Unusual Isotope Effects of Molybdenum in Chemical Exchange Reaction Using Dicyclohexano-18-Crown-6

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Molybdenum isotopes were fractionated in a liquid–liquid extraction system using dicyclohexano-18-crown-6 (DC18C6). The enrichment factors showed a breakdown of the conventional mass-dependent rule. Some unusual and larger isotope effects were observed in the even atomic mass isotopes, ^{92}Mo and ^{94}Mo. The unusual features in the present study were not responsible for the field shift effect, which was regarded as a primary factor of the anomalous isotope effect in the recent theory, but were due to an anomaly on the vibrational levels. The largest isotope effect was observed in the isotope pair of ^{94}Mo–^{96}Mo, it was $\varepsilon_{96,94}$ = 0.0086±0.0007, its initial aqueous phase was 0.91 M molybdenum chloride, and its organic phase was 0.2 M DC18C6 in chloroform: this was 0.0043±0.0004 in terms of the enrichment factor for unit mass difference.

A partition function ratio of one isotope to another accounts for the isotope effect in a chemical exchange reaction. In 1947, Bigeleisen and Mayer[1] have established the mass-dependent isotope effect for relatively heavier elements: i.e., the enrichment factor is shown by the change of reduced partition function ratios between one isotopomer and the other. The well-known Bigeleisen–Mayer function is described by the logarithm of the reduced partition function ratio,

$$\ln(s/s')f = (1/24)(h\nu/kT)^2(\delta m/mm')nM, \quad (1)$$

where δm is the isotopic mass difference of the masses m and m'. The mass of the ligand and the number of ligands are shown by M and n, respectively. The vibrational frequency is shown by ν, and h, k, and T have the usual meanings in physical chemistry. This formulation shows that the isotope enrichment factor must have the linear dependency on the atomic mass difference of the isotopes in the isotopomer.

Recent studies[2—14] have shown that isotope effects are not always in linear dependencies to the mass differences of the isotopes. Nishizawa and co-workers[2] have first reported the isotope effects as contrary to the mass-dependent isotope effects on zinc isotope enrichment in a solvent extraction using a macrocyclic ligand of dicyclohexano-18-crown-6 (DC18C6). In 1995, they have commented during a study of strontium isotope separation[3] that the isotope enrichment factors have similar features with the changes in the nuclear charge distributions, $\delta\langle r^2\rangle$.

The nuclear charge distribution gives an electronic field that determines the energy of the atomic electrons. A change in the energy level arising from a difference in this field between isotopes is well known as a field shift of isotope shifts in atomic spectra.[15,16] The chemical isotope effect due to the field shift is called the field shift effect or the nuclear size and shape effect. The Bigeleisen–Mayer equation is based on the Born–Oppenheimer approximation and uses an isotope-independent potential energy and simple harmonic oscillations. The field shifts due to the different sizes and shapes of isotope nuclei lead to shifts in the minimum in the potential energy. The field shift effect in the minimum in the potential energy was independently suggested by Bigeleisen[17,18] and by Fujii et al.[19] regarding the anomalous isotope effect of ^{235}U. In 1996, they have presented the new theory which adds a correction term to the field shift effect in Eq. 1.[17—19] The isotope enrichment factor, ε, is shown as

$$\varepsilon = a(hc/kT)fs + b(1/24)(h/2\pi kT)^2(\delta m/mm'), \quad (2)$$

where fs is the field shift, and a is the scaling factor of the field shift effect term and b is the scaling factor of the Bigeleisen–Mayer term. The anomalous aspects of the isotope enrichment factors are described as the field shift effect in the first term of this equation in recent experiments on the unusual isotope effects.[5—14,17—19]

The field shift effect in the vibrational-rotational frequency of diatomic molecules has been investigated by Tiemann[20] and by Schlembach.[21] They have reported that the field shift effect dominates the isotopic change of the vibrational frequency in lead or thallium compound, and have theoretically deduced the nuclear size and shape effect. The chemical isotope effect involves the field shift effect in the minimum in the potential energy and that in the vibrational levels. However, the field shift effect in the vibrational levels is calculated to be small compared with that in the minimum in potential curve by Bigeleisen.[22]

