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**ON THE FEASIBILITY OF ISOTOPIC ABUNDANCE
MEASUREMENTS USING RAMAN SCATTERING**

R. C. Harney
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ON THE FEASIBILITY OF ISOTOPIC ABUNDANCE MEASUREMENTS USING RAMAN SCATTERING

Abstract

The possibility of using gas-phase Raman scattering of laser beams for measuring the isotopic abundances of light elements is studied. A design for a Raman scattering isotopic abundance spectrometer is presented, and the data collection rate for a natural isotopic abundance determination in nitrogen

gas is calculated. An analysis of noise sources indicates that isotopic variations of less than 100 parts per billion may be measured in times of the order of a few minutes. It appears that laser Raman scattering should be a valuable new tool for precision assays of isotopic abundance ratios.

Isotopic abundance measurements are being used at an ever-increasing rate in chemical and biological research.¹ For radioactive isotopes, the abundances are easily determined using nuclear counters. For nonradioactive isotopes, mass spectrometers have been essentially the only available tools. In general, a precision measurement (error of $\pm 0.1\%$ or less) of an isotopic abundance ratio takes on the order of tens of minutes or more using a mass spectrometer. In addition, the sample is altered (i. e., ionized and possibly fragmented) as well as consumed during the measurement. A technique in which the measurement time is reduced significantly and the sample is neither consumed nor altered might be of considerable interest. Here, we describe a new approach, laser Raman scattering, which should fulfill these conditions. We

limit our study (for the present) to the light elements (hydrogen, boron, carbon, nitrogen, and oxygen), though some mention of heavier elements is made later. We begin with a discussion of isotope effects in Raman scattering and then describe a design for a practical system incorporating the necessary dispersive elements as well as an argon ion laser source. Finally, estimates are made of the range of applicability of the Raman scattering technique.

Raman scattering is the inelastic scattering of light by molecules.² The elementary processes are indicated in Fig. 1 for the case of the excitation of molecular vibrations, which is of prime interest in the present context. In Stokes Raman scattering, a laser photon of energy $\hbar\omega_L$ scatters from a molecule in its ground state, losing an amount of

Fig. 1. The Raman effect: Stokes and anti-Stokes scattering.

energy equal to one quantum of vibrational energy ($\hbar\omega_v$). The molecule is left in an excited state, while the scattered photon has an energy $\hbar(\omega_L - \omega_v)$. In anti-Stokes scattering, the laser photon scatters from a molecule in its first excited vibrational state, gaining an amount of energy equal to one quantum of vibrational energy. In this case the scattered photon has an energy $\hbar(\omega_L + \omega_v)$. The relative intensities of Stokes and anti-Stokes scattering are temperature dependent; the ratio is given by the Boltzmann factor,

$$\frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} = e^{-\hbar\omega_v/kT} \quad (1)$$

The Raman cross section will depend on ω_L , as well as on ω_v and other char-

acteristics of the scattering molecule. Substitution of one isotope for another in a molecule usually changes the vibrational frequency roughly inversely as the square root of the effective mass. In simple molecules this frequency shift, known as the isotope effect, can be sufficiently large (1 cm^{-1} or greater) so that the Raman frequencies corresponding to different isotopes can be easily resolved by a monochromator. Table 1 lists the natural isotopic abundances of some important elements while Table 2 shows the isotope effect in the vibrational frequencies of several simple molecules.

If the element to be analyzed in a sample can be quantitatively converted to a single molecular species that exhibits an easily detectable Raman isotope effect, then Raman scattering may be

Table 1. Natural isotopic abundances of selected elements.

Element	Isotope	Abundance (%)	Element	Isotope	Abundance (%)
Hydrogen	^1H	99.985	Chlorine	^{35}Cl	75.77
	^2H	0.015		^{37}Cl	24.23
	^3H	—	Potassium	^{39}K	93.08
Lithium	^6Li	7.56		^{40}K	0.0118
	^7Li	92.44		^{41}K	6.91
Boron	^{10}B	19.8	Iron	^{54}Fe	5.8
	^{11}B	80.2		^{56}Fe	91.7
Carbon	^{12}C	98.89		^{57}Fe	2.14
	^{13}C	1.11		^{58}Fe	0.31
	^{14}C	—	Rubidium	^{85}Rb	72.15
Nitrogen	^{14}N	99.63		^{87}Rb	27.85
	^{15}N	0.37	Mercury	^{196}Hg	0.146
Oxygen	^{16}O	99.759		^{198}Hg	10.02
	^{17}O	0.037		^{199}Hg	16.84
	^{18}O	0.204		^{200}Hg	23.13
Silicon	^{28}Si	92.21		^{201}Hg	13.22
	^{29}Si	4.70		^{202}Hg	29.80
	^{30}Si	3.09		^{204}Hg	6.85
Sulfur	^{32}S	95.00	Uranium	^{234}U	0.0057
	^{33}S	0.76		^{235}U	0.72
	^{34}S	4.22		^{238}U	99.27
	^{36}S	0.014			

