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**LAWRENCE LIVERMORE LABORATORY**

University of California/Livermore, California

STABLE ISOTOPE RATIO MEASUREMENTS IN HYDROGEN, NITROGEN, AND OXYGEN  
USING RAMAN SCATTERING

R. C. Harney, S. D. Bloom, and F. P. Milanovich

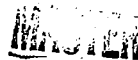
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STABLE ISOTOPE RATIO MEASUREMENTS IN HYDROGEN, NITROGEN,  
AND OXYGEN USING RAMAN SCATTERING\*

F. C. Harney and F. D. Bloom  
Department of Applied Science, University of California,  
Davis-Livermore  
and  
Lawrence Livermore Laboratory

and

F. P. Milanovich  
Lawrence Livermore Laboratory, Livermore, California 94550

ABSTRACT

A method for measuring stable isotope ratios using laser Raman scattering has been developed which may prove of significant utility and benefit in stable isotope tracer studies. Crude isotope ratio measurements obtained with a low-power laser indicate that with current technology it should be possible to construct an isotope ratio measurement system using laser Raman scattering which is capable of performing 0.1% accuracy isotope ratio measurements of  $^{16}\text{O}/^{18}\text{O}$  in natural abundance oxygen gas or  $^{14}\text{N}/^{15}\text{N}$  in natural abundance nitrogen gas in times less than two minutes per sample. Theory pertinent to the technique, designs of specific isotope ratio spectrometer systems, and data relating to isotope ratio measurements in hydrogen, nitrogen, and oxygen will be presented. In addition, the current status of several studies utilizing this technique will be discussed.

\*This work performed under the auspices of the U.S. Energy Research and Development Administration.

The research described in this paper relates to a recent idea of ours concerning the applicability of Raman scattering as an analytical tool for precision stable isotope ratio measurements.<sup>1</sup> We first review some of the theory of Raman scattering pertinent to the technique. Next, Raman spectra and relative cross section data for several simple isotopic molecules are presented. This baseline data is then analyzed in terms of our proposed measurement technique to obtain realistic estimates of the performance of a Raman-scattering isotope ratio spectrometer. Finally, a brief review of work in progress is given.

Raman scattering<sup>2</sup> is the inelastic scattering of light by atoms or molecules (SLIDE 1). In Raman Stokes scattering a photon of energy  $h\nu_L$  scatters from a molecule in the ground state losing energy  $h\nu_V$ . The scattered photon carries off energy  $h(\nu_L - \nu_V)$  while the molecule is left in an excited state of energy  $h\nu_V$ . These excited states can be either rotational, vibrational, nuclear, or electronic in character. In Raman anti-Stokes scattering, a photon of energy  $h\nu_L$  scatters from a molecule in an excited state of energy  $h\nu_V$ . The scattered photon carries off energy  $h(\nu_L + \nu_V)$  leaving the molecule in its ground state. Because the scattered intensity is proportional to the number of molecules in the initial state, the ratio of anti-Stokes intensity to Stokes intensity is given by the Boltzmann factor,  $e^{-h\nu_V/kT}$ . In the remainder of this paper we will consider only Stokes vibrational scattering.

The key to our technique lies in the Raman isotope effect: molecules containing different isotopes have different scattered frequencies. The origin of this effect is the mass difference between different isotopes and is illustrated in SLIDE 2. Molecule XX has a manifold of vibrational energy levels with level separation  $\hbar\omega_V \propto M^{-1/2}$  ( $M$  is the reduced molecular mass) while the isotopically-substituted molecule XX' has a manifold of vibrational energy levels with level separation  $\hbar\omega_V' \propto M'^{-1/2}$ . For a fixed incident photon energy  $\hbar\omega_L$ , the scattered photon energy for molecule XX is  $\hbar\omega_S = \hbar(\omega_L - \omega_V)$  while for molecule XX' it is  $\hbar\omega_S' = \hbar(\omega_L - \omega_V')$ . SLIDE 3 tabulates the isotope effect in the vibrational frequencies of several simple molecules. It is important to note that in many instances the isotope shift is several  $\text{cm}^{-1}$  or larger, sufficiently large to be easily resolved by a monochromator.

In view of the magnitude of typical isotope shifts and the extremely high intensities available from modern ion lasers, we wondered if laser Raman scattering might not be a useful technique for making stable isotope ratio measurements. In SLIDE 4 we show a simple system for making such measurements. The beam from an intense argon ion laser is focused into a cell containing the sample to be analyzed. The Raman-scattered light is analyzed by two (or more, if necessary) monochromators each tuned to the frequency characteristic of a different isotopic species. The photons passed by each monochromator are detected by a photomultiplier tube coupled to photon-counting electronics. The raw data from each detector is either an intensity ( $\text{photons}\cdot\text{sec}^{-1}$  or  $\text{watts}\cdot\text{sec}^{-1}$ ) or the number of total photon counts. The relation of this data to system parameters is shown in SLIDE 5 while the

fractional isotopic abundances and isotope ratios are related to the raw data in SLIDE 6. At this point it is instructive to consider a hypothetical example: a gas near atmospheric pressure composed of two isotopic species, one of which has an abundance which is 0.1% of the other. In SLIDE 7 we see that using typical values of the scattering cross section, spectrometer efficiency, and laser flux,  $10^6$  counts-sec<sup>-1</sup> could be obtained from the high abundance species while  $10^3$  counts-sec<sup>-1</sup> could be obtained from the low-abundance species. Since the precision of the measurement is determined by the statistics of the low-abundance species and Raman scattering obeys Poisson statistics only  $10^6$  counts are needed from this species to yield a 0.1% precision isotope ratio measurement. This would require only  $10^3$  seconds or about 15 minutes, which is performance comparable to that which can be obtained from a good mass spectrometer.

Buoyed by the apparent feasibility of the Raman technique and armed with the knowledge that the use of stable isotopes in medicine and research (caused by the increased availability of these isotopes produced by the ICONS program at Los Alamos<sup>3</sup>) will soon outstrip the current capability to make isotope analyses,<sup>4</sup> we investigated further. Very quickly it was discovered that the complexity of molecular vibrational spectra might prohibit the isolation of frequencies which were specific to individual isotopic species. The vibrational Raman spectrum of a typical diatomic molecule is illustrated schematically in SLIDE 8. There are three branches to the spectrum which refer to different rotational transitions superimposed on the basic  $v=0$  to  $v=1$  vibrational transition ( $v$  is the vibrational quantum number).

The O-, Q-, and S-branches refer to transitions in which the rotational quantum number  $J$  changes by  $-2$ ,  $0$ , and  $+2$ , respectively. Each line in the spectrum corresponds to a transition with a different initial state  $J$ . The spacing of the individual lines in the Q-branch is somewhat exaggerated with respect to the spacing of lines in the O- and S-branches. Also shown in the slide is the Q-branch of a low-abundance isotopic molecule. As shown, the majority of the intensity of this branch could be passed by a monochromator without passing any of the intensity from the adjacent O-branch lines of the high-abundance molecule. However, if it had been displaced slightly higher or lower in frequency, only a fraction of its intensity could be isolated without passing any O-branch intensity. The presence of light scattered into the same frequency interval from two different isotopic molecules will degrade the accuracy of any isotope ratio measurement.

To determine if there were interesting species which did not have this drawback we constructed a Raman spectrometer with unique capabilities.<sup>5</sup> This system is shown schematically in SLIDE 9. The requisite photon beam is typically provided by a 1.5 watt argon ion laser although a 100 mwatt He-Ne Laser is also available. The laser beam is polarized by a Glan-Thompson prism, passed through a narrow-band interference filter, and focused into a scattering cell. A portion of the laser beam is split off and directed onto a monitor photomultiplier (PM) tube. The Raman-scattered light is collected by a lens and directed onto the entrance slit of a SPEX<sup>6</sup> double monochromator (0.75m,  $f/6.8$ ) equipped with 2400 groove/mm holographic gratings. The

holographic gratings reduced the normal stray light problem by two orders of magnitude and eliminated grating ghosts entirely.<sup>7</sup> The photons passed by the monochromator are detected by a specially-selected RCA C31034A-02 photomultiplier tube, cooled to  $-70^{\circ}\text{C}$  by a thermoelectric cryostat with a methanol chiller for heat exchange. This system has a detection quantum efficiency of 30% in the visible with an indiscriminated dark noise less than 4 counts-sec<sup>-1</sup>. Pulses from the monitor PM tube are fed into an amplifier, discriminator, and scaler system with 10 MHz response. Pulses from the signal PM tube are amplified and discriminated and then fed into either a ratemeter-chart recorder system or a scaler. An automatic controller allows operation of the system in a pure photon-counting mode described as follows. First counts are obtained for a preset time. The data is then recorded on a line printer and the wavelength drive turned on for a short period of time to move the spectrometer passband a small increment. This procedure is repeated until the desired spectrum is obtained. The entire spectrometer is shown in SLIDE 10 while SLIDE 11 gives a close-up view of the electronics especially the automatic controller.

