ASSESSMENT OF RESONANCE IONIZATION MASS SPECTROMETRY FOR ANALYTICAL CHEMISTRY AND SPECTROSCOPY

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Resonance ionization mass spectrometry (RIMS) is a natural outgrowth
of RIS (Hurst et al 1979). The result of an RIS process is an ion
pair. The electron can be used to detect the process, and single atom
detection has been demonstrated by this method (Hurst et al 1977).
The cation resulting from the RIS process actually carries more easily
accessible and useful information (i.e. the mass of the ion). There
are some statistically related questions as to the usefulness of sin-
gle atom identification by this member of the ion pair, but certainly
RIMS is useful in mass analysis. The first published description of a
RIMS process involved the demonstration of isotopic separation of
potassium (Beekman et al 1980). The analytical application and demon-
stration of RIMS followed (Donohue et al 1982, Miller, et al 1982,
Fassett et al 1983). The development of RIMS has proceeded along
several different directions, using CW or pulsed lasers, narrow or
wide band laser energies, different kinds of sample generation, and
different kinds of mass separations. Various other presentations in
this symposium address a number of these points. Our assessment of
these aspects will be given in this paper, but the individual papers
should be consulted for an independent understanding. Keep in mind
that RIMS in various forms can be used to obtain either element or
isotope selectivity.

Even though the RIMS technique has developed along several lines,
several things are common to all approaches. Ultimately RIMS requires
gaseous, free, atoms. RIMS makes use of the photoionization of these
atoms by absorption of photons through allowed transitions involving
real energy levels. The ion once formed is detected by standard mass
spectrometric techniques.

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1. Experimental

There are papers in this symposium dealing with a variety of atom generating techniques, such as thermal (Donohue et al 1984c, Travis et al 1984), electrical (Harrison 1984), and particle beam (Parks 1984). Atomic species can also be generated by other techniques such as by laser (Beekman et al 1980), or oven (Bekov and Letokhov 1983) to name a few. The initial state, or states, of the neutral species generated determines the analytical RIS route. More will be said about this subject later.

RIMS techniques have involved the use of both pulsed (Donohue et al 1982, Miller et al 1982, Fassett et al 1983) and CW lasers (Miller and Nogar 1983). These approaches can be compared in the individual papers of this symposium. On the basis of our present assessment of these two alternatives for RIMS analysis of uranium, we tend to favor pulsed RIMS (Donohue et al 1984b). It may turn out that certain elements can be analyzed better by one approach, other elements by the alternate approach. There has not yet been enough individual element comparisons to reach definite conclusions. The ultimate individual choice may resolve around sample volatility, interfering element, spectral properties, etc.

In the present analytical development of RIMS, single color photons are generally used. Ions are generated by absorption of 2, or more, photons though allowed transitions to ultimately yield an ion. If two photons are involved, it is a scheme 1 RIS process (Hurst et al 1979). We have been developing RIMS analyses using lower energy photons in order to minimize experimental problems which can result from the use of higher energy photons, e.g. dye lifetime, multiphoton processes, etc. In operating with such low energy photons and since we are presently developing RIMS techniques for lanthanides and actinides, we find that 3, or perhaps even 4, photons can be resonantly absorbed to yield the resultant ion. Such a scheme could be considered a modification of an RIS scheme 1 or a modification of scheme 3 in which λ_1 as equal to λ_2. The red dyes do have a longer, but still limited lifetime than do blue dyes in flash-lamp pumped dye lasers. The lifetime for the rhodomine dyes can be further extended by the addition of cyclooctatetraene, $\sim$ 50 fold molar excess, to the dye solution and by removing O_2 and for the dye solution. Typically R6G dye solution so treated will last $\sim$ 20 hours in a CMX-4 laser at 30 pps.

