Laser separation of lithium isotopes by double resonance enhanced multiphoton ionization of Li2

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Laser separation of lithium isotopes by double resonance enhanced multiphoton ionization of Li_2

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Multiphoton ionization spectra of $^7Li_2$, $^6Li_2$, and $^7Li^6Li$ vapors have been measured in the 570–650 nm region using a single, low resolution, multimode cw dye laser. A number of wavelengths provide selective multiphoton ionization of one isotopic species demonstrating the possibility of efficient laser-driven isotopic separation in lithium in this wavelength region.

Laser-induced isotope separation is a subject of considerable current interest because of its potentially higher efficiency compared to more traditional methods. For light isotopic species, such as ^6Li and ^7Li, the mass difference is sufficiently large that distillation methods of isotope separation provide an economical means of gross separation. Nevertheless, if high isotopic purity is desired, a uniquely selective method must be used such as that offered by laser excitation or mass spectrometry. Rothe *et al.* have reported[1,2] the separation of the two natural lithium isotopes by the sequential two photon ionization of Li_2 using an argon laser:

$$Li_2(X\,^1\Sigma_g^+) \xrightarrow{h\nu} Li_2(B\,^1\Pi_u) \xrightarrow{h\nu} Li_2(X\,^2\Sigma_g^+)\,. \qquad (1)$$

A theoretical analysis of the two photon ionization approach to the isotope separation was reported by Cremaschi[3] who also predicted other transitions via the $B\,^1\Pi_u$ state that would be useful. All previous work has been based upon the use of the $B\,^1\Pi_u$ state as an intermediate where all transitions fall in the 20 000–21 000 cm^{-1} energy range.

Isotope separation of ^6Li and ^7Li has also been demonstrated for the atomic species in a molecular beam and with a single mode laser.[4] The combination of isotope shift, fine structure, and hyperfine interactions[5,6] result in the ^6Li $2\,^2P_{1/2}$–$2\,^2S_{1/2}$ and ^7Li $2\,^2P_{3/2}$–$2\,^2S_{1/2}$ transitions being separated by about 10 GHz from a region of spectral congestion involving both isotopes.

In the present work we investigate the *double* resonance enhanced *three* photon ionization of the isotopic species of Li_2 and experimentally demonstrate the feasibility of ^6Li–^7Li isotope separation. These transitions, which use the $A\,^1\Sigma_u^+$ state and the $F\,^1\Sigma_g^+$ or $G\,^1\Pi_g$ state as intermediate levels, occur in the 16 000–17 000 cm^{-1} range, where tunable lasers of high average power are available. Moreover, a low resolution cw dye laser can be used to effect the isotope separation.

Earlier work[7] has shown that a single low resolution tunable dye laser operating in the 570–650 nm region can induce a number of optical–optical double resonance (OODR) transitions in $^7Li_2$ of the type

$$Li_2(X\,^1\Sigma_g^+) \xrightarrow{h\nu} Li_2(A\,^1\Sigma_u^+) \xrightarrow{h\nu} Li_2(F\,^1\Sigma_g^+)$$
$$\searrow^{h\nu} Li_2(G\,^1\Pi_g) \qquad (2)$$

In the present work we have used $^6Li_2$, $^7Li_2$, and $^6Li^7Li$ as target molecules and have detected the ions formed when a third photon ionizes the $F\,^1\Sigma_g^+$ or $G\,^1\Pi_g$ molecules:

$$Li_2(X\,^1\Sigma_g^+) \xrightarrow{h\nu} Li_2(A\,^1\Sigma_u^+) \xrightarrow{h\nu} Li_2(F\,^1\Sigma_g^+) \xrightarrow{h\nu} Li_2^+$$
$$\searrow^{h\nu} Li_2(G\,^1\Pi_g) \nearrow^{h\nu} \qquad (3)$$

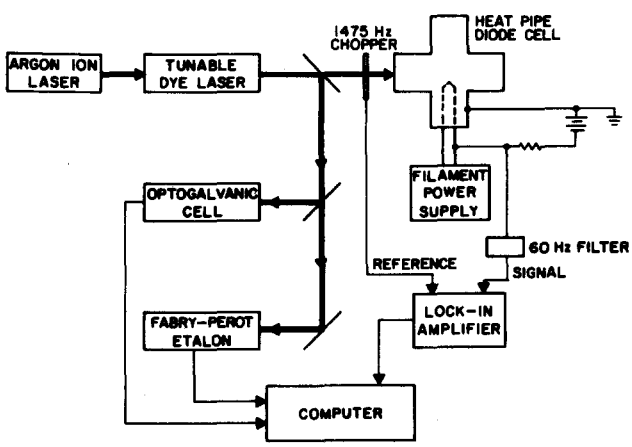

FIG. 1. Experimental schematic for the double resonance enhanced multiphoton ionization of the isotopic lithium dimers.

