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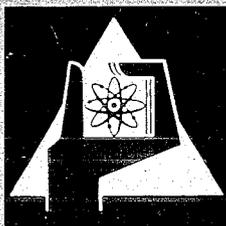
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THE DEPENDENCY OF THE CHEMICAL BEHAVIOUR OF MOLYBDENUM RECOIL ATOMS IN METAL CARBONYLS ON THE ENERGY AND THE ISOTOPE

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ABSTRACT

Different isotopes recoiling from nuclear reactions show sometimes
a difference in their chemical behaviour. With the view of studying
the causes for this difference target elements ranging from molybdenum
to indium were irradiated in close contact with $Cr(CO)_6$ with 600 MeV
protons. The ^{90}Mo and ^{93m}Mo recoil atoms having energies dependent
on the mass difference between target and product reacted with the
$Cr(CO)_6$ forming $Mo(CO)_6$. The yield of this reaction was determined
in dependency on the individual isotopes and their recoil energy.
Further $Mo(CO)_6$ was irradiated with 600 MeV protons, fast neutrons and
thermal neutrons. The percentage of ^{90}Mo, ^{93m}Mo and ^{99}Mo having the
configuration of the target (retention) was analysed dependent on
the individual isotopes and the irradiation conditions.

It was found in all cases that the retention of ^{93}Mo was higher than
that of ^{90}Mo and ^{99}Mo. The magnitude of this isotope effect was
independent of the recoil energy and the irradiation conditions. The
existence or non-existence of nuclear levels with sufficient life-time
($> 10^{-12}$ sec) in the deexcitation cascade of the excited recoiling
isotopes is quoted as cause for their different chemical behaviour.

10. Oktober 1969

INTRODUCTION

Atoms recoiling from nuclear reactions break in nearly all cases their chemical bonds.Having lost their excitation energy, they may react again chemically with their environment. The product spectrum resulting from these reactions depends on the chemical environment and the nuclear reaction.

Several studies showed, that different isotopes of the same element formed sometimes different product spectra in the same chemical environment. Mostly the different isotopes were produced by different nuclear reactions[1-5]. Sometimes, when the isotopic composition of the target was suitable, they were generated by thermal neutron capture[6-10]. In some cases also a different chemical behaviour of an isomeric state compared with the ground state was found[11,12].

This isotope effect must have its cause in the conditions, which are created by the irradiation and the nuclear reaction. The following factors affect these conditions:

1. The radiation dose received by the target.
2. The recoil energy of the atoms.
3. The decay mode of the originally highly excited recoil atoms.

When the isotope effect is studied with isotopes arising from different nuclear reactions, all three factors are of importance. When the different isotopes are produced by the same nuclear reaction, the radiation dose is constant and only the two remaining factors are important. Finally, isomers should have recoil energies which are not very different from the recoil energies of the same isotope in the ground state. Thus, it is probable at least in this case that the decay mode of the recoil atom is the most important factor resulting in an isotope effect, although a contribution of the recoil energy and the radiation dose can

not be excluded completely. Nuclear reactions with high energy particles (spallation) make it possible to study the influence of the recoil energy and of the decay mode of the excited isotopes independently. On one hand the different isotopes are produced under constant radiation conditions by the same nuclear reaction. On the other the dependency of the recoil energy on the mass difference between target and product gives the chance to vary the recoil energy using different target elements for the production of the same isotopes.

For this reason we irradiated target elements ranging from molybdenum to indium with 600 MeV protons. The targets were in close contact with metal carbonyl catchers. Thus the recoiling molybdenum isotopes ^{90}Mo and ^{93m}Mo could penetrate into the catcher and form molybdenum carbonyl. The percentage of the carbonyl formation (retention) was analysed for both isotopes and compared with experimentally determined recoil ranges (which are proportional to the recoil energies).

In another experiment we irradiated molybdenum carbonyl as a target with 600 MeV protons, fast neutrons and thermal neutrons and determined the retentions of ^{90}Mo, ^{93m}Mo and ^{99}Mo with respect to the different irradiation conditions.

The metal carbonyls were chosen as targets and catchers because of their very specific reaction with molybdenum recoil atoms[15]. Preceding studies which will be described elsewhere[16] showed that in our experiments molybdenum was the only spallation product which reacted with the metal carbonyls.

EXPERIMENTAL

Irradiations   Figure 1 shows the "mixed targets". They consisted of several metal foils of thickness 10 mg/cm^2 covered with a 0,5 mm layer of powdered Cr(CO)$_6$ serving as catcher. As target metals, Mo, Rh, Pd, Cd, Ag and In were chosen. The targets were

irradiated for 1 h at room temperature in the external beam of the CERN Synchrocyclotron. The flux of 600 MeV protons was 2.10^{10} p/cm^2.sec.

Figure 1

The Mo(CO)$_6$ targets consisted of powdered material which was sublimed under vacuum before the irradiation. The following irradiation conditions were chosen:

1. 200 mg Mo(CO)$_6$ packed in polyethylene foil were irradiated for 1 h and 10 h with 600 MeV protons.

2. 200 mg Mo(CO)$_6$ wrapped in silver foil (0,2 mm thick) were activated for 30 minutes with neutrons produced by the reaction of the 50 MeV deuterons of the Karlsruhe cyclotron with a beryllium target. The temperature did not exceed 30°C. The flux was 5.10^{11} n/cm^2.sec.

3. 20 mg Mo(CO)$_6$ packed in polyethylene foil were activated for 10 minutes in the thermal column of the Karlsruhe FR2 reactor with a flux of 3.10^{11} n/cm^2.sec. The irradiation temperature was either 60-70° C or dry ice temperature (- 79° C).

Chemical separations The retention was determined by separating the organic from the inorganic fraction either by extraction or by sublimation. In the case of the mixed targets, the Cr(CO)$_6$ layer was separated from the foils and sublimed under vacuum at 90°C. The yield of the sublimation was determined by weight. The Mo in the residue was separated from the other spallation products by the following procedure: The residue was dissolved in aqua regia and a known amount of Mo-VI was added. The solution was made 6,5 N with HCl and the Mo extracted with MIBK and backextracted with water. After a Fe(OH)$_3$ scavenger precipitation, the Mo was precipitated with α-benzoinoxime in 2N HCl, the precipitate extracted with ethylacetate and backextracted

with 2N ammonia. Acetic acid was added until pH 3 was reached and
the Mo precipitated with 8-hydroxyquinoline, filtered, dried, weighed
for the yield determination and mounted for counting. The sublimate
was dissolved in fuming nitric acid and handled in the same way as
the residue.

For the $Mo(CO)_6$ irradiated with 600 MeV protons the same procedure
was used, as far as the residue was concerned. The sublimate could
be measured directly because of the absence of the disturbing ^{48}Cr-
and ^{48}V-activities.

The $Mo(CO)_6$ targets irradiated with fast and thermal neutrons were
sublimed and the sublimate and the residue measured directly, since
no disturbing activities were present. The targets irradiated with
thermal neutrons at dry ice temperature were dissolved in cold $CHCl_3$,
the inorganic part extracted with 2N nitric acid and both solutions
measured directly.

Measurements   The γ-spectra of the Mo-fractions in the sublimate
and in the residue were recorded with a NaI(Tl) detector, but not
the fast neutron irradiated targets, for which a planar Ge(Li)
detector was used. The photopeaks of ^{93m}Mo, ^{99}Mo and ^{90}Nb (the daughter
of ^{90}Mo) were evaluated as to quantity. In the case of the samples
from the thermal neutron irradiations, the total γ-activity was
counted with a well type NaI(Tl) detector.

Determination of recoil ranges   The "thick target, thick catcher"
method[17] was used for an crude estimation of the ranges of ^{90}Mo and
^{93m}Mo atoms recoiling during the 600 MeV proton bombardment of
different target elements. Mo, Pd, Ag and In target foils were covered
with aluminum catcher foils in forward and backward direction with
respect to the proton beam. Each foil was thicker than the range of
the recoiling atoms. ^{90}Mo and ^{93m}Mo in the foils were separated and
counted according to the procedure described above for the mixed targets.

RESULTS

The results of the experiments are summarized in table I and table II.

Table I

In table I, the percentage of ^{90}Mo and ^{93m}Mo (the retention) which sublimed together with $Cr(CO)_6$, is given for the different target elements. In addition the recoil ranges are quoted for all cases where experimental determinations were done. There seems to be no significant difference in the retention values with increasing mass distance between target and product. However, the recoil ranges which are proportional to the recoil energy, increase by a factor of five, going from Mo to In. The retention of ^{93m}Mo was about 8 % higher as the retention of ^{90}Mo. The difference was not dependent of the target element. From these results, we conclude that in our system the retention is different for different isotopes and that it is independent of the recoil energy in the investigated energy region.

Table II shows the results of irradiations of $Mo(CO)_6$, this compound serving simultaneously as target and catcher. The bombarding particles varied as well as the irradiation conditions.

Table II

The ^{93m}Mo retention seems to be independent of the type of the nuclear reaction and also of the irradiation time. Thus, it is independent of the radiation dose received from the target. The ^{90}Mo retention shows some variation. But since the accuracy of the determination of this values was not very high, the variation may be accidental.

A comparison of the values of Table I and Table II shows nearly no difference between the "mixed targets" and the $Mo(CO)_6$ targets. Besides ^{90}Mo and ^{93m}Mo, also ^{99}Mo is generated with neutrons. Its retention is a little lower than that of ^{90}Mo and significantly lower than that of ^{93m}Mo. The magnitude of the isotope effect is about the same as in the case of the mixed targets. Our values for ^{90}Mo and ^{99}Mo are in good agreement with the results of Harbottle and Zahn[18]. Bombarding $Mo(CO)_6$ at liquid nitrogen temperature with 2 GeV protons, they found 75 % retention for ^{90}Mo and 73,7 % for ^{99}Mo.

The retention of ^{99}Mo produced with thermal neutrons was a little lower than that produced with fast particles. In this case the irradiation temperature had an pronounced effect on the magnitude of the retention. Thus, the $Mo(CO)_6$ irradiated with thermal neutrons showed annealing reactions. Attempts to anneal $Mo(CO)_6$, irradiated with fast particles, failed.

DISCUSSION

We do not want to speculate in the following section on the formation mechanism of the retention. From our experimental results we just want to draw some conclusions, concerning the isotope effect. In all cases investigated in this work evidently ^{93m}Mo had a higher retention than ^{90}Mo and ^{99}Mo. Mainly the three factors quoted in the introduction can be the reason for that. The first one, a different radiation dose received by the targets, can be excluded. The different isotopes were namely produced always together in the same target. Thus, ^{93m}Mo originated under exactly the same irradiation conditions as the other Mo isotopes. The second factor, the energy of the recoil atoms, can also be

excluded for the following reason. Variations of the recoil
energy by a factor of five did neither affect the absolute
retention values, nor the difference in retention between the
individual isotopes. A decrease in recoil energy by several
orders of magnitude, as in the case of the thermal neutron
irradiations, brought only a small reduction of the retention.
It is more probable that this reduction is caused by the
different irradiation conditions than by recoil energy. Our
results as well as other studies show namely that $Mo(CO)_6$
irradiated with moderate doses in the thermal column of
reactors is sensitive to radiation and thermal annealing. In
contrast to that, the conditions of the fast particle irradia-
tions do not affect the behaviour of the molybdenum recoil
atoms in the metal carbonyls. The relatively high doses seam
to lead to a saturation, at which variations have no further
effect.

There remains now the third factor, a difference in the
deexcitation mode of the individual excited molybdenum isotopes.
This cause which was proposed by several authors[13,14], we shall
discuss now a little more in detail. We shall restrict the
discussion to solids, since their retentions are mostly high
and the product spectra less manifold than in the liquid or
gas phase. Figure 2 shows the energy level scheme[21] of ^{60}Co and
its isomeric state ^{60m}Co. Producing this isotopes by thermal
neutron irradiation of inorganic Co-complexes Lazzarini found[12,22]
nearly always a higher retention for ^{60m}Co than for ^{60}Co. Keeping
in mind, that a fraction of ^{60}Co results from the decay of ^{60m}Co
during the irradiation, this isotope effect can be interpreted
in terms of a "two step" reaction. After the nuclear reaction,
the ^{60m}Co as well as the ^{60}Co recoil atoms slow down and react
in a first step with their chemical environment, forming a
certain percentage of retention.

Figure 2

A part of the ^{60}Co atoms, however, results from a secondary nuclear transformation, namely the decay of the ^{60m}Co. This highly converted isomeric transition leads in a second step to a destruction of the bonds formed in the first step, followed partly by a reformation. This effect causes consequently a decrease in retention. Or to say, the Co recoil atoms come to rest in a latice site with a certain defect concentration. This leads to the retention of the first step. For the case of a following isomeric transition, the defect concentration increases in the second step which causes mostly a decrease in retention.