Using this system spectra of nitrogen and oxygen in air were obtained at  $1.3\text{ cm}^{-1}$  resolution using the ratemeter-chart recorder system. These are shown in SLIDE 12 and SLIDE 13. In both cases, there is distinct evidence of the low-abundance isotopic molecules ( $^{14}\text{N}\ ^{15}\text{N}$  in nitrogen and  $^{16}\text{O}\ ^{18}\text{O}$  in oxygen). In SLIDE 14 we show a spectrum of  $^{14}\text{N}\ ^{15}\text{N}$  in nitrogen obtained using the photon-counting system.<sup>8</sup> Resolution was  $1.5\text{ cm}^{-1}$ , spacing between data points was  $0.03\text{ cm}^{-1}$ , and the integration time was 1000 seconds per point. The  $\Delta J=0$  band of  $^{14}\text{N}\ ^{15}\text{N}$

is clearly resolved between the  $J=6 \rightarrow J=4$  and  $J=5 \rightarrow J=3$  lines of  $^{14}_N \ ^{14}_N$ . In SLIDE 15 we show a spectrum of  $^{16}_O \ ^{18}_O$  in oxygen under almost identical conditions as the nitrogen spectrum. In this case the  $\Delta J=0$  band of  $^{16}_O \ ^{18}_O$  is clearly resolved between the  $J=9 \rightarrow J=7$  and  $J=7 \rightarrow J=5$  lines of  $^{16}_O \ ^{16}_O$ . These are two very important cases as their well-resolved character indicates that  $^{14}_N/^{15}_N$  and  $^{16}_O/^{18}_O$  isotope ratio measurements can in principle be made near natural abundance.

Further scans were made at  $4 \text{ cm}^{-1}$  resolution (sufficient to integrate 95% of a  $\Delta J=0$  band without any contribution from neighboring  $\Delta J=-2$  lines) through the  $\Delta J=0$  bands of  $^{14}_N \ ^{14}_N$ ,  $^{14}_N \ ^{15}_N$ ,  $^{16}_O \ ^{16}_O$ , and  $^{16}_O \ ^{18}_O$ . From these scans ratios of the isotopic scattered intensities were obtained (SLIDE 16<sup>9</sup> while mass spectrometer analyses<sup>10</sup> of the gas samples yielded the ratios of the isotopic molecular number densities. Division of these two sets of ratios yielded the scattering cross sections of  $^{14}_N \ ^{15}_N$  relative to  $^{14}_N \ ^{14}_N$  and  $^{16}_O \ ^{18}_O$  relative to  $^{16}_O \ ^{16}_O$ . Comparison with tabulated cross section data for  $^{14}_N \ ^{14}_N$  and  $^{16}_O \ ^{16}_O$  then yielded the scattering cross sections for  $^{14}_N \ ^{15}_N$  and  $^{16}_O \ ^{18}_O$ . It is of theoretical interest that the ratios of the isotopic cross sections is not unity (the value one would expect at first thought). This can be qualitatively explained by considering the effects of the vibrational wavefunctions on the cross section. This dependence is shown explicitly in SLIDE 17. The factors  $\langle B_v | I_v \rangle$  and  $\langle I_v | A_v \rangle$ , called Franck-Condon factors, are of order unity and may have arbitrary phase. Since the cross section is the result of a coherent summation of a large number of contributions, each



of which is of the same order of magnitude as the total cross section, a tremendous cancellation of contributions may and must occur as a result of the randomness of the phases of the Franck-Condon factors. Since these factors are affected by mass-related differences in the vibration wavefunctions, it is evident that even with all other factors being equal, the cross section of one isotopic molecule has no direct relation to that of another isotopic molecule. The problem is unfortunately too complicated for numerical calculations of the cross section differences to be made at this time.

Our measurement of the isotopic cross sections of  $^{16}\text{O } ^{18}\text{O}$  and  $^{14}\text{N } ^{15}\text{N}$  is equivalent to calibration of our spectrometer for measuring  $^{16}\text{O}/^{18}\text{O}$  and  $^{14}\text{N}/^{15}\text{N}$  isotope ratios at the 5% precision level. These measurements would be accomplished by scanning through the  $\Delta J=0$  bands of both the low- and high-abundance isotopic species at  $4 \text{ cm}^{-1}$  resolution and 60 seconds per point. Scanning is necessary to assure that the maximum scattered intensity is measured because the spectrometer is only resettable to  $\pm 0.5 \text{ cm}^{-1}$ .

In our measurements of the isotopic cross sections total count rates of approximately  $20 \text{ counts-sec}^{-1}$  were obtained in the  $\Delta J=0$  bands of both  $^{16}\text{O } ^{18}\text{O}$  and  $^{14}\text{N } ^{15}\text{N}$  with only 1.2 watts in the laser beam. This data can be used to obtain a concrete estimate of the performance which can be obtained with the Raman-scattering technique. First, however, it is of interest to note a possible improvement to the instrument, namely, placing the sample cell inside the laser cavity (SLIDE 18). In this case, intensities up to 1000 watts can be obtained as

compared to a maximum of about 30 watts for a sample placed in the external beam. As mentioned earlier only  $10^6$  counts are needed in the low-abundance peak to yield a 0.1% precision measurement. At a laser power of 1.2 watts we measured 20 count-sec<sup>-1</sup>, so  $5 \times 10^4$  seconds are required for a 0.1% precision measurement (SLIDE 19). The spectrometer used for the cross section measurements is essentially one-half of the isotope ratio spectrometer of SLIDE 4 so that a direct extension of data from the cross section measurements to isotope ratio measurements is possible. Extrapolating to the 1000 watts available in the intracavity system, a count rate of 17,000 counts-sec<sup>-1</sup> is expected. At this rate only 60 seconds would be required for a 0.1% precision measurement. This performance is an order of magnitude improvement over the performance expected from a typical mass spectrometer.

As a result of the preceding work, we have shown that Raman scattering should be a useful tool for stable isotope ratio measurements in certain light elements. In SLIDE 20 we list some of the possible advantages of the Raman scattering technique over mass spectrometry. Among these include conservation of the sample and probable increases in either speed or accuracy or both. To be fair, in SLIDE 21 we list several disadvantages of the technique. Foremost among these is that only certain molecules are amenable to analysis. Finally, in SLIDE 22 we present a cost analysis of the Raman-scattering technique. Based on the assumption that a recently available small double monochromator can be modified to our purposes, a Raman-scattering

isotope ratio spectrometer might be constructed for as low as \$40,000. This is a substantial reduction compared to the \$50,000-\$150,000 cost of a good mass spectrometer.

In SLIDES 23 and 24 we present two additional spectra of interest. SLIDE 23 is the Raman spectrum (1.0  $\text{cm}^{-1}$  resolution, 3600 sec-point<sup>-1</sup>) of  $^{16}\text{O}^{16}\text{O}$  in oxygen. In this case the  $J=5 \rightarrow J=3$  line of  $^{16}\text{O}^{16}\text{O}$  lies right on top of the  $J=2$  band of  $^{16}\text{O}^{17}\text{O}$ . Thus,  $^{16}\text{O}/^{17}\text{O}$  isotope ratios cannot be measured in molecular oxygen at natural abundance without either suffering a large increase in measurement time (due to the fact that only a fraction of the band can be isolated from the  $^{16}\text{O}^{16}\text{O}$  lines) or by complicating the data analysis to account for the  $^{16}\text{O}^{16}\text{O}$  contributions to the measured  $^{16}\text{O}^{17}\text{O}$  intensity. SLIDE 24 is the Raman spectrum (1.0  $\text{cm}^{-1}$  resolution, 600 sec-point<sup>-1</sup>) of  $^{16}\text{O}^{16}\text{O}$  in  $^{18}\text{O}$ -enriched oxygen. Coupled with similar data on  $^{18}\text{O}^{18}\text{O}$  in  $^{16}\text{C}^{16}\text{C}$ , this spectrum indicates that  $^{16}\text{O}^{16}\text{O}/^{18}\text{O}^{18}\text{O}$  molecular ratio measurements are possible at almost any abundance ratio. This type of measurement is of extreme interest in studies of isotopic fractionation in oxygen adsorption. One study currently being planned<sup>11</sup> on the oxygen-hemoglobin system requires numerous 0.01% precision measurements to be performed on nearly equal mixtures of  $^{16}\text{O}^{16}\text{O}$  and  $^{18}\text{O}^{18}\text{O}$ . Routine measurements of this type are beyond the capability of most mass spectrometers yet should be feasible with the Raman scattering technique.

