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ISOTOPE SEPARATION BY LASER-ENHANCED CHEMICAL REACTION

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Reactivity enhancement was studied using a reaction between a laser excited atomic beam and a molecular beam. This method was applied to lithium isotope separation, in which the excited Li isotopic atom reacts with $CHClF_2$. It is found that the specified lithium isotope is enriched in the reaction product LiF, whereas LiCl has no selectivity.

1. Introduction

In the field of the laser isotope separation, especially for the method which uses an atomic beam as a processing material, the fixation and recovery of laser-excited atoms is one of the most important steps. The photoionization method in which the excited atoms are ionized by laser irradiation has been widely utilized. It needs usually several kinds of laser beams [1]. On the other hand, the laser-enhanced chemical reaction method by which the excited atoms are recovered in the form of some chemical compounds, can exclude a photoionization laser system. And moreover, any type of chemical forms can easily be produced by choosing a partner molecule. Reactions of laser-excited atom with molecules have been achieved for the system $Na(2P_{3/2}) + Ne$ [2], $Na(2P_{3/2}) + Hg$ [3], $Na(2P_{3/2}) + Ar,Kr$ and Xe [4], and $Li(4S_{1/2}) + (NO_2, Cl_2$ and $F_2)$ [5]. However they are not referred to the laser-induced chemical reaction process of atoms from the view point of isotopic selectivity. Our target of this study is to make reaction products enriched with a specified isotope of lithium atom through a method in which a laser-excited atomic beam reacts with a crossed molecular beam of halogenated compounds.

2. Experimental

Fig. 1 shows the experimental arrangement, which is composed of an atomic beam source, a molecular beam source, a reaction cell and a detection system. The lithium atomic beam is produced by heating and vaporizing lithium metal of natural isotopic abundance ratio placed in a crucible with a bombardment of electrons emitted from an electron gun and then by collimating it through three sets of skimmers. On the other hand, the molecular beam is obtained through a nozzle–skimmer system. A chamber between the nozzle and skimmer is evacuated at the level of 0.01 Pa by a differential vacuum system. The gas pressure in the nozzle is kept constant to obtain a stable molecular beam intensity. The laser light irradiates the crossing part or a reaction spot of the atomic and molecular beam in the direction perpendicular to the plane involving these two beams. The reaction products are introduced into an ion chamber and detected by a quadrupole mass spectrometer which is made so as to rotate about the reaction zone or beam crossing spot on the above plane. The laser beam is emitted from a dye laser with 0.5 mg peak energy and 10 Hz repetition rate which is optically pumped with a Nd:YAG laser. A mixture of R

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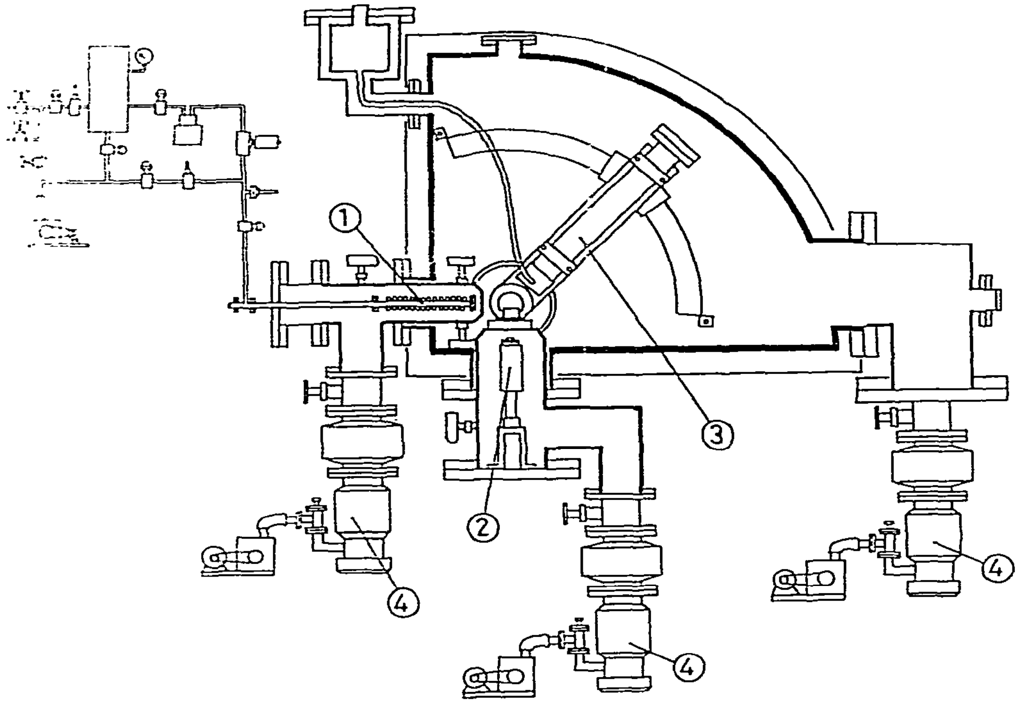

Fig. 1. Experimental arrangement. 1, molecular beam source; 2, atomic beam source; 3, quadrupole mass filter; 4, vacuum system.

640 dye and NBAP dye is used for excitation of lithium from the ground state (2S) to the lower excitation levels ($2P_{1/2}$ and $2P_{3/2}$ of Li) as shown in fig. 2. Mixture of dye R 640 + NBAP and C 500 dye is used for the excitation to the higher excitation level ($4S_{1/2}$) which can be reached from the ground state ($2S_{1/2}$) via the lower excitation level(2P) by the two-step photoexcitation method. The laser linewidth used is around 1. 1 GHz. Care is taken that the atomic spectrum may not be considerably broadened due to the power broadening effect in the high optical power density.

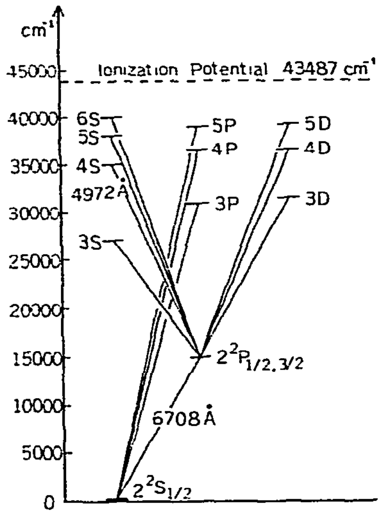

Fig. 2. Schematic energy diagram of lithium atom.

The $CHClF_2$ molecule is selected as a reaction partner, since it has reasonable chemical reactivity with alkali atoms, that is, its reaction with alkaline atoms is neither too high nor too low. It is shown from the experiment that the divergences of the atomic beam and the molecular beam are about 2° and 12° respectively. Zero laboratory angle corresponds to the center peak of the atomic lithium beam when no molecular beam is crossed.

The activation energy is obtained from an Arrhenius plot of the reaction product yields by changing the molecular-beam temperature which is achieved by heating the molecular-beam source.

Temperatures of the atoms or molecules are obtained by the time-of-flight method. In this method the change in the molecular-beam intensity which is modulated by a beam chopper is monitored by a quadrupole mass spectrometer. Assuming that the gas velocity distribution at the inlet of the skimmer is maxwellian, the time-dependent signal intensity $s(t)$ of the detected species is given by

$$s(t)=\frac{A}{t^4}\exp\left[-\frac{mX_{\mathrm{h}}^2}{2\kappa T_{\mathrm{t}}}\left(\frac{1}{t}-\frac{1}{t_{\mathrm{M}}}\right)^2\right], \qquad (1)$$

where t is the time of flight, X_{h} the flight distance, t_{M} the mass average time of flight, m the molecular weight, κ Boltzmann's constant, and A a constant.

The experimentally obtained beam signal intensity profile is deformed from the real one, because the width of the molecular beam and the slit of the chopper influence this profile. The modified signal is described as follows.

$$s(t)=\int_{-\infty}^{\infty} G(\tau)s(t-\tau)\mathrm{d}\tau, \qquad (2)$$

where $G(t)$ is a triangular gate function of the beam chopping:

$$\begin{aligned} G(t) &= t/t_1, && \text{for } 0 \leqslant t \leqslant t_1; \\ &= 2-t/t_1, && \text{for } t_1 < t \leqslant t_2. \end{aligned} \qquad (3)$$

Accordingly the temperature of the molecular beam can be obtained by fitting eq. (2) to the experimental data.

On the other hand the flux of the atomic beam is determined by the oven temperature which is equilibrated with lithium atomic vapor.

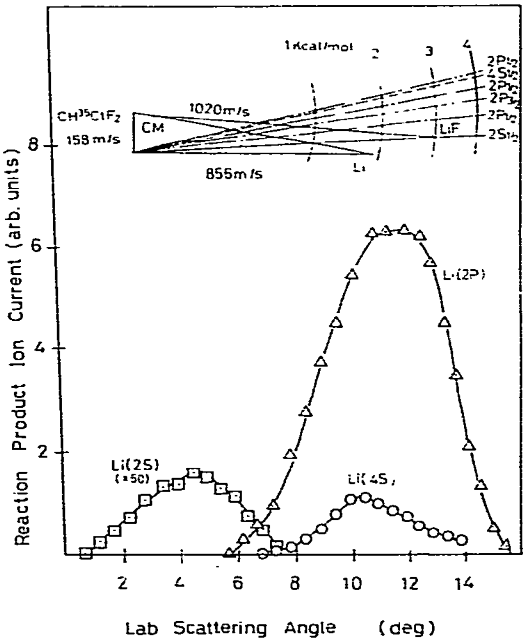

Fig. 3. Angular distribution of the isotopically non-selective reaction product LiF produced by the reaction of CHClF$_2$ with the lithium atom excited with a broadband laser. The molecular isotope detected is LiF: the states used are the ground state (2S) and the excited states (2P and 4S).

3. Results

3.1. Reactivity of excited Li

When a lithium atom reacts with CHCl$_2$F, reaction products LiF and LiCl are observed. Fig. 3 shows the angular distribution of the product LiF obtained from reaction of Li atoms in the ground state (2S), lower excited level (2P) and higher excited level (4S) respectively. It is seen from fig. 3 that the 2P excited state Li has the highest reactivity and ground-state Li has very low reactivity against the target molecule. It is also found that although the LiF signal peak appears at 4.5° in the case of the reaction of the ground-state atom, it appears at around 11° in the case of a reaction with an excited atom (2P and 4S). The position of the peak is considered to depend on how much internal energy is converted to kinetic energy. The scattering angle would be much smaller, according as more internal energy is transferred to kinetic energy. These peaks which appear in the reaction process of the excited lithium atoms would actually consist of two separate peaks, if selectively excited as shown in the following sections. However in this case a single peak appears, because simultaneously excitation and reaction of ^{6}Li and ^{7}Li with CHCl$_2$F takes place.

In the case of the angular distribution of the other reaction product, LiCl, taken under the same experimental conditions as mentioned above, the trend of the angular distribution of reactivity is similar to the one obtained for LiF, while the peak positions are closer to the atomic beam position. This would mean that LiCl has less energy distributed to the internal state and much energy is given to the translational mode. A Newton diagram for this reaction system is shown in fig. 3 for the case of LiF production, where the directions of the reaction products are illustrated for the 2S ground state and the 2P and 4S excited states.

3.2. Apparent activation energy

Fig. 4 shows an Arrhenius plot of the LiF and LiCl products for the ground (2S) and excited state (2P and 4S) lithium atom, from which the apparent activation energies are obtained, i.e. 0.349 kcal/mol (LiF) or 0.196 kcal/mol(LiCl) for ground-state Li, and 0.125 kcal/mol (LiF) and 0.0768 kcal/mol(LiCl) for excited-state Li. Accordingly the apparent activation energy is lowered by 0.224 kcal/mol(LiF) and 0.119 kcal/mol(LiCl) for reactions of laser-excited Li. The changes in activation energy obtained for reactions between the ground state and the excited states are very small compared with the photon energy incident on the atoms. This might be due to the fact that there are many paths included in these reactions and moreover there are differences in the reaction paths between the excited lithium atoms and the ground-state ones. These apparently small energy changes for the reactivity enhancement are compensated, if the activation entropy is taken into consideration.

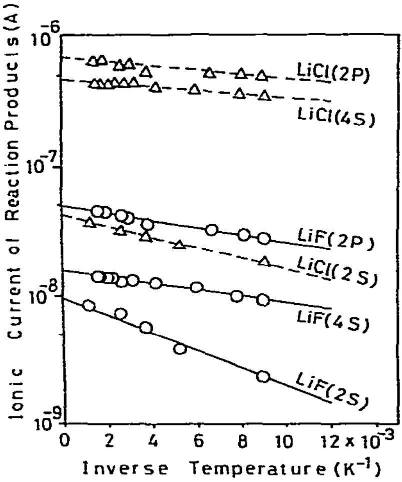

Fig. 4. Arrhenius plot for the reaction products LiF and LiCl with and without chemical reaction enhancement by laser irradiation. The molecular isotopes detected are LiF and LiCl; the atomic isotopes excited are both ^{6}Li and ^{7}Li; the states used are the excited state (2P, 4S) and the ground state (2S) of ^{7}Li.

From the thermodynamic point of view, reactivity $\bar{k}$ can be described as follows.

$$\bar{k} = (\kappa T/h)\exp(\Delta S^{\neq}/R)\exp(-\Delta H^{\neq}/RT) \quad (4)$$

for the reaction system

$$A + BC \rightarrow A..B..C \rightarrow AB + C, \quad (5)$$

where A = Li, BC = CCl_2FH, AB = LiF or LiCl, C denotes radicals such as $\cdot$CHClF or : CHF_2, A..B..C is an activated complex (≠), h is Planck's constant, $\Delta H^{\neq}$ the activation energy and $\Delta S^{\neq}$ the activation entropy.

From the experimental data, the difference in the change of activation entropy are obtained with (ΔS_L) and without (ΔS_0) laser for LiF and LiCl reactions, i.e. $(\Delta S_L - \Delta S_0)/R = \ln(5.1 - 60/t)$ for LiF and $\ln(15 - 584/t)$ for LiCl respectively.

3.3. Isotope separation

Fig. 5 shows schematically the isotope shifts of lithium atom resulting from 2S–2P and 2S–4S transitions. This isotope shift causes the isotopically selective reactivity. The laser linewidth used in this case is so narrow as to excite selectively each isotope via two transition schemes $2S_{1/2}$–$2P_{1/2}$ (^{6}Li) and $2S_{1/2}$–$2P_{3/2}$(^{7}Li) which are spectroscopically separated by more than 20 GHz, but is not so narrow as to excite the ^{6}Li isotope selectively via the transition $2S_{1/2}$–$2P_{1/2}$ (^{6}Li) as shown in fig. 5, because the energy difference between $2P_{1/2}$(^{7}Li) and $2P_{3/2}$(^{6}Li) is only 0.84 GHz.

The difference in the chemical reactivity shown in the previous section can be applied to the isotope separation of ^{7}Li or ^{6}Li.

Fig. 6 shows the angular distribution of ^{6}LiF and ^{7}LiF when ^{6}Li, excited selectively to the $2P_{3/2}$ state, reacts with the partner molecule. It is found that the natural ^{6}Li isotopic abundance of 7.5% enhances up to ≈ 50% at the peak position of the

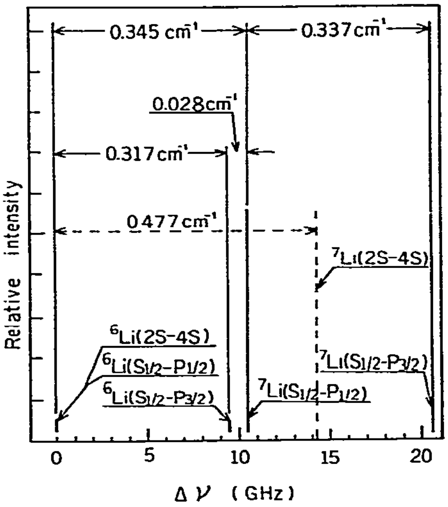

Fig. 5. Isotope shifts resulting from 2S–2P and 2S–4S transitions. Relative positions are shown. Solid lines: 2S–2P; dotted line: 2S–4S.

