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# Mass of astrophysically relevant ${ }^{31} \mathrm{Cl}$ and the breakdown of the isobaric multiplet mass equation 

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#### Abstract

The mass of ${ }^{31} \mathrm{Cl}$ has been measured with the JYFLTRAP double-Penning-trap mass spectrometer at the Ion Guide Isotope Separator On-Line (IGISOL) facility. The determined mass-excess value, $-7034.7(34) \mathrm{keV}$, is 15 times more precise than in the Atomic Mass Evaluation 2012. The quadratic form of the isobaric multiplet mass equation for the $T=3 / 2$ quartet at $A=31$ fails ( $\chi_{n}^{2}=11.6$ ) and a nonzero cubic term, $d=-3.5(11) \mathrm{keV}$, is obtained when the new mass value is adopted. ${ }^{31} \mathrm{Cl}$ has been found to be less proton-bound, with a proton separation energy of $S_{p}=264.6(34) \mathrm{keV}$. Energies for the excited states in ${ }^{31} \mathrm{Cl}$ and the photodisintegration rate on ${ }^{31} \mathrm{Cl}$ have been determined with significantly improved precision by using the new $S_{p}$ value. The improved photodisintegration rate helps to constrain astrophysical conditions where ${ }^{30} \mathrm{~S}$ can act as a waiting point in the rapid proton capture process in type-I x-ray bursts.


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${ }^{31} \mathrm{Cl}$ is a short-lived $\left[T_{1 / 2}=190(1) \mathrm{ms}\right.$ [1] ] $s d$-shell nucleus and a well-known beta-delayed proton emitter [1-5]. However, its mass-excess value ( $\Delta=-7066(50) \mathrm{keV}$ [6]) is still based on a single $Q$-value measurement of the ${ }^{36} \mathrm{Ar}\left({ }^{3} \mathrm{He},{ }^{8} \mathrm{Li}\right)^{31} \mathrm{Cl}$ reaction performed at Michigan State University in the 1970s [7]. The mass of ${ }^{31} \mathrm{Cl}$ is relevant for testing the isobaric multiplet mass equation (IMME) $[8,9]$ because it is a member of the $T=3 / 2$ isobaric quartet with isospin projection $T_{Z}=$ $(N-Z) / 2=-3 / 2$. According to the IMME, the masses of the isobaric analog states (IASs) in a mass multiplet should show purely quadratic behavior: $M\left(A, T, T_{Z}\right)=a(A, T)+$ $b(A, T) T_{Z}+c(A, T) T_{Z}^{2}$ after treating the Coulomb interaction by using first-order perturbation theory. Previous IMME evaluations have shown that the quadratic form works well for the $T=3 / 2$ quartet at $A=31[10-14]$ but the test has not been very stringent, mainly due to the uncertainty in the ${ }^{31} \mathrm{Cl}$ mass. Overall, the quadratic form of the IMME has failed only in a few cases, such as at $A=8$ [15], $A=9$ [16], $A=21$ [17], $A=32$ [18,19], $A=35$ [20], and $A=53$ [21]. The breakdown of the IMME has been explained, e.g., by isospin mixing of the states and charge-dependent effects [16,22]. However, for some cases, such as for the $A=53$ quartet [21], even detailed shell-model calculations have not been able to describe the breakdown.

The mass of ${ }^{31} \mathrm{Cl}$ is also relevant for the rapid proton capture $(r p)$ process occurring in type-I x-ray bursts (XRBs) [23,24]. There, most of the nucleosynthetic flow proceeds through ${ }^{30} \mathrm{~S}$, which can act as a waiting point due to its half-life [1.178(5) s [25] ] and low proton-capture $Q$ value establishing $\mathrm{a}(p, \gamma)-(\gamma, p)$ equilibrium towards ${ }^{30} \mathrm{~S}$ at high temperatures. The route via the ${ }^{30} \mathrm{~S}(\alpha, p){ }^{33} \mathrm{Cl}$ reaction is hindered by the Coulomb barrier at typical XRB temperatures of around 1 GK. Waiting points, such as ${ }^{30} \mathrm{~S}$, have been proposed to be responsible for the double-peaked structure observed in XRB luminosity curves [23].