used for performing the isotopic analysis. Examples of such elements are carbon and nitrogen. Carbon in any substance is readily converted to CO_2 upon combustion, and nitrogen in almost any form is converted to N_2 by the Dumas method.⁸ The intensity I_i (in photons-sec⁻¹-sr⁻¹) of Stokes Raman scattering from molecules of type i is given by

$$I_i = \rho_i \sigma_i \phi L, \quad (2)$$

where we suppress the dependence on scattering angle and polarization, since

these are not important in the present discussion. In Eq. (2) ρ_i is the number density in cm⁻³ and σ_i is the differential Raman cross section (usually at 90°) in cm²-sr⁻¹, both pertaining to type i molecules; ϕ is the incident laser intensity (photons-sec⁻¹); and L is the length of the scattering volume. Since the isotopic molecular abundances N_i are given by

$$N_i = \rho_i / \sum_{\text{all } j} \rho_j, \quad (3)$$

it is clear that, given the quantities $\sigma_i \phi L$, the N_i can be obtained by measuring the I_i .

Table 2. The isotope effect in selected molecules.

Molecule	ω_v (cm^{-1})	Ref. No.	Molecule	ω_v (cm^{-1})	Ref. No.
H ₂	4161.1	3	¹⁰ BF ₃	482.0	6
HD	3632.1	3	¹¹ BF ₃	480.4	6
D ₂	2994.4	4	¹² C ¹⁶ O ₂	1388.2	7
HT	3433.1	4	¹³ C ¹⁶ O ₂	1369.9	7
DT	~2686.0 ^a	4	¹² C ³² S ₂	658.0	7
T ₂	2466.1	4	¹² C ³² S ³³ S	653.0	7
⁶ Li ₂	~373.9 ^a	4	¹² C ³² S ³⁴ S	648.4	7
⁶ Li ⁷ Li	~360.3 ^a	4	¹² C ₆ H ₆	981.6	6
⁷ Li ₂	346.2	4	¹² C ₅ ¹³ CH ₆	984	6
¹⁴ N ₂	2330.7	4	¹² C ₆ D ₆	944.7	6
¹⁴ N ¹⁵ N	~2291.5 ^a	4	¹² C ₅ ¹³ CD ₆	939.5	6
¹⁵ N ₂	~2251.7 ^a	4	¹² C ³⁵ Cl ₄	461.5	6
¹⁶ O ₂	1556.3	5	¹² C ³⁵ Cl ₃ ³⁷ Cl	458.4	6
¹⁷ O ₂	~1509.8 ^a	5	¹² C ³⁵ Cl ₂ ³⁷ Cl ₂	455.1	6
¹⁸ O ₂	~1467.3 ^a	5	¹² C ³⁵ Cl ³⁷ Cl ₃	~452.0 ^a	6
¹⁶ C ¹⁷ O	~1533.2 ^a	5	¹² C ³⁷ Cl ₄	~448.9 ^a	6
¹⁶ O ¹⁸ O	~1512.5 ^a	5			
¹⁷ O ¹⁸ O	~1488.7 ^a	5			

^aA calculated frequency.

Consider the proposed system shown in Fig. 2. A laser beam is focused into a cell containing the sample to be analyzed. The scattered light is collected by a pair of lenses and directed into two double monochromators. Each monochromator isolates a particular isotopic Raman frequency. A photomultiplier and scaler system at the output slit of each monochromator counts the number of Raman-scattered photons. For the *i*th isotopic line and the *m*th monochromator, the count rate R_{im} is given by

$$R_{im} = \epsilon_m \gamma_{mi} \rho_i \sigma_i \phi L \approx \epsilon_m \gamma_{mi} I_i, \quad (4)$$

where ϵ_m is the collection efficiency of the *m*th lens system and γ_{mi} is the efficiency of the *m*th monochromator and photomultiplier system at the scattered wavelength. The ratio of the count rates observed for two lines *i* and *j* is

$$\frac{R_{i1}}{R_{j2}} = \left(\frac{\epsilon_1 \gamma_{1i} \sigma_i}{\epsilon_2 \gamma_{2j} \sigma_j} \right) \frac{\rho_i}{\rho_j} = \alpha_{ij} \frac{\rho_i}{\rho_j}. \quad (5)$$

Calibration with a sample whose ρ_i and ρ_j values have been determined by mass spectrometer measurements yields the constants α_{ij} . Once the α_{ij} are known, the ρ_i of other samples may be determined

Fig. 2. Schematic diagram of a laser Raman scattering isotopic abundance spectrometer.

by measuring the R_i . It is of course possible to use a single monochromator by using a periodic scanning procedure to sample the different isotopic lines.