In SLIDE 25 we show a modification of the technique which should be useful for hydrogen-deuterium isotope ratio measurements. In the hydrogen system, the isotope shifts are so large that

there is almost no overlap of the vibrational spectrum of one species with that of another. The shifts are also large enough and sufficiently far from the laser wavelength that interference filters may be used to isolate the  $\nu_1$  bands of  $H_2$ ,  $HD$ , and  $D_2$ . Placing the filters between two f/1 lenses, whose focal points are at a photomultiplier tube and the scattering cell, results in a detector with an overall efficiency of 0.01. This is two orders of magnitude greater than a typical monochromator and should result in a system capable of making 0.1% precision H/D isotope ratio measurements at any degree of enrichment in times of the order of a few minutes. A system such as the one shown is currently being built to test its utility for use in the isotope separation program at Livermore.

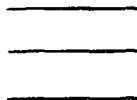
Finally, in SLIDE X6 we show a far-out concept which may hold promise for analysis of any isotope ratio. In this system a beam of monoenergetic gamma rays (such as produced by neutron capture in a suitable target placed in a fission reactor or by a gamma ray laser) scatters from a sample (solid, liquid, or gas) via the nuclear Raman effect. The inelastically-scattered gamma rays are detected by Ge(Li) detectors coupled to a multichannel analyzer. Such a system is not currently feasible for precision isotope ratio measurements because gamma ray sources of sufficient intensity are not yet available. Should they become available this nuclear Raman scattering technique should remove the major disadvantage of the vibrational Raman technique, namely limited applicability to a few special molecular species.

## REFERENCES

1. R.C. Harney and S.D. Bloom, "On the Feasibility of Isotopic Abundance Measurements Using Raman Scattering," Lawrence Livermore Laboratory report UCRL-51558 (April 1974).
2. Detailed discussions of the Raman effect may be found in:
  - a) G. Herzberg, Spectra of Diatomic Molecules, Van Nostrand Reinhold 1950 and Infrared and Raman Spectra, Van Nostrand Reinhold 1945.
  - b) A. Anderson, The Raman Effect, Vols. I and II., Marcel Dekker 1971.
  - c) M. Tobin, Laser Raman Spectroscopy, John Wiley and Sons 1971
3. Descriptions of the ICONS program are contained in the following references:
  - a) R.E. Schreiber " ICONS at LASL," Los Alamos Scientific Laboratory report LA-4759-MS (1971).
  - b) N.A. Matwyoff, M.J. Reinfeld, T.R. Mills, B.B. McInteer, and M. Goldblatt, "The Stable Isotopes ( ICONS ) Research and Development Program at the Los Alamos Scientific Laboratory," Proceedings of the IAEA Symposium on Isotopes and Radiation Techniques in Studies of Soil Physics, Irrigation and Drainage in Relation to Crop Production, Vienna, Austria, Oct. 3-5, 1973.
  - c) N.A. Matwyoff and D.G. Ott, Science, 181, 1125 (1973).
4. P.R. Stout (deceased), private communication (1975).
5. R.C. Harney and F.P. Milanovich, Rev. Sci. Instr., 46, 1047 (1975).
6. Reference to a company or product name does not imply recommendation or endorsement by either the University of California or the U.S. Energy Research and Development Administration to the exclusion of others that may be suitable.
7. J. Cordell et al., in Optical Instruments and Techniques, Oriel Press 1970, pp. 117-124.
8. S.D. Bloom, R.C. Harney, and F.P. Milanovich, to appear in Jan.-Feb. 1976 issue of Applied Spectroscopy. Some of the data on nitrogen and oxygen are published in this work.
9. Data on the cross sections of  $^{14}\text{N}$ ,  $^{14}\text{N}$  and  $^{16}\text{O}$ ,  $^{16}\text{O}$  were obtained from W.R. Fenner, H.A. Hyatt, J.M. Kellam, and S.P.S. Porto, J. Opt. Soc. Amer., 63, 73 (1973).
10. C.H. Otto, private communication (1975).
11. M. Anbar and H. Heck, private communication (1975).

# THE RAMAN EFFECT

Excited electronic states  $\hbar\omega_e$



Virtual intermediate states  $\hbar(\omega_v + \omega_e)$   
 $\hbar\omega_e$



First excited vibrational state  $\hbar\omega_v$



Ground state 0



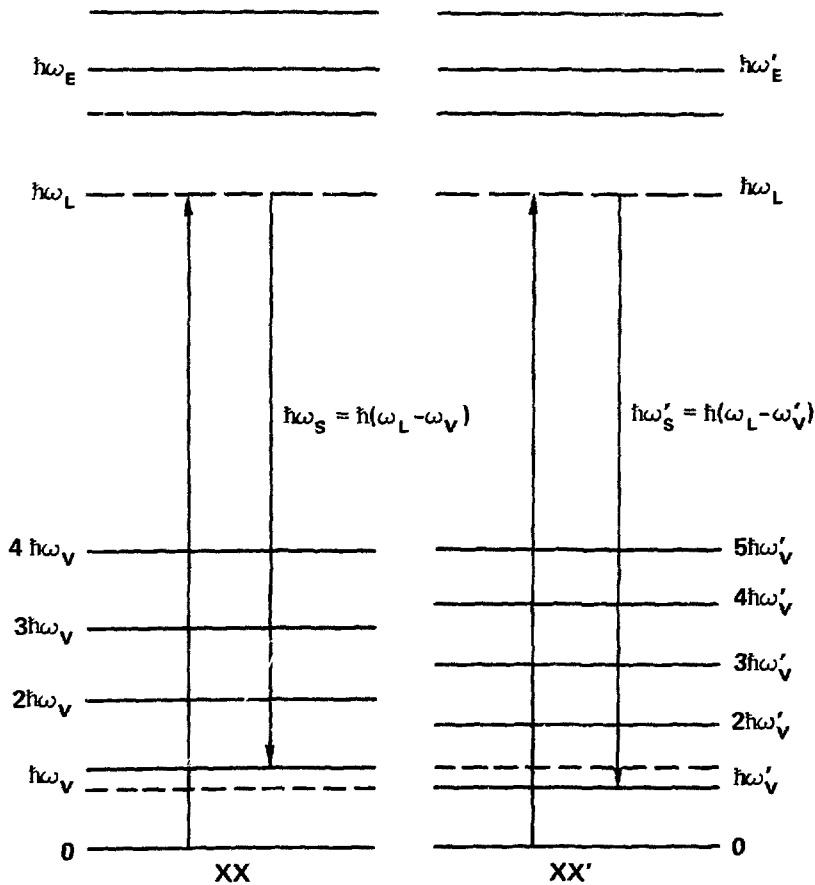
incident photon  $E = \hbar\omega_L$   
scattered photon  $E = \hbar(\omega_L - \omega_v)$

incident photon  $E = \hbar\omega_L$   
scattered photon  $E = \hbar(\omega_L + \omega_v)$

