Major mechanism of photoactivation for the $^{115}In(\gamma,\gamma')^{115}In^m$ process by ^{60}Co γ-ray irradiation

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The $^{115}In(\gamma,\gamma')^{115}In^m$ photoactivation process was studied by γ-ray irradiation with an intense ^{60}Co source. The nonresonant activation of ^{115}In to the 1078 keV level proposed was reinvestigated. No evidence was obtained for such a direct process but an indirect process of resonance absorption of Compton-scattered γ rays offered a reasonable explanation for the experimental results. Hot atom chemical studies using *tris*(acetylacetonato) indium (III) as a target material indicated that the excitation of the isomeric level via nonresonant process must be less than 3.3% of the resonance effect.

Many authors have studied the photoactivation of stable nuclides to metastable levels.[1-13] The application of this (γ,γ') process to radiation dosimetry,[14-16] activation analysis,[17,18] and hot atom chemistry[19,20] is an important area of research.

Intense γ-ray sources of radioisotopes such as ^{60}Co are able to activate various nuclides via resonance absorption of Compton-scattered γ rays, and it was reported that the experimental results could quantitatively be interpreted by calculation using the Klein-Nishina formula.[5,6] In 1981, however, Ljubičić, Pisk, and Logan[21] presented a different view on the photoactivation phenomenon of ^{115}In to its metastable level with a ^{60}Co γ-ray source. They suggested that a new nonresonant-type process might be dominantly concerned with the nuclear excitation. The cross section of this process was estimated to be 3.8×10^{-31} cm^2, being much larger than ever found for photoactivation by ^{60}Co γ rays (the order of 10^{-32} cm^2). In their experiment, the lead scatterer thickness was changed and the result of activation was analyzed. The $^{115}In^m$ isomeric activities found were supposed as being induced by both resonant and nonresonant processes. The dominance of the nonresonant reaction was concluded from the fitting of experimental and calculated values.

We investigated the nuclear excitation of ^{115}In by a 2.6×10^{15} Bq (70 kCi) strong ^{60}Co γ-ray source of cage type in the Institute of Isotopes of the Hungarian Academy of Sciences in Budapest. Our results have shown that, in principle, the resonant process of Compton-scattered γ rays was much more important than the nonresonant one even if the latter was assumed to be present. The nonresonant process could not be verified by means of the Szilard-Chalmers process of *tris*(acetylacetonato) indium (III) [$In(acac)_3$] with (γ,γ') reaction of ^{115}In. The magnitude of recoil energy of the metastable atom of $^{115}In^m$ produced by the (γ,γ') reaction is expected to be in an appropriate range for comparison with the chemical bond rupture of the indium complex compounds.

The arrangement of the source and the γ-flux distribution are shown in Figs. 1(a) and 1(b). Irradiations were carried out in the center, where the dose rate was 2.65×10^4 Gy/h (2.65×10^6 R/h). This was larger than that in the experiment using 370 TBq (10 kCi) ^{60}Co source in the Japan Atomic Energy Research Institute in Tokai, Japan, although the shape of the irradiation assembly was similar to that in Tokai.

High purity metallic indium was irradiated in a small glass tube. Similarly, $In(acac)_3$ synthesized from indium chloride and acetylacetone was irradiated in the same type of glass tube.

Radioactivity was measured with a 1024 channel γ spectrometer equipped with a well-type NaI(Tl) detector. The detection efficiency for the photopeak of the 336 keV γ radiation of $^{115}In^m$ was 30%.

