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Model Calculations of Continuous- Wave Laser Ionization of Krypton

B. D. Cannon

July 1999

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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Summary

This report describes modeling of a scheme that uses continuous-wave (CW) lasers to ionize selected isotopes of krypton with high isotopic selectivity. The models predict that combining this ionization scheme with mass spectrometric measurement of the resulting ions can be the basis for ultra-sensitive methods to measure ^{85}Kr in the presence of a 10^{11} excess of the stable krypton isotopes. Two experimental setups are considered in this model: the first setup is for krypton as a static gas, the second is for krypton in an atomic beam.

In the static gas experiment, for a total krypton press of 10^{-4} torr and 10 W of power in the cavity, the model predicts a total krypton ion current of $4.6 \times 10^8 \text{ s}^{-1}$ and for a $^{85}\text{Kr}/\text{Kr}$ of 10^{-11} a ^{85}Kr ion current of 3.5 s^{-1} or about 10,000 per hour. The atomic beam setup allowed higher isotopic selectivity; the model predicts a ^{85}Kr ion current of 18 s^{-1} or 65,000 per hour.

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1.0 Introduction

This report describes modeling of a scheme that uses continuous-wave (CW) lasers to ionize selected isotopes of krypton with high isotopic selectivity. The results of these model calculations predict that combining this ionization scheme with mass spectrometric measurement of the resulting ions can be the basis for ultra-sensitive methods to measure ^{85}Kr in the presence of a 10^{11} excess of the stable krypton isotopes. Two experimental setups are considered in this model, which have much different isotopic selectivities, ionization rates, and configurations of the mass spectrometer's vacuum system. The first setup is for the krypton as a static gas such as found in a static mass spectrometer. This setup could make measurements on smaller samples but would require measurement times of a few hours. The second setup is for the krypton in an atomic beam and could make measurements in several minutes but would require much larger samples than the static mass spectrometer. This report will first describe the laser ionization scheme and the two different experimental setups that were modeled. Then it will present the results of the model calculations and finally detailed discussions of the calculations are presented in the sections "Calculation of Excitation Rates" and "Calculation of Spectra."

2.0 Excitation Scheme

Figure 2.1 shows the excitation scheme considered in this model. Continuous-wave single-frequency light with a wavelength near 215 nm excites krypton atoms in the ground state, $1p_0$ to an excited state, $2p_6$ by a two-photon transition. A build-up cavity is used to increase the light intensity, which will increase the excitation rate for this step, and give the equal intensity counter-propagating beams needed for efficient Doppler-free two-photon excitation. Approximately 70% of the atoms excited to the $2p_6$ state radiate to the metastable $1s_5$ state while the remainder return to the ground state by way of one of two short lived intermediate states.¹ The atoms in the $1s_5$ state are subsequently excited to the $4d_4$ state where they are ionized by light from a high power near-infrared laser. There are interfering ionization processes that can limit the total isotopic selectivity of this ionization scheme. The two such processes considered in this model are ionization of the $2p_6$ and $1s_5$ states by the 215 nm light. These ionization pathways have the isotopic selectivity of the first two-photon excitation but they are less efficient than the main scheme. For the other wavelengths of light used in this scheme, the photon energies are too low to cause any interfering ionization process.

3.0 Experimental Setups Modeled

Two experimental approaches are considered in this model that have much different isotopic selectivities, ionization rates, and configurations of the mass spectrometer's vacuum system. The first

Figure 2.1. Schematic Diagram of Excitation Scheme. Two-photon excitation at 215 nm selectively excites krypton atoms of a desired isotope from the $1p_0$ ground state to the $2p_6$ state from which they decay by spontaneous emission to the metastable $1s_5$ state. A second laser beam selectively excites the desired krypton isotope from the $1s_5$ state to the $4d_4$ state from which they are ionized by a high power infrared laser. The energy levels of the interfering isotopes in the $2p_6$ and $4d_4$ states are also shown to indicate the origin of the isotopic selectivity. For both two-photon transitions, the laser wavelengths are tuned to energy levels of the desired isotope and are detuned from the levels of the interfering isotopes.

setup corresponds to the krypton being a static gas such as in a static mass spectrometer. For this case, both two-photon excitations occur in the same place and ionization by the 215 nm light limits the selectivity. Attempts to spatially separate the two excitation regions when using a static gas would result in prohibitive losses because only a small fraction of the atoms excited to the $1s_5$ state would reach the region for the second excitation before colliding with a wall and being deactivated. The second setup assumes the krypton is in an atomic beam and the second two-photon excitation is down stream from the first excitation. The very long radiative lifetime of the $1s_5$ state (calculated to be 85 seconds!) allows the excitations to be well separated in time and space. The spatial separation combined with electrodes to sweep away ions formed by the 215 nm light allows the full selectivity of the second excitation step to be realized. To maximize ionization efficiency of the atoms in the $1s_5$ state, the beams for the second excitation must be larger than the 215 nm beam waist by the product of the beam divergence and the distance from the atomic beam nozzle. With a divergence of 20 mrad and a distance of 50 mm, the beams in the second region would need to be 1 mm high to intercept all the $1s_5$ atoms. However, the larger beam size in the second region is not a problem for two reasons. First, watts of power are available at 811 nm

rather than the milliwatts available at 215 nm. And second, the two-photon cross-section for the second transition is enormous because the virtual intermediate level is only 7 cm^{-1} from a real state^{2,12} rather than the $33,000\text{ cm}^{-1}$ separation for the first step.

Both approaches begin with a two-mirror enhancement cavity with a near-spherical geometry that builds up the power of the 215 nm light to increase the rate of the first two-photon excitation. This cavity geometry gives a very small beam diameter at the waist, which is mid-way between the two mirrors so electrodes can be positioned close to the waist without touching the mirrors. The small beam radius is important since the two-photon excitation rate is proportional to the fourth power of the inverse of the beam radius. Cavity mirrors with radii of 15 mm and a separation of 29.9 mm were chosen which give a spatial mode that has a $15\text{ }\mu\text{m}$ diameter at the waist and a $266\text{ }\mu\text{m}$ diameter at the mirrors.³ Analytically integrating the square of the intensity of this mode over the radial and angular coordinates gives the relative two-photon excitation rate as a function of the distance from the waist along the optical axis. This tightly focused geometry concentrates the excitation region to within 2.5 mm from the waist, which simplifies coupling to the other laser beams and extracting ions into a mass spectrometer. The selected mirror separation gives a free spectral range for this cavity of 5 GHz and a bandwidth of 20 MHz for mirror reflectivities of 99%. This will allow efficient coupling of the $\sim 1\text{ MHz}$ wide 215 nm light into the cavity.

4.0 Results of Model Calculations

4.1 Static Gas

Figure 4.1 is a plot of the isotopic selectivity calculated from the model favoring ^{85}Kr over the adjacent mass isotopes ^{84}Kr and ^{86}Kr , which are the most abundant of the six stable krypton isotopes. The selectivity against these two isotopes is the same to better than 10%. This selectivity drops linearly with the reciprocal of the 215 nm power in the cavity for powers between 50 mW and 10 W. The cause of this drop in selectivity is the increase in the non-selective ionization of the $2p_6$ and $1s_5$ excited states by the 215 nm light. In the static gas setup, these ions cannot be differentiated from those produced by the subsequent selective ionization via the $4d_4'$ state. For a total krypton pressure of 10^{-4} torr and 10 W of power in the cavity, the model predicts a total krypton ion current of $4.6 \times 10^8\text{ s}^{-1}$ and for a $^{85}\text{Kr}/\text{Kr}$ of 10^{-11} a ^{85}Kr ion current of 3.5 s^{-1} or about 10,000 per hour. The combination of the isotopic selectivities from the laser ionization and a static mass spectrometer would not allow direct measurement of ^{85}Kr at the isotope ratio given above. However, by implanting the mass separated ions and then releasing them after pumping out the remaining krypton gas, then abundance of ^{85}Kr could be measured in the released gas. If the volume of the vacuum system of the static mass spectrometer is 1 liter, the ^{85}Kr ion current from 10,000 released ^{85}Kr atoms would be 1 s^{-1} .

Figure 4.1. Isotopic Selectivity and Ionization Rate Constant Versus 215 nm Power for a Static Gas. The calculated selectivity of the laser ionization scheme for ^{85}Kr against the adjacent mass isotopes, ^{84}Kr and ^{86}Kr , is plotted versus the 215 nm power in the enhancement cavity for the static gas setup. The 215 nm power in the enhancement cavity is the product of the enhancement factor times the input power. The selectivity against ^{86}Kr differs from that against ^{84}Kr by less than 10% while the selectivity against ^{83}Kr is about a factor of 2 better. The calculated ionization rate constant is also plotted and at 10 watts of ultraviolet light (UV) in the cavity corresponds to formation of $1\ ^{85}\text{Kr}$ ion per second for $9\ ^{85}\text{Kr}$ atoms per cm^3 .