Stokes Scattering

Anti-Stokes Scattering

# ORIGIN OF THE ISOTOPE EFFECT IN VIBATIONAL RAMAN SCATTERING



## ISOTOPE EFFECT IN SELECTED MOLECULES

Molecule	$\nu(\text{cm}^{-1})$	Ref.	Molecule	$\nu(\text{cm}^{-1})$	Ref.	
H <sub>2</sub>	4161.1	A	B <sup>10</sup> F <sub>3</sub>	482.0	D	
HD	3632.1	A	B <sup>11</sup> F <sub>3</sub>	480.4	D	
D <sub>2</sub>	2994.4	B	C <sup>12</sup> O <sub>2</sub> <sup>16</sup>	1388.2	E	
HT	3433.1	B		C <sup>13</sup> O <sub>2</sub> <sup>16</sup>	1369.9	E
DT	~2686.0	B	C <sup>12</sup> S <sub>2</sub> <sup>32</sup>	658.0	E	
T <sub>2</sub>	2468.1	B		C <sup>12</sup> S <sup>32</sup> S <sup>33</sup>	653.0	E
Li <sub>2</sub> <sup>6</sup>	~ 373.9	B		C <sup>12</sup> S <sup>32</sup> S <sup>34</sup>	648.4	E
Li <sup>6</sup> Li <sup>7</sup>	~ 360.3	B	C <sub>6</sub> <sup>12</sup> H <sub>6</sub>	991.6	D	
Li <sub>2</sub> <sup>7</sup>	346.2	B		C <sub>6</sub> <sup>12</sup> C <sup>13</sup> H <sub>6</sub>	984	D
N <sub>2</sub> <sup>14</sup>	2330.7	B	C <sub>6</sub> <sup>12</sup> D <sub>6</sub>	944.7	D	
N <sup>14</sup> N <sup>15</sup>	~2291.5	B		C <sub>6</sub> <sup>12</sup> C <sup>13</sup> D <sub>6</sub>	939.5	D
N <sub>2</sub> <sup>15</sup>	~2251.7	B	C <sup>12</sup> Cl <sub>4</sub> <sup>35</sup>	461.5	D	
O <sub>2</sub> <sup>16</sup>	1556.3	C		C <sup>12</sup> Cl <sub>3</sub> <sup>35</sup> Cl <sup>37</sup>	458.4	D
O <sub>2</sub> <sup>17</sup>	~1509.8	C	C <sup>17</sup> Cl <sub>2</sub> <sup>35</sup> Cl <sup>37</sup>	455.1	D	
O <sub>2</sub> <sup>18</sup>	~1467.3	C	C <sup>12</sup> Cl <sub>2</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup>	~ 452.0	D	
O <sup>16</sup> O <sup>17</sup>	~1533.2	C	C <sup>12</sup> Cl <sub>4</sub> <sup>37</sup>	~ 448.9	D	
O <sup>16</sup> O <sup>18</sup>	~1512.5	C				
O <sup>17</sup> O <sup>18</sup>	~1488.7	C				

~ denotes a calculated frequency

A - Stoicheff, Can. J. Phys. 32 630 (1954)

B - Herzberg, Spectra of Diatomic Molecules

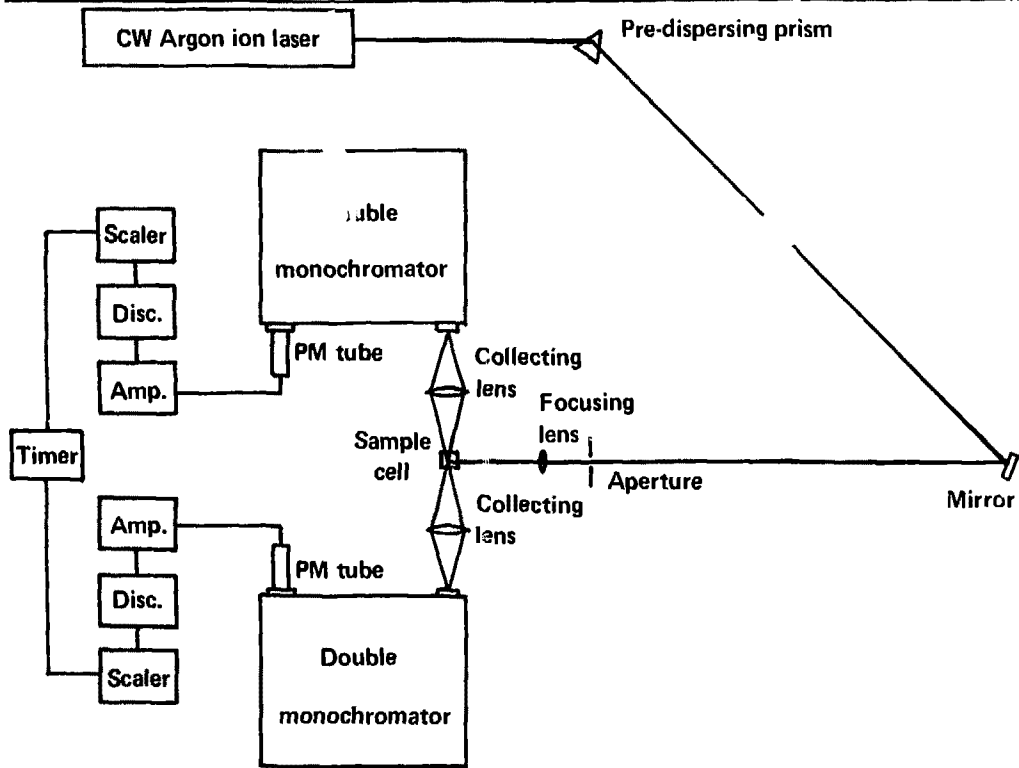
C - Woher and McGinnis, J. Mol. Spectry. 4 195 (1960)

D - Herzberg, Infrared and Raman Spectra

E - Stoicheff, Can. J. Phys. 36 218 (1958)



# RAMAN SCATTERING ISOTOPIC ABUNDANCE SPECTROMETER



SLIDE 4

## INTENSITY MEASUREMENTS



Measured intensity

$$I_{mi} = \epsilon_i' \sigma_i \rho_i L I_o$$

Measured counts

$$N_{mi} = \epsilon_i' \sigma_i \rho_i L \int_{\tau_{oi}}^{\tau_{fi}} I_o dt$$

$\sigma_i$  — cross section of  $i^{\text{th}}$  species

$\rho_i$  — number density of  $i^{\text{th}}$  species

$\epsilon_i'$  — detection efficiency of  $i^{\text{th}}$  species

$I_o$  — incident intensity

$L$  — length of scattering volume

$\tau_{oi}$  — time at which counting began

$\tau_{fi}$  — time at which counting ended



**Fractional isotopic abundance (of isotope j of element X)**

$$f_j \equiv \frac{\sum_k n_{kj} \rho_k}{\sum_k n_{kX} \rho_k} = \frac{\sum_k n_{kj} I_{mk} \epsilon_k^{-1}}{\sum_k n_{kX} I_{mk} \epsilon_k^{-1}} = \frac{\sum_k n_{kj} N_{mk} \epsilon_k^{-1}}{\sum_k n_{kX} N_{mk} \epsilon_k^{-1}}$$

**isotope ratio (of isotopes i and j)**

$$R_{ij} \equiv \frac{f_i}{f_j} = \frac{\sum_k n_{ki} I_{mk} \epsilon_k^{-1}}{\sum_k n_{kj} I_{mk} \epsilon_k^{-1}} = \frac{\sum_k n_{ki} N_{mk} \epsilon_k^{-1}}{\sum_k n_{kj} N_{mk} \epsilon_k^{-1}}$$

$n_{kj}$  - number of atoms of isotope j in species k

$n_{kX}$  - number of atoms of element X in species k

$$\epsilon_k^{-1} \equiv (\epsilon_k' \sigma_k L)^{-1}$$

## BACK-OF-THE-ENVELOPE CALCULATION OF RAMAN ISOTOPE MEASUREMENT FEASIBILITY

$$\text{Count rate} = \epsilon \sigma \rho \phi L$$

$$\epsilon \sim 10^{-4} \text{ (typical spectrometer efficiency)}$$

$$\sigma \sim 10^{-29} \text{ cm}^2 \text{ (typical diatomic Raman cross section)}$$

$$\rho \sim 10^{19} \text{ cm}^{-3} \text{ (gas at } 300^\circ\text{K, } 0.5 \text{ atm)}$$

$$\phi \sim 10^{20} \text{ photons-sec}^{-1} \text{ (30 watts at } 4880 \text{ \AA)}$$

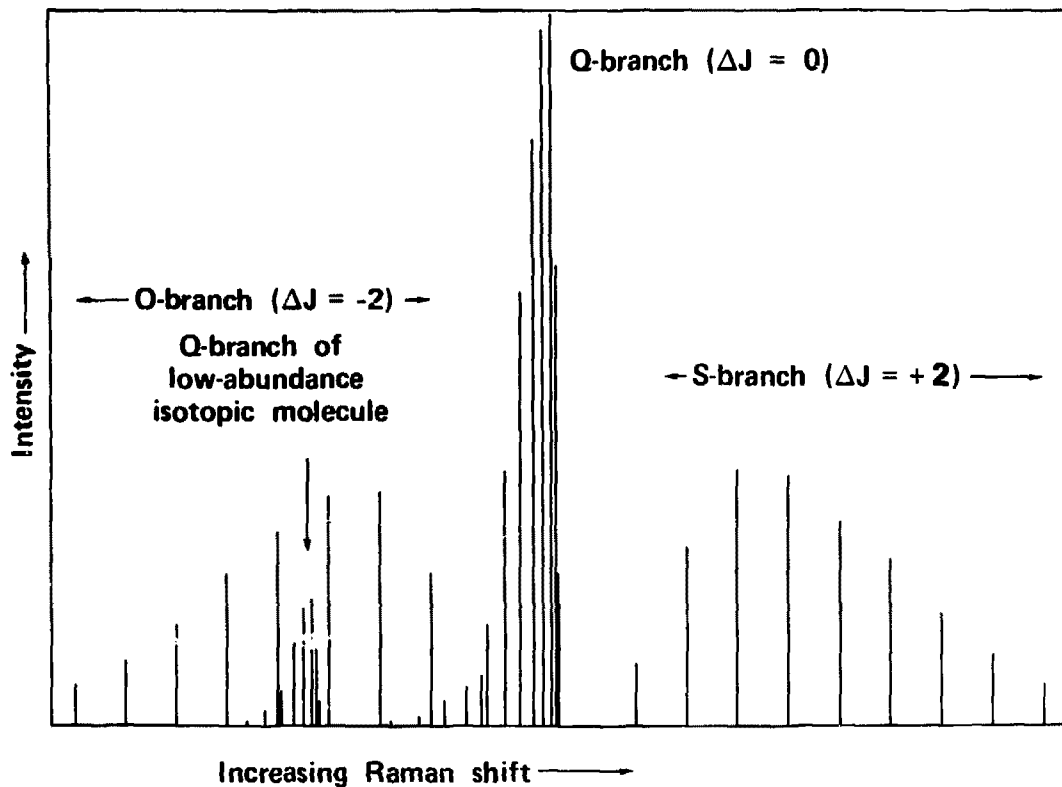
$$L \sim 1 \text{ cm}$$

$$\text{Count rate} \sim 10^6 \text{ sec}^{-1}$$

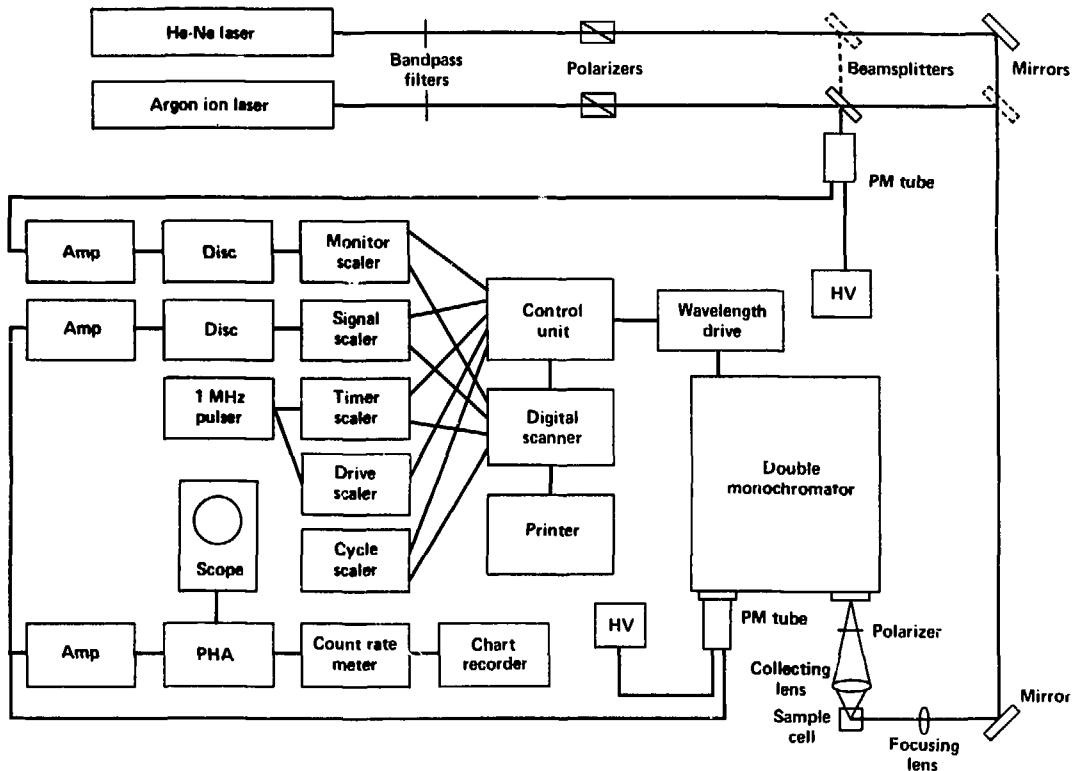
For an isotopic molecule of 0.1% abundance, count rate  $\sim 10^3 \text{ sec}^{-1}$

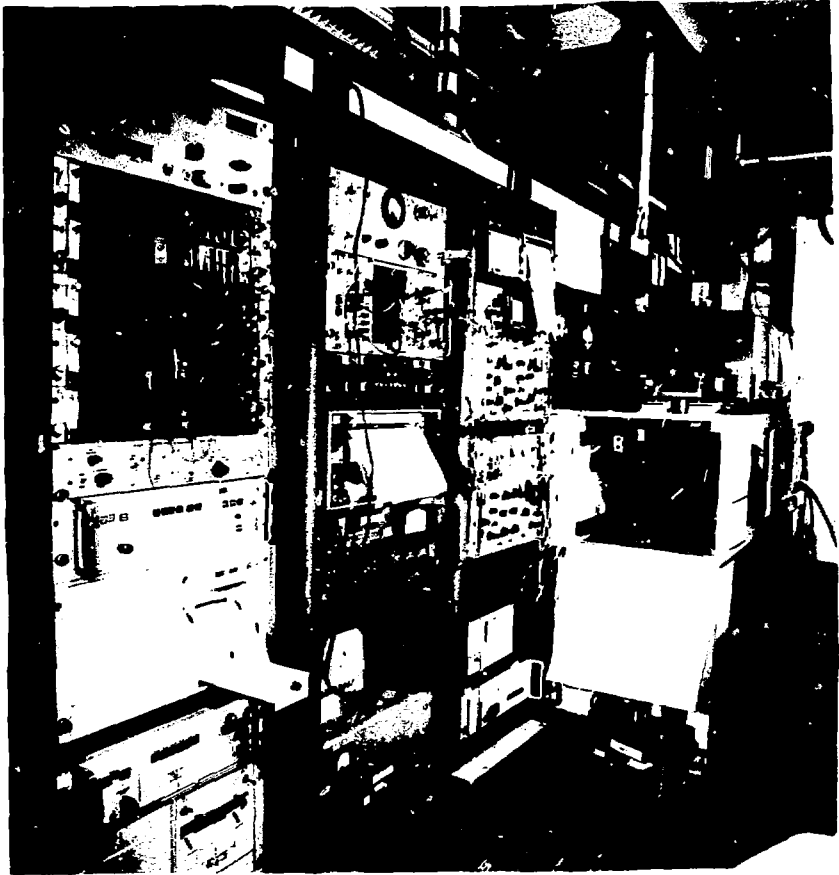
Time required for 0.1% precision measurement is  $10^3 \text{ sec}$  (15 min)

**TYPICAL VIBRATION-ROTATION RAMAN SPECTRUM OF A DIATOMIC MOLECULE**

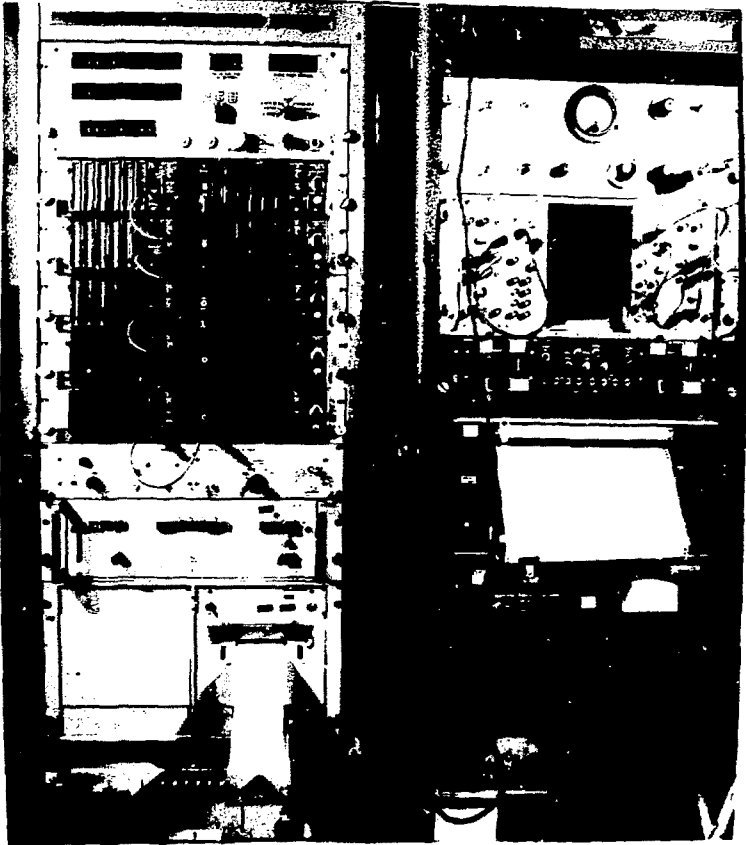


# MULTI-FUNCTION LASER RAMAN SPECTROMETER





SLIDE 10

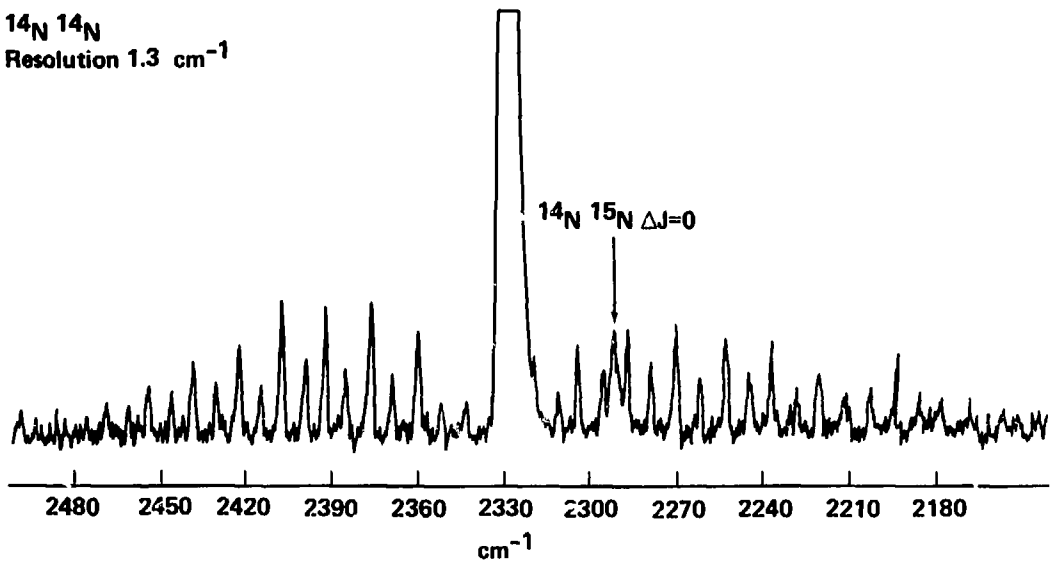


SLIDE 11





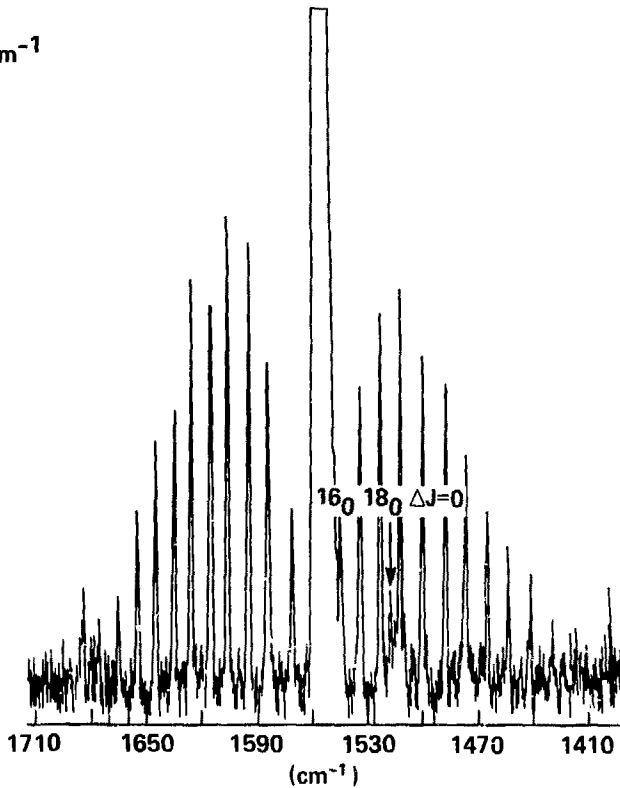
$^{14}\text{N } ^{14}\text{N}$   
Resolution  $1.3 \text{ cm}^{-1}$