Once the ion is formed by the RIS process, it is extracted by reasonably straight forward mass analysis techniques. The unique part of RIMS is really the ion generation. In the various RIMS studies many forms of mass analyzers have been used, magnetic, quadrupole, time-of-flight. The choice of mass analyzer is perhaps independent of the RIMS technique. The detection of the resultant ions, though, must be considered in the successful application of RIMS. A pulsed RIMS process will result in a relatively large number of ions reaching the

detector in a relatively short period of time. Saturation of the detector is possible and the dynamic range of the measurement is small. On the other hand, CW RIMS generates ions in a continuous mode which is more adaptable to a larger dynamic range of measurement. Possible ways to improve the range of pulsed RIMS detection is a fruitful area of investigation.

2. Results

It has been shown that RIMS competes quite favorably with thermal ionization mass spectrometry for the analysis of uranium and plutonium in 10 ng samples (Donohue et al; 1984a). Under the reported conditions of analysis, RIMS offers the advantage in this application of eliminating the isobaric interference of ^{241}Am or ^{241}Pu and reducing the isobaric interference of ^{238}U on ^{238}Pu. Other applications of RIMS are being pursued, e.g. other papers in this symposium, which will expand the range of elements analyzed and greatly increase the sensitivity of the RIMS technique. With the present state of the art, it appears that the most sensitive RIMS analysis will involve a pulsed laser system coupled with a pulsed sample system. An alternative CW laser system, particularly with narrow band lasing, offers a different approach that can give unique isotopic analyses which will also, obviously, eliminate isobaric interference, but a relatively larger sample may be required.

From our experience in thermal generation of atoms and from a knowledge of the experience of others, it is reasonable to say that atoms are not necessarily generated in a ground state configuration. From the analysis of RIMS spectral results, it seems quite apparent that atoms are found in a number of initial states (Young and Donohue 1983). In many cases the presence and density of atom population in these states can be predicted by a Boltzman distribution. In other cases the population does not follow such a classical case. A study by europium by RIMS (Young et al 1984a) has shown that the atoms are present in initial states of 13000 to 20,000 cm^{-1} under thermal conditions that are less than 1200°K. The mechanism for populating these high-lying initial states is not known for certain, but may well involve a "hybrid resonance" effect (Collins et al 1976) as represented in Figure 1. If this is the cause, molecular Eu species, such as Eu$_2$ or other molecules, are non-resonantly excited to some state that dissociates yielding an excited and, in this case, a ground state atom. The excited state atoms then absorb 2 photons during the same laser flash, through a resonant level, to ionize. No matter what the cause of multiple initial states for atoms, the phenomenum is real and represents a dilution of accessible RIMS-active species. In considering the analytical limit of this technique this characteristic must be considered, and future improvements in sensitivity will ultimately require a reduction in the number of such initial atomic states.

Since electronic energy levels of atoms are involved in the RIMS process, RIMS can be considered as a spectral tool. In a simple consideration, RIMS can be used as an atomic spectrometer with absorption of light ultimately being measured by ion-multiplier detectors in a mass spectrometer, rather than the usual photomultiplier. The fact that lasers can cause the multistep photoionization of lanthanide and actinides is not new and has been used very successfully in the past (Worden and Conway 1980). What should be realized about the application of RIMS in this regard is that the laser scheme need not be complex; further, a very small amount of sample is required. In the reported RIMS application to U and Pu analysis (Donohue et al 1984a), quantitative analytical data were obtained for ^{241}Pu on a total of 0.4 ng of that isotope absorbed on a resin bead. Spectral information can be obtained on this size, or even smaller, sample. To demonstrate the usefulness of such a study, spectra of Th, U, Np, Pu, and Am were taken from 580 to 607 nm, the R6G dye region, in our RIMS apparatus with a CMX-4 laser (Donohue et al 1984b). An example of the RIMS spectrum of uranium is shown in Figure 2. It is interesting to note that for all of these actinides over this wavelength region, except Am, the most intense peak observed corresponds to a ground state transition and involves 3 photon absorption for ionization. For Am many more RIMS peaks were observed than for the rest of the actinides studied; it should be remembered that the energy level diagram of Am is similar to that of Eu. What is not known is whether a hybrid-resonance effect enhances RIMS spectra, giving more RIMS peaks for Am, or whether such an effect is only observed when sensitivity is maximized in an effort to observe a result. Even in the case of Am, however, the main RIMS peak corresponds to a ground state transition. A summary of the peaks, and starting level for these actinides is given in Table 1.