[^0]Nonresonant proton captures contribute to the total protoncapture rate of ${ }^{30} \mathrm{~S}$ at lower temperatures, whereas above $T \approx 0.13 \mathrm{GK}$, the rate is dominated by resonant proton captures to the two lowest excited states in ${ }^{31} \mathrm{Cl}$. These have been studied via beta-delayed proton decay of ${ }^{31} \mathrm{Ar}$ [26-29] with observed laboratory energies of 446(15) and 1415(5) keV [26] and 1416(2) keV [28]. Recently, ${ }^{31} \mathrm{Cl}$ has been studied via Coulomb breakup of ${ }^{31} \mathrm{Cl}$ at high energy in inverse kinematics by using the $\mathrm{R}^{3} \mathrm{~B}$-LAND setup at GSI [30]. The two lowest-lying levels, $1 / 2^{+}$at $782(32) \mathrm{keV}$ and $5 / 2^{+}$at 1793(26) keV [30], were found to be in a reasonable agreement with the estimates, $745(17)$ and $1746(9) \mathrm{keV}$ [31], based on the IMME and beta-delayed proton data. A similar Coulomb dissociation study of ${ }^{31} \mathrm{Cl}$ performed at RIKEN resulted in resonance energies around 0.45 and 1.3 MeV [32]. In order to compare the results from $\mathrm{R}^{3} \mathrm{~B}$-LAND with the beta-delayed proton data and to verify the excitation energies of the lowest resonance states in ${ }^{31} \mathrm{Cl}$, the proton separation energy of ${ }^{31} \mathrm{Cl}$, i.e., its mass, has to be known more precisely.

To estimate the waiting-point conditions for ${ }^{30} \mathrm{~S}$, also the rate for photodisintegration reactions on ${ }^{31} \mathrm{Cl}\left(\lambda_{\gamma, p}\right)$ has to be taken into account. The ratio of $\lambda_{\gamma, p}$ to the proton-capture reaction rate $N_{A}\langle\sigma v\rangle$ depends exponentially on the protoncapture $Q$ value on ${ }^{30} \mathrm{~S}$ (i.e., the proton separation energy $S_{p}$ of ${ }^{31} \mathrm{Cl}$ ) [33]:

$$
\begin{align*}
\frac{\lambda_{\gamma, p}}{N_{A}\langle\sigma v\rangle}= & 9.8685 \times 10^{9} T_{9}^{3 / 2} \frac{g_{S} g_{p}}{g_{C l}}\left(\frac{G_{S} G_{p}}{G_{C l}}\right) \\
& \times\left(\frac{m_{S} m_{p}}{m_{C l}}\right)^{3 / 2} e^{-11.605 Q / T_{9}} \tag{1}
\end{align*}
$$

where $m_{i}$ are the masses in atomic mass units, $g_{i}$ are the statistical factors $g_{i}=2 J_{i}+1$, and $G_{i}$ are normalized partition functions for ${ }^{30} \mathrm{~S}, p$, and ${ }^{31} \mathrm{Cl}$. The normalized partition functions [34] are close to one in the relevant energy region. The uncertainty in the present $Q$ value has been shown to significantly affect XRB nucleosynthesis calculations in a high-temperature ( $T_{\text {peak }}=2.50 \mathrm{GK}$ ) scenario with normal


