems.

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*B. A. Morrow, "Raman Spectroscopic Studies of Surface Species," Vibrational Spectroscopies for Adsorbed Species, A. T. Bell and N. L. Hair, eds. ACS Symp. 137, American Chemical Society, 119-140 (1980).

APPENDIX D

REPRESENTATIVE COMMERCIALLY AVAILABLE RAMAN SYSTEMS

Two representative commercially supplied Raman Systems, SPEX nd Jobin-Yvon, are considered in this section. If adequate signals ⁓ obtained in current experiments at ORGDP on their older J-Y system, then either system will probably work and the choice between them and any other comparable system would depend more on mechanical layout and accessories such as sample chamber, multipass cells, etc.

Table D1 is a comparison of the specifications assuming an 1800 grooves/mm grating in each. As previously noted, higher dispersion is accompanied by less coverage based on an assumed width of the detector to be covered by the spectrum.

The J-Y Ramonor 1000 uses two monochromators in additive dispersion and from the table has ~4x the dispersion of the SPEX "TRIPLEMATE" which uses a double monochrometer in subtractive dispersion as a filter to reduce stray light. The third, dispersing monochromator of 0.22 m focal length is used in the SPEX to project the spectrum onto a multichannel detector. The table compares the two systems with each using 1800 g/mm gratings. The SPEX is equipped with a turret for holding three gratings in the third monochromator. Selection is by an external knob. As may be seen from Table D2, the different gratings enable trade offs to be made in resolution and spectral coverage. The gratings can be changed in seconds. This appears to be a very useful feature for the fission product experiment since it permits low and high resolution work. The latter will be important if surface Raman is done on small specimens from the thermal gradient column. There will then be time enough to operate at full resolution. Table D3 gives the manufacturer's performance specifications and Table D4 shows an approximate cost breakdown for a system based on the SPEX "TRIPLEMATE".

Retroflective Raman Cells

Retroflective, multipass cells for effectively increasing laser power have been found very useful for Raman spectroscopy with gas phase and a number of designs have been published. Gains of 10-50 in signal have been reported.* Several cells are available commercially which could possibly be adapted for use in the hot cell. Consideration will be given to purchasing the SPEX illumination chamber with large sample adapter for possible use in the hot cell. With some cooling added, this two compartment chamber which has removable sides and already aligned optics could save the expense of designing a special chamber.

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*R. A. Hill and D. A. Hartley, "Focused, Multiple-Pass Cell for Raman Scattering," App. Opt. 13, 186-192 (1979); T. W. Kowicz and A. D. May, App. Opt. 14, 3092-3094 (1975).

Table D1. Comparison of two commercial Raman systems

	RAMANOR U1000 "Double"	SPEX "TRIPLE MATE"
Focal Length	1 m	0.22 m
Dispersion	9.2 cm^{-1}/mm with 1800 g/mm grating	34 cm^{-1}/mm with 1800 g/m
Grating	Ruled or holographic (plane)	Holographic
Aperture	f/8	
Resolution	0.2 cm^{-1} at 5791 Å	0.7 cm^{-1}
Stray Light Rejection	10^{-14} at 20 cm^{-1} from Rayleigh line	10^{-14} at 10 band-pass units
Accuracy	± 1 cm^{-1} over 5000 cm^{-1}	± 18.7 cm^{-1}
Repeatability	± 0.2 cm^{-1}	± 7.6 cm^{-1}
cm^{-1} on 25.4 mm detector	229 cm^{-1} (1800 gm)	870 cm^{-1} (1800 gm)
$cm^{-1}/25$ μ pixel	0.01 cm^{-1}/px	0.03 cm^{-1}/px

Table D2. SPEX "TRIPLEMATE" specifications

Spectral coverage, (4) 185-1000 nm (54000-10000 cm^{-1})
 Wavelength accuracy, ±0.5 nm

Wavelength resettability, ±0.2 nm

Stray light, 10^{-14} at 10 bandpass units from laser (Rayleigh line)

Filter Stage

Two modified Czerny-Turner monochromators coupled in subtractive
 mode

Gratings plane, 50 × 50 mm, kinematically interchangeable (5)

Wavelength Readout, 4-digit, nm

Slits, bilateral, 25-5000 μm, continuously adjustable

Spectrograph Stage

Asymmetrical Czerny-Turner

Entrance slit, bilateral, 25-2000 μn, continuously adjustable

Gratings, 64 × 64 mm, plane (6) 3-position turret provides
 external selection

Dispersio.., 1.4 nm/mm

Bandpass per 25 μm, selectable, .017-27nm

Wavelength display, 5-digit indicating central wavelength for any
 grating in the turret mount