Besides the nuclear mass effect and the nuclear size and

shape effect, the larger isotope effect have been observed on the odd atomic mass isotopes of the even atomic number elements,[7,9,11] which have the nuclear spin. The isotope effect of the isotopes arising from the nuclear spin requires another correction term of the nuclear spin effect, $\ln K_{hf}$,[17] in Eq. 2. In the recent works on the spectroscopic analysis of rovibrational lines, Knöckel[23] and Tiemann[24] have reported that the vibrational levels have the hyperfine structure as in the case with the atomic orbital. We have estimated the nuclear spin effect as a function of the number of the hyperfine splitting vibrational levels on titanium isotope enrichment.[6]

We have investigated the isotope separation effects of numerous elements in the liquid–liquid extraction using DC18C6,[6–9,12–14] and have found that the unusual aspect occurs clearly on the transition elements. We have already reported the isotope effects on such transition elements as titanium,[6] chromium,[7] iron,[8] nicke,[9] and zinc[10,11] in the first long period and zirconium[12] in the second long period. In the present study, we will report molybdenum isotope effects fractionated by a liquid–liquid extraction method using DC18C6: we deal with the even atomic mass isotopes of molybdenum, because they are free from the nuclear spin effect.

Experimental

Liquid–Liquid Extraction Procedure. Dicyclohexano-18-crown-6 (DC18C6) was a product of Aldrich Chemical Company. Molybdenum(V) chloride, 99.9% purity, was obtained from Wako Pure Chemical Industries. A stock solution of 0.91 mol dm^{-3} molybdenum(V) in 0.1 M HCl (1 M = 1 mol dm^{-3}) was prepared by dissolving molybdenum chloride in hydrochloric acid. This solution was then diluted with water and hydrochloric acid in order to obtain 0.18 M molybdenum in various concentrations of HCl. These solutions served as the aqueous phase for the liquid–liquid extraction. The organic phase was 0.2 M solution of DC18C6 in chloroform.

Each 20 cm^3 solution of the aqueous solution of molybdenum(V) chloride and the organic solution of DC18C6 was mixed in a flat-bottomed flask and stirred by a magnetic stirrer for 30 min. Then the mixed solution was transferred into a separating funnel and kept motionless for 90 min. These procedures were carried out at 273.2±0.5 K. After the extraction procedures, two phases were separated. The separated organic phase was scrubbed with 0.1 M HCl. Molybdenum concentration in the stripping water was analyzed by ICP-AES (Shimadzu ICPS-7500).

Isotopic Analysis. The molybdenum chloride salt in the back-extraction solution was dried once by heating. In order to decompose residual organic substances, 3 cm^3 of 14 M HNO_3 was added to the dried salt and heated for 30 min on a hot plate at 423 K; after that, 1 cm^3 of 30% H_2O_2 was added. Then the solution was heated to dryness at 373 K.

The salt was dissolved in the mixed acid of 2.0 M HNO_3 and 2.0 M HCl and 3 drops of H_2O_2, and the sample solution of 1000 ppm molybdenum was prepared for the analysis of isotopic composition. Each solution of 10 μl (10 μg of Mo) was loaded onto a rhenium evaporation filament of a double filament system. The yellow-white salt on the filament was confirmrd to be MoO_2Cl_2.[25] The isotopic analysis was performed using a mass spectrometer with a multicollector system (Finnigan MAT262).

Rhenium filaments contained trace amounts of zirconium, molybdenum, and ruthenium. The ion current was measured with a secondary electron multiplier; the ion currents of the impurities contained in the filaments were thus found to be less than 0.5 mV in digital output, which was below the detection limit of Faraday cups. Interference of these isotopes in the filaments was small enough to be negligible in the isotopic analysis. The ionization filament was heated to the 500 mV of ^{187}Re in digital output. Then the temperature of the evaporation filament raised to attain the appropriate measurement range in 1 V as the total molybdenum ion beam. Because there was less interference to ^{95}Mo, we measured the isotope ratio, ^{m}Mo/^{95}Mo as the isotope composition, where the superscript m signifies mass number 92, 94, 96, 98, or 100. We monitored the digital output of ^{90}Zr and ^{99}Ru before starting the isotope ratio measurement; it was under the detection limit of the mass spectrometer. The isotopic analysis of the present study was free from the interference of zirconium and ruthenium as the contaminants in the sample solution. The species of $MoO^+$and $MoCl^+$ were also undetectable. The multicollector system made it possible to obtain accurate data of molybdenum isotope ratios. The precision of the measured isotope ratio was less than 0.045% (1 SD).

Results and Discussion

Definitions. The single stage isotope separation factor, $\alpha_{98,m}$, for molybdenum in the present system is defined as

$$\alpha_{98,m} = ([^m\mathrm{Mo}]/[^{98}\mathrm{Mo}])_{org}/([^m\mathrm{Mo}]/[^{98}\mathrm{Mo}])_{aq}, \quad (3)$$

where $([^m\mathrm{Mo}]/[^{98}\mathrm{Mo}])_{org}$ and $([^m\mathrm{Mo}]/[^{98}\mathrm{Mo}])_{aq}$ are the isotope ratios of ^{m}Mo relative to ^{98}Mo found in the organic and aqueous phases, respectively. The superscript m signifies mass number 92, 94, 96, or 100. The isotope enrichment factor, $\varepsilon_{95,m}$, is defined as

$$\varepsilon_{98,m} = \alpha_{98,m} - 1 \approx \ln \alpha_{98,m} \quad (|\ln \alpha_{98,m}| \ll 1). \quad (4)$$

Isotope Enrichment Factors. The equation of the extraction equilibrium is simply shown as

$$(Mo^{5+})_{aq} + 5(Cl^-)_{aq} + (L)_{org} = (MoLCl_5)_{org}, \quad (5)$$

where $(L)_{org}$ and $(MoLCl_5)_{org}$ are DC18C6 and the molybdenum complex in the equilibrium, respectively. Suffix aq or org indicates the chemical species in parentheses found in the aqueous phase or that in the organic phase. The equilibrium constant, K, in Eq. 5 is shown as a function of the activities of the chemical species:

$$K = [MoLCl_5]_{org}/([Mo^{5+}]_{aq}[Cl^-]_{aq}^5[L]_{org}). \quad (6)$$

The partition coefficient is

$$D = [Mo]_{org}/[Mo]_{aq}. \quad (7)$$

We can obtain the following equation from Eqs. 6 and 7:

$$\log D = 5\log [Cl^-]_{aq} + \log [L]_{org} + \log K, \quad (8)$$

If the concentration of the extracted complex, $(MoLCl_5)_{org}$, is very much smaller than the concentrations of $(Mo^{5+})_{aq}$, $(Cl^-)_{aq}$, and $(L)_{org}$ in the equilibrium, the activities of $(Cl^-)_{aq}$ and $(L)_{org}$ in the initial phases can be applied into Eq. 8. Since we fixed the concentration of DC18C6 at 0.2 M in this study, Eq. 8 can be rewritten,

$$\log D = 5\log [Cl^-]_{aq} + C, \quad (9)$$

where C is a constant. The logarithm of the partition coefficient is illustrated in Fig. 1 as a function of the logarithm of the initial concentration of the chloride ion which is supplied from molybdenum chloride and HCl. We can delineate two straight lines having different slopes in Fig. 1. In the diluted aqueous phase, the molybdenum chloride and HCl dissociate completely, so the activity coefficient can be treated as unity, and thus the activity of Cl^- can be treated as the concentration of it. The slope of the line in the diluted region is 4.0. This means that the extracted species do not have the configuration of 1 : 5 for molybdynum : chlorine, but the atomic ratio of chlorine to molybdenum in the crown-complex is 4.0.

The color of the initial aqueous solutions in the diluted region is red-brown: The stock solution remained dark red-brown. The color turns into green with increase of the concentration of hydrochloric acid. We can obtain a larger partition coefficient by use of the green solution of the molybdenum chloride in the concentrated HCl than the brown solution in the diluted HCl. In the aqueous chemistry of molybdenum, the emerald green pentachlorooxomolybdate(V) ion, $[MoOCl_5]^{2-}$, is well known to exist in the concentrated HCl.[26] With the decrease of acidity, equilibria involving dimeric oxo species of molybdenum(V) occur: The red-brown species is recognized to be $[(MoOCl_4)_2O]^{4-}$ with a Mo–O–Mo bridge.[26] This red-brown complex has the configuration of 1 : 4 for molybdenum : chlorine. Thus, $H_4(MoOCl_4)_2O$ is assured to be extracted in the diluted region of HCl, while H_2MoOCl_5 is extracted in the concentrated region of HCl. We evaluate the isotope enrichment factors on 0.91 M molybdenum in 0.1 M HCl system as the isotope effect on $H_4(MoOCl_4)_2O$-crown complex and those on 0.18 M molybdenum in 4.0 M HCl system as the isotope effect on H_2MoOCl_5-crown complex. The maximum partition coefficient is observed on 0.18 M molybdenum in the concentrated HCl of 9.6 M system; $D = 13.8$. This means 93% molybdenum in the initial aqueous phase is extracted into the organic phase. Without the crown ether, the partition coefficient on this system is under the detection limit of ICP-AES; $D \ll 10^{-6}$.