FIG. 1. TOF-ICR spectrum of ${ }^{31} \mathrm{Cl}^{+}$with a quadrupolar radiofrequency excitation of 50 ms . The spectrum represents a typical resonance of ${ }^{31} \mathrm{Cl}$ obtained in 140 minutes. The blue squares indicate the number of ions in each time-of-flight bin: the darker the color, the greater the number of ions.
burst duration ( $\approx 100 \mathrm{~s}$ ) as well as in a short-burst ( $\approx 10 \mathrm{~s}$ ) scenario with $T_{\text {peak }}=1.36 \mathrm{GK}$ [35].
${ }^{31} \mathrm{Cl}^{+}$ions were produced via ${ }^{32} \mathrm{~S}(p, 2 n){ }^{31} \mathrm{Cl}$ reactions by using a 40 MeV proton beam impinging on a $1.8-\mathrm{mg} / \mathrm{cm}^{2}$ thick ZnS target at the IGISOL facility [36]. The reaction products were stopped in helium gas and extracted with a sextupole ion guide [37] and accelerated to 30 keV before mass separation with a $55^{\circ}$ dipole magnet. A radio-frequency quadrupole cooler and buncher [38] was implemented to convert the continuous $A=31$ beam into short ion bunches which are released into the JYFLTRAP double-Penning-trap mass spectrometer [39]. Simultaneous magnetron and cyclotron excitations were applied for the ions in the purification trap for 40 ms to select the ${ }^{31} \mathrm{Cl}^{+}$ions by using the mass-selective buffer gas cooling method [40]. In the precision trap, a $10-\mathrm{ms}$ magnetron excitation was followed by a short, 50 ms cyclotron excitation to minimize the decay losses of ${ }^{31} \mathrm{Cl}$. The ion's cyclotron resonance frequency $v_{c}=q B /(2 \pi m)$, where $q$ and $m$ are the charge and mass of the ion, respectively, was determined by using the time-of-flight ion cyclotron resonance (TOF-ICR) technique [41] (see Fig. 1). The magnetic field strength $B$ was calibrated by using ${ }^{31} \mathrm{P}^{+}$ions as a reference $\left[m\left({ }^{31} \mathrm{P}\right)=30.9737619984(7) \mathrm{u}[6]\right.$ ]. Thus, the atomic mass of ${ }^{31} \mathrm{Cl}$ was determined using $m\left({ }^{31} \mathrm{Cl}\right)=r\left(m_{\text {ref }}-m_{e}\right)+m_{e}$, where $r=\frac{v_{c}, \text { ref }}{v_{c}}$ is the cyclotron frequency ratio of ${ }^{31} \mathrm{P}^{+}$ and ${ }^{31} \mathrm{Cl}^{+}, m_{\text {ref }}$, and $m_{e}$ are the ${ }^{31} \mathrm{P}$ and electron masses, respectively. The weighted mean of the measured frequency ratios was $r=1.00060330(12)$ resulting in a mass-excess value $\Delta=-7034.7(34) \mathrm{keV}$ (see Fig. 2), which is 31 keV higher than the value in the Atomic Mass Evaluation 2012 (AME12) [6]. The uncertainty is dominated by the statistical error of the frequency fit. The systematic uncertainties, as described in Ref. [42], have a negligible contribution to the final result.

The IMME was studied at $A=31$ by using the new mass value for ${ }^{31} \mathrm{Cl}$. The ground-state masses for the other


FIG. 2. Mass-excess values determined in this work. The red line shows the weighted mean of the results and the dashed blue lines $1 \sigma$ error bands.
members of the multiplet have been taken from AME12 [6] (see Table I). The mass values of ${ }^{31} \mathrm{~S}$ and ${ }^{31} \mathrm{P}$ are based on Penning-trap measurements at JYFLTRAP [18] and the Florida State University trap [43], respectively. The mass of ${ }^{31} \mathrm{Si}$ is linked via $(n, \gamma)$ measurements (see, e.g., Refs. [44-47]) to ${ }^{29} \mathrm{Si}$, which has been precisely measured with a Penning trap at the Massachusetts Institute of Technology [48]. The excitation energy for the $T=3 / 2$ IAS in ${ }^{31} \mathrm{~S}$ is based on data from beta-delayed $\gamma$ rays of ${ }^{31} \mathrm{Cl}[1,5]$ as well as from ${ }^{31} \mathrm{P}\left({ }^{3} \mathrm{He}, \mathrm{t}\right)$ [49] and ${ }^{33} \mathrm{~S}(p, t)$ reactions [50]. The energy for the IAS in ${ }^{31} \mathrm{P}$ has been determined with high precision by using the Gammasphere detector array [51]. A similar excitation energy, $E_{x}=6380.0(20) \mathrm{keV}$, has also been obtained via ${ }^{30} \mathrm{Si}(p, \gamma)$ measurements [52-54]. Thus, the data for the IMME are based on various independent measurements which do not show any significant discrepancies.