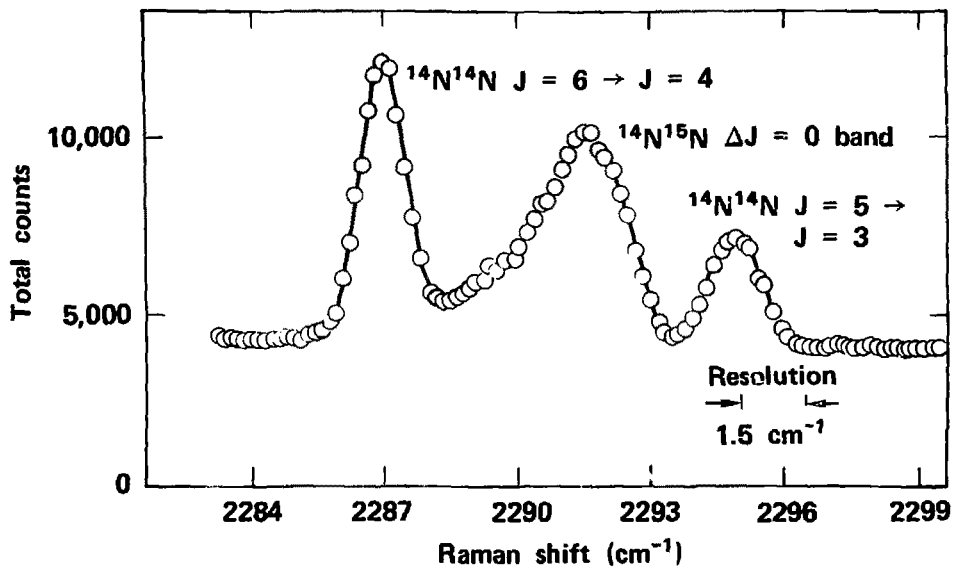
SLIDE 12



$^{16}\text{O}^{16}\text{O}$   
Resolution  $1.3\text{ cm}^{-1}$

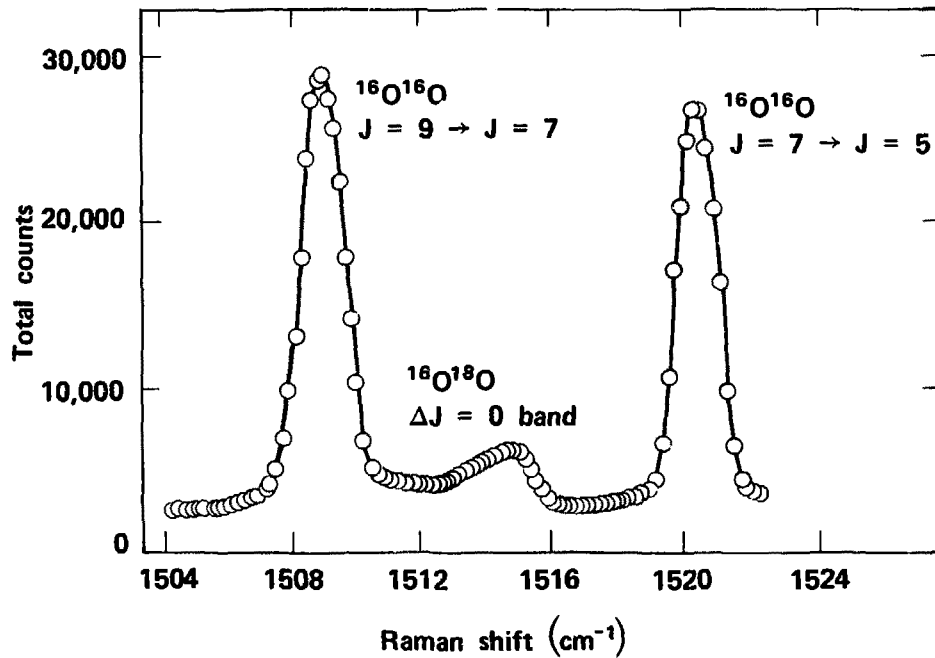


# ISOTOPE STRUCTURE IN THE RAMAN SPECTRUM OF NITROGEN



SLIDE 14

**ISOTOPE STRUCTURE IN THE RAMAN SPECTRUM OF OXYGEN**



 ISOTOPIC CROSS SECTION DATA

Nitrogen		Oxygen	
$I_{14-15}/I_{14-14}$	$0.0081 \pm 0.0002$	$I_{16-18}/I_{16-16}$	$0.0043 \pm 0.0001$
$N_{14-15}/N_{14-14}$	$0.0072 \pm 0.0001$	$N_{16-18}/N_{16-16}$	$0.0041 \pm 0.0001$
$\sigma_{14-15}/\sigma_{14-14}$	$1.13 \pm 0.05$	$\sigma_{16-18}/\sigma_{16-16}$	$1.05 \pm 0.05$
$\sigma_{14-14}$ ( $\text{cm}^2\text{-sr}^{-1}\text{-mol}^{-1}$ )	$3.3 \pm 1.1 \times 10^{-31}$	$\sigma_{16-16}$ ( $\text{cm}^2\text{-sr}^{-1}\text{-mol}^{-1}$ )	$4.3 \pm 1.4 \times 10^{-31}$
$\sigma_{14-15}$ ( $\text{cm}^2\text{-sr}^{-1}\text{-mol}^{-1}$ )	$3.7 \pm 1.4 \times 10^{-31}$	$\sigma_{16-18}$ ( $\text{cm}^2\text{-sr}^{-1}\text{-mol}^{-1}$ )	$4.5 \pm 1.5 \times 10^{-31}$

## RAMAN CROSS SECTION FORMULA

$$\sigma \propto \omega_i \omega_s^3 \left| \sum_{l, l_v} \langle B_v | l_v \rangle \langle l_v | A_v \rangle \langle B | r | l \rangle \langle l | r | A \rangle \left( \frac{1}{\Delta E_l} + \frac{1}{\Delta E_l'} \right) \right|^2$$

$\omega_i$  – incident frequency

$\omega_s$  – scattered frequency

$|A\rangle$  – combined nuclear, rotational, and electronic wavefunction of initial state

$|B\rangle$  – combined nuclear, rotational, and electronic wavefunction of final state

$|l\rangle$  – combined nuclear, rotational, and electronic wavefunction of intermediate state

$|A_v\rangle$  – vibrational wavefunction of initial state

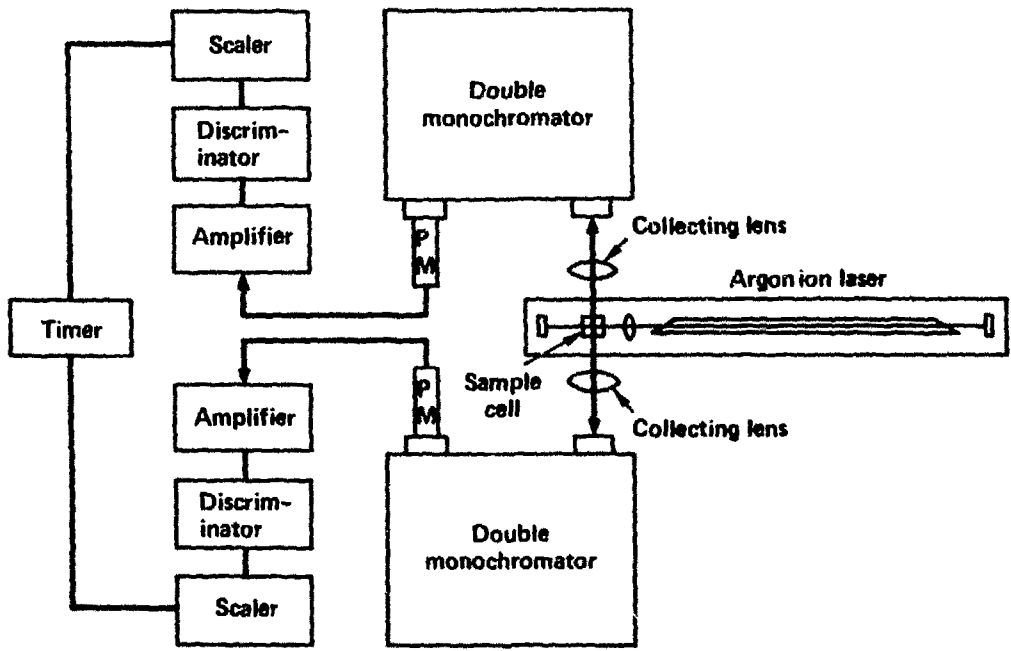
$|B_v\rangle$  – vibrational wavefunction of final state

$|l_v\rangle$  – vibrational wavefunction of intermediate state

$\Delta E_l$  – resonant denominator for state  $l$

$\Delta E_l'$  – anti-resonant denominator for state  $l$

# ISOTOPE MEASUREMENT TECHNIQUE USING INTRACAVITY LASER EXCITATION



SLIDE 1F

## ACHIEVED AND EXPECTED RESULTS



### Achieved results

20 counts/sec on  $^{16}\text{O}^{18}\text{O}$  and  $^{14}\text{N}^{15}\text{N}$  peaks with 1.2 watts in laser beam.  
A 0.1% accuracy measurement requires  $10^6$  counts or  $5 \times 10^4$  sec.

### Expected results

17,000 counts/sec on  $^{16}\text{O}^{18}\text{O}$  and  $^{14}\text{N}^{15}\text{N}$  peaks with 1000 watts inside the laser cavity.  
A 0.1% accuracy measurement requires  $10^6$  counts or 60 sec.

### Mass spectrometer results

A typical mass spectrometer requires  $10^3$  sec to make a 0.1% accuracy measurement.