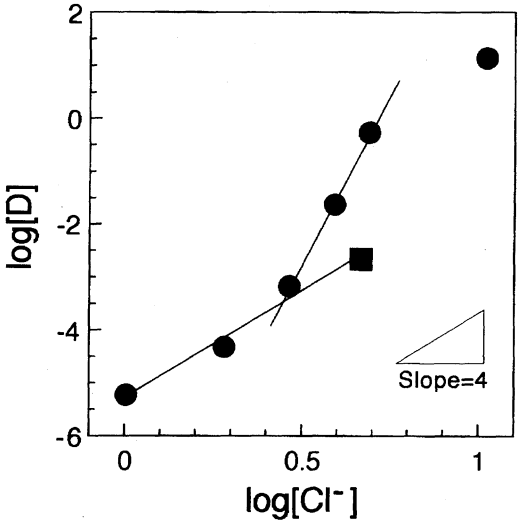

Fig. 1. Logarithm of partition coefficient (D) against logarithm of concentration of Cl^- in the initial aqueous phase. The initial molybdenum concentration of the solid circles is fixed at 0.18 M, and the initial HCl concentrations of them are 0.1 M, 1.0 M, 2.0 M, 3.0 M, 4.0 M, and 9.6 M (from left to right). The initial aqueous phase of the solid square is the stock solution of 9.1 M molybdenum in 0.1 M HCl. The concentration of Cl^- in the diluted region can be treated as the activity.

The isotope enrichment factors of molybdenum are illustrated as a function of mass number in Figs. 2 and 3 together with the experimental errors. The enrichment factors shown in Fig. 2 are obtained under the condition of 0.91 M molyb-

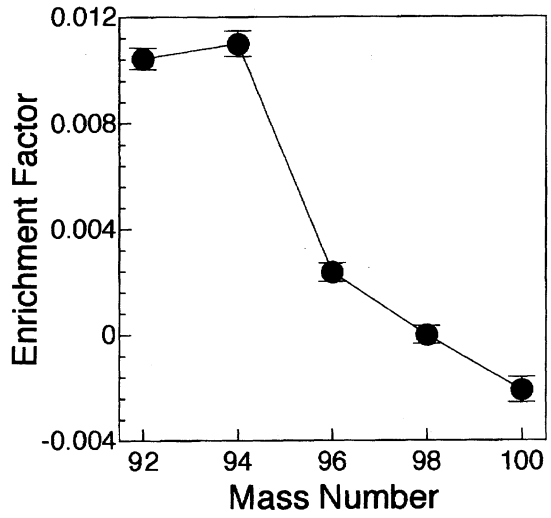

Fig. 2. Isotope enrichment factors as a function of mass number.
The initial condition of aqueous phase is 0.91 M of molybdenum in 0.1 M HCl.

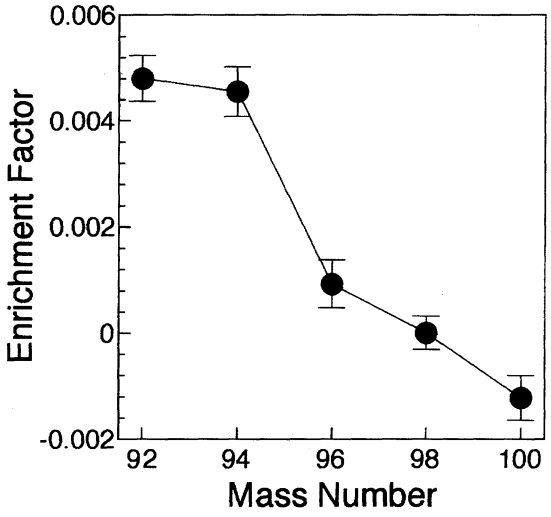

Fig. 3. Isotope enrichment factors as a function of mass number.
The initial condition of aqueous phase is 0.18 M of molybdenum in 4.0 M HCl.

