Krypton Isotope Analysis Using Near-Resonant Stimulated Raman Spectroscopy

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EXECUTIVE SUMMARY

The Krypton Isotope Laser Analysis (KILA) method has been developed at the Pacific Northwest Laboratory in an attempt to measure small (typically, $<10^{-10}$) ratios of unstable to stable krypton isotopes in air samples. This technique uses high-resolution lasers to induce a specific isotope of krypton to fluoresce for optical detections.

Previous measurements have shown the sensitivity for non-isotopically-selective detection of krypton in 1 Torr of helium to be slightly better than one part-per-trillion, which translates into <1000 krypton atoms in the detection volume. This sensitivity is adequate to detect ^{85}Kr in sample volumes of less than one liter. Besides extremely high sensitivity, a measurement of ^{85}Kr content in a sample of air would require extremely high selectivity to differentiate between ^{85}Kr and stable krypton isotopes present to roughly 1 part per million in the atmosphere. The selectivity of the laser-based KILA technique is limited by the spectral linewidth of the transitions of interest. The Doppler-broadened lineshapes for the transitions studied here are approximately 500 MHz. However, hyperfine shifts in krypton are more typically between 50-200 MHz so that higher resolution is needed to de-excite individual isotopes. Stimulated near-resonant Raman spectroscopy has the potential to offer sub-Doppler linewidths and, therefore, higher selectivity. The selectivity needed for trace ^{85}Kr analysis at the levels indicated above has not been met. Initial characterization of the near-resonant Raman lineshapes needed to achieve the higher resolution indicated de-excitation rates that were much too broad and weak. In an effort to understand the suppression of the near-resonant Raman process, a computer model was developed that incorporated the physical parameters affecting the radiative excitation transfer. The results of this analysis indicate that diffusion of resonance radiation out of the excitation region is the largest damping term and limits the selectivity of the process to a value below that required for demonstration of the KILA technique.

Efficient population transfer during the stimulated near-resonant Raman process requires higher laser intensities and more tightly focused beams. Diffusion of metastable Kr atoms out of the excitation volume defined by the focused laser beams introduces a large background and decreases the sensitivity of the technique. A discussion of these and other factors limiting realization of the KILA technique are presented.

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INTRODUCTION

A method for measuring low relative abundances of ^{85}Kr in one liter or less samples of air has been under development here at Pacific Northwest Laboratory.^(a) The goal of the Krypton Isotope Laser Analysis (KILA) method is to measure ratios of 10^{-10} or less of ^{85}Kr to more abundant stable krypton. Mass spectrometry and beta counting are the main competing technologies used in rare-gas trace analysis and are limited in application by such factors as sample size, counting times, and selectivity. The use of high-resolution lasers to probe hyperfine levels to determine isotopic abundance has received much attention recently. In this study, we report our progress on identifying and implementing techniques for trace ^{85}Kr analysis on small gas samples in a static cell as well as limitations on sensitivity and selectivity for the technique. High-resolution pulsed and cw lasers are employed in a laser-induced fluorescence technique that preserves the original sample. This technique, outlined in Figure 1, is based on resonant isotopic depletion spectroscopy (RIDS) in which one isotope is optically depleted while preserving the population of a less abundant isotope (Makarov 1983; Janik et al. 1989).

The KILA method consists of three steps. In the first step, the $1s_5$ metastable level of krypton is populated via radiative cascade following two-photon excitation of the $2p_6$ energy level. Next, using RIDS, the stable krypton isotopes are optically depleted to the ground state through the $1s_4$ level with the bulk of the ^{85}Kr population being preserved. Finally, the remaining metastable population is probed to determine ^{85}Kr concentration. The experimental requirements for each of these steps are outlined below.

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Figure 1. Energy-level Diagram of Excitation/De-excitation Scheme. Following two-photon excitation to $2p_6$, the atom radiatively relaxes to the $1s_5$ level with 71% probability. At this time, the cw lasers, detuned by Δ from the $1s_5$ - $2p_8$ transition, transfer population from $1s_5$ to $1s_4$ in a near-resonant, stimulated Raman transition. Once in the $1s_4$ level, each atom decays to the ground state by emitting a photon with a wavelength of 123.6 nm. Each VUV photon represents a de-excited metastable.

EXPERIMENTAL CONSIDERATIONS

Figure 2 shows the experimental apparatus. The sample cell is a stainless steel cube with MgF_2 windows obtained from Optovac, Inc. on three sides. The two windows on opposing sides are for laser propagation, while the third is for vacuum-ultraviolet (VUV) monitoring of the excitation region. Fused silica windows were originally used for the laser ports but exhibited noticeable fluorescence under pulsed laser exposure. While this fluorescence did not appear to contribute to the VUV background, the fused silica windows were replaced with MgF_2 , from which fluorescence could be observed only in a darkened room. A Thorn-EMI 9423B solarblind photomultiplier (PMT) viewed the excitation region transverse to laser propagation through the third MgF_2 window, while a Lyman α filter (Acton Research Corp. model 122-N-2D) with a peak transmission at 123.6 nm and a 10-nm bandwidth provided discrimination against scattered laser light and other background counts. The output of the VUV PMT is sent to a Pacific AD6 combination 100x amplifier/discriminator whose NIM output is counted by a multi-channel scaler (MCS) board (Santa Fe Energy Research model MCS-II) installed in the AT bus of a 386-SX personal computer. The MCS had a maximum count rate of 200 MHz and a dead time between channels of <10 nsec.

A detail of the pulsed laser system that produces the intense tunable radiation needed to populate the metastable level is shown in Figure 3. A single-longitudinal-mode oscillator of the Littman design (Liu and Littman 1981) is transversely pumped by ~ 1 mJ of 532-nm light from a frequency-doubled Continuum Nd:YAG laser (model YG-661) operating at 10 Hz with 330 mJ per pulse total output. DCM dye at a concentration of 0.14 millimolar in methanol is flowed through the oscillator cell using a gravity-fed circulation system. The output from the oscillator is spatially filtered and first pre-amplified in a transversely pumped dye cell and further enhanced during longitudinal pumping of three amplifier cells tilted at Brewster's angle for the incoming beam. The four stages of amplification yield up to 55 mJ of light at 642 nm in a well-collimated TEM_{00} Gaussian beam. This output is frequency-doubled and then mixed with the fundamental beam to produce ≤ 5 mJ of frequency-tripled coherent light at 214 nm with a 2-mm beam diameter. With a pulsewidth for the ultraviolet beam of ~ 4 nsec, the measured laser bandwidth of 220 MHz is approximately twice the Gaussian transform limit. This beam is sent through the sample cell unfocused and then retro-reflected onto itself for Doppler-free two-photon excitation of the $1s_0$ - $2p_6$ transition. The Paschen notation for designating energy levels is used throughout for

Figure 2. Schematic Diagram of the Experimental Apparatus Showing Laser Systems and Sample Cell. Auxilliary cells are for tuning cw and pulsed lasers relative to krypton resonances.

Figure 3. Detail of Pulsed Laser System for Metastable Production.

simplicity. A fraction ($\sim 0.2\%$) of the irradiated krypton atoms is then excited to the $2p_6$ energy level by two-photon absorption of the 214-nm radiation. At the pressures in a typical gas sample (≤ 1 mTorr krypton in 2 Torr helium), the decay of $2p_6$ is dominated by its radiative lifetime of 26 nsec. Approximately 70% of the atoms in the $2p_6$ level then radiatively decay to the $1s_5$ metastable level, with the remaining fraction radiating to $1s_4$. The $1s_4$ energy level relaxes to the ground state by emitting a VUV photon at 123.6 nm so that the remaining 30% of the $2p_6$ population ends up back in the ground state after a time characteristic of the radiation-trapped $1s_4$ lifetime (~ 500 nsec). A small fraction of the pulsed beam is split off and sent through a second cell filled with 50 mTorr krypton. The infrared fluorescence from this cell is used to tune to the peak of the $1s_0$ - $2p_6$ transition.