Table II summarizes the IMME fit results. With the new ${ }^{31} \mathrm{Cl}$ mass value, the quadratic IMME fails $\left(\chi_{n}^{2}=11.6\right)$ and a significant nonzero cubic coefficient $d=-3.5(11) \mathrm{keV}$ is obtained. The more precise mass for ${ }^{31} \mathrm{Cl}$ reveals the breakdown of the IMME: with the AME12 mass value for ${ }^{31} \mathrm{Cl}$ the quadratic IMME fits perfectly well $\left(\chi_{n}^{2}=0.08\right)$. So far, only $A=9$ [16], $A=35$ [20], $A=53$ [21], and recently $A=21$ [17], of the known $T=3 / 2$ quartets have shown significant nonzero

TABLE I. Mass-excess values $\Delta$ and excitation energies $E_{x}$ for the $J^{\pi}=3 / 2^{+}, T=3 / 2$ isobaric analog states at $A=31$. The massexcess value of ${ }^{31} \mathrm{Cl}$ is from this work, the others are from the AME12 [6].

| Nucleus | $T_{Z}$ | $\Delta(\mathrm{keV})$ | $E_{x}(\mathrm{keV})$ |
| :--- | :---: | :---: | :---: |
| ${ }^{31} \mathrm{Cl}$ | $-3 / 2$ | $-7034.7(34)$ | 0 |
| ${ }^{31} \mathrm{~S}$ | $-1 / 2$ | $-19042.52(23)$ | $6280.60(16)[60]$ |
| ${ }^{31} \mathrm{P}$ | $+1 / 2$ | $-24440.5411(7)$ | $6380.8(17)[51]$ |
| ${ }^{31} \mathrm{Si}$ | $+3 / 2$ | $-22949.04(4)$ | 0 |

TABLE II. Coefficients for the quadratic and cubic IMME fits (in keV) for the $T=3 / 2$ quartet at $A=31$.

|  | Quadratic | Cubic |
| :--- | :---: | :---: |
| $a$ | $-15465.4(26)^{\mathrm{a}}$ | $-15463.2(10)$ |
| $b$ | $-5302.7(32)^{\mathrm{a}}$ | $-5296.9(20)$ |
| $c$ | $209.1(32)^{\mathrm{a}}$ | $209.5(10)$ |
| $d$ | 11.6 | $-3.5(11)^{\mathrm{b}}$ |
| $\chi_{n}^{2}$ |  |  |

${ }^{\text {a }}$ The parameter uncertainty has been scaled with $\sqrt{\chi_{n}^{2}}$.
${ }^{\mathrm{b}}$ During the review process, $E_{x}=6279.0(6) \mathrm{keV}[59]$ for the IAS in
${ }^{31} \mathrm{~S}$ was published. The new value, which differs $2.6 \sigma$ from Ref. [60], yields $\chi^{2} / n=16.2$ for the quadratic IMME and a cubic coefficient of $d=-4.3(11) \mathrm{keV}$.
cubic coefficients (see Fig. 3). New precision measurements pave the way toward a more fundamental understanding of the reasons behind the breakdown. Isospin mixing has successfully explained the breakdown of the IMME at $A=9$ [16] and $A=32$ [22] but failed at $A=21$ [17], albeit detailed shell-model calculations were carried out.

The role of isospin mixing in the IMME is not straightforward. The quadratic IMME works well for the $A=33, J^{\pi}=$ $1 / 2^{+}, T=3 / 2$ quartet ( $\chi_{n}^{2}=0.06$ [13]), although isospinforbidden beta-delayed protons observed from the IAS at 5548 keV in ${ }^{33} \mathrm{Cl}$ (see, e.g., Refs. [55,56]) imply that there must be isospin mixing in the IAS. Interestingly, the cubic coefficients for the $A=31[d=-3.5(11) \mathrm{keV}]$ and $A=35$ [ $d=-3.37$ (38) keV [13] ] $J^{\pi}=3 / 2^{+}, T=3 / 2$ quartets are very similar, which motivates further theoretