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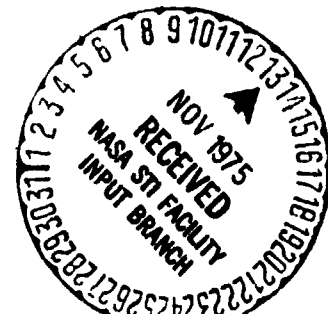
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## Introduction

The potential advantages in which micro-gravity environments holds for manufacturing processes has created the need to better define some of these processes. A good example is shown in the excellent work of Dr. Heribert Wiedemeir of Rensselaer Polytechnic Institute.<sup>1</sup> In his vapor transport experiments, the zero gravity results always gave higher transport rates than the theoretically predicted rates. Needless to say there is a substantial need to understand certain processes better if we are to utilize them to their potential.

This work was intended to improve upon the basic understanding of such processes and to demonstrate the ability to make measurements in situ for the vapor transport process. In order to achieve these goals, we considered the Raman technique as a potential in situ probe. Due to the technological advances in the laser industry, high intensity sources are readily obtainable and Raman spectroscopy has become a very useful analytical tool. Excellent texts on Raman spectroscopy and its application are available.<sup>2,3</sup> Very little theory is given in this report. We have intended only to provide a foundation for the types of measurements which can be made with the Raman technique.

## Technical Approach

Raman spectroscopy is an alternate approach to vibrational spectroscopy which has become extremely popular since the laser has become available to scientific laboratories. The ability to perform molecular identifications, concentration monitoring, structure analysis and temperature measurements. The Raman effect arises when an electromagnetic field interacts with an oscillating vibration within a molecule. This interaction is coupled through the configurational changes in the nuclear and electronic positions, or the polarizability of the molecule. For the Raman effect to be an allowed effect, the molecular polarizability must vary with the vibrational motion of the molecule. When the above condition is satisfied and the molecule is irradiated with monochromatic light of frequency  $\nu_0$ , then light of frequencies  $\nu_0 + \nu_i$ , and  $\nu_0 - \nu_i$  is emitted, where  $\nu_i$  is a fundamental vibration of the molecule. Figure 1 illustrates this schematically.

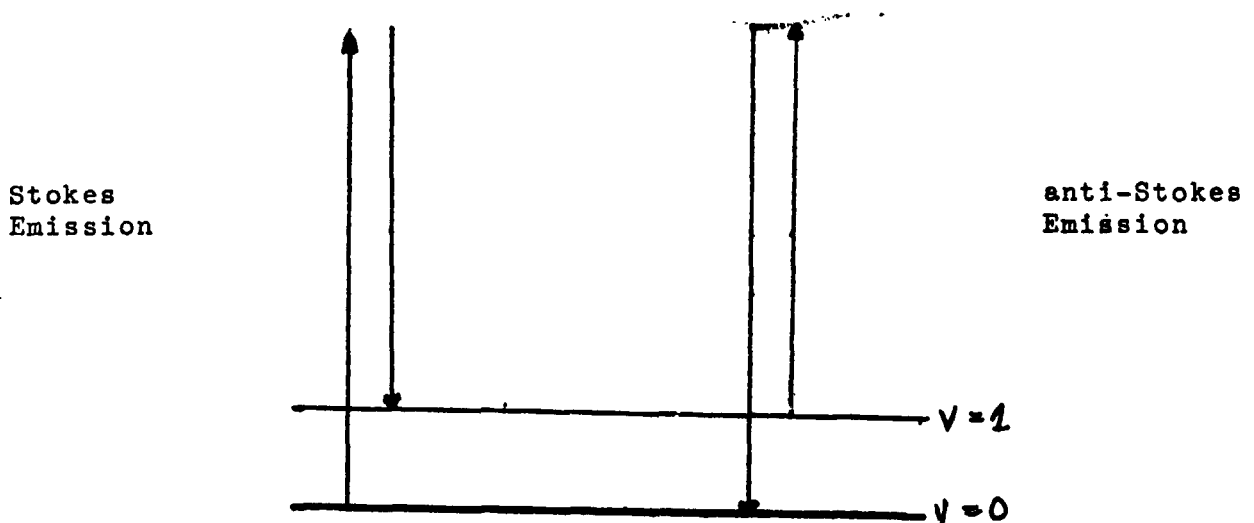


Fig. 1

By convention the latter term is called Stokes emission and the former, anti-Stokes emission. The major differences between infra-red and Raman transitions are determined by the symmetry properties of the molecules and the vibrations,  $\nu$ . Since infra-red absorption depends on a change in the dipole moment of the molecule with high symmetry (e.g.  $O_h$ ,  $T_d$ , or  $D_h$  point groups) does allow infra-red absorption for these vibrations. However, the polarizability of the molecule does change during the motion of the vibration and these transitions are allowed for the Raman effect.

In general the rule states that molecules which have a center of symmetry, those vibrations which preserve the center of symmetry cannot be infra-red active, whereas vibrations which do not preserve the center of symmetry cannot be Raman active. If both the Raman and the infra-red spectra are observed for the same vibration, then we can say that the molecule does not have a center of symmetry. Germanium tetraiodide is an example of the former and germanium di-iodide is an example of the latter. For  $GeI_4$ , the  $A_1$  and E vibrations can only be observed with the Raman technique, whereas we can observe the  $F_2$  vibrations with either infra-red or Raman since these vibrations transform as the x, y, z, xz, xy, and yz axes. Hence we do have an exception in the rule for this case. Likewise, all transitions for  $GeI_2$  are allowed in both the infra-red and with Raman excitation.

Since the Raman measurement involves excitation from an intense, monochromatic light source (satisfied by laser sources in general), the amount of light received by the detector system is directly

proportional to the number of molecules excited by the laser source. Hence this technique measures concentration directly without going through Lambert-Beers type calibrations. All that is required is to measure the Raman cross-section or calibrate an intensity versus concentration for a specific power input into the ampoule in which the measurement is to be made. Since vapor transport experiments will be performed with the optical system parameters pretty well constant, this technique should be very effective for these types of experiments.

Another technique or measurement in which the Raman effect provides a convenient approach is the measurement of temperature in a gaseous sample. As seen in Fig. 1, the molecular signals which we call Stokes and anti-Stokes signals are merely the differences in population of the ground vibrational level relative to the first excited vibrational level. Thus the difference in population is given by the Maxwell Boltzman distribution, and the ratio between the Stokes and the anti-Stokes signals is given by:

$$\frac{I(\text{anti-Stokes})}{I(\text{Stokes})} = \left( \frac{\nu_0 + \nu_i}{\nu_0 - \nu_i} \right)^4 e^{-\frac{h\nu_i}{kT}}$$

An example of this calculation for the I<sub>2</sub> system is given in Table I for the temperature range 300-1000 degrees K. Similar ratios are obtainable for GeI<sub>2</sub> and GeI<sub>4</sub>.

## Conclusions

It is evident from the Raman experiments performed on  $I_2$ ,  $GeI_2$ , and  $GeI_4$  that the Raman technique is an excellent probe for molecular and temperature parameters in vapor transport experiments. Using an argon ion laser of 1 to 2 watts power, a number of different types of information can be obtained including molecular identification, concentration and temperature profiles.

It is suggested that more applications of laser physics to vapor transport kinetics be considered to improve the depth of knowledge for these processes.

## Summary

The vapor systems  $GeI_2$  and  $I_2$  and solid  $GeI_4$  have been analyzed using Raman spectroscopic techniques. The Raman bands of  $I_2$  and  $GeI_4$  have been confirmed and Raman bands for  $GeI_2$  at  $230\text{ cm}^{-1}$  and  $360\text{ cm}^{-1}$  have been reported for the first time. The application of the Raman technique as a temperature probe in vapor transport kinetics has been studied and its feasibility is considered to be very good.

Acknowledgements are to Dr. Gary L. Workman and Mike Lenox for assistance on this project.



R.C. McNutt  
Principal Investigator

TABLE I

T (°K)	Ratio for $\frac{I(\text{anti-Stokes})}{I(\text{Stokes})}$
300	0.634
400	0.688
500	0.730
600	0.765
700	0.793
800	0.817
900	0.838
1000	0.856

## Experimental Results

The Raman spectra which have been observed for  $\text{GeI}_4$  solid,  $\text{GeI}_2$  vapor and  $\text{I}_2$  are given in Fig. 2-4. Also a spectrophotometric scan for  $\text{I}_2$  dissolved in carbon tetrachloride is shown in Fig. 5. Note that radiation is absorbed much more efficiently at 514.5 nm than at 488.0 nm. This leads to the large number of fluorescence bands for  $\text{I}_2$  as given in Fig. 2.

All Raman spectra were obtained with a modified Cary 81 Raman Spectrophotometer. It was originally built for Toronto arc excitation, but our work required laser excitation. All the Toronto arc apparatus was subsequently removed and the beam from a Spectra-Physics Model 164 Argon Ion Laser was directed into the sampling volume. We did have a number of problems in obtaining high quality spectra originally because of the optical train designed for Toronto arc excitation.

We were able to optimize the Raman signals after some manipulation of sampling geometry. A compilation of our results is given in Table II. We were unable to find any previous data on  $\text{GeI}_2$ , so our results are the first for this species.



Fig. 2 GeI<sub>2</sub> VAPOR

EXCITATION LINE = 488.0 (only)

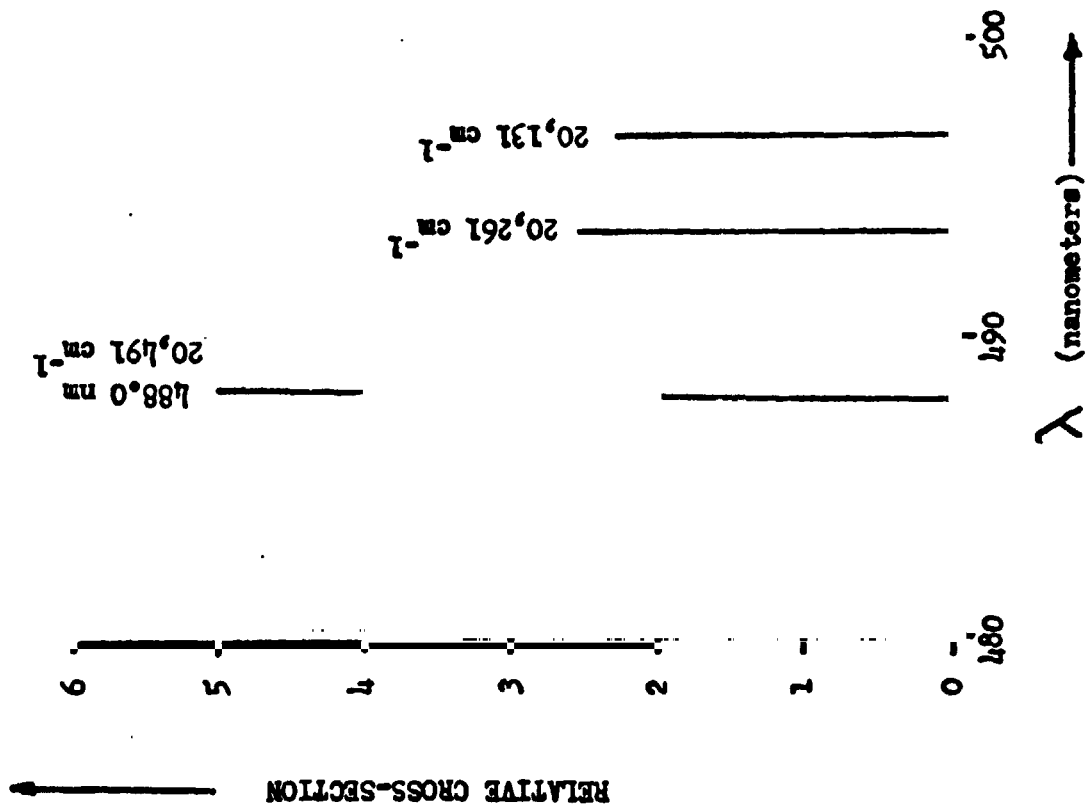


Fig. 3

BACKSCATTER FROM GeI<sub>4</sub> (solid)

EXCITATION LINE = 514.5

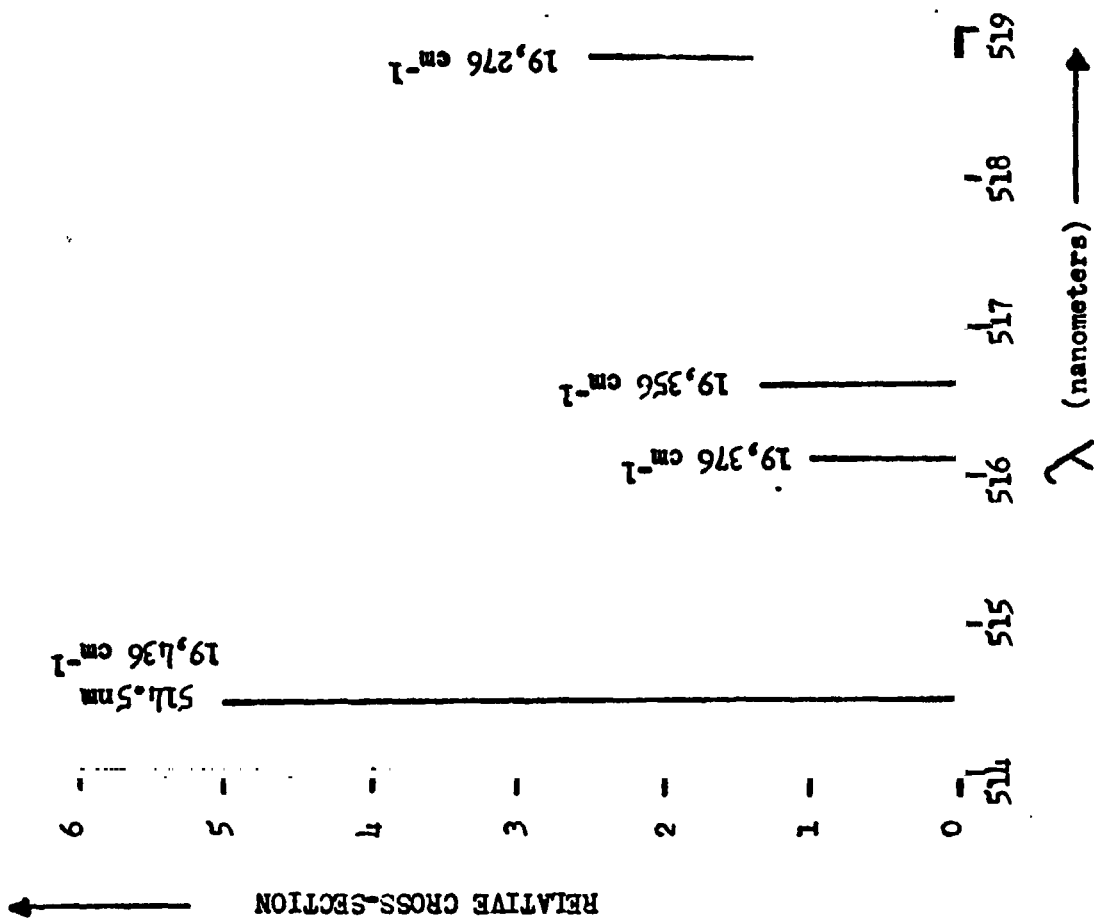
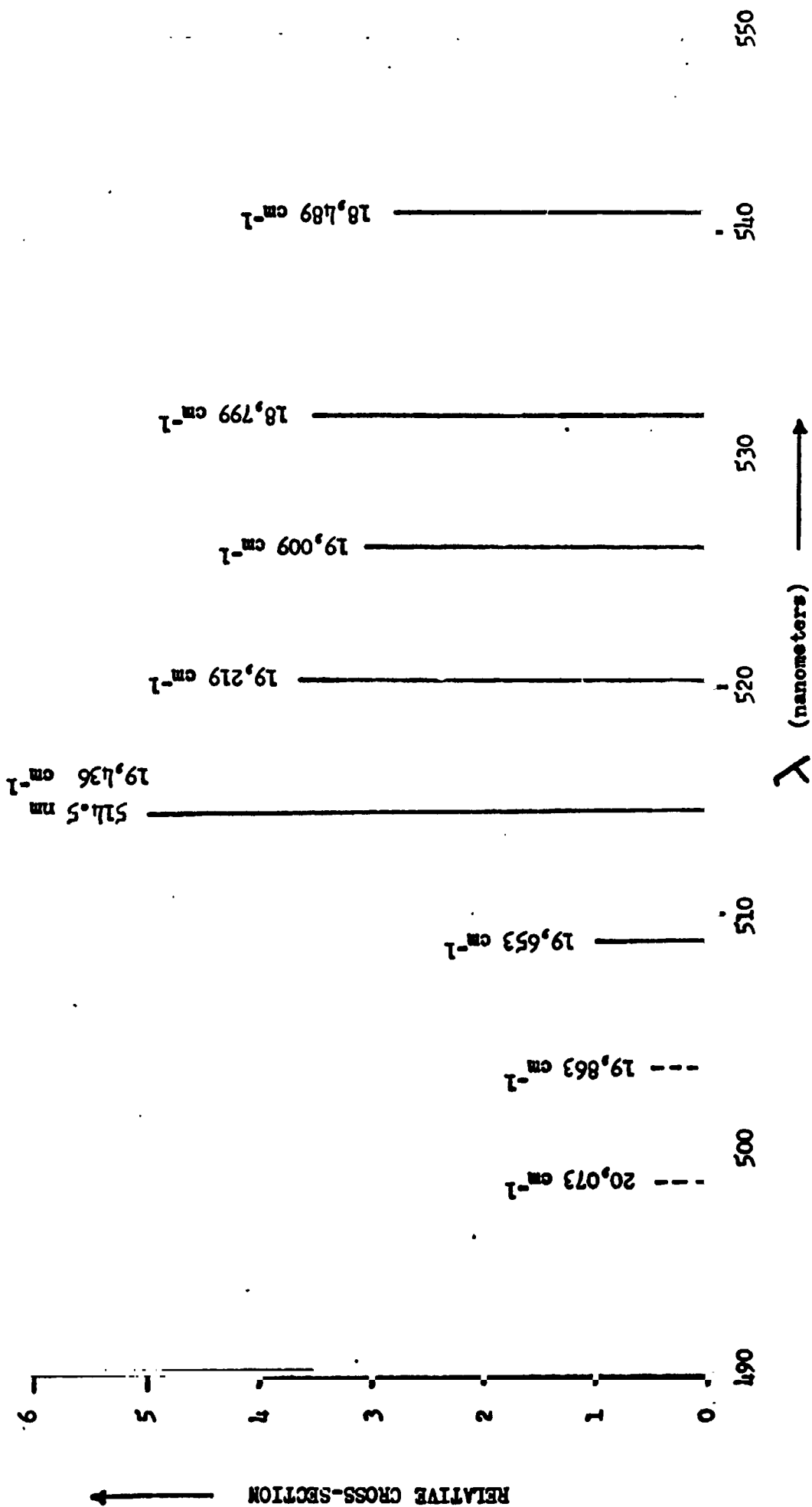


FIG. 4 IODINE VAPOR

EXCITATION LINE = 514.5 nm (only)



ABSORPTION SPECTRUM OF I<sub>2</sub> IN CCl<sub>4</sub>

Fig. 5

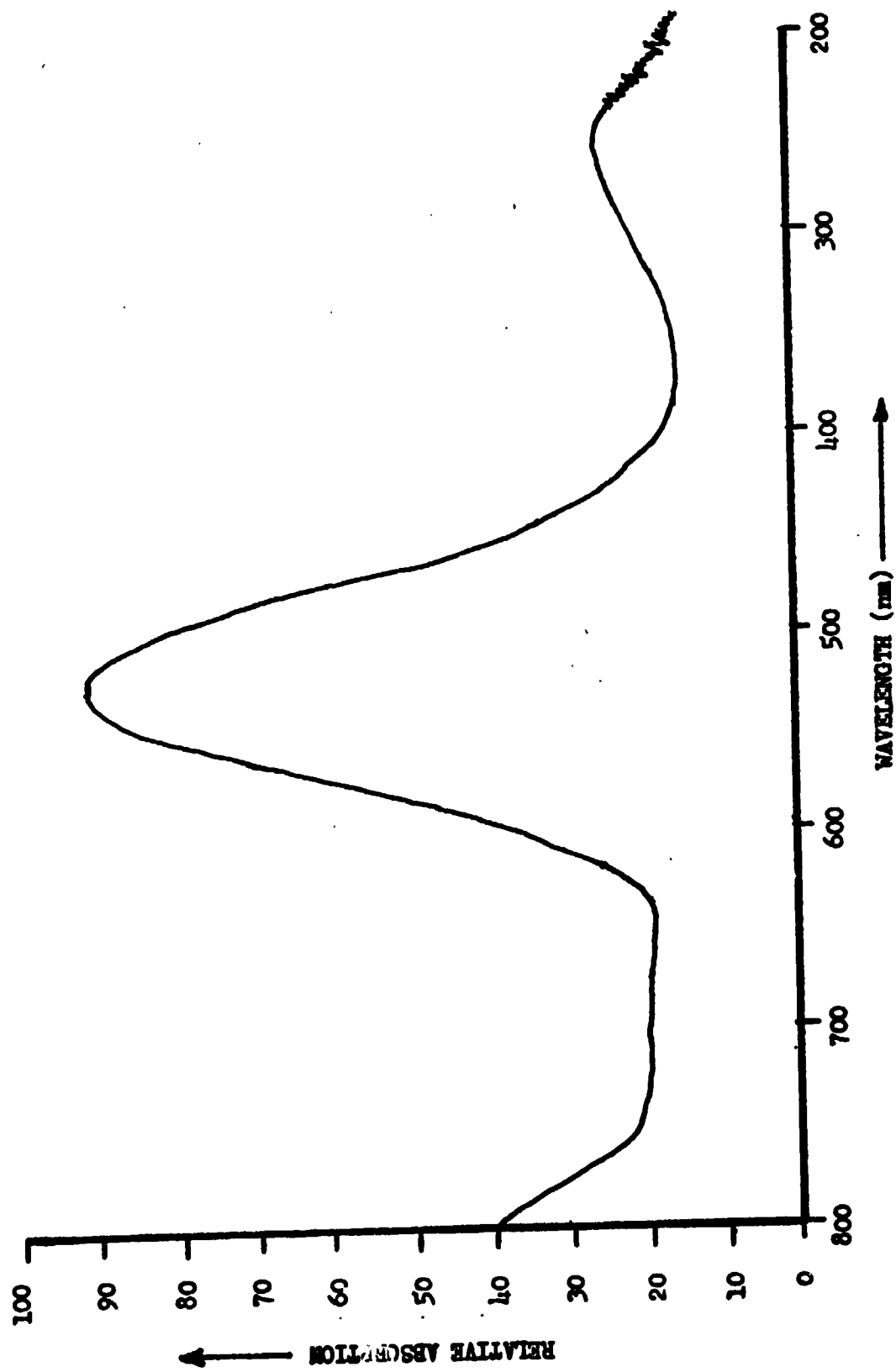


Table II. Raman Measurements on the Germanium Iodides

<u>Vibration</u>	<u>Symmetry</u>	<u>Motion</u>	<u>Measurement</u>	<u>Literature (Reference 4)</u>
<b>Germanium Tetraiodide - Point group <math>T_d</math></b>				
	$A_1$	symmetric stretch	160 $\text{cm}^{-1}$	159 $\text{cm}^{-1}$
	$E$	symmetric bending	60	56
	$F_2$	anti-symmetric bending and stretching	80	83
	$F_2$	anti-symmetric bending and stretching	--	263
<b>Iodine - Point group <math>D_h</math></b>				
	$A_1$	symmetric stretch	217	213
<b>Germanium Di-iodide - Point group <math>C_{2v}</math></b>				
	$A_1$	symmetric stretch	230	---
	$A_1$	symmetric bending	---	---
	$B_1$	anti-symmetric stretching	360	---

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