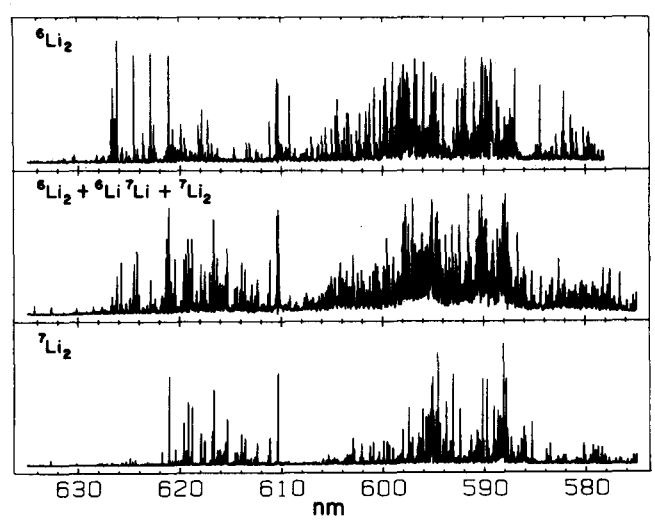

FIG. 2. Double resonance enhanced multiphoton ionization signal from 92% $^6Li_2$, 8% $^6Li^7Li$ (top); 50% $^6Li^7Li$, 25% $^6Li_2$, 25% $^7Li_2$ (middle); and 99% $^7Li_2$ (bottom). Intensity in arbitrary units, and wavelength in nm.

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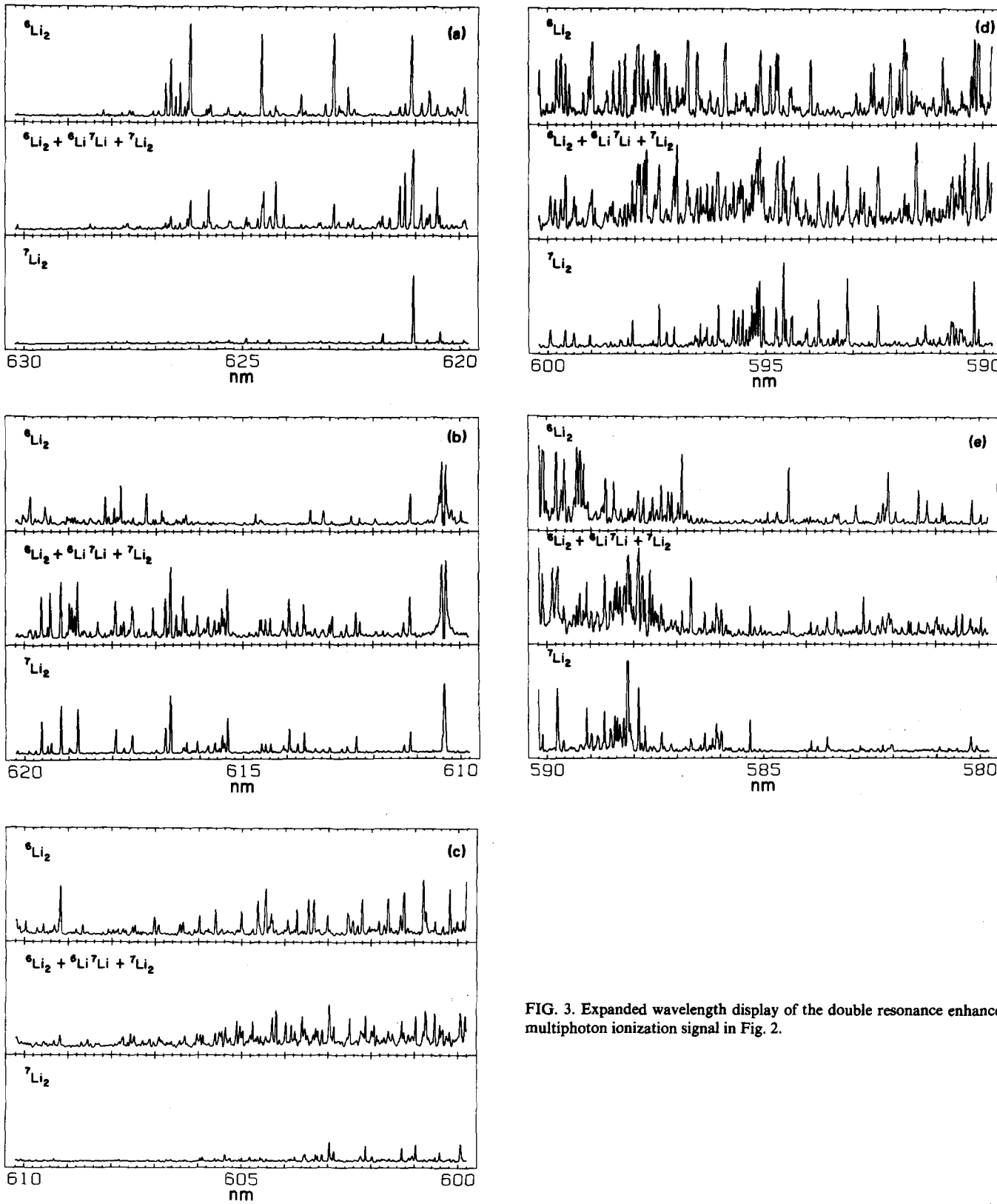