The experimental data are shown in Table I. The radioac-

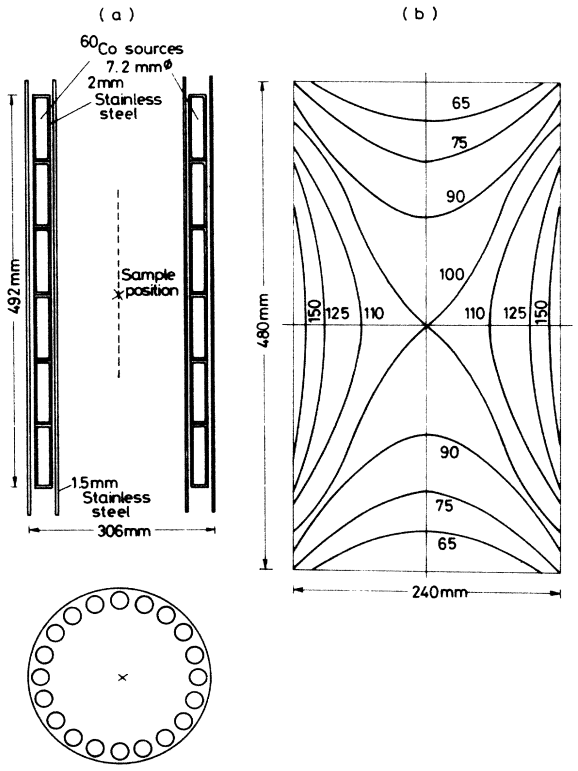

FIG. 1. Intense ^{60}Co γ-ray irradiation assembly. (a) source arrangement, (b) dose rate distribution (normalized to 100% at the central position).

TABLE I. Produced radioactivity of $^{115}In^m$.

Material (g)	Radioactivity of $^{115}In^m$ (Bq) Observed	Nonresonant estimated	Resonant estimated
In metal 0.7902	217	1770	257
$In(acac)_3$ 0.0557[a]	14.1	109	15.7

[a]In content of 0.20 g $In(acac)_3 = In(CH_3COCHCOCH_3)_3$.

tivity produced was corrected to the saturation value. In Table I the data are compared with those calculated according to the cross sections of nonresonant and resonant activation. For the nonresonant absorption of γ rays, the cross section of 3.8×10^{-31} cm^2 is used as stated by Ljubičić *et al.*[21] For resonant absorption of the Compton-scattered γ rays the cross section is calculated as follows:[4] The overall cross section (σ) for resonant absorption of γ rays is expressed by the formula

$$\sigma = \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 \ , \tag{1}$$

where σ_1 is the term for the Compton scattering in the cobalt source, σ_2 for that in the scatterer located between the source and the target, σ_3 for wall scattering, and σ_4 for scattering in the target itself. Usually σ_3 and σ_4 can be neglected when wall scattering is not so significant and the indium target is thin. σ_1 and σ_2 are

$$\sigma_1 = Kn_{01}\Theta G e^{-(\mu_1'-\mu_1)R}(1-e^{-\mu_1 R})/\mu_1 \ , \tag{2}$$

$$\sigma_2 = n_{02}\Theta G(1-e^{-(\mu_2'-\mu_2)\rho})/(\mu_2'-\mu_2) \ , \tag{3}$$

where n_{01} and n_{02} are the electron densities in the source and scatterer of thicknesses R and ρ, respectively; μ_1 and μ_2 are the corresponding absorption coefficients of the primary beam; μ_1' and μ_2' are those of effective (1078 keV) Compton-scattered γ rays. $K = e^{-(\mu_2'-\mu_2)\rho}$, Θ is the integrated cross section for photoactivation, and G is the Klein-Nishina differential cross section for the scattering of a photon of primary energy into the unit energy interval at 1078 keV level.

The value of the integrated cross section Θ of photoactivation of ^{115}In via its 1078 keV level in the previous report[4] (where 1040 keV was used instead of 1078 keV) was reestimated, and it was confirmed that the value was $(2.3\pm0.4)\times10^{-25}$ cm^2 eV. Using this integrated cross section, the overall cross section σ of photoactivation in Eq. (1) was calculated. In Table I radioactivity calculated for the resonant process is based on the σ thus obtained. As seen in Table I it is obvious that the experimental data are different from the values expected for the nonresonant process,[21] whereas they agree with those for the resonant process. The agreement between the experimental data and the calculated ones based on the resonance absorption of Compton-scattered γ rays is good, although the details of the irradiation assembly of Budapest are not the same as those of Tokai. The results in Table I show that the nonresonant process cannot be the major mechanism of activation to the metastable level.

To confirm this, we tried to find further experimental evidence. In the Szilard-Chalmers effect, which is also known as the hot atom effect,[22-24] chemical bonds are broken when

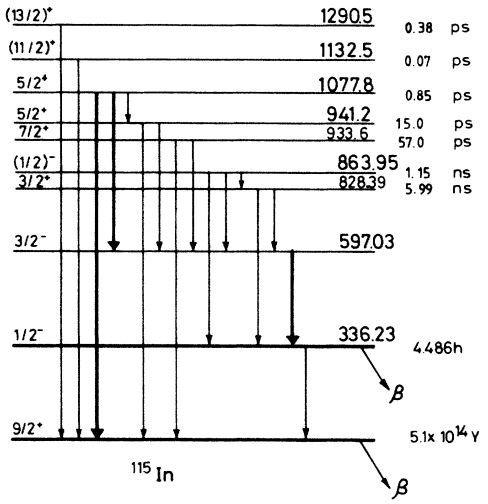

FIG. 2. Level structure of ^{115}In, together with lifetime and spin data.