At this point it is instructive to calculate R for the case of nitrogen gas, because it is a practical example for the types of problems one would expect in real isotopic abundance measurements. Consider a sample at 1 atm ($p = 2.7 \times 10^{19} \text{ cm}^{-3}$), with $L = 1 \text{ cm}$, and a photon flux of $\phi = 1.2 \times 10^{19} \text{ photons-sec}^{-1}$. This flux corresponds to a laser power of 5 W at 4880 Å and is characteristic of commercially available argon ion lasers. From Table 3, the 90° differential cross

section for nitrogen is $\sigma = 3.3 \times 10^{-3} \text{ cm}^2\text{-sr}^{-1}$. Thus, from Eq. (2)

$$I = 1.1 \times 10^8 \text{ photons-sec}^{-1}\text{-sr}^{-1}.$$

An $f/7$ monochromator (effective solid angle of 0.02 sr) and a photomultiplier tube with a quantum efficiency of 25% (e.g., a selected RCA C31034^{*}) yields $\epsilon\gamma \approx 0.005 \text{ sr}$, which is a reasonable figure. Thus from Eq. (4),

$$R = 5.5 \times 10^5 \text{ counts-sec}^{-1}.$$

^{*}Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Atomic Energy Commission to the exclusion of others that may be suitable.

Table 3. Raman cross sections for selected molecules (4880 Å excitation).

Molecule	Raman shift, ω_v , (cm^{-1})	Differential cross section, $d\sigma/d\Omega$ ($\text{cm}^2\text{-mol}^{-1}\text{-sr}$)	Ref. No.
C_6H_6	992	$3.25 (\pm 0.10) \times 10^{-29}$	9
$\text{C}_5\text{H}_5\text{CH}_3$	1002	$1.83 (\pm 0.06) \times 10^{-29}$	9
$\text{C}_6\text{H}_5\text{NO}_2$	1345	$1.03 (\pm 0.04) \times 10^{-28}$	9
CS_2	656	$4.35 (\pm 0.13) \times 10^{-29}$	9
CCl_4	459	$2.25 (\pm 0.07) \times 10^{-29}$	9
N_2	2331	$3.3 (\pm 1.1) \times 10^{-31}$	10
O_2	1556	$4.3 (\pm 1.4) \times 10^{-31}$	10
H_2	4161	$7.9 (\pm 2.6) \times 10^{-31}$	10
CO_2	1388	$4.6 (\pm 1.5) \times 10^{-31}$	10
H_2O	3652	$8 (\pm 3) \times 10^{-31}$	11
NH_3	3334	$1.65 (\pm 0.55) \times 10^{-30}$	10
ND_3	2420	$9.9 (\pm 3.3) \times 10^{-31}$	10

This is of course the rate characteristic of the high-abundance peak ($^{14}\text{N}_2$). The low-abundance peak ($^{14}\text{N}^{15}\text{N}$) would have a rate of approximately 4000 counts-sec $^{-1}$. Thus an isotope ratio measurement to a precision of approximately $\pm 0.1\%$ would require 5 to 10 min, exclusive of possible noise limitations, which we now consider.

The precision limit of the Raman scattering technique as well as the minimum detectable quantity is prescribed by the counting statistics. For example, in a totally noise-free situation, 100 counts on the weak line must be obtained to determine the isotope ratio to an accuracy of 10%. At the 1 part per million level of the low-abundance element, 10^8 counts will be obtained on the strong line. This takes about 5 min at the typical count rate calculated earlier. However, two factors contribute to noise in the Raman scattering technique: stray light and ghosts from the gratings, and thermal noise in the photomultiplier. Cooling the photo-

multiplier tube to liquid nitrogen temperature reduces the thermal noise to less than 0.1 counts-sec $^{-1}$. In a double monochromator using holographic gratings, ghosts are absent, and the stray light intensity is less than 10^{-12} of the input intensity.¹² The majority of this input intensity is Rayleigh-scattered light from the sample.* Since the Rayleigh attenuation factor of nitrogen at 1 atm is 0.02 km^{-1} (Ref. 13), which corresponds to $\rho\sigma = 1.6 \times 10^{-8} \text{ cm}^{-1}\text{-sr}^{-1}$, the Rayleigh-scattered intensity is $I \approx 3.2 \times 10^{11}$ photons-sec $^{-1}\text{-sr}^{-1}$. Applying the spectrometer efficiency $\epsilon\gamma \approx 0.005 \text{ sr}$ and the 10^{-12} attenuation factor, the stray-light noise is approximately 10^{-3} counts-sec $^{-1}$. Thus, we see that only the noise level of the photomultiplier limits the minimum detectable quantity.

