Highly excited metastable states, or isomers, of nuclei are considered as a potential new form of energy storage, if the energy of a long-lived isomer can be released by a controllable rapid process (isomer depletion). Chiara et al.\(^1\) provided the first experimental evidence of isomer depletion caused by nuclear excitation by electron capture (NEEC)\(^2\), with a rather large excitation probability of \(P_{\text{exc}} = 0.010(3)\), by exciting an isomer of molybdenum-93 to a higher state. By assessing the reported experimental results and analysis methods, we found that the complex \(\gamma\) background in that work was treated using two idealistic assumptions. Therefore, the observed isomer depletion could have been overestimated owing to residual contamination.

In the reported work\(^1\), the 268-keV \(\gamma\)-ray emission was used to mark the NEEC process. Because this \(\gamma\)-ray is mainly emitted from the fusion-evaporation reaction, the real NEEC events were identified by their coincidence with transitions above the 2.4-MeV isomer. In a \(\gamma\)-rich environment, a considerable number of false events due to contamination cannot be excluded by event by event according to the time coincidence and the \(\gamma\)-ray energy. Here, contamination means events that are not induced by isomer depletion—mainly chance coincidences and coincidences with Compton background and with other transitions of similar energy—and was treated on the basis of two assumptions, which we believe are too idealistic (see methods section of ref. \(^1\)). First, the number of chance coincidences was considered to be negligible. Second, only the smooth Compton background was taken into account.

According to the spectra in extended data figure 3 of ref. \(^1\), the presence of the 263-keV peak indicates that chance coincidences are not negligible. This transition, emitted from the isomer with half-life \(T_{1/2} = 6.85\) h, is in coincidence only with the 685-keV and 1,478-keV transitions. Considering these effects, it cannot be assumed that the ratios \(k\) in ref. \(^1\) of background events in coincidence with events in the peak energy range to background in coincidence with channels close to the gating transition are the same for different transitions.

Owing to these idealistic assumptions, it is possible that contamination was not properly excluded in ref. \(^1\). In figure 3b of ref. \(^1\), the 263-keV transition is clearly seen as a peak, and marked as a known transition of \(^{90}\)Mo. There is a known 262-keV transition above the gating transitions\(^3\), but it should be excluded, because a Doppler-shifted transition could not appear as a peak in a spectrum without Doppler correction.

Therefore, the only known transition in \(^{90}\)Mo at this energy is the one below the isomer, which is expected to be absent in this spectrum if the contamination is properly excluded. Furthermore, the intensity of this peak is about twice that of the peak at 268 keV; this intensity ratio is similar to that observed in the spectrum gated by the 1,478-keV transition (see figure 2b of ref. \(^1\)). Considering that only the 268-keV transition contributes to isomer depletion, the similar intensity ratios indicate that the peak at 268 keV comes mainly from contamination. Therefore, the deduced excitation probability of \(P = 0.010(3)\) should be regarded as an upper limit for isomer depletion.

By contrast, the peak at 263 keV did vanish in a spectrum doubly gated by the 1,478-keV and 2,475-keV transitions (see figure 2a of ref. \(^1\)), which was regarded as proof of existence of isomer depletion. However, this observation can be explained without invoking the isomer depletion mechanism. As mentioned, the 263-keV peak cannot be caused by true events in a spectrum gated by the 2,475-keV transition. However, the situation for the 268-keV transition is quite different, because it is mainly populated via a series of transitions involving high-energy statistical \(\gamma\)-rays. The background induced by the high-energy \(\gamma\)-rays would cover the gating range of the Doppler-shifted 2,475-keV transition, allowing the appearance of the 268-keV peak in this spectrum.
Matters arising

Fig. 1 | Experimental setup and estimated cross-section of 90Mo as a function of bombarding energy. Top right, multi-layers in the path of the beam and bombarding energies at the interfaces. Shown are the effective thicknesses of the layers, considering a 12% increase due to the angle with the beam path (see methods section in ref. 1). The cross-sections were calculated using the Monte Carlo fusion–evaporation code PACE4.

from true events. Therefore, compared to the 268-keV transition, the 263-keV one is considerably reduced in figure 2a of ref. 1. Because it is partly populated from the isomer, the 685-keV transition is less affected. The intensities of the 123-keV, 203-keV, 770-keV and 963-keV transitions are much lower, and it is not surprising that they are indiscernible in figure 2a of ref. 1, owing to the poor statistics.

Furthermore, the spectrum shown in figure 2a of ref. 1 could have been affected by the chosen background parameters. As described in the methods section of ref. 1, a ratio \( k \), defined as \( k = \frac{(g \cdot g_1 - b \cdot b_1)}{(b \cdot g_2 - b \cdot b_2)} \), is employed to subtract the background of doubly gated spectra, where a gate is regarded to be composed of the peak of interest \( (p) \) atop a smooth background \( (b) \). Here, one transition is assumed to be in true coincidence with the transitions of interest, denoted by subscript 2, whereas the other one is not in true coincidence with them without the isomer depletion mechanism, marked by subscript 1.

Extended data figure 3 of ref. 1 shows an example of deducing the \( k \) ratios. If the spectra, subscripts 1 and 2 correspond to the transitions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41586-021-03333-5.

Fig. 2 | Re-examination of \( k \) ratios. This figure was obtained by overlapping extended data figure 3a (g·g1, orange) and extended data figure 3c (b·g2, black) of ref. 1. The y axis of the b·g2 spectrum is extended so that the ordinates of the g·g1 spectrum are 1.33 times those of the b·g2 spectrum, thus reaching the same peak heights. The g·g1 spectrum is slightly shifted to the left for easier comparison. The 770-keV peaks are located on the left shoulder of the stronger 773-keV peaks.

Because, from our point of view, the reported excitation probability is only an upper limit, it should be measured again, possibly with a setup that can fully exclude contamination. In a possible refined method, the residues should be delivered to another location by adding an extra beam line. Using a beam line with a length of several metres, the prompt γ-rays are left behind, and only those from isomer depletion are measured, which can give rise to the observation of characteristic γ-rays such as the 268-keV transition of \(^{90}\)Mo. The time coincidence between the γ-rays and the stopped residues can further help to distinguish isomer depletion from spontaneous decay. By comparing the yields of isomer depletion and spontaneous decay from the isomer, it would be easy to deduce the excitation probability. Using this method, it is possible to measure isomer depletion with a precision of \( 10^{-4} \)–\( 10^{-6} \). The appropriate stopping material is expected to maximize the probability of NEEC, which is possible with a realistic theoretical estimation. Such a measurement can be performed in several facilities, such as RIBLL (Radioactive Ion Beam Line in Lanzhou) at HIRFL (Heavy Ion Research Facility in Lanzhou).

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41586-021-03333-5.

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Reply to: Possible overestimation of isomer depletion due to contamination

We appreciate the interest of Guo et al., the points that they raise, and the opportunity that we have to provide additional details that are not included in ref. 1. This allows us to strengthen our experimental case while, in parallel, recent developments are improving our theoretical understanding of nuclear excitation by electron capture (NEEC), such as the exploration of a substantial increase in predicted NEEC probability when considering capture by an ion in an excited state or the impact of the momentum distribution of target electrons. In the accompanying Comment, Guo et al. focus on whether potential background contributions were underestimated in our analysis. As discussed below, these concerns are mostly unwarranted; aside from a small systematic uncertainty that could possibly slightly reduce our reported NEEC excitation probability \( p_{\text{exc}} = 0.010(3) \), our original conclusions still stand.