denum in 0.1 M HCl as the initial aqueous phase and those in Fig. 3 are of 0.18 M molybdenum in 4.0 M HCl. Experimental results in Figs. 2 and 3 show a breakdown of the mass-dependent rule of the Bigeleisen–Mayer formulization. Unusual and larger isotope effects can be seen on the isotopes, ^{92}Mo and ^{94}Mo: the magnitude of $\varepsilon_{98,92}$ is equal to that of $\varepsilon_{98,94}$ within their experimental errors. The magnitudes of enrichment factors in Fig. 2 are almost twice as large as those in Fig. 3. This shows that the isotope enrichment in $H_4(MoOCl_4)_2O$-crown complex is more effective than that in H_2MoOCl_5-crown complex, but the unusual isotope effects of ^{92}Mo and ^{94}Mo occur in both complexes. The largest isotope effect is observed in the isotope pair of ^{94}Mo–^{96}Mo, to be $\varepsilon_{96,94} = 0.0086 \pm 0.0007$, on 0.91 M molybdenum in 0.1 M HCl system as shown in Fig. 2: this is 0.0043±0.0004 in terms of the enrichment factor for unit mass difference.

Unusual Isotope Effect of ^{92}Mo and ^{94}Mo. The obvious unusual isotope effects of the even atomic mass isotopes, ^{92}Mo and ^{94}Mo, can be recognized in Figs. 2 and 3. These isotopes are not interfered with by the zirconium contaminants of ^{92}Zr and ^{94}Zr that we mentioned above. The nuclear spins of the even atomic mass isotopes of molybdenum have the finite value of zero. Thus, they are irrelevant to the nuclear spin effect. Suppose the field shift term in the recent theory of Eq. 2 is the reason of the unusual isotope effect, the anomalous aspect of isotope enrichment factors should imitate closely the nuclear charge distributions. The nuclear charge distributions of molybdenum isotope nuclei are precisely measured by muonic X-ray spectra.[27] The changes in mean square radii, $\delta\langle r^2\rangle$, from ^{98}Mo are shown in Fig. 4, which are reproduced from the data obtained by the muonic atoms. It is clear that the mean square radii have almost a linear dependency to the atomic mass. Because of the linearity of $\delta\langle r^2\rangle$ to the mass number, it is hard to estimate separately the contribution of the nuclear mass ($\delta m/mm'$), and that of the nuclear size and shape. In all cases, the unusual isotope

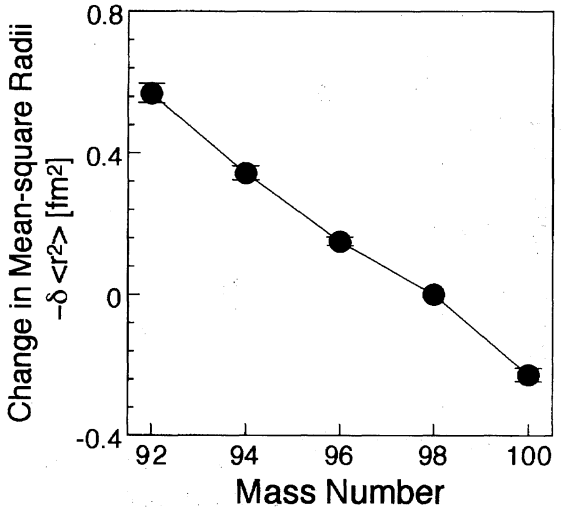

Fig. 4. Change in mean square radii as a function of mass number.
The magnitudes of $\delta\langle r^2\rangle$ are obtained by Schellenberg et al.[27] via muonic X-ray spectra.

effects of ^{92}Mo and ^{94}Mo are unconcerned with the nuclear mass effect and the field shift effect. The field shift effect of the recent theory in Eq. 2 is not an appropriate reason for the unusual isotope effect of ^{92}Mo and ^{94}Mo in the molybdenum-crown complex.

Isotope Effect due to Anomalies in Vibrational Levels. Generally, the vibrational frequency is regarded as $\nu = (\varkappa/\mu)^{1/2}/2\pi$, where $\varkappa$ and μ are the force constant and the reduced mass between the isotope and the ligand, respectively. The isotopic difference of the vibrational frequency results from the isotopic difference of the force constant, $\delta\varkappa$, and that of the reduced mass, $\delta\mu$. The conventional mass-dependent theory as shown in Eq. 1 is derived from $\delta\mu$ by use of the isotope-independent force constant, $\delta\varkappa = 0$. The force constant difference is expressed as a function of the change in the nuclear charge radii, $\delta\langle r^2\rangle$.[21] Hence, the isotope effect due to the force constant results in another nuclear field shift effect in addition to the field shift effect in the minimum potential energy. The vibrational frequency shift of the isotopes is a function of the reduced mass and the nuclear charge distribution. The change in mean-square radii of the even atomic mass isotope of molybdenum shows the linear dependency to the atomic mass that we mentioned above. The field shift effect in the vibrational frequency cannot account for the unusual isotope effect of ^{92}Mo and ^{94}Mo. There must be unusual and large shifts in the vibrational frequency between the isotopomers of molybdenum-crown complex along with the field shift and the mass shift.