A comparison of the behaviour of the isotopes ^{128}J and ^{130}J produced in NaJO$_3$ by thermal neutron irradiation led to similar results. The retention[9] of ^{130}J was ≈ 40 % lower than that of ^{128}J. Corresponding to the interpretation of the ^{60}Co results, the level schemes in figure 2 show, that a part of the ^{130}J is formed by a highly converted isomeric transition[23], coming from an isomeric state with 9 minutes half-life. Thus, a one step reaction causes probably the retention of ^{128}J and a two step reaction that of ^{130}J.

^{99}Mo and ^{90}Mo, the level schemes[21] of which are presented in figure 3, have no isomeres, contrary to these examples.

Figure 3

To understand this case, we have to pay attention to the fact that recoil atoms, after slowing down in solids, take their position in the lattice[23,24] in $\approx 10^{-12}$ sec, whilst the reformation of their electron shell is completed in $\approx 10^{-8}$ sec. This has the consequence that every deexcitation taking place 10^{-12} sec after the nuclear reaction or later may have an influence on the defect concentration around the recoil atom or requiring more than 10^{-8} sec may again destroy the

reformed electron shell. In principle there is no difference between such a transition if partly converted and the deexcitation of an isomeric state. In particular the transitions coming from rather long lived low-lying states are often highly converted. Figure 3 shows now that ^{99}Mo has such a low-lying level with a 10^{-5} sec life time. This is far long enough to cause a two step reaction and the corresponding decrease in retention. We can be quite sure that the retention is formed in a one step reaction for ^{93m}Mo, since its spin has the unusual high value 21/2. Above this level no states with higher spins are known[25]. Thus, converted transitions with life times long enough for a second step should be very seldom events. This interpretation agrees with the findings of a higher retention for ^{93m}Mo than for the other isotopes. Unfortunately no data concerning the ^{90}Mo levels are available.

Not for all systems studied, the two step reaction yields a lower retention than the one step reaction. Comparing ^{80m}Br with ^{82}Br which originates partly from the decay of an isomer of 6 minutes half-life, a higher retention for ^{82}Br was determined in some compounds[10,25]. But since in other compounds no difference[26] or a higher retention[8] for ^{80m}Br were found, this case can not be understood on all evidence that is available. Summarizing, we can say that the existence or non-existence of nuclear levels with sufficient life-time ($> 10^{-12}$ sec), decaying partly by internal conversion in the deexcitation cascade, may cause differences in the chemical behaviour of isotopes recoiling from a nuclear reaction. Predictions about the magnitude and the direction of the isotope effect are difficult in the light of the experimental data presently available.

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TABLE I

The percentage of the retention of molybdenum recoil atoms, produced by 600 MeV protons in different target elements in contact with $Cr(CO)_6$.

target	Mo	Rh	Pd	Ag	Cd	In	mean value
^{93m}Mo - Retention %	79.0 ± 2	80.6 ± 2	81.2 ± 2	81.0 ± 2	78.6 ± 2	80.5 ± 2	80.2
^{90}Mo - Retention %	70.0 ± 3	70.6 ± 3	—	74.5 ± 3	73.0 ± 3	71.1 ± 3	71.8
recoil ranges ^{90}Mo in mg/cm^2 of the target	0.11	—	0.49	0.53	—	0.64	
^{93m}Mo	0.21	—	0.64	0.60	—	0.64	

TABLE II

The percentage of the retention of molybdenum recoil atoms, produced under different irradiation conditions in $Mo(CO)_6$.

Irradiation conditions	protons 600 MeV 1 h	protons 600 MeV 10 h	neutrons 50 MeV 30 m	thermal neutrons 60°C	thermal neutrons -78°C
^{93m}Mo-Retention %	80.6 ± 2	79.7 ± 2	79.6 ± 1		
^{90}Mo-Retention %	72.0 ± 2	69.0 ± 2	75.0 ± 2		
^{99}Mo-Retention %			70.0±1.5	66 ± 2	40 ± 4