Due to the relatively high laser powers and large photon energy required to efficiently excite krypton, the selectivity between krypton and other species present in air (N_2 , O_2 , H_2O , Ar, CO_2 , Ne, etc.) is limited by multi-photon ionization of and accidental coincidences in electronic and ro-vibrational energy levels of other species not of interest. In general, this low selectivity would not pose a problem since subsequent cw laser probing of krypton electronic levels would provide extremely high selectivity; however, ionic recombination of atmospheric constituents resulting in VUV fluorescence would potentially interfere with the laser-induced VUV fluorescence of krypton and cannot be ignored. Of even greater concern is the collisional deactivation of the krypton metastables. The metastable lifetime, in the absence of collisional deactivation, is limited by diffusion to the walls of the sample cell and is ~ 3 msec in a buffer gas of 1 Torr helium. Collisions with the molecular constituents of air would shorten this lifetime by 5-6 orders of magnitude with oxygen being the most abundant quencher (Velasco et al. 1978; Sobczynski and Setser 1991). For these reasons, modest sample preparation must be done to remove deactivating collisional partners and add a buffer gas (typically, a rare gas) to limit diffusion. Experiments with argon, neon, and helium have shown helium to be superior at limiting diffusion while not contributing significantly to the background VUV fluorescence.

Attached to a flange on one port of the stainless steel cube is a gas-handling system for mixing krypton and helium samples. Both the gas-handling system and the sample cell are evacuated to below 10^{-7} Torr before gas samples are added. For these experiments, ultra-high purity (99.999%) helium was used as the buffer gas, although a review of the collisional quenching rates for Kr $1s_5$ for typical impurity levels (Sobczynski and Setser 1991; Velasco et al. 1978) indicates that even modest purity helium (99.99%) would not substantially shorten the metastable lifetime. Validation of ultra-trace detection of krypton is limited, ultimately, by the impurity level of krypton in the helium buffer charge. No information on krypton impurity levels

is provided by the supplier (Matheson Gas Products), and subsequent queries could only guarantee <23 parts per million (ppm). Measurements made during the development of our laser-induced fluorescence (LIF) techniques and discussed later indicate that the actual level is several orders of magnitude lower and consistent with expectations based on the differences of vapor pressures produced during cryogenic distillation. However, the implicit assumption that higher purity helium contains less krypton impurities is not necessarily accurate. We believe that our measurements of the krypton impurity level are the most accurate available. Isotopically enriched samples of ^{86}Kr (99.3%) and of ^{78}Kr (99.0%) were obtained from Isotec, Inc. with guaranteed elemental purities of 99.5%. Isotopic impurities for both samples are overwhelmingly adjacent isotopes. Given the low krypton partial pressures in these experiments, collisional deactivation of metastables by impurities in the krypton sample was negligible.

The sensitivity of our optical detection technique depends strongly on the efficiency of krypton metastable production via two-photon absorption to $2p_6$. Metastable production in turn depends strongly on the pulsed laser power. Production efficiencies were measured by diode laser absorption at 811.5 nm from the $1s_5$ - $2p_9$ transition following pulsed laser excitation. A metastable production efficiency of 0.15% was obtained with this method for a 3-mm beam diameter. At higher laser fluxes, two-photon resonant, three-photon ionization competes with radiative relaxation of $2p_6$ to $1s_5$. By collecting the ions on a charged plate inside the sample cell, we observed that the number of ions created is comparable to the number of metastables produced. However, no noticeable VUV background is generated by these ions since the time-resolved VUV fluorescence signal is unchanged when the ions are swept out of the detection region.

Once krypton atoms are excited to the metastable level, the isotopic abundances are probed using two collinear single-frequency cw lasers. A cw ring dye laser (Coherent model 699-21) was detuned outside the Doppler profile (typically 2-4 GHz) of the $1s_5$ - $2p_8$ transition and overlapped spatially with the pulsed excitation laser. A second cw ring laser (Coherent model 899-21 Ti:Sapph) was detuned by the same amount from the $1s_4$ - $2p_8$ transition and overlapped collinearly with the first cw laser. Both ring lasers have a root-mean-square linewidth $\leq 1\text{MHz}$, are linearly polarized in the same direction, and are frequency stabilized to $\sim 5\text{MHz/day}$ using a computer-controlled stabilization circuit. Laser 1 (699-21) was collimated with a beam diameter of 3 mm and 150 mW of power. Laser 2 (899-21) was kept larger (5 mm diameter) but had 500 mW of power. By detuning both lasers outside the Doppler width of the transition, population transfer from $1s_5$ to $1s_4$ is achieved without passing through $2p_8$. Each atom in the $1s_4$ level decays by emission of a VUV photon during relaxation to the ground state. These VUV photons

are collected as a function of the frequency of the downward pumping laser and a histogram displayed on the MCS.