In the study of the optical spectroscopy of $^{m}Mo^{16}O$, the unusual isotopic frequency shifts of the vibrational band have been observed.[28] In the transition from the ground state to an excited state, the upper vibrational band of $v = 2$ in the excited state has one unusual feature, which is irrelevant to the reduced mass and the nuclear charge radius. The changes in wave numbers from ^{98}Mo of this transition are shown in Fig. 5, as reproduced from the optical spectra. We can see that the positive deviation from ^{100}Mo is maximized at ^{94}Mo, and the negative deviation from the calminant of ^{94}Mo to ^{92}Mo.

The characteristics of the unusual isotope effects of ^{92}Mo and ^{94}Mo in Figs. 2 and 3 show close similarity to the aspect of the changes in wave numbers in Fig. 5. Suppose the vibrational levels of the vibration motion between molybdenum and oxygen in DC18C6 have the same feature as shown in Fig. 5; the anomalies of the vibrational energy will account for the unusual isotope effects of ^{92}Mo and ^{94}Mo. In the present study on the chemical isotope effect of molybdenum even atomic mass isotopes using DC18C6, we suggest the following equation adding yet another correction term to Eq. 2:

$$\varepsilon = \alpha\delta\langle r^2\rangle + b(\delta m/mm') + \ln K'. \quad (10)$$

The first term is the nuclear size and shape effect, the second term is the conventional Bigeleisen–Mayer term, the third term is the chemical isotope effect due to the anomalies in the vibrational levels.

In some recent works, the nuclear size and shape effect and/or the nuclear spin effect are explained as an unusual

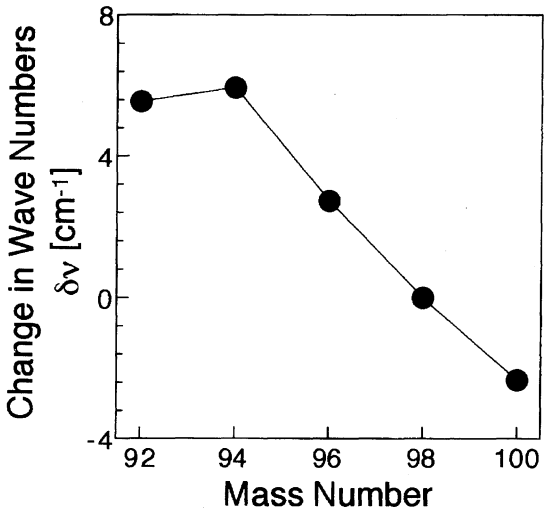

Fig. 5. Isotope shifts of vibrational band $v = 2$ in excited $^{m}Mo^{16}O$.
The changes in wave numbers in the optical spectra of $^{m}Mo^{16}O$ are measured by Hamrick et al.[28] within the uncertainty of 2%.

isotope effect disobeying the conventional Bigeleisen–Mayer formulization. However, if the vibrational levels have the anomalies, which are unconcerned with the nuclear mass, the nuclear size and shape or the nuclear spin, we must take account of the isotope effect due to the anomalous vibrational levels as shown in the last term in Eq. 10.

Conclusions

Molybdenum isotopes were fractionated in a liquid–liquid extraction system using DC18C6. The enrichment factors show a breakdown of the conventional Bigeleisen–Mayer approximation. Some unusual and larger isotope effects are observed in the even atomic mass isotopes, ^{92}Mo and ^{94}Mo. These unusual features are not due to the field shift effect in the recent theory, but to the anomalies on the vibrational levels. The largest isotope effect is observed in the isotope pair of ^{94}Mo–^{96}Mo, to be $\varepsilon_{96,94} = 0.0086 \pm 0.0007$, on 0.91 M molybdenum chloride system: This is 0.0043 ± 0.0004 in terms of the enrichment factor for unit mass difference.

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