Table 1. Spectral Interpretation of Actinide RIMS-Peaks

Element	Peak, nm	Starting level, cm^1	Photons
Th	580.4	0	3
U	591.5	0	3
Np	587.8	0	3
Pu	586.4	0	3
Am	605.6	0	3

It is interesting to note that we were unsuccessful in an attempt to obtain a RIMS spectrum of Cm in the R6G dye region; Cm has no allowed ground-state transitions possible, based on published energy levels, in the region from 580 to 607 nm.

As described in an earlier paper in this symposium (Donohue et al 1984c), there are many spectroscopic factors involved in the overall RIMS technique, and these spectroscopic factors effect mass bias in the analytical results. Control or correction of these spectroscopic factors is necessary for good analytical numbers. Conversely, measurement of these spectroscopic factors can be accomplished by RIMS. Again, the mass spectrometer becomes the detector for a spectrometer; in this case an isotopically selected spectrometer since

the mass to be detected can be selected. As a demonstration of the application, we measured the isotopic shift (I.S.) of several levels in uranium and composed these to the I.S. reported in the work of others (Miron 1979). The measurement involves two lasers for the 3-photon uranium resonant photoionization. One low powered, 0.5 mJ, pulsed, wide-band laser (4 cm^{-1} band width) saturates a transition, of all isotopes, from the ground state to a first intermediate state (E_1), e.g. $^5L^{\circ}_6-^5K_6$. At the same time a higher powered, 5 mJ, narrow band laser (0.1 cm^{-1}) is tuned across known transitions to a second intermediate state (E_2); absorption of the second photon of this narrow band laser promotes ionization from state E_2 for RIMS detection of that particular isotope. The wavelength of the maximum RIMS signal is observed and compared with the wavelength observed for ^{238}U. The isotope shift of state E_2 is calculated from

$$S_{E_2} = S\ obs + S_{E_1}$$

where
S_{E_2} = isotope shift of level E_2
$S\ obs$ = the observed isotope shift
S_{E_1} = known isotope shift of level E_1

The results of this study are shown in Table 2.

Table 2. Measured isotope shifts in uranium, $^{238}U-^{235}U$

E_1, cm^{-1} = 16900.38 cm^{-1}; S_{E_1} = 0.19 cm^{-1} (Blaise et al 1976)

E_2, cm^{-1}	Uranium isotopes (shifts in cm^{-1}			
	238	236	235	233
33800.75				
observed shift	0	−0.40	−0.72	−1.12
S_{E_2}			−0.53	
33723.80				
observed shift	0	−0.51	−0.83	−1.28
S_{E_2}			−0.64	
S_{E_2} (Miron 1979)			−0.57	
33752.03				
observed shift	0	−0.48	−0.77	−1.17
S_{E_2}			−0.58	
S_{E_2} (Miron 1979)			−0.60	

As presently experimentally constructed, our RIMS technique is only good for a qualitative measurement of I.S., precision of ± 10%. With a better experimental arrangement much better I.S. information could be obtained. From the data given in Table 2, it can be seen that I.S. information can be readily obtained for each individual isotope under study.