Focal plane, 25 mm wide × 10 mm high, unvignetted

Table D3. "TRIPLEMATE" spectrograph performance specifications

Grating gr/mm	Spectral Coverage nm/25 mm (cm^{-1} at 19435 cm^{-1})	Bandpass (nm) per 25 μm
150	138* Δ (5257)	.27
300	138 Δ (5257)	.14
600	70 (2646)	.07
1200	35 (1320)	.035
1800	23 (870)	.023
2400	17 (1) (1326)	.017 (1)
3600	11.5 (2) (1840)	.011 (2)

*Limited by bandpass of filter stage   Δ With 7 mm slit opening

Notes

1. At 357 nm (28,000 cm^{-1})

2. At 250 nm (40,000 cm^{-1})

3. Where applicable, figures pertain to a 1200 gr/mm grating at 500 nm in Order 1.

4. 600 gr/mm gratings are recommended for first (filter) stage general purpose work in visible region.

5. Up to three gratings (150, 300, 600, 1200, 1800, 2400, 3600 gr/mm) may be mounted in externally actuated turret for spectrograph stage.

Table D4. Cost estimate based on a
commercial Raman systems

Triple Mate	$ 14,000
3-Gratings	3,000
UV-Visible Illuminator	6,800
Laser Filter	1,250
Large Sample Adapter	1,100
Polarization Scrambler	550
External Resonating Cavity (multipass device)	1,180
	$ 27,880
Intensifier Camera	15,000
Image Memory & Controller Disks	25,000
Analog Tape Recorder	2,500
	$ 70,380
	30,000
Laser	$100,380

NOTE ADDED IN PROOF:

ANASPEC, Inc., Acton, MA has recently announced a complete laser Raman system equipped with an intensified 1024-diode array detection and computer control. Approximately 1000 cm^{-1} can be covered in a single measurement. A fiber optic probe for remote analysis is listed as an option. The cost of the complete system is approximately $148 thousand.

APPENDIX E

OPTICAL MULTICHANNEL ANALYZERS

Included in this appendix are representative specifications from two manufacturers of TV and diode array detectors and associated electronics including computer-based storage and analysis systems.

To achieve single photon sensitivity, an intensifier camera tube such as the ISIT (Princeton App. Research Mod. 1257) or intensified-photodiode array (Princeton App. Res. Mod. 1420 or the Tracor Northern TN-1223-41) (Table E1). A disadvantage of the PAR-ISIT device is the limited width of 12.5 mm. When used with the SPEX TRIPLE MATE for example, only half of the available spectrum could be recorded. The intensifier diode arrays are 25 mm wide thus utilizing the full output, but the effective slit height is only 2 mm maximum compared with the camera tube which has a scanned area of 12.2 × 12.5 mm.

Camera tubes with 25-40 mm diam inputs are available. We have successfully used the Secondary Electron Conduction (SEC) vidicon with a minifying, 150 mm diam image intensifier in the TV-Echelle 2-D spectrograph. A similar arrangement for a conventional linear spectrum could be used to give 50-80 mm input widths. However, as mentioned above the SPEX and J-Y systems require only 25 mm. If suitable spectrograph optics could be obtained, a 50-80 mm input could improve the resolution. Alternatively, the ORNL-TV-Echelle spectrograph equipped with a state-of-the-art, large format, high resolution camera (probably custom-built) could provide more than adequate resolution. The optical resolution (photographically determined) is better than 0.01 nm which is 10X better than our present overall, electronics-limited resolution. Further study is underway to find a suitable filter monochromator which could be used with the TV-Echelle spectrograph.

Table E1. Detector comparison

	ISIT TUBE	Int. Diode Array "A"	Int. Diode Array "B"
Number of channels	500	700	1024
Channel width	25μ	25	~25
Linewidth (FWHM)	~4	1	3
Active area	$12.2 \times 12.5 \text{ mm}^2$	$2.5 \times 25 \text{ mm}^2$	$2.5 \times 25 \text{ mm}^2$
Sensitivity Photoelectrons/count	1	1	1
Uniformity of sensitivity	±10%	±10%	
Noise c/channel	1.5 per scan	1 per scan	5 per scan
Spectral range nm	365-900	200-800	200-800

Tube = Princeton App. Research 1257

A = Princeton App. Research 1420

B = Tracor-Northern TN1223-41

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