FIG. 3. Expanded wavelength display of the double resonance enhanced multiphoton ionization signal in Fig. 2.

A schematic diagram of the experimental apparatus is shown in Fig. 1. Radiation was produced with a Coherent 599 cw tunable dye laser operated with rhodamine 6G and pumped with a Spectra Physics 171 argon-ion laser. The dye laser output power was typically 0.9 W in the center of the dye laser gain curve. Wavelength calibration was achieved by sampling the laser radiation with a neon optogalvanic cell and Fabry–Perot interferometer. Spectra were recorded with a sample of ^6Li (mole fraction 0.9558), a sample of ^7Li (mole fraction 0.9992), and an approximately equimolar mixture. Both isotopes were obtained from Oak Ridge National Laboratory. Several grams of the lithium sample under study were placed in a cruciform heat pipe cell together with about 2 Torr of helium at room temperature; the cell

was then heated to about 1000 K. At this temperature, the composition at the center of the cell was estimated to be 0.7 Torr Li, 0.02 Torr Li_2, and 3 Torr helium. Ions were detected by operating the cell as a space-charge-limited thermionic diode[8] with a heated filament in the cell; the filament acted as both the cathode and electron source, while the cell body served as the anode. Introduction of a cation into the space charge region produced an increase in the diode current. The laser beam was chopped at 1475 Hz, and the change in diode current observed with a lock-in detector. Using a birefringent filter as the only tuning element, the laser bandwidth was approximately 1 cm^{-1} and positions of individual spectral transitions could be determined to about 0.1 cm^{-1}.

The resulting spectra are shown in Figs. 2 and 3 for the three samples of different ^6Li and ^7Li isotopic composition. The top spectrum in each figure, labeled $^6Li_2$, is due primarily to $^6Li_2$, having been obtained from the sample with 0.9558 mole fraction of ^6Li. Therefore, about 8% of the lithium dimer vapor is composed of the mixed isotopic species $^6Li^7Li$. The bottom spectrum, labeled, $^7Li_2$, is $>99\%$ ^7Li. The middle spectrum was obtained from a sample made from the approximately equimolar mixture of isotopes. The lithium dimer concentration in this sample is, therefore, about 50% $^6Li^7Li$, 25% $^6Li_2$, and 25% $^7Li_2$. Figure 2 shows the three spectra on a compressed wavelength scale that covers the entire gain curve of rhodamine 6G, and Fig. 3 shows the three spectra on an expanded wavelength scale where differences between the spectra of isotopic species can easily be seen.

The intensities of the ionization signals, which are in arbitrary units in Figs. 2 and 3, were found to have a quadratic dependence on laser power. Quadratic dependence on laser power was simultaneously observed in the UV fluorescence detected OODR spectra.

A number of wavelengths offer a high specificity of excitation and ionization yield. Table I lists those wavelengths which appear to give the highest selectivity and relative yield. There are a number of good ionization possibilities for each isotope, and it is concluded that the lithium isotopes can be separated using these convenient wavelengths.

The actual efficiency of the isotope separation will depend upon factors other than the strengths of the multiphoton ionization signals. For example, the present experiments do not reveal to what extent intermolecular energy transfer will affect the efficiency of the laser isotope separation. The possibility exists that the two-photon excited state energy of one isotopic species could be transferred to a molecule of different mass before the final ionization step occurs.

TABLE I. Wavelengths of OODR transitions in Li_2 with high isotopic selectivity. Wavelengths are in air; frequencies are in vacuum.

Wavelength (nm)	Frequency (cm^{-1})	Isotope
626.190	15 965.1	6
622.877	16 050.1	6
619.610	16 134.7	7
619.168	16 146.2	7
618.162	16 172.5	6
617.804	16 181.9	6
617.217	16 197.3	6
616.664	16 211.8	7
613.942	16 283.7	7
613.597	16 292.8	7
609.177	16 411.1	6
585.306	17 070.4	7
584.409	17 106.6	6

In conclusion, it should be pointed out that the present approach to ^6Li–^7Li isotopic separation does not require the use of single frequency dye lasers. Instead, one can take advantage of the higher conversion efficiency for production of multimode, low resolution laser radiation.

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