The detection volume is defined by the cw beam diameter of 2 mm and assumes that the PMT detects photons over a 30-mm length of the laser beam path. The PMT has an effective photocathode area of 45 mm and views the excitation region through a 5-cm diameter Lyman α filter and a 2.5-cm diameter MgF₂ window. The pulsed laser passes parallel to and 1 cm from the MgF₂ detection window. The factors limiting the laser path length seen by the PMT are the Lyman α filter and the MgF₂ detection window. The peak transmission of the Lyman α filter decreases and shifts to shorter wavelengths for light incident at increasing angles to the normal. Even more detrimental to efficient transmission are the increased pathlengths through the MgF₂ substrate of the Lyman α filter and the MgF₂ detection window.

NEAR-RESONANT STIMULATED RAMAN PROCESS

The data of Figure 4 represent a typical scan obtained by detuning Laser 1 from the $1s_5$ - $2p_8$ transition by $\Delta_{12}=+2$ GHz and scanning Laser 2 around the same detuning from $1s_4$ - $2p_8$. The narrow spectral feature at $\Delta_{12}=2$ GHz is due to the two-photon transition affected on the Λ system, $1s_5 \rightarrow 2p_8 \rightarrow 1s_4$, while the broad dip at zero detuning is due to competition between the two lasers, one resonant and one off-resonant. The energy levels and parameters relevant to the transition are shown below.

The states $|1\rangle$, $|2\rangle$, $|3\rangle$ are $1s_5$, $2p_8$, $1s_4$, respectively, while Δ_{12} and Δ_{23} are the detunings for the

Figure 4. Near-resonant Raman Spectrum for 1 mTorr ^{86}Kr in 200 mTorr He. The detuning of Laser 1 (Δ_{12}) = 2000 MHz. Each data point represents a 5-sec counting time and 8-MHz stepsize.

transitions $|1\rangle \rightarrow |2\rangle$ and $|2\rangle \rightarrow |3\rangle$. The population of level $|3\rangle$ is monitored in the scan of Figure 4 and can be predicted by numerical solution of the time-dependent optical Bloch equations:

$$\begin{aligned} d\rho_{11}/dt &= i\Omega_{12}(\rho_{12}-\rho_{21}) + \Gamma_{12}\rho_{22} \\ d\rho_{33}/dt &= i\Omega_{23}(\rho_{32}-\rho_{23}) + \Gamma_{23}\rho_{22} - \Gamma_3\rho_{33} \\ d\rho_{12}/dt &= i[(\Delta_{23}-\Delta_{12})\rho_{13} + \Omega_{23}\rho_{12}/2 - \Omega_{12}\rho_{23}] \\ d\rho_{13}/dt &= i[\Omega_{12}(\rho_{11}-\rho_{22})/2 + \Omega_{23}\rho_{13}/2 - \Delta_{12}\rho_{12}] - \Gamma_{123}\rho_{13}/2 - \Gamma_3\rho_{13} \\ d\rho_{32}/dt &= i[\Omega_{23}(\rho_{33}-\rho_{22})/2 + \Omega_{12}\rho_{31}/2 - \Delta_{23}\rho_{32}] - \Gamma_{123}\rho_{32}/2 - \Gamma_3\rho_{32} \end{aligned}$$

Here, the Γ 's are damping constants, Δ 's are detunings, and Ω 's are Rabi frequencies. For a steady-state approximation, an analytical solution for ρ_{33} can be found (Liao et al. 1979; Berman 1977) for the two regimes, $\Delta_{12} \approx \Delta_{12} \gg$ Doppler width and $\Delta_{23} \approx 0$, that takes into account Doppler broadening and collisional effects. For pulsed excitation of ρ_{11} , the population transfer from $1s_5 \rightarrow 1s_4$ is not strictly steady-state. However, the radiative damping terms for ρ_{11} , ρ_{22} , and ρ_{33} are, in general, larger than the diffusional or collisional rates for these states and the lineshapes for ρ_{33} are well described by the following equations:

$$\rho_{33} = C\left(\frac{k_1}{k_2}\right)\left(\frac{k_1 u}{\Delta_{12}}\right)^2 \left(\frac{2\Gamma_{12}}{\Gamma_2} - 1\right) Z_i\left(\frac{i\Gamma_{23} + \Delta_{23}}{k_2 u}\right) + B\left(\frac{\Gamma_{23}}{\Gamma_2}\right)$$

for $\Delta_{23} \approx 0$ and

$$\begin{aligned} \rho_{33} = C\left(\frac{k_1 u}{\Delta_{12}}\right)^2 \{ & \frac{k_1}{k_2 - k_1} Z_i\left(\frac{i\Gamma_{13}}{(k_2 - k_1)u}\right) [1 + \left(\frac{k_1 u}{\Delta_{12}}\right)^2 \alpha\left(\frac{\Gamma_{13}}{(k_2 - k_1)u}\right)] \\ & + 2\left(\frac{k_1 u}{\Delta_{12}}\right)^2 \frac{\Gamma_{12}\Gamma_{23}}{\Gamma_2 k_1 u} \} + B\left(\frac{\Gamma_{23}}{\Gamma_2}\right) \end{aligned}$$

for $\Delta_{23} \approx \Delta_{12}$. Here, Z_i is the imaginary part of the plasma dispersion function given by

$$Z_i(y) = -\Pi^{1/2} \int e^{-x^2} (y \pm x)^{-1} dx$$

For these equations, C is a constant proportional to $(\Omega_{12} \Omega_{23})^2$, B is a constant proportional to Ω_{12}^2 and accounts for one-photon excitation to $2p_8$ followed by radiative relaxation to $1s_4$, $u =$

most probable speed for Kr atoms, and k 's are wavevectors for the two lasers. Fits of the spectral features at $\Delta_{23}=\Delta_{12}$ and $\Delta_{23}=0$ for large detunings ($\Delta_{12}\gg k_1u$) are shown in Figures 5 and 6.

The selectivity of the KILA technique for measurement of ^{85}Kr over stable krypton is given by the following equation and depends on the linewidth of the stimulated Raman transition.

$$S = \exp\left(\frac{4\Delta^2}{\Gamma}\right) \quad \text{where } \Delta = \text{isotope shift and } \Gamma = \text{Lorentzian linewidth}$$

The lineshape for large detunings is well described by a Voigt profile with a Gaussian full-width at half-maximum of 34 MHz and a Lorentzian linewidth of 69 MHz. Hyperfine constants for the $1s_4$ and $1s_5$ energy levels indicate line shifts on the order of 100 MHz so that the Lorentzian component of the lineshape will be the dominating factor in determining the selectivity and $S=4.5\times 10^3$ – well below the factor of 1×10^{11} required for the measurement of ^{85}Kr in ambient air samples. The width of the stimulated Raman lineshape is determined by the factor, $\Gamma_{13}/(k_2-k_1)u$, with $\Gamma_{13}=(\Gamma_1+\Gamma_3)/2$ being the loss rate from states $|1\rangle$ and $|3\rangle$. The loss rate of state $|1\rangle$ is limited by diffusion of the metastables out of the 3-mm diameter of Laser 1, while the state $|3\rangle$ loss rate is limited by diffusion of radiation-trapped fluorescence out of Laser 1 and is inherently higher than that of gaseous diffusion. The diffusion rate of fluorescence to the walls of an infinite cylinder (Holstein et al. 1951) with a 3-mm radius is calculated to be $\Gamma_3 = 2\pi(54\times 10^6 \text{ rad/sec})$ for 1 mTorr of krypton while gaseous diffusion out of the same cylinder is typically $\Gamma_1 \leq 2\pi\times 10^6 \text{ rad/sec}$ for the buffer gas pressures used here. The fits of Figures 5 and 6 were performed using these loss rates. For the data at $\Delta_{23}=0$, the model consistently underestimates the linewidth by ~15% indicating power-broadening of the resonant Doppler-broadened $1s_4$ - $2p_8$ transition by Laser 2.

Increasing the beam diameters of Lasers 1 and 2 reduces the loss rates from states $|1\rangle$ and $|3\rangle$ and, consequently, the Lorentzian linewidths are reduced, yielding better selectivity; however, the peak height decreases relative to the one-photon background and effectively decreases the sensitivity of the technique. Measurements of one part in 10^{10} ^{85}Kr in ambient air samples require photon-counting on a background equivalent to ~100 counts/sec. To achieve this background level during the 5-msec lifetime of the $1s_5$ metastables would require a peak height-to-background of 30. The largest signal-to-background we have been able to achieve is ~3 (approximately a factor of 10 below what would be required). This enhancement factor is confirmed in the time-resolved spectra of Figure 7 where the increase in the $1s_5$ - $1s_4$ transfer rate is apparent with Laser 2 on. By plotting the ratio of the Raman peak height for $\Delta_{23}=\Delta_{12}$ versus laser intensity, as in Figure 8, we can extrapolate to the laser intensities required for the measurement of

Figure 5. Stimulated Raman Spectrum for $\Delta_{23} \approx \Delta_{12}$. Solid line is fit of the model explained in text.

Figure 6. Stimulated Raman Spectrum for $\Delta_{23} \approx 0$. Solid line is fit to model explained in text.

Figure 7. Time-resolved Spectra of Stimulated Raman De-excitation.

Figure 8. Plot of Ratio of Raman Peak Height to One-photon Background Versus Laser Intensity. Solid line is a least squares fit to data. Slope of fit = 3.3.

^{85}Kr . Lasers 1 and 2 would require output powers of 9 and 22 Watts, respectively, of single frequency output to yield both sufficiently narrow lineshapes and a peak-height-to-background of 30 assuming no power broadening of the transitions. These power levels are beyond currently available ring dye laser technology and are well into the power-broadened regime. For these reasons, the KILA technique does not appear feasible at this time.

In order to quantify the analytical properties of the KILA technique, measurements were performed on a prepared sample of ^{78}Kr in ^{86}Kr . Figure 9 shows a LIF spectra of the resolved stimulated Raman lineshapes on a sample of 0.07 mTorr ^{78}Kr , 0.1 mTorr ^{86}Kr , and 200 mTorr helium. The solid line represents a fit of the two convolved lineshapes and yields an isotope shift of 123.3 MHz for the $1s_5-1s_4$ transition. The $1s_5-2p_8$ transition isotope shift has been measured by several researchers (Cannon and Janik 1990; Jackson 1979) to be 293 MHz. The isotope shift for the $1s_4-2p_8$ transition would be $293 + 123.3 = 416.3$ MHz. This agrees well with the only value available in the literature: 418.5 MHz (Jackson 1979). The detection limit for this relatively small isotope shift is roughly one part in 10^7 ^{78}Kr in ^{86}Kr with a signal-to-background of 1 using LIF spectroscopy. This value is limited by the shot-to-shot noise of the pulsed laser. The expected selectivity using the KILA technique would be <1 part in 10^5 but is limited by the purity of the krypton samples (Whitehead et al. 1993).

Figure 9. Near-resonant Raman Spectrum on $^{78}\text{Kr}/^{86}\text{Kr}$ Isotopic Mixture. Sample was 0.07 mTorr ^{78}Kr , 0.1 mTorr ^{86}Kr , and 200 mTorr helium. Solid line is least-squares fit to convolved lineshape.

CONCLUSIONS

While the techniques developed here are very sensitive to overall detection of krypton, the combination of sensitivity and selectivity needed for ^{85}Kr analysis of ambient air samples has not been achieved. Limitations on the technique are such that pursuit of a trace analytical method for measuring ^{85}Kr using this technology should be discouraged.

The stimulated near-resonant Raman lineshapes posed the largest obstacle to realization of the KILA technique. The substantial improvements in peak height and linewidth that need to be met are not realistic in terms of current laser technology and known line-broadening parameters. While the physical parameters, such as Doppler broadening and velocity-changing collisions, are well described by the current model for population transfer from $1s_5$ to $1s_4$, no practical solution is apparent from the model. The technique has potential application to hyperfine spectroscopy in a static sample as well as to low-selectivity isotopic measurements where the expense of elaborate atomic beam machines would be prohibitive. The goals for which the project were originally funded were not met and, as a consequence, this paper represents the final report on the KILA project.

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