4.2 Atomic Beam

For the atomic beam setup, interfering ions, ionized by 215 nm are removed, which allows much higher isotopic selectivity. However, the fraction of krypton atoms excited to the $1s_3$ state that are ionized must also be reduced to optimize the isotopic selectivity. The predicted ionization rate constants versus 215 nm power in the enhancement cavity are reduced by a factor of 3 from those shown in Figure 4.2 because lower laser intensities were assumed to reduce power broadening that would reduce the isotopic selectivity. The isotopic selectivity has a much larger dependence on which isotope is being considered and there is a new parameter that strongly affects the isotopic selectivities; the divergence of the atomic beam. The beam divergence controls the distribution of velocity transverse to the atomic beam direction, which is along the direction of the laser beams. This velocity distribution is characterized by an effective Doppler temperature with a 33 mrad half angle divergence from a source at 300°K giving a 10°K effective Doppler temperature. Figure 3 is a plot of the predicted isotopic selectivity for ^{85}Kr against the

Figure 4.2. Isotopic Selectivities for Laser Ionization in a Krypton Atomic Beam. The calculated selectivity for ^{85}Kr against ^{83}Kr , ^{84}Kr , and ^{86}Kr are plotted as a function of Doppler temperature in the atomic beam. Without the interference from ionization by the 215 nm light, the isotopic selectivity is independent of the 215 nm power for achievable powers in the enhancement cavity.

three major mass spectral interferences versus Doppler temperature. The model predicts the selectivity of the laser ionization of ^{85}Kr against the even mass isotopes increases from ^{86}Kr to ^{78}Kr . However, the odd mass isotope ^{83}Kr shows a much different behavior as a result of having the same nuclear spin as ^{85}Kr and so very similar hyperfine spectra. The highest Doppler temperature plotted is 300°K, which corresponds to what the static gas selectivity would be without the interfering ionization by the 215 nm light. For an atomic beam that has 5×10^{13} krypton atoms per cm^3 at the waist of the enhancement cavity and a $^{85}\text{Kr}/\text{Kr}$ isotope ratio of 10^{-11} , the model predicts a ^{85}Kr ion current of 18 s^{-1} or 65,000 per hour. The extremely high selectivity of the laser ionization for this setup combined with easily attainable abundance sensitivity from either quadrupole or magnetic sector mass spectrometers would easily allow single pass measurement of ^{85}Kr . A source that would generate such an atomic beam is a linear array of capillaries with 25 micron inside diameters that are 2.5 mm long and have 1 torr of krypton behind them. The resulting gas load of $0.2 \text{ torr cm}^3 \text{ s}^{-1}$ is easily compatible with the vacuum requirements for obtaining the high vacuum required for good abundance sensitivity.

5.0 Calculation of Excitation Rates

5.1 First Transition

The excitation rate to the metastable $1s_5$ state via the first transition was calculated by integrating the krypton number density times the square of the light intensity in the enhancement cavity times the effective two-photon cross section for excitation to the $1s_5$ state. This effective cross section is the product of the two-photon cross section and the radiative branching from the $2p_6$ state to the $1s_5$ state. The integration was done analytically from zero to infinity in the radial coordinate, from 0 to 2π in the angular coordinate, and from -2.5 mm to $+2.5$ mm from the waist along the laser beam. The intensity is given by the product of the power incident on the enhancement cavity (P_{215}), the enhancement factor of the cavity (E_{cavity}), and the normalized spatial distribution of the mode. The incident power and the enhancement factor are parameters that can be varied in the model. The effective two-photon cross section was determined by scaling the effective cross section previously measured at this laboratory⁴ with pulsed lasers by the ratio of the linewidths. This measured cross section of $1.2 \times 10^{-10} \text{ cm}^4 \text{ watt}^{-2} \text{ s}^{-1}$ was based on 0.15% production of krypton atoms in the $1s_5$ state using 5 mJ in a 4 ns pulse with a 2-mm beam diameter in a Doppler-free excitation with a linewidth of 1300 MHz. From the 6 MHz natural linewidth of the $2p_6$ state, the effective two-photon cross section for continuous-wave single-frequency excitation is $2.6 \times 10^{-8} \text{ cm}^4 \text{ watt}^{-2} \text{ s}^{-1}$.

This cross section is for the even isotopes, which have no hyperfine splitting. For the odd isotopes, this is reduced by two factors. The first factor, which is 0.28, reflects the relative strength of the desired hyperfine transition from the $F=9/2$ level of the ground state to the $F=13/2$ level of the $2p_6$ state, where F is the total angular momentum quantum number. The second factor, which is 0.75, reflects the radiative branching from the $2p_6$ $F=13/2$ hyperfine level to the $1s_5$ $F=13/2$ hyperfine level, which is given by the ratio of the products of the degeneracy times the squared 6-J symbol for each level.⁵ The radiative branching from the $2p_6$ state to the $1s_5$ state is included in the 2-photon cross section.