Figure 1

Arrangement of the "mixed targets" consisting of metal foils as target and $Cr(CO)_6$ as catcher.
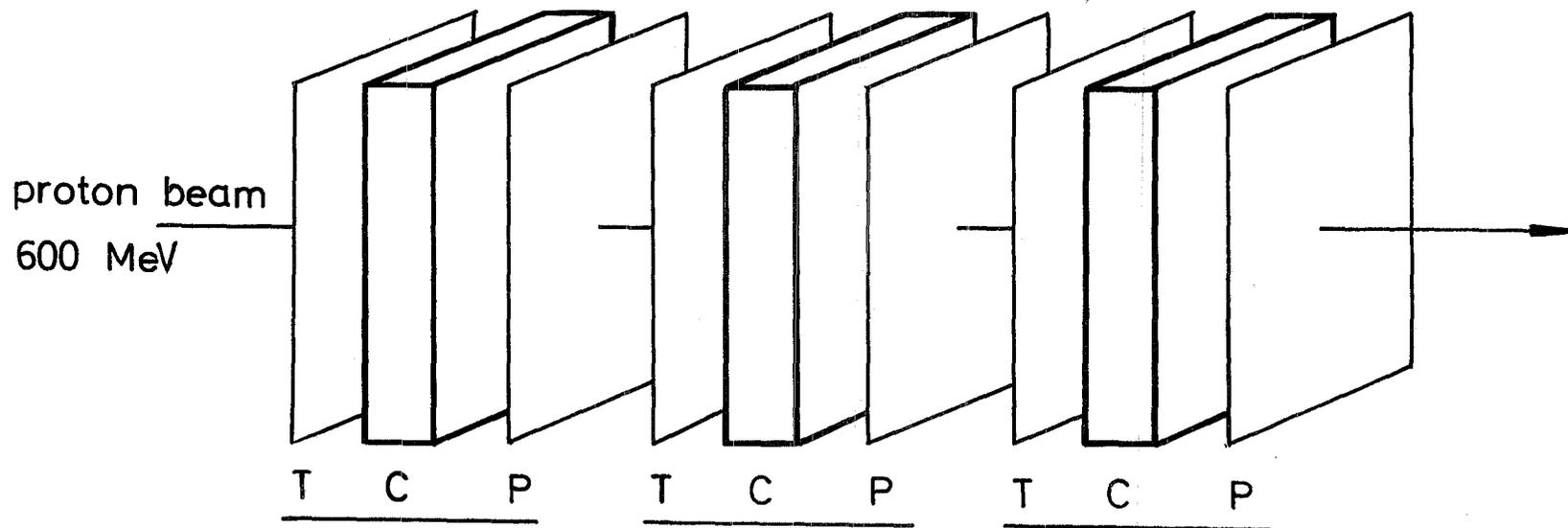
T   target foil   (Mo, Rh, Pd, Ag, Cd, In)

C   powdered $Cr(CO)_6$ layer, 0.5 mm thick

P   PVC foil

Figure 2

Energy levels of the isomeric pair ^{60m}Co and ^{60}Co and of ^{128}J and ^{130}J.
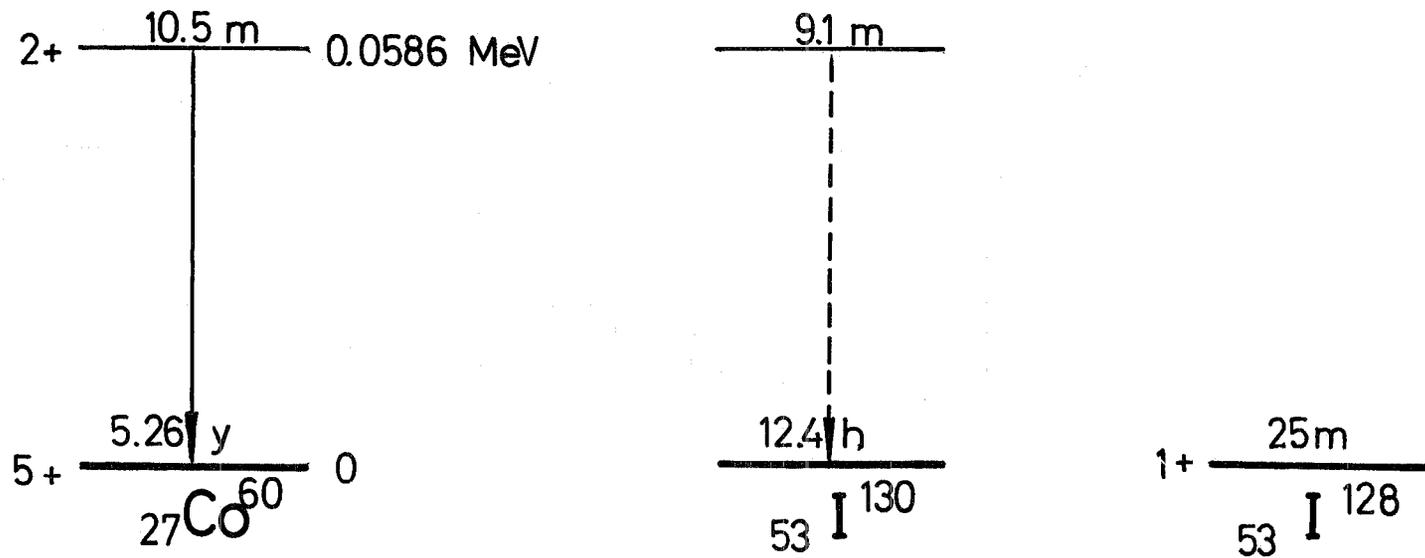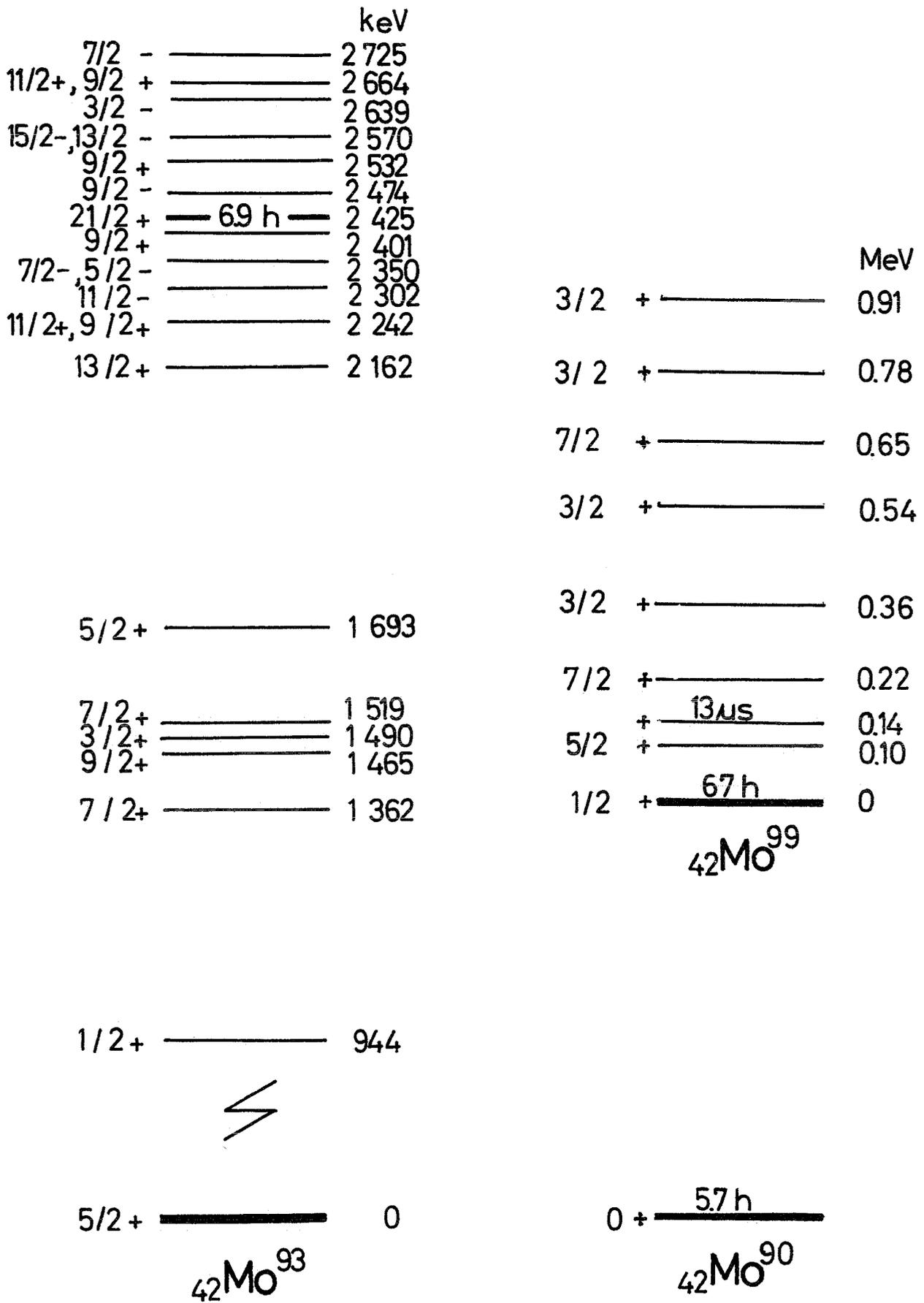
Figure 3   Energy levels of ^{90}Mo, ^{93m}Mo and ^{99}Mo.