Guo et al. rightly note that the 263-keV isomeric transition (half-life \( T_{1/2} = 6.85 \text{ h} \)) is not expected to be observed in true, prompt coincidence with any \( \gamma \)-rays with energies higher than 1,478 keV. However, the authors appear to argue that the NEEC-indicative 268-keV transition \( (T_{1/2} = 3.5 \text{ ns} \text{; short enough to be in prompt coincidence}) \) should behave more like the delayed 263-keV \( \gamma \)-ray—and appearing in the gated spectrum solely through chance coincidences—than like the four other prompt \( ^{90} \text{Mo} \) lines at 123, 203, 770 and 963 keV that could be eliminated from the spectrum through background subtraction. The opposite is true. With a half-life much longer than the 82.47 ns between ATLAS beam pulses, there is no way to correlate between the isomer decays and the specific reaction (or beam pulse) that created the isomer. The essentially uniform time distribution would indeed result in chance coincidences between the 263-keV isomeric transition and \( \gamma \)-rays arising from other reactions. However, this chance-coincidence rate would differ from that of prompt \( ^{90} \text{Mo} \) \( \gamma \)-rays (including the four aforementioned background lines, as well as the 268-keV \( \gamma \)-ray) that can be produced in two independent reactions within the same coincidence window. The behaviour of the 263-keV peak thus cannot be used as a reliable gauge, as Guo et al. propose, for what to expect for prompt \( \gamma \) transitions.

To estimate the rate of chance coincidences between two unrelated \( ^{90} \text{Mo} \) decays, we can follow the steps outlined by Guo et al., with some corrected values. Adopting the PACE4 cross-sections, along with our experimental parameters (beam intensity and target thicknesses) and the 90% factor for populating above spin 17/2, gives a 263-keV production rate of \(-8.4 \text{ kHz}\). The approximate yield passing through the 268-keV transition is at the low end of their quoted range, \(-20\%\), giving a rate of 1.7 kHz for the production of the 268-keV \( \gamma \)-ray. The coincidence window of 90 ns (Guo et al. assumed 100 to 1,000 ns) gives a chance-coincidence probability of \(-0.03\%\), well below the NEEC excitation probability \( p_{\text{exc}} = 1.0(3)\%\).

We can deduce the chance-coincidence probability more directly from the data, instead of relying solely on the above estimates. Data were recorded using a 2-\( \mu \)s coincidence window, encompassing many beam pulses, with a narrow 90-ns window defined in the offline analysis. For a given reaction occurring within a specific 90-ns window, the probability of a second reaction occurring in either the same window or a similar one associated with a different beam pulse is equivalent. Events were selected for which the 268-keV and 1,478-keV transitions were observed within one 90-ns coincidence window, along with a 685-keV \( \gamma \)-ray that could arrive at any time within the full 2-\( \mu \)s window. The time difference between the 685-keV and 268-keV transitions shows that most events correspond to the 685-keV \( \gamma \)-ray that arrives within the same 90-ns window as the other two \( \gamma \)-rays (prompt coincidence). By taking the ratio of the number of events detected with the 685-keV \( \gamma \)-ray to their number in prompt coincidence (same 90-ns window), we find that the probability for chance coincidences between two \( ^{90} \text{Mo} \) decays is 0.08(8)\%, consistent with the above estimate using the PACE4 cross-sections. Again, we conclude that such chance coincidences are fairly small by comparison.

As for true coincidences with statistical \( \gamma \)-rays, we see no reason to expect a dramatic difference in the behaviour of the prompt 268-keV \( \gamma \)-ray compared to other prompt \( ^{90} \text{Mo} \) transitions. Placing a double gate on the 1,478-keV transition and one of the prompt lines (268 keV, as well as the 123-keV and 203-keV lines used for determining the \( k \) background parameter in ref. 1) produces spectra with no noteworthy differences in the continuum at high energies—see Fig. 1. Whereas any residual counts in the 123-keV and 203-keV peaks might be identifiable in figure 2a of ref. 1 because of low statistics after background subtraction, they can be clearly seen (and fitted) in two of the component spectra in external data figure 3 of ref. 1; this was the basis for determining the \( k \) value for the background subtraction. The lower intensities of the background lines compared to the 268-keV transition are reflected in the corresponding statistical uncertainties from the fits to the \( g_{p1} \) and \( b_{p2} \) spectra. The values of \( k \) for each of the four background lines are plotted in blue in the inset to Fig. 1. The weighted average of these \( k \) values has a statistical uncertainty comparable to those of the 268-keV and 685-keV transitions (in green), even though the individual uncertainties for the background lines are larger.
to background, even though they should be similarly coincident with statistical γ-rays. We attribute this excess of counts to NEEC.

