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AN EVALUATION OF THE SUITABILITY OF LASER-INDUCED FLUORESCENCE FOR MEASUREMENTS OF FISSION-PRODUCT IODINE SORPTIVITY IN THE MHTGR

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S. A. Sherrow

SUMMARY

Experiments and calculations indicate that laser-induced fluorescence (LIF) lacks the sensitivity needed for sorptivity measurements of I_2 or other molecular species at partial pressures below 10^{-11} atm. Although the technique may have sufficient sensitivity for measurements of atomic species, the species of interest are, in all likelihood, not atomic. Methods of measurement which would allow the determination of species are proposed.

1. OBJECTIVE

In order to predict the release of fission products from the modular high-temperature gas-cooled reactor (MHTGR) under accident conditions, such as a cooling system leak, it is necessary to know the distribution of fission product species within the system. One area of particular concern is the extent to which fission products removed from circulation (by adsorption or reaction with cooling circuit components) are re-entrained following a change in temperature or pressure. This experimental program seeks to address that area by supplying data on fission product sorption and desorption by primary circuit alloys under conditions which approximate, as nearly as possible, those expected for the MHTGR.

2. INTRODUCTION

The determination of sorption/desorption isotherms is, in principle, straightforward. The vapor pressure (or some related quantity) of the species of interest is measured in the presence of the adsorbent, and the quantity is compared to a reference measurement. The problem in practice is that the vapor pressures expected for key fission product species are on the order of 10^{-14} atm; ordinary methods of vapor pressure determination lack the sensitivity for quantitative measurements at this level.

A previous evaluation of LIF for fission product sorption/desorption measurements was based on data obtained for cesium and on literature reports of very low detection limits achieved for some species by LIF.¹ Although molecular iodine was the experimental focus of this evaluation, the discussion of the technique and the conclusion apply equally to other species. In the sections that follow, the technique of LIF will be described and the factors which determine detection limits will be discussed. The equipment and procedures used for iodine measurements will be described. An approximate formula for calculating signal levels will be presented with numerical examples. Finally, the problems inherent in the LIF approach will be addressed, and methods which might more readily provide useful data will be discussed.

3. ASPECTS OF LIF

Fluorescence is radiation emitted by an atom or molecule as it relaxes from an excited state. The technique of LIF employs a laser to prepare the excited state. The laser wavelength must coincide with an allowed transition (for our purposes, an electronic absorption) of the sample. The emission may be at the same wavelength as the excitation (resonance fluorescence) or at a different wavelength, and also corresponds to an allowed transition. The specific transition energies and the selection rules that determine which transitions are permitted vary from one species to the next; thus a laser/detector combination that yields adequate results for one species may be wholly unsuited for another.

The observed signal in LIF experiments may be viewed as the product of three factors: the probability that a laser photon is absorbed, the probability that a photon is emitted at the selected detection wavelength, and the combined efficiencies of the collection optics and detector. The last factor is determined by geometry and hardware and has nothing to do with the sample. The first two quantities depend on the sample species itself, on the experimental conditions, and on the concentration (number density) of the sample.

The tendency of a sample species to undergo a transition from one particular energy level to another is called the transition probability; this is a fixed property of the sample. The number of photons absorbed by a given sample is the product of the transition probability, the intensity of the light source, and the number of available sample atoms or molecules. In the case of an atomic sample, there are only electronic energy levels. Even at fairly high (1000°C) temperatures, most of the

atoms are in the lowest electronic state and are available for an excitation to another level. Molecules possess, in addition to electronic energy, vibrational and rotational energy. Excitation is from a particular vibration/rotation sublevel of the ground electronic state to a particular vibration/rotation sublevel of the excited electronic state. Because the molecules are thermally distributed among the vibration/rotation sublevels, the number found in any given state is a function of temperature and of the particular vibration/rotation energies of the molecule. Typically, the number of molecules available to undergo a specified transition is a small fraction of the total sample. Also, because the number of possible energy states for a molecule is much greater than that for an atom, the probability of a transition to any one state is often much smaller than the probability of an atomic transition.

An atom or molecule in an excited state may dispose of its excess energy in a number of ways: it may ionize or dissociate, it may react or otherwise interact with another species, or it may emit. The likelihood of the first two processes may be minimized by the selection of the excited state and the laser power and by controlling the concentration and composition of the background gas. In the absence of other relaxation paths, the tendency of the sample to return via emission to the initial or to an intermediate state is governed by the transition probability. Because of the disparity in the number of possible transitions, atomic emissions appear as a few sharp lines while molecular emissions appear as a series of bands, each of which is composed of many closely spaced lines.

What should be clear from the preceding discussion is that the LIF experiment must be tailored to the species of interest. The sample itself dictates what laser wavelength(s) may be used for excitation. Molecular samples allow some latitude in wavelength selection, but it comes at the expense of intensity. Limits of detection vary with experimental conditions and with hardware, and the ultimate lower limits are established by fixed transition probabilities.

4. EXPERIMENTS WITH IODINE

The purpose of the LIF experiments with iodine was to ascertain whether the laser equipment already purchased for the program and the LIF technique itself could be expected to yield reliable data for iodine sorptivity at moderate (500°C) temperatures and very low (10^{-14} atm) partial pressures.

The laser equipment used for these experiments was a Quanta-Ray DCR 1-A Nd:YAG, which was purchased by General Atomics for LIF studies of cesium and was inherited by this program. The laser fundamental is in the infrared at 1064 nm; frequency doubling crystals for generating second (532-nm) and third (355-nm) outputs were supplied with the laser. Also supplied with the laser was a Quanta-Ray PDL-1 dye laser; either of the harmonics could be used to pump the dye laser so that any laser wavelength between 355 and 800 nm could be generated. The detection equipment was selected for sensitivity and response over a wide range of wavelengths (200-900 nm) and consisted of a Jarrell-Ash 0.27-m spectrograph, a Princeton Applied Research model 1421 intensified diode array

detector, and a model 1463 optical multichannel analyzer. The spectrograph was adjusted to reject the laser frequency and disperse the remainder of the incoming signal; the array detector, after calibration with a standard lamp, registered signal intensity as a function of wavelength. The detector exposure time could be varied from 17 ms to about 10 min; any number of exposures could be added to improve the signal to noise. A schematic drawing of the experimental arrangement is shown in Fig. 1.

Energy level diagrams and possible fluorescence schemes for atomic² and molecular³ iodine are shown in Figs. 2 and 3. The longest wavelength atomic iodine absorption from the ground state is at 183 nm. This wavelength can be obtained from excimer lasers or from frequency doubling a dye laser; it is not possible to obtain wavelengths in this region with the existing laser equipment. Iodine has a strong absorption that begins at 636 nm and extends beyond 500 nm; any laser wavelength in this region could be used to excite fluorescence. The YAG harmonic at 532 nm was selected for excitation because of its stability and ease of generation. At this wavelength, the laser excites I_2 molecules from the $v = 0$, $J = 51$ and 54 sublevels of the ground electronic state to the $v' = 32$, $J' = 50$ and 55 sublevels of the excited state.⁴ Emission is from $v' = 32$ to all possible vibrational levels of the ground electronic state.

Iodine samples were prepared by resubliming purified iodine into cold fingers attached to evacuated pyrex or quartz gas cells. Iodine vapor pressures from 10^{-4} to 10^{-9} atm were controlled by adjusting the temperature of the cold finger;⁵ the gas cells were at ambient (20°C) temperature. To ensure a constant I_2 vapor pressure it was necessary,

Fig. 1. Experimental configuration for LIF measurements of I_2 .
(The dashed line indicates the laser path.)

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Fig. 2. Simplified energy level diagram showing the lowest energy levels of I atoms.

(The upward arrow indicates excitation; the downward arrow indicates fluorescence. Single photon transitions from the $5s^2 5p^5$ ground state to the $5s^2 5p^4 6p$ state are forbidden.)

Fig. 3. Simplified energy level diagram for I_2 .

[The vibrational spacings shown are $\approx 213 \text{ cm}^{-1}$ for the lower state and 125 cm^{-1} for the upper state. Each vibrational level is further subdivided into rotational levels (not shown). The upward arrow indicates 532 nm excitation; the downward arrows indicate the first few lines of the fluorescence series.]

particularly at the lower pressures, to maintain the vapor in contact with the temperature-controlled solid. Very small pressures of I_2 cannot be maintained in sealed cells because of reaction with residual gases and other trace impurities.

Spectra for various I_2 vapor pressures are shown in Figs. 4-6. Exposure times were varied as necessary in order to obtain acceptable signals. Figure 6 shows the spectrum of 2×10^{-9} atm I_2 measured with the maximum exposure time of 10 min. This was the smallest quantity measured during these experiments. The 10-min limit on exposure was due to saturation of the detector by dark current at the lowest operating temperature; this represented the operating limit of the detector, and no substantial improvement could be made with this system. The apparent lower limit of 10^{-9} atm was several orders of magnitude above the region of interest for the sorption/desorption studies. Detection limits must be even higher at elevated temperatures because dissociation reduces the number of I_2 molecules.

5. SIGNAL CALCULATIONS

In the first section it was noted that detection limits are determined by experimental hardware and conditions and by the properties of the sample species itself. We have established that the lower limit of detection for I_2 in our system is $\sim 10^{-9}$ atm. In order to determine whether and how improvement might be gained, it is useful to examine the factors contributing to the signal.

Fig. 4. LIF spectrum of 1.2×10^{-6} atm I_2 . The most intense line is the transition which terminates in $v = 2$ of the ground state. (These data were obtained with a 10-s detector exposure and 150 mJ per pulse laser energy.)

Fig. 5. LIF spectrum of 3.2×10^{-7} atm I_2 ; data were obtained with a 10-s detector exposure and 40 mJ per pulse laser energy.

Fig. 6. LIF spectrum of 2.1×10^{-9} atm I_2 ; data were obtained with a 10-min detector exposure and 40 mJ per pulse laser energy.

The LIF signal, in detector counts per second, is given by

$$S = \alpha N V \frac{E}{2(E + E_s)} DAfQ,^6$$

where

- N = the number density of sample molecules,
- V = the sampled volume (1 cc),
- α = the fraction of molecules capable of absorbing a photon.⁷

For atomic samples, α is usually unity; for heavy diatomics such as I_2 , it is about 0.01. The product $\alpha N V$ is the number of atoms or molecules actually being observed.

E is the intensity of the laser, and E_s is half the intensity needed to saturate the transition. E_s is related to the absorption probability and is typically about 10^6 W/cm². At $E = E_s$, we assume a steady excited population of one-fourth of the available molecules; in the limit of infinite laser power, this fraction increases to one-half. D is the duty cycle of the laser, the fraction of time that the laser is on (pulse duration multiplied by repetition rate). Pulsed lasers achieve very high peak powers by delivering their energy in short bursts. Our laser, for example, delivers 0.1 J in 10 ns at 10 Hz. The intensity is 10^7 W/cm², but the duty cycle is 10^{-7} . Although CW lasers provide a much lower peak power (not enough to saturate), they have a duty cycle of unity. The result is that for experiments lasting 1 s or longer, comparable signals are obtained from pulsed or CW lasers having the same average power. The factor $\alpha N V E D / 2(E + E_s)$ is a time-averaged number of molecules excited in 1 s.

A is the Einstein coefficient for spontaneous emission;⁸ multiplied by the number of excited molecules, it yields the signal photon emission

rate. Spontaneous emission probabilities for I_2 are on the order of 10^4 s^{-1} for a single strong line and 10^6 s^{-1} for the entire series from a single upper state. For allowed atomic transitions, typically $A = 10^8 \text{ s}^{-1}$.

Signal photons are emitted in all directions; the fraction collected and directed to the detector is given by f . With a fast collection lens and high throughput optical configuration, as many as 0.1% of the emitted photons may be transmitted to the detector. Q is the detector quantum efficiency, the number of signal counts produced for each photon detected. Detector efficiencies vary widely, and the efficiency of a single detector may vary with wavelength. For a broadband detector such as ours, a quantum efficiency of about 7% at 550 nm is typical.

An I_2 pressure of 10^{-11} atm corresponds to a room temperature number density of 10^8 molecules/cc. The total LIF signal expected ($A = 10^6/\text{s}$, $E \gg E_s$, other values as given above) is

$$S = 0.01 \times 10^8 \times 1 \times 1/2 \times 10^{-7} \times 10^6 \times 0.001 \times 0.1$$

$$= 5 \text{ counts per second,}$$

which is less than the background generated by a cooled, low-noise detector. (Detector noise may be as low as 10 cps; ours is ~25 cps per channel at -40°C .) With 25 cps detector background and 5 cps signal, a signal to noise of 10 may be achieved with an integration of 2 min.

In our experiments, because the fluorescence is dispersed into individual lines, the appropriate value of the Einstein coefficient is $10^4/\text{s}$; thus we have the higher detection limit of 10^{-9} atm. It should be emphasized that this is an optimistic calculation; it does not consider impurity quenching, reaction, or dissociation. At a temperature of

300°C, 10^{-11} atm of iodine vapor is 99% dissociated⁹ and contains only about 10^6 I_2 molecules/cc.

For atomic species, the prospects for LIF are certainly better since dissociation is not a concern and all of the atoms are in the same initial state. It is indeed possible to detect atomic species at pressures as low as 10^{-14} atm if the transition is strong, if quenching and other impurities can be eliminated, and if an appropriate laser is available. In practice, the last two conditions may be extremely difficult to fulfill.

6. ALTERNATIVES TO LIF

As stated earlier, the object of this experimental program is to provide meaningful data about the sorption and desorption behavior of relevant fission product species. The key term is relevant. Given the reactivity of the elements and the abundance of impurities, it is extremely unlikely that free fission product atoms exist in the cooling circuits. Before any additional effort is given to the development of species-specific detection techniques, the identities of the species should be established.

LIF and other species-specific techniques may be disadvantageous for this application even if the species are known. Cesium, for example, may be present in the system as Cs, CsI, CsOH, CsO, or Cs_2O , just to name a few possibilities. Species-specific detection requires a separate set of experiments (often involving different equipment) for each species.

A more effective approach to this problem is to develop an experimental technique that yields meaningful results for all species and that indicates which species are present. Two techniques that are considered promising are mass spectrometry and absorption spectroscopy.

Both techniques provide direct indications of the species present and may monitor all species in a single experiment. The relatively inexpensive mass spectrometers sold as "residual gas analyzers" are capable of real time detection of species at 10^{-14} atm and in the presence of at least a 10^6 -fold excess of background gas. For absorption spectroscopy a long path gas cell could be used, or the sample gas could be condensed on a cold spectroscopic window. An experimental plan employing absorption spectroscopy is being prepared; a very high quality spectrophotometer is already available.

7. CONCLUSIONS

It has been demonstrated that molecular LIF lacks the sensitivity needed for fission product sorptivity measurements at the levels of interest. Under carefully controlled conditions, conditions which do not approximate those of the HTGR, atomic LIF does possess the required sensitivity for some elements. In all likelihood, however, the relevant species are not atomic in nature. It is strongly recommended that efforts be directed toward establishing the identities of species in this system.

8. REFERENCES AND NOTES

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2. Iodine atomic energy levels taken from C. E. Moore, Atomic Energy Levels, vol. 3, NSRDS-NBS 35, U.S. Government Printing Office, Washington, 1971.
3. Molecular iodine energies taken from P. Luc, J. Mol. Spectrosc. 80, 41 (1980), and from F. Martin, R. Bacis, S. Churassy, and J. Verges, J. Mol. Spectrosc. 116, 71 (1986).
4. This was determined by using molecular constants given in the references above and by calculating energy differences for ground state levels $v = 0-4$, $J = 0-120$, and excited state levels $v' = 30-55$, $J' = J \pm 1$.
5. The vapor pressure of I_2 was calculated as

$$\log_{10} P(\text{torr}) = A - B/(T + C),$$

where

$$\begin{aligned} A &= 9.8109, \\ B &= 2901, \\ C &= 256, \\ T &= \text{the temperature in } ^\circ\text{C}. \end{aligned}$$

The equation is taken from Lange's Handbook of Chemistry (McGraw-Hill, 1979).

6. The signal expression is adapted from J. D. Winefordner and M. Rutledge, Appl. Spectrosc. 39, 377 (1985).
7. This is the fraction of molecules in the ground state sublevels v, J , that are connected to the excited state by the laser frequency. For our case, it is the fraction in $v = 0$, $J = 51$ or 54. This fraction is given by

$$\alpha_{vJ} = \frac{(2J+1)\exp[-hcBJ(J+1)/kT]\exp[-vhc\nu/kT]}{(kT/hcB)[1/(1-\exp[-hc\nu/kT])]},$$

where

$$\begin{aligned} h &= \text{Planck's constant,} \\ k &= \text{Boltzmann's constant,} \\ c &= \text{speed of light (cm/s),} \\ T &= \text{temperature (K),} \\ v &= \text{vibrational quantum number,} \\ J &= \text{rotational quantum number,} \\ B &= \text{molecular rotational constant (0.037 cm}^{-1} \text{ for } I_2), \\ \nu &= \text{vibrational fundamental (213.3 cm}^{-1} \text{ for } I_2). \end{aligned}$$

8. The Einstein coefficient is given by

$$A = 64\pi^4\mu^2/3h\lambda^3;$$

where

h = Planck's constant,
 λ = emission wavelength,
 μ = transition strength.

For molecules, μ^2 is approximated as $\mu^2 \times \text{FC}$, the product of an average electronic transition strength with the Franck-Condon factor for the particular sublevels involved. Franck-Condon factors for I_2 are given by Martin et al. in ref. 3.

9. In the absence of any background gas, the percent dissociation of I_2 may be written as

$$D = [K_p/(K_p + 4P)]^{1/2};$$

where

P = total pressure of molecular and atomic iodine,
 K_p = equilibrium constant for dissociation.

Values of K_p are derived from JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Government Printing Office, 1985.

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