the recoil energy of the atom produced by the nuclear process is larger than the binding energy. The threshold energy for this in the gas phase is usually considered to be a few eV, or probably 5 eV at most. For the ^{115}In $(\gamma,\gamma')^{115}In^m$ reaction we can calculate the recoil energy (E_r) for $^{115}In^m$. For incident γ of energy E_γ for an atom of mass m the equation for calculating the energy is

$$E_r \text{ (in eV)} = \frac{537E_\gamma^2}{m} \quad (E_\gamma \text{ in MeV}) \ . \tag{4}$$

If the recoil atom is bound to the rest of the given molecule (total mass M), this energy is not fully available to the ^{115}In atom, because of the law of momentum conservation. In this way, the effective energy (E_{eff}) needed to break the bond is reduced:

$$E_{\text{eff}} = (M-m)E_r/M \ . \tag{5}$$

This is usually known as the Suess effect. Looking at the level structure[25] of ^{115}In shown in Fig. 2, it can be seen that the most important level for isomer activation by the (γ,γ') process is at 1078 keV. The excited atom loses its energy by the cascade emission of two γ rays and it reaches the metastable level. Using the relation given in Eqs. (4) and

TABLE II. Calculated recoil energy for the Szilard-Chalmers process in the irradiated indium compound.

	Nonresonant γ:1332 keV	Resonant γ:1078 keV
Incident γ:E_{in}	8.29 eV	5.43 eV
Outgoing γ:E_{out}^1 1078 → 597 keV	1.08 eV	1.08 eV
Outgoing γ:E_{out}^2 597 → 336 keV	0.32 eV	0.32 eV
E_{in} corrected by Suess effect	5.98 eV	3.92 eV

(5) and in Fig. 2, we obtain the recoil energy data for the $^{115}In(\gamma,\gamma')^{115}In^m$ reaction as shown in Table II. In the nonresonant process the initial recoil energy of the atom is 8.29 eV for the incident ^{60}Co γ ray of 1332 keV, provided that the momentum of γ is immediately transferred to the atom. This value reduces to 5.98 eV when the Suess effect is taken into account. This is sufficient for bond breaking in ordinary chemical compounds, while in the resonant process the recoil energy (3.92 eV) is fairly small compared with the nonresonant case. For the successive decay the recoil events may separately be considered from the initial recoil caused by the incident γ ray because the lifetime of the 1078 keV level is 0.85 ps, which is much larger than one vibration period for typical molecular systems.

Purified $In(acac)_3$ was put at the bottom of a jacket of the evacuated glass container shown on Fig. 3. At elevated temperatures ($>200\,^{\circ}C$) the substance was vaporized in the glassware dipped in a liquid silicone bath, which was used to maintain a temperature high enough to keep the substance in gaseous form. Irradiation was also performed for the vapor of $In(acac)_3$.

If the bond rupture occurs during irradiation of $In(acac)_3$ in the gas phase at higher temperature, the radioactivity of $^{115}In^m$ (half-life 4.486 h) should be detected on the wall of the glassware. After the irradiation the wall was washed repeatedly with hydrochloric acid. The washing solutions were combined and measured by the NaI(Tl) detector, but no radioactivity was detected; see Table III. All the radioactivity was found in the jacket where the gas of $In(acac)_3$ was condensed by cooling with liquid nitrogen. The number of counts was extrapolated to the end of the irradiation taking into consideration the time delay until the counting period started. The intensity decay of the sample during the counting period was also considered by introducing

$$t=\frac{T}{0.693}(1-e^{-0.693t'/T}) \quad , \tag{6}$$

where t and t' are the reduced and actual counting periods, respectively. The value of 4.486 h was taken[25] for the half-life T of $^{115}In^m$, which is practically the same as we have found (4.48 ± 0.03 h). The result of the second run was multiplied by the ratio of the saturation factors of 2 hours to 1 hour irradiation, in order to relate corrected data uniformly for the 2-hour irradiation period. Since the measurements of the washing solutions resulted in practically background spectra, evaluation was done by summarizing the channel contents falling in the expected position of the missing 336 keV photopeak, in order to establish an upper limit for the nonresonant process. The criterion for estimating the detection limit from the background intensity as $1.64\sqrt{2C_B}/t_B$ was applied, which corresponds to a 90% confidence level. Correction was also made for the time delay between the end of irradiation and the start of the counting, as if the measured sample had contained $^{115}In^m$. Thus, C_B stands here for the corrected figure of background counts collected during period t_B. On the basis of this estimate, the contribution of the nonresonant process must be less than 3.3%, as can be seen from Table III.

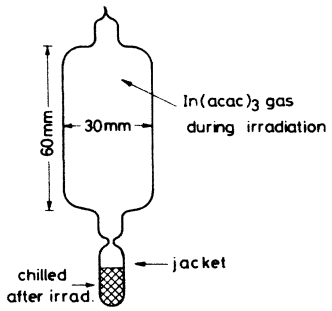

FIG. 3. Glassware for the irradiating $In(acac)_3$ sample in the gas phase.

This result shows that for all practical purposes the parent compound was not broken at the nuclear event of the $^{115}In(\gamma,\gamma')^{115}In^m$reaction. As stated before, bond rupture in the indium complex compound is naturally expected when the recoil energy is more than 5 eV. From the experimental results obtained in Table III, the nonresonant process is rather questionable. Of course, if the process is caused by the inelastic photoelectric effect, the recoil energy value will be changed; however, this case also leads to the inner shell ionization followed by the Auger cascade, which results in multiple ionization. In such a case the chemical bond is very easily broken by Coulombic repulsion in the molecule.[26] The nonresonant process does not reasonably explain the eperimental results.

Theoretical considerations published so far[21,27,28] have not been able to indicate a possible mechanism that might be responsible for nonresonant excitation. Cross sections calculated for inelastic photoelectric effects, nuclear Raman scattering, etc., are several orders of magnitude less than would be necessary for a reasonable explanation.

In view of this, we argue that the resonant process in the $^{115}In(\gamma,\gamma')^{115}In^m$ reaction for ^{60}Co γ-ray irradiation be considered as a major one. Using the radioactivity of $^{115}In^m$ produced by irradiation with the intense ^{60}Co source, the value of integrated cross section Θ was calculated. This is listed in Table IV and compared with those in other reports.

TABLE III. Recoil experiment in the gas phase.

			Produced radioactivity of $^{115}In^m$ (counts per second)			
			Jacket		Wall	
Sample	Amount (g)	Irradiation period (h)	Net counts detected	Net counts corrected	Detected (background)	Detection limit $1.64\sqrt{2C_B}/t_B$
$In(acac)_3$	0.20	2.0	967/200	0.55 ± 0.05	2915/5000	0.018
$In(acac)_3$	0.20	1.0	343/1000	0.70 ± 0.10	35 198/60 000	0.016

TABLE IV. Integrated cross section values for photoactivation of $^{115}In^{m}$.

Authors	Θ 10^{-26} cm^2 eV
Ikeda and Yoshihara (Ref. 4)	23 ± 4
Veres (Ref. 8)	20 ± 4
Chertok and Booth (Ref. 9)	7.1 ± 2.3
Booth and Brownson (Ref. 10)	11.5 ± 4.0
Boivin, Cauchois, and Héno (Ref. 11)	30^{+40}_{-20}
Watanabe and Mukoyama (Ref. 13)	19 ± 1
Ljubičić, Pisk, and Logan (Ref. 21)	5.39 ± 0.64
This work	18.1 ± 1.5

The value obtained here is in good agreement with those in the previous works[4,8,13] with the use of intense ^{60}Co sources.

The ground state transition width Γ_0 can be derived from the integrated cross section by using the relation

$$\Theta = \frac{\Gamma_{iso}}{\Gamma} \int_0^\infty \sigma_{abs}(E)\, dE = g\pi^2 \lambda \Gamma_0 \frac{\Gamma_{iso}}{\Gamma} \tag{7}$$

assuming that the branching ratio Γ_{iso}/Γ is known. A few data for this branching ratio based on Coulomb excitation and $(n,n'\gamma)$ experiments are available, viz., 0.157,[29] 0.44,[30] 0.19,[31] and 0.24.[32] Related Γ_0 values deduced from the result of 18.1×10^{-26} cm^{2}eV obtained in the present work vary as 58.1, 20.7, 48, and 38 meV, respectively, for the 1078 keV transition for ^{115}In. While such large variations exist, comparison of Γ_0 values obtained from photoactivation experiments with those provided directly by other techniques is rather difficult. Further investigations are needed for decisive conclusions to be drawn.

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