^{6}LiF ionic current. An enrichment of 25% is obtained if the ionic current is integrated between 4 and 18°.

On the other hand, from the angular distributions of the two isotopes in the reaction products ^{7}LiF and ^{6}LiF produced by the reaction of Li and $CHClF_2$, it is found that natural lithium with 92.5% ^{7}Li isotopic abundance is enriched up to 99.9% and a ^{7}Li enrichment of 98% will be obtained for the integrated ionic current between 4 and 16°, when the laser wavelength is tuned to the resonant excitation level of ^{7}Li.

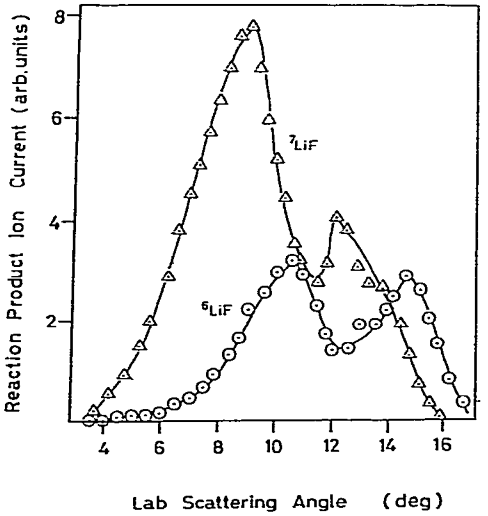

Fig. 6. Angular distribution of the isotopically selective reaction products LiF produced by the reaction with $CHClF_2$. The molecular isotopes detected ^{6}LiF and ^{7}LiF; the atomic isotope excited is ^{6}Li; the state used is the excited $2P_{3/2}$ state.

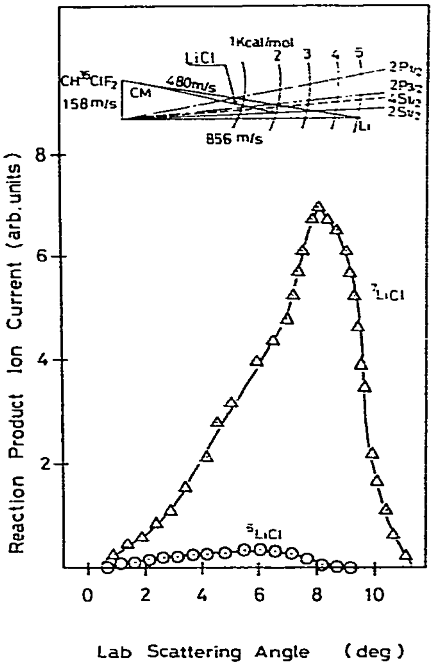

Fig. 7. Angular distribution of the isotopically non-selective reaction product LiCl produced by the reaction with $CHClF_2$. The molecular isotopes detected ^{6}LiCl and ^{7}LiCl; the atomic isotope excited is ^{6}Li; the state used is the excited $2P_{3/2}$ state.

Fig. 7 shows the angular distributions of ^{6}LiCl and ^{7}LiCl in the same experimental conditions. In this case no change in the isotopic abundance ratio, that is, no enrichment is observed.

In the above experiments the LiF peak is split into two different peaks, whereas LiCl has a single peak.

4. Discussion

The following results are obtained in the laser enhanced chemical reaction of Li with $CHClF_2$.

(1) LiF is more easily produced when ground-state Li reacts, and LiCl is more easily produced when laser-excited Li reacts with $CClF_2H$. This may happen because the reaction paths in the two processes are different.

(2) There are some angle differences in the maximum yield of reaction products among the ground and the two excited states. The difference might be based on the discrepancies of the reaction paths and the internal state of final reaction products.

(3) When one of the lithium isotopes is excited by the laser beam with a specified wavelength, it is isotopically enriched in the reaction product LiF, but not in the other reaction product LiCl.