## **ADVANTAGES OF RAMAN SCATTERING ISOTOPIC MEASUREMENT TECHNIQUE**

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- **Increased speed of measurement**
- **Increased ease of measurement**
- **Increased accuracy**
- **Increased sensitivity**
- **Smaller samples may be used**
- **Sample is neither altered nor consumed**
- **Measurement is repeatable on same sample**
- **Technique is adaptable to time-resolved studies**
- **Liquid samples (in certain cases) may be analyzed**

## **DISADVANTAGES OF RAMAN SCATTERING ISOTOPIC MEASUREMENT TECHNIQUE**

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- **Technique is not readily adaptable to all elements**
- **Samples must be prepared in standard form in advance of measurement**

## **COST COMPARISONS**

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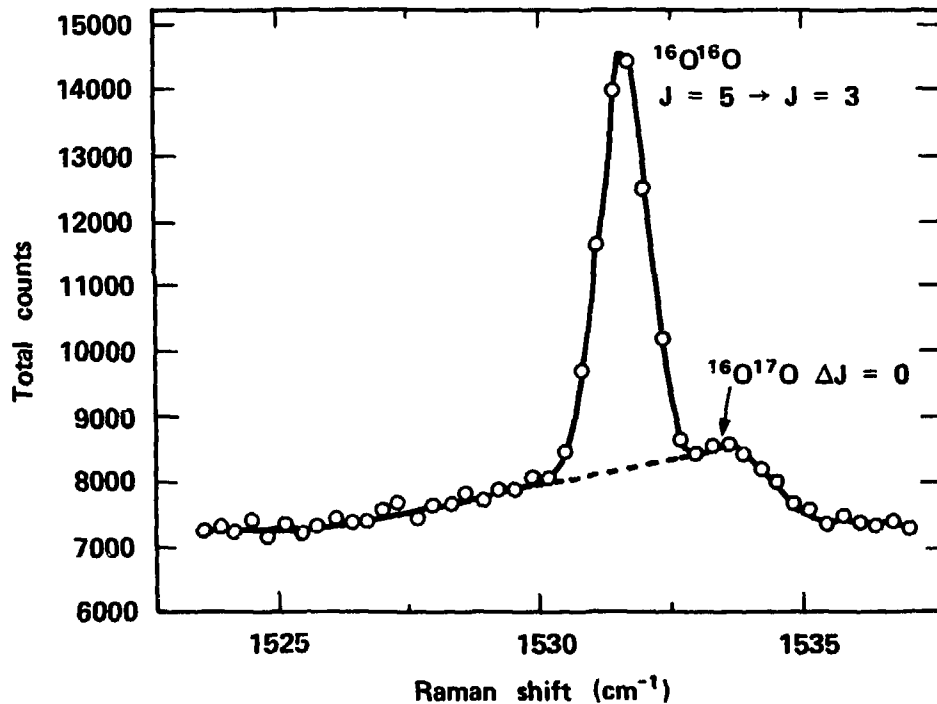
### **Raman Spectroscopy**

<b>Laser</b>	<b>\$23,000</b>
<b>(2) Monochromators (with holographic gratings)</b>	<b>7,000</b>
<b>(2) Photomultiplier tubes</b>	<b>2,400</b>
<b>(2) Cryostats</b>	<b>2,600</b>
<b>Miscellaneous electronics</b>	<b><u>5,000</u></b>
	<b>\$40,000</b>

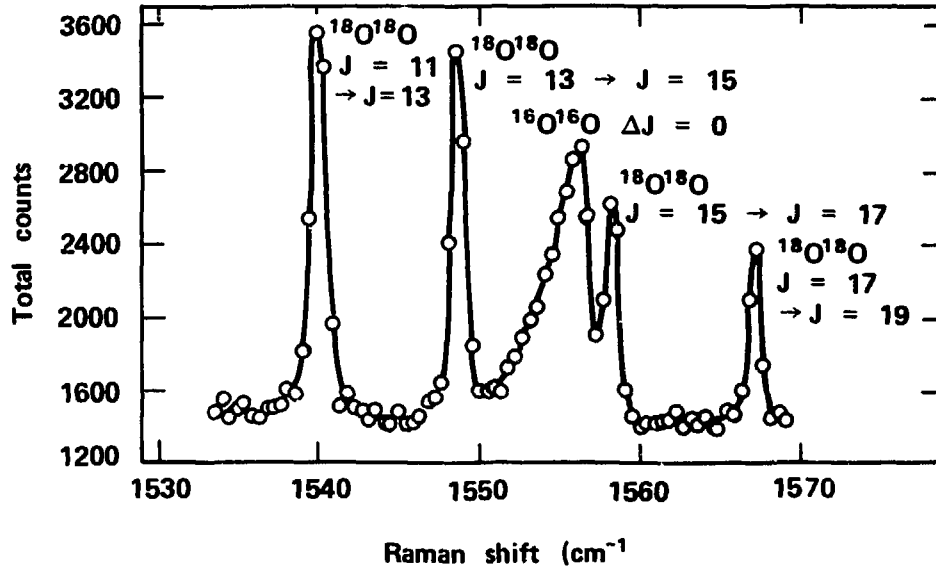
### **Mass Spectrometry**

<b>Mass spectrometer</b>	<b>\$50,000—\$150,000</b>
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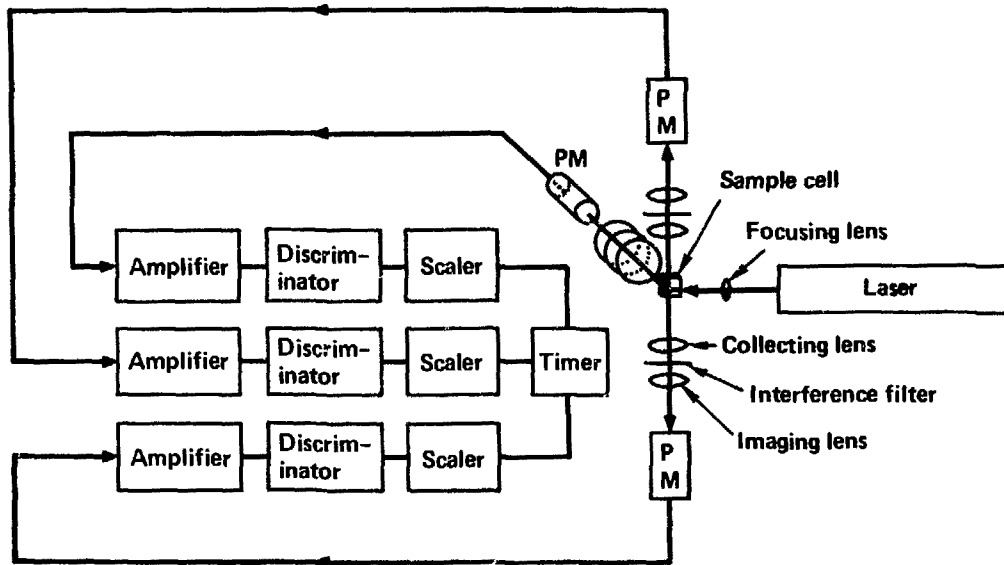
ISOTOPE STRUCTURE IN THE RAMAN SPECTRUM OF OXYGEN



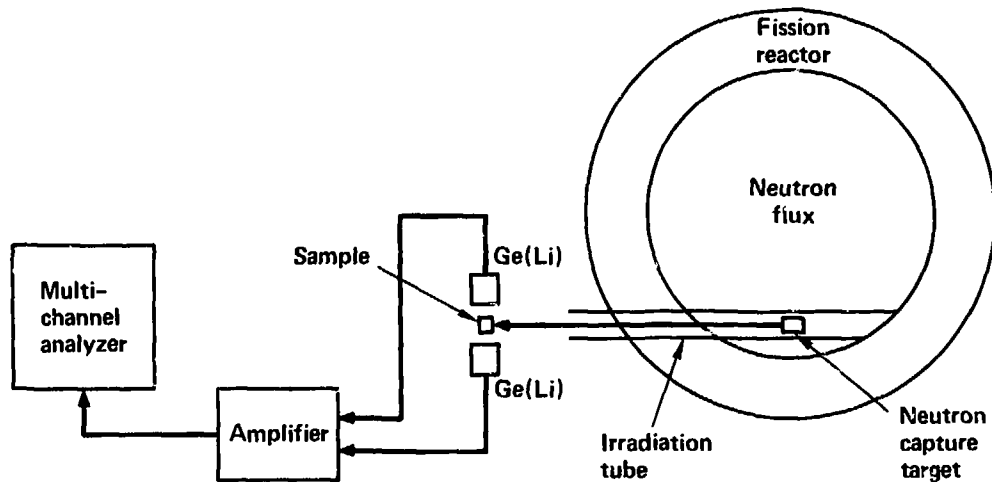
**OXYGEN-16 ISOTOPE STRUCTURE IN THE RAMAN SPECTRUM OF ENRICHED OXYGEN**



# HYDROGEN-DEUTERIUM ISOTOPE MEASUREMENT APPARATUS



# ISOTOPE MEASUREMENT APPARATUS UTILIZING NUCLEAR RAMAN SCATTERING



SLIDE 26