The enhancement factor for the cavity, E_{cavity} , is the ratio of the power circulating in the cavity to the power incident from outside the cavity. This factor depends on the reflectivities of the mirrors and their losses due to absorption and scatter and is given by

$$E_{\text{cavity}} = \frac{T_1}{[1 - \sqrt{R_1 R_2 (1 - L)}]^2}$$

where T_1 and R_1 are respectively the transmission and reflectivity of the input mirror, R_2 is the reflectivity of the other mirror, and L is the round trip loss due to factors other than mirror transmission. The quoted reflectivities and losses of commercially available mirrors at 215 nm range from 96% with losses of 0.5% to 99% with losses of 0.3% that give calculated enhancement factors of 17 and 42 respectively for R_1 equal to R_2 . With unequal reflectivities, the enhancement can be increased to over 50. There is also a company that specializes in custom high performance coatings, MLD Technologies, that claims they can make low loss mirrors for 215 nm that could give an enhancement factor of 100. The model calculations

are presented for E_{cavity} between 25 and 100, but the two-photon excitation rates scale as the square of E_{cavity} while the rate for photoionization of the excited states by 215 nm light scales linearly with E_{cavity} , so it is simple to scale these results to other values of the cavity enhancement factor.

5.2 Second Transition

In previous work from this laboratory, we showed that the two-photon excitation from the $1s_5$ state to the $4d_4'$ state could be saturated with 70 mW of single-frequency light focussed to a 180 μm diameter with the light retro-reflected.² Since several watts of single-frequency light at 811 nm are available using diode laser technology (for example, by using a tapered amplifier from SDL Inc. or injection locking a high power diode, such as the OPC-A003 series from Opto Power Corp.), this second transition can be saturated for either experimental setup considered. For the static gas setup, the 811 nm beam overlaps the 215 nm beam and a beam diameter of less than 100 μm is required. For the atomic beam setup, the 811 nm beam would need to be 1 mm high by 0.150 mm wide, which would require less than 500 mW to saturate. Thus, we assume that we can excite any desired fraction of $1s_5$ atoms in the proper hyperfine level to the $4d_4'$ state, but with a corresponding loss of selectivity due to power broadening. The optimum tradeoff between selectivity and excitation efficiency depends on the experimental setup. For the static gas setup, selectivity is limited by photoionization from the 215 nm beam and so 75% excitation efficiency was used for that case. For the atomic beam setup, 25% excitation efficiency was used.

5.3 Photoionization Rates

The photoionization cross section for the $4d_4'$ state at 1064 nm is $32 \pm 5 \text{ Mbarn}^{10}$ and, together with the radiative lifetime of $142 \pm 12 \text{ ns}$, gives a saturation intensity of 41 kW/cm^2 . For an ionizing beam with a cross section of 1 mm x 0.15 mm, this gives 33% ionization efficiency for 30 watts of power. This 33% photoionization efficiency is assumed for the atomic beam setup. For the static gas setup, where a smaller beam can be used and loss of selectivity in the second transition is less important, 75% photoionization efficiency is assumed in this model, which would require 10 watts of infrared in a 0.1 mm diameter beam. Rather than using the 1064 nm wavelength from a neodymium-YAG laser for ionization, 980 nm diode lasers developed for pumping fiber-optic amplifiers offer a smaller and less expensive alternative that also requires less electrical power and cooling and provides more than enough power. For example, the Opto Power model OPC-B060-980-FC provides 60 watts at 980 nm from a filter bundle.

The interfering processes of photoionization of the $2p_6$ and $1s_5$ states by the 215 nm light are not as well studied as photoionization of the $4d_4'$ state. The photoionization cross sections for the $1s_5$ state at 257.34 nm and 244.06 nm have been measured to be $0.29 \pm 0.11 \text{ Mbarn}$ and $0.21 \pm 0.067 \text{ Mbarn}$ respectively.⁶ There are no autoionizing resonances, which could give large changes in cross section with wavelength, in the energy region reached by these two wavelengths or the 215 nm wavelength from the $1s_5$ state. Also, calculations of the photoionization cross section predict only small changes for changing the photoionizing wavelength to 215 nm.⁶ Thus, the model uses a cross section of 0.25 Mbarn for photoionizing krypton atoms in the $1s_5$ state by 215 nm photons. For photoionization of the $2p_6$ state, there is no published experimental data. The lack of any saturation behavior in our previous measurements of production of $1s_5$ by 2-photon excitation to the $2p_6$ state gives an upper limit for this

cross section of 2 Mbarn. There are measurements of the photoionization cross section of a similar state in krypton, the $3p_6$ state, at 193 nm that found cross sections of 0.3-0.6 Mbarn.^{7,8} Based on this limited information, the model uses 0.5 Mbarn for the a cross section for photoionization of the $2p_6$ state at 215 nm.

Table 5.1 lists the rate constants for production of krypton atoms in the $1s_5$ state for the assumed enhancement cavity geometry for various cavity enhancement factors and amounts of 215 nm power incident on the input mirror of the cavity. These rates are for the laser wavelength tuned to the center of the transition for any even isotope. For a particular hyperfine line of one of the odd isotopes, these rate constants must be multiplied by the relative line strength given in Table 6.3. For example, the rate constant for excitation of ^{85}Kr on the $F=9/2$ to $F=13/2$ hyperfine transition is 0.28 times the value given in Table 5.1, which gives a rate constant of $0.193 \text{ cm}^3 \text{ s}^{-1}$ for 100 mW and E_{cavity} of 100. For a room temperature partial pressure of krypton of 1×10^{-4} torr, the number density of ^{85}Kr is 32 cm^{-3} at a 10^{-11} abundance. Thus, $0.193 \times 32 = 6.2$ ^{85}Kr atoms would be excited to the $1s_5$ state each second and $0.112 \times 6.2 = 0.7$ ^{85}Kr ions would be produced each second by 215 nm photoionization. Of these ^{85}Kr atoms in the $1s_5$ state, 75% would be in the correct hyperfine level for subsequent excitation to the $4d_4'$ state.

Table 5.1. Rates for Production of Kr in the $1s_5$ State and the Fraction of Excited States Photoionized by 215 nm Light. These rate constants for the production of $1s_5$ states of krypton are for the even mass isotopes and need to be multiplied by the relative intensities given in Table 6.3 to obtain the rates for a particular hyperfine line for the odd mass isotopes. The fraction of the excited states photoionized by 215 nm light assumes thermal velocities for the krypton atoms, a temperature of 300K, and a beam radius of 7.5 microns.

215 nm Power (mW)	Cavity Enhancement Factor (E_{cavity})	Rate Constant for Production of $1s_5$ ($\text{cm}^3 \text{ s}^{-1}$)	Fraction of Excited States Photoionized by 215 nm Light
2	25	1.72×10^{-5}	5.6×10^{-4}
2	50	6.88×10^{-5}	1.12×10^{-3}
2	100	2.75×10^{-4}	2.24×10^{-3}
10	100	6.88×10^{-3}	1.12×10^{-2}
50	100	0.172	5.6×10^{-2}
100	100	0.688	1.12×10^{-1}

6.0 Calculation of Spectra

Calculating the isotopic selectivity of a laser excitation scheme for krypton requires knowing the spectra of the transitions; that is the lineshapes, spectral positions, and relative strengths for all the krypton isotopes for the transitions involved. For isotopes that have zero nuclear spin, the relative strengths are given by the relative abundance of each isotope. For isotopes with non-zero nuclear moments, 6-J angular momentum coupling coefficients must be included to account for the relative strengths of all the hyperfine transitions. Both transitions used in this approach are 2-photon transitions with counterpropagating beams where the virtual intermediate level is far from any real level and they have no levels in common. This means that a rate equation model can accurately describe the process and that many phenomena such as optical pumping of hyperfine levels and optical coherence between the two transitions can be neglected.

The rate equation model for two-photon excitation predicts that the lineshape for each transition can be described as the sum of two terms with equal areas, one describing the Doppler broadened excitation and the other describing the Doppler-free excitation. A Gaussian lineshape

$$G(\nu) = \frac{2}{\Delta\nu_D} \cdot \sqrt{\frac{\ln(2)}{\pi}} \cdot \exp\left[-\frac{4\ln(2)(\nu - \nu_0)^2}{\Delta\nu_D^2}\right]$$

describes the Doppler broadened component for the cases considered here, a static gas and perpendicular excitation of a moderately collimated atomic beam, where ν is twice the laser frequency, ν_0 is the center frequency, and $\Delta\nu_D$ is the full width at half maximum (FWHM). The Doppler-free component has a Voigt lineshape

$$V(\nu) = \int_{-\infty}^{+\infty} G(\nu - x) \cdot L(x) dx$$

which is a convolution of a Lorentzian

$$L(\nu) = \frac{2 \cdot \Delta\nu_H}{\pi} \cdot \left[\frac{1}{\Delta\nu_H^2 + 4(\nu - \nu_0)^2} \right]$$

that reflects lifetime and power broadening with a FWHM of $\Delta\nu_H$ and a Gaussian that reflects laser frequency jitter.

However, in calculating the selectivity in this model, a Lorentzian lineshape is used in place of a Voigt lineshape. The natural linewidth of the first transition, $1p_0 \rightarrow 2p_6$, is 6.07 MHz FWHM that is determined by the 26.2 ns lifetime of the $2p_6$ level.⁹ The natural linewidth of the second transition, $1s_5 \rightarrow 4d_4'$, is 1.12 MHz FWHM, which is determined by the 142 ns lifetime of the $4d_4'$ state¹⁰ since the lifetime of the metastable $1s_5$ state is very long. For both of these transitions, the natural linewidths are greater than or equal to the expected jitter widths, which means that the error in using a Lorentzian

lineshape is less than 25% at the peak and less than 1% in the wings. Thus the errors in using this approximation are small compared to other uncertainties in calculating the overall selectivity, such as the abundance selectivity of the mass spectrometer. In addition, this approximation avoids the need to do the numerical integration that is required to calculate each point in the Voigt lineshape.

The spectral positions of the even mass isotopes can be specified by the transition frequency for one isotope, for example ^{86}Kr , and the transition isotope shifts relative to this reference isotope for all the other isotopes. Calculating the spectral positions for the odd mass krypton isotopes, ^{83}Kr and ^{85}Kr , requires the hyperfine constants, A and B, for each electronic state that has an electronic angular momentum, J, different from zero. The energies of hyperfine levels ν_F relative to a reference energy level are described by

$$\nu_F = \nu_J + A(C/2) + B(3/4)C(C+1) - I(I+1)J(J+1)/(2I(2I-1)J(2J-1))$$

where F and I are respectively the total and nuclear spin angular momentum quantum numbers and $C = F(F+1) - I(I+1) - J(J+1)$. A and B are respectively the magnetic-dipole and electric-quadrupole hyperfine constants, and ν_J is the center-of-mass shift relative to the reference level. Use of this equation for the upper and lower levels of a transition allows the hyperfine spectrum for each isotope to be calculated relative to the reference isotope using the transition isotope shift and between zero and four hyperfine constants, which depend on the isotope and electronic angular momenta of the states.

Transition isotope shifts are the differences between the isotope shifts for the levels involved, which means that the isotope shift for a transition from level A to C can be calculated by adding the transition isotope shift for A to B and B to C and remembering that the transition isotope shift from B to C is the negative of that for C to B. With this rule, transition isotope shifts for the even krypton isotopes can be calculated from existing experimental data, but the data are not quite as complete for ^{83}Kr and are quite sparse for ^{85}Kr . However the transition isotope shifts between ^{85}Kr and ^{83}Kr can be accurately estimated using the fact that isotope shifts are the sum of a mass effect term and a nuclear field term and that for krypton the mass effect term is much larger than the field effect term. The mass effect term for the ^{85}Kr - ^{83}Kr shifts is one half of the mass term between ^{86}Kr and ^{82}Kr to better than 0.03% because the mass term scales with the nuclear masses as $(M_1 - M_2)/(M_1 \times M_2)$. The error, Δ , in using one-half the ^{86}Kr - ^{82}Kr isotope shift to approximate the ^{85}Kr - ^{83}Kr shift is due almost entirely to the field effect and for five transitions it was found to range from -10 MHz to -21 MHz¹¹ with an average of -14 MHz. This is in agreement with the results of a number of studies of krypton isotope shifts showing that nuclear field shifts are small.^{12,13} The ratio of Δ s for a pair of transitions is equal to the slope of the King plot for this same pair of transitions, and this slope can be determined using only the even mass isotope shifts.¹¹ Thus the error in estimating the ^{85}Kr - ^{83}Kr isotope shifts is a few megahertz. Because of the even-odd staggering of isotope shifts, it is more accurate to estimate the ^{85}Kr to ^{83}Kr shift and subtract the ^{83}Kr to ^{86}Kr shift to estimate the ^{85}Kr to ^{86}Kr shift than to directly mass scale the ^{84}Kr to ^{86}Kr shifts.

The first transition in this scheme is a two-photon transition from the krypton ground state ($1p_0$) to the $2p_6$ state. Isotope shifts for this transition have not been directly measured but can be calculated using the experimental data shown in Table 6.1 for the first four transitions. The dominant uncertainty is the errors associated with the first transition. Isotope shifts for the second transition in the proposed detection scheme, from $1s_5$ to $4d_4'$, are given in the last row of Table 6.1.

6.1 Isotope Shifts Used in this Work

The isotope shifts for the two-photon transition from the ground state ($1p_0$) to the $2p_6$ state of krypton are calculated by summing the shifts for the first four transitions in Table 6.1. The ^{85}Kr - ^{83}Kr shifts for the $1p_0 \rightarrow 2p_6$ and $1s_5 \rightarrow 4d_4'$ transitions are calculated using the procedure described in the text. The one standard deviation error estimates are given in parenthesis in units of the least significant digit shown.

The hyperfine constants for ^{85}Kr can be accurately predicted by scaling the constants for ^{83}Kr using the relations

$$\begin{aligned} {}^{85}\text{A}/{}^{83}\text{A} &= 1.0359(3) \\ {}^{85}\text{B}/{}^{83}\text{B} &= 1.711(4) \end{aligned}$$

where the superscripts on the A's and B's refer to the particular isotope.¹¹ These ratios depend only on the ratios of nuclear properties and not on the electronic states. Table 6.2 shows the hyperfine constants for ^{85}Kr and ^{83}Kr used to calculate the line positions. The hyperfine constants have been measured for all three states of ^{83}Kr and for two of the states for ^{85}Kr . The scaling relationships given above were used to calculate the ^{85}Kr hyperfine constants for the $4d_4'$ state.

Table 6.1. Isotope Shifts

	$^{86}\text{V} - ^{84}\text{V}$ (MHz)	$^{84}\text{V} - ^{82}\text{V}$ (MHz)	$^{82}\text{V} - ^{80}\text{V}$ (MHz)	$^{80}\text{V} - ^{78}\text{V}$ (MHz)	$^{85}\text{V} - ^{83}\text{V}$ (MHz)	$^{86}\text{V} - ^{83}\text{V}$ (MHz)	Source
$1p_0 \rightarrow 1s_2$	44.4(80)	60.0(60)	53.4(60)	48.9(60)		130.1(60)	Ref. ¹³
$1s_2 \rightarrow 2p_3$	97.1(15)	99.8(18)	109.1(30)	115.4(21)		134.0(50) ^(a)	Ref. ¹⁴
$2p_3 \rightarrow 1s_5$	-87.5(6)	-84.6(6)	-94.6(8)	-102.3(8)		-119.5(20)	Ref. ^{15,16}
$1s_5 \rightarrow 2p_6$	73.4(11)	69.3(11)	78.6(8)	85.5(7)	60.6(30)	94.1(14)	Refs. ^{10,11}
$1p_0 \rightarrow 2p_6$	127.4(80)	144.5(64)	146.5(68)	147.5(64)	149.8(85) ^(b)	238.7(82)	See Text
$1s_5 \rightarrow 4d_4'$	159.8(25)	145.0(40)	174.9(37)	170.1(28)	132.0(80) ^(b)	216.9(23)	Refs. ^{10,11}
(a) Estimated from $^{86}\text{V} - ^{83}\text{V}$ shift for the $1s_2 \rightarrow 2p_4$, which has the same lower state, the same upper state J, and almost identical even mass isotope shifts.							
(b) Calculated including field shift by scaling Δ for the $1s_5 \rightarrow 2p_6$ by the King plot slope.							

The values shown in Table 6.2 for the hyperfine constants used are the weighted averages of the measured values tabulated in References 1 and 2. The one standard deviation error estimates are given in parenthesis in units of the least significant digit shown. The constants for the $1s_5$ state of ^{83}Kr were measured in a microwave-atomic beam experiment to an accuracy of a few kilohertz or better.

Table 6.2. Hyperfine Constants

State	^{83}Kr		^{85}Kr	
	A(MHz)	B(MHz)	A(MHz)	B(MHz)
$1s_5$	-243.97()	-452.16()	-252.83(8)	-775.7(11)
$2p_6$	-108.50(8)	-87.2(11)	-112.47(13)	-153.3(22)
$4d'_4$	-73.66(2)	-455.2(8)	-76.30(3)	-778.8(22)

6.2 Relative Positions and Intensities of $1p_0 \rightarrow 2p_6$ Transitions for Krypton

Table 6.3 gives the positions and relative absorption cross sections for the two-photon transition in krypton from the ground state to the $2p_6$ state for the stable krypton isotopes and ^{85}Kr calculated using the isotope shifts and hyperfine constants in Tables 6.1 and 6.2. The relative intensities do not reflect any differences in the relative abundances of the different isotopes. Table 6.4 gives the same information for the two-photon transition from the metastable $1s_5$ state to the $4d'_4$ state.

The line positions and relative strengths for the two-photon transition from the krypton ground state to the $2p_6$ state for the stable krypton isotopes and ^{85}Kr are shown in Table 6.3. The transition energy for ^{86}Kr is $93123.3337 \text{ cm}^{-1}$,¹⁷ which requires laser wavelength in vacuum of 214.769 nm.

Table 6.3. Relative Positions and Intensities of $1p_0 \rightarrow 2p_6$ Transitions for Krypton

Frequency Shift (MHz)	Relative Intensity	Lower State F	Upper State F	Isotope
-1237.0	0.28	9/2	13/2	83
-1139.5	0.28	9/2	13/2	85
-565.9	1.00	0	2	78
-484.5	0.24	9/2	11/2	83
-418.4	1.00	0	2	80
-325.4	0.24	9/2	11/2	85
-271.9	1.00	0	2	82
-127.4	1.00	0	2	84
0.0	1.00	0	2	86
112.2	0.20	9/2	9/2	83
293.2	0.20	9/2	9/2	85
573.2	0.16	9/2	7/2	83
751.4	0.16	9/2	7/2	85
914.8	0.12	9/2	5/2	83
1078.0	0.12	9/2	5/2	85

The line positions and relative strengths for the two-photon transition from the krypton $1s_5$ metastable state to the $4d_4'$ state for the stable krypton isotopes and ^{85}Kr is shown in Table 6.4. The transition energy for ^{86}Kr is 24659.83 cm^{-1} ,⁷ which requires laser wavelength in vacuum of 811.069 nm.

Table 6.4. Relative Positions and Intensities of $1s_5 \rightarrow 4d_4'$ Transitions for Krypton

Frequency Shift (MHz)	Relative Intensity	Lower State F	Upper State F	Isotope
-1909.3	0.0076	5/2	9/2	83
-1666.3	0.0076	5/2	9/2	85
-1651.0	0.0216	5/2	7/2	83
-1606.2	0.0263	7/2	11/2	83
-1469.0	0.0337	5/2	5/2	83
-1451.3	0.0263	7/2	11/2	85
-1448.2	0.0216	5/2	7/2	85
-1349.3	0.0349	5/2	3/2	83
-1310.9	0.0337	5/2	5/2	85
-1281.4	0.0222	5/2	1/2	83
-1253.2	0.0480	7/2	9/2	83
-1230.3	0.0349	5/2	3/2	85
-1188.9	0.0222	5/2	1/2	85
-1120.8	0.0480	7/2	9/2	85
-1119.6	0.0606	9/2	13/2	83
-1036.8	0.0606	9/2	13/2	85
-994.9	0.0472	7/2	7/2	83
-902.7	0.0472	7/2	7/2	85
-813.0	0.0290	7/2	5/2	83
-765.4	0.0290	7/2	5/2	85
-693.2	0.0095	7/2	3/2	83
-684.8	0.0095	7/2	3/2	85
-649.8	1.0000	2	4	78
-649.6	0.0707	9/2	11/2	83
-555.9	0.0707	9/2	11/2	85
-479.7	1.0000	2	4	80
-391.2	0.1162	11/2	15/2	83
-322.8	0.1162	11/2	15/2	85
-304.8	1.0000	2	4	82
-296.7	0.0460	9/2	9/2	83
-225.5	0.0460	9/2	9/2	85
-159.8	1.0000	2	4	84
-38.4	0.0188	9/2	7/2	83
-7.3	0.0188	9/2	7/2	85

Table 6.4. (contd)

Frequency Shift (MHz)	Relative Intensity	Lower State F	Upper State F	Isotope
0.0	1.0000	2	4	86
129.9	0.0040	9/2	5/2	85
143.6	0.0040	9/2	5/2	83
222.2	0.0796	11/2	13/2	83
353.8	0.0796	11/2	13/2	85
652.2	0.2000	13/2	17/2	83
692.2	0.0336	11/2	11/2	83
816.4	0.2000	13/2	17/2	85
834.6	0.0336	11/2	11/2	85
1045.2	0.0093	11/2	9/2	83
1165.1	0.0093	11/2	9/2	85
1303.5	0.0013	11/2	7/2	83
1383.2	0.0013	11/2	7/2	85
1439.5	0.0615	13/2	15/2	83
1740.8	0.0615	13/2	15/2	85
2052.9	0.0154	13/2	13/2	83
2417.3	0.0154	13/2	13/2	85
2522.9	0.0028	13/2	11/2	83
2875.9	0.0003	13/2	9/2	83
2898.2	0.0028	13/2	11/2	85
3228.6	0.0003	13/2	9/2	85

7.0 References

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