(4) Two different peaks are found in the angular distribution of the reaction product yield between ^{6}LiF and ^{7}LiF, when one of Li isotopes is selectively excited, and moreover the peaks differ in their positions. This difference is based on the mass difference of the lithium atoms.

(5) Even when ^{6}Li is selectively excited and ^{7}Li is not, the ^{7}LiF production rate is extremely enhanced. And in this case, the peak height of the LiF yield at lower angles is considerably decreased as compared with ^{7}LiF, but the peak in LiF yield at higher angular position is almost the same among the two isotopic reaction products of LiF. This may be due to the fact that LiF pertaining to the latter peak is not influenced by the laser excitation.

(6) In the reaction product LiCl, there are no isotopic changes in the Li atoms.

From the above results, the following reaction processes are considered to be included.

(i) Main reactions not related to the laser irradiation:

$$Li + CHClF_2 \rightarrow LiCl + {}^{\cdot}CHF_2, \qquad (R1)$$

$$Li + {}^{\cdot}CHF_2 \rightarrow LiF + :CHF. \qquad (R2)$$

(ii) Main reactions directly related to the laser irradiation:

$$Li + h\nu \rightarrow Li^*, \qquad (R3)$$

$$Li^* + CHClF_2 \rightarrow LiF + {}^{\cdot}CHClF, \qquad (R4)$$

$$Li^* + CHClF_2 \rightarrow LiCl + {}^{\cdot}CHF_2. \qquad (R5)$$

(iii) Main reactions indirectly related to the laser irradiation (this may be frequently caused in a relatively reactive atomic or molecular beam collision):

$$Li + {}^{\cdot}CHClF \rightarrow LiCl + :CHF, \qquad (R6)$$

$$Li + {}^{\cdot}CHClF \rightarrow LiF + :CHCl. \qquad (R7)$$

It can be assumed that the laser-excited lithium atoms rarely react with the radicals which are previously produced through the reaction of excited Li and the target molecule, because the lifetime of lithium atoms is as short as 15 ns (2P state). And moreover any reaction product is thoroughly swept away by the subsequent laser pulse.

The –F and –Cl bond have about 120 and 80 kcal/mol bonding energy respectively. Therefore under a selective excitation conditions, LiCl tends to be produced more easily. However, in the above reactions, reactivities of the reaction schemes (R1) and (R2) without laser irradiation are so low that the reaction products LiF and LiCl have no great influence on the laser-enhanced reaction. Excited Li denoted by the symbol Li* which is shown in process (R3) produces LiF selectively through (R4). The ·CHClF radical generated by this reaction leads to a reaction with ground-state Li atom, and LiCl is produced. Laser-enhanced LiF product is produced through processes (R4) and (R7). This results in the two separate peaks, one of which is produced by the isotope-selective reaction (R4) and the other is related with the non-selective process (R7). And all of the LiCl products are produced via isotopically non-selective chemical reaction processes (R1) and (R6).

To summarize the reaction processes of LiF formation, they are explained as follows. Without laser excitation, the –F bond which has ≈ 120 kcal/mol reacts with Li against the 0.349 kcal/mol activation energy and 3.3 kcal/mol K activation entropy and it is fixed as LiF with a bonding energy of 137 kcal/mol. And the Li atom excited to the higher level which has 41.3 kcal/mol more energy than the ground state for the 2S–2P excitation reacts with the –F bonding against 0.224 kcal/mol activation energy and 3.3 kcal/mol K activation entropy. As a result, the selectively excited LiF isotope is produced with an enhanced reaction rate. Therefore the amount of LiF produced through reaction (R4) exceeds that from reaction (R7), which results in isotope separation.

On the other hand the –Cl bond which has somewhat lower bonding energy than the –F bond reacts with Li more easily than the –F bond under the condition of no laser irradiation, against 0.196 kcal/mol activation energy and 5.4 kcal/mol K activation entropy. In contrast to the LiF formation process, however, the amount of LiCl which is produced through the isotope selective reaction (R5) is far less than that produced by reaction (R6). That is, the laser-excited Li reacts with $CClF_2H$ and produces LiF resonantly, whereas LiCl is mainly produced through non-resonant processes.

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