*Rayleigh (or Brillouin) scattering is several orders of magnitude stronger than Raman scattering in transparent liquids or gases.

A signal-to-noise ratio of 1 yields better than 10% accuracy if 10^3 counts are obtained. Thus for a count time of 10^4 sec and a maximum count-rate of 10^6 sec⁻¹ (achievable with fast electronics) one could collect 10^{10} counts on the strong line and 10^3 noise counts. This means that an abundance of 100 parts per billion is measurable to less than about 10% accuracy. Since the noise figure used is an upper limit, abundances down to 10 parts per billion should be measurable. Another way of exhibiting the potential performance of the Raman technique is in the precision to which isotopic abundances such as $^{12}\text{C}/^{13}\text{C}$ could be measured. Using the same basic data as above it is easy to show that an isotope ratio measurement with a precision of $\pm 0.1\%$ would require 2 to 5 min, similar to the results already quoted for $^{14}\text{N}/^{15}\text{N}$. Measuring the $^{16}\text{O}/^{18}\text{O}$ ratio would also yield results in the same time range. A typical mass spectrograph measurement of any of these ratios to the same precision would require approximately 30 min.

The main limitation of the Raman technique is that the element to be analyzed must be quantitatively incorporated into a molecule, showing an easily detectable isotope effect. A similar problem is present in mass spectroscopy. However, in the Raman scattering technique samples can be prepared and encapsulated in standard forms in advance of any measurement. Furthermore, the measurement itself is easily standardized and can be repeated as often as desired on the same sample. Finally, many new media, otherwise totally intractable, are approachable using the Raman technique, liquids in certain cases being a good

example. Examples of tractable (for our purposes) substances are: hydrogen in H_2O , lithium in Li_2 vapor (at 1000°C), boron in BF_3 , carbon in CO_2 , nitrogen in N_2 , oxygen in CO_2 and H_2O , sulfur in SO_2 , chlorine in CCl_4 (liquid), and uranium in UF_6 or UO_2^{2+} (acidic aqueous solution). In molecules where three or more isotopes may be present, a large number of isotopic lines may have to be monitored. This is possible, but the time required to collect all the necessary data is in direct proportion to the number of lines. Of the materials in the list we have given, only BF_3 and N_2 escape this possible difficulty. In BF_3 there are only two isotopic molecules; while there are three in N_2 . However, N_2 is a special case. For an ^{14}N concentration x and an ^{15}N concentration y , the kinetics of N_2 formation favor the statistical $x^2:2xy:y^2$ ratio for $^{14}\text{N}_2: ^{14}\text{N}^{15}\text{N}: ^{15}\text{N}_2$. The equilibrium value of these ratios is not $x^2:2xy:y^2$, yet the equilibration time is so long that in practice equilibrium will never be reached. As a result, the ^{14}N and ^{15}N concentrations can be determined by inference from a measurement of only the $^{14}\text{N}_2$ and $^{14}\text{N}^{15}\text{N}$ lines.

As already noted, sample preparation and handling in the laser Raman scattering technique are generally the same for gaseous samples as in the mass spectroscopic technique. For best results the scattering cells should be filled on a cryogenic vacuum line. For the Raman technique sample size should not pose a serious drawback. A typical reusable sample cell would have a volume of 1 cm^3 , while a sealed-capillary cell could have a volume as small as 10^{-2} cm^3 , all at 1 atm. Using the latter, micromole

quantities of gas may be analyzed. It is also possible to analyze smaller samples by using lower pressure, although the count rates will be decreased proportionately.

In conclusion, we suggest that laser Raman scattering using photon counting techniques should be useful for measuring isotopic abundances of many elements. A

typical spectrometer (Fig. 2) would consist of a high-power argon ion laser, a scattering cell and collecting optics, two double monochromators, and two photon counting systems. The technique's applicability to nitrogen and oxygen should prove of significant utility in the use of ^{15}N and ^{18}O as nonradioactive tracers.

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