Comparing the $g_{g2}$ and $b_{g2}$ spectra by graphically overlaying them as a means of evaluating the background subtraction can be misleading. Statistical variations by channel make the height of a peak a less reliable gauge of its size than the fitted area. Nevertheless, we follow the example of Guo et al.\(^4\) and similarly plot in Fig. 2 an overlay of the $g_{g1} + g_{g2} - b_{b2}$ and $b_{g1} + b_{g2} - b_{b2}$ spectra (including the important background contributions $g_{b1}$ and $b_{b1}$, neglected by Guo et al.) that were used to deduce the $k$ values in ref.\(^1\), with the latter spectrum scaled by 1.33. The four background lines at 123, 203, 770 and 963 keV would all be underestimated if $k = 1.33$ was used. (Here, the peak heights visually suggest the same conclusion as the areas.) The actual ratios of areas (the correct approach) are the $k$ values plotted in the inset to Fig. 1. We also note that the 235-keV and 244-keV peaks arising from the strong\(^93\)Mo channel, visible in the spectra in Guo et al.\(^4\), would not be eliminated by the simple construction $g_{g2} - 1.33b_{g2}$; however, the full background subtraction in figure 2 of ref.\(^1\) (and as evident in Fig. 2) does remove this background.

The excitation (NEEC) probability $P_{\text{exc}}$ was determined from figure 3 of ref.\(^1\). From the sum of the spectra double-gated on 1,442/241 keV and 686/241 keV, by comparing the 268-keV and 2,475-keV peak areas, corrected for efficiency and internal conversion. Given the successful background subtraction with $k = 1$ in the spectra in figure 2 of ref.\(^1\), we adopted $k = 1$ for the spectra of figure 3 as well. We note that the strong 1,734-keV transition that feeds the isomer parallel to the 2,475-keV γ-ray\(^4\) (not shown in ref.\(^1\)) is in true coincidence with the 241-keV and 1,442-keV γ-rays, but not with the one at 686 keV. Thus, we can perform a similar analysis as before, with gates 1 and 2 corresponding to 686 keV and 241 keV, respectively, yielding $k = 1.07(14)$. Furthermore, adjusting $k$ between 0.7 and 1.3 for the summed spectra in figure 3 of ref.\(^1\) only changes the deduced value of $P_{\text{exc}} = 0.010(3)$ by -9%–small compared with the uncertainty—so the result is fairly robust.

Guo et al.\(^4\) are concerned by the presence of a 263-keV peak in figure 3b of ref.\(^1\). They are correct that the high-lying 262-keV transition identified in ref.\(^1\) would be weak and Doppler-shifted, and thus could not be the peak observed in this spectrum. However, it does not arise from the isomer decay. There is an additional (so far unpublished) 262-keV γ-ray, emitted from stopped\(^93\)Mo nuclei, that was identified in our benchmark experiment at the Australian National University (ANU)\(^5\). This is the peak that appears via the 686/241-keV double gate, and it has the correct size relative to the 278-keV peak, expected from the unpinned level scheme (both peaks are marked with asterisks in figure 3 of ref.\(^1\)). No coincidences in the control reactions were found to interfere with the NEEC signature itself\(^6\).

In summary, our result of $P_{\text{exc}} = 0.010(3)$ is largely supported by the suitable background subtraction and analysis techniques described in ref.\(^1\) and clarified here. A potential systematic error arising from chance coincidences may reduce this somewhat (from 0.0096 to 0.0088, quoting additional precision)—a small change relative to the uncertainty of 0.003. NEEC has not been ruled out, nor have any more likely candidate mechanisms been proposed. That said, we do encourage others to explore NEEC using different experimental approaches, as it would be valuable to have independent confirmation of this long-sought phenomenon.

Data availability

Data analysed for the original publication were re-examined for this Reply; no new data were generated.

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