3. References

Beekman D W, Callcott, T A Kramer S D, Arakara E T, Hurst G S and
  Nussbaum E 1980 Int. J. Mass Spectrom. Ion Phys. 34 89
Bekov G I and Letokhov V S 1983 Trends in Anal. Chem. 2 252
Blaise J E and Rodziemski Jr L J 1976 J. Opt. Soc. Am. 66 644
Collins C B, Curry S M, Johnson, B W, Mirza M Y, Chellehmalzadeh J A,
  Anderson J A, Popescu D and Popescu I 1976 Phys. Rev. A 14 1662
Donohue D L, Young J P and Smith D H 1982 Int. J. Mass Spectrom. Ion
  Phys. 43, 293
Donohue D L, Smith D H, Young J P, McKown H S and Pritchard C A 1984A
  Anal. Chem. 56 379
Donohue D L, Young J P and Smith D H 1984B Appl. Spec. (In Press)
Donohue D L, Smith D H, Young J P, and Ramsey J M 1984C Paper #   ,
  this symposium
Fassett J D, Travis J C, Moore L J and Lytle F E 1983 Anal. Chem. 55
  765.
Harrison W W 1984 Paper #   , this symposium
Hurst G S, Nayfeh M H and Young J P 1977 Appl. Phys. Lett. 30 229
Hurst G S, Payne M G, Kramer S D, Young J P 1979 Rev. Mod. Phys. 51
  767
Miller C M, Nogar N S, Gancary A J, Shields W R 1982 Anal. Chem. 54
  2377
Miller C M and Nogar N S 1983 Anal. Chem. 55 1606
Miron E 1978 Israel Atomic Energy Comm., Beersheba, Nuclear Research
  Center - Negev, NRCH - 441, January.
Parks J E 1984, paper #   , this symposium
Travis J C, Fassett J D and Moore L J 1984, Paper #   , this
  symposium
Worden E F and Conway J G 1980 Am. Chem. Soc. Symp. Ser. 31 381 and
  references therein
Young J P and Donohue D L 1983 Anal. Chem. 55 88
Young J P, Donohue D L, Smith D H 1984A Int. J. Mass Spectrom. Ion
  Phys. 56 307

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Figure 1. Possible mechanism for populating high-lying energy levels of Eu. Laser induced photo-dissociation of Eu_2 dimer molecules would result in the formation of excited fragment atoms having energies in the range of 13,000–20,000 cm^{-1}.
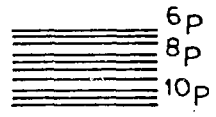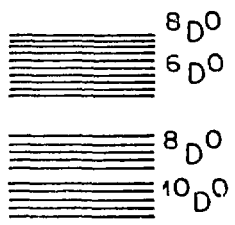
Figure 2. Optical ionization spectrum of uranium.

ORNL-DWG 83C-17209
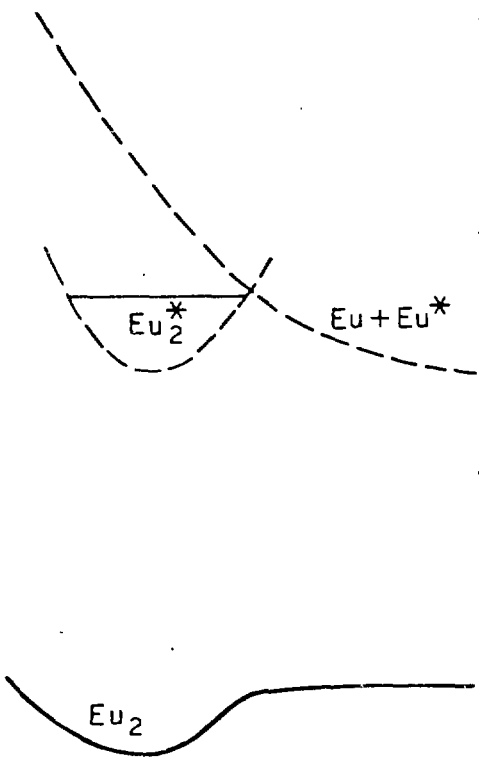
URANIUM

RELATIVE INTENSITY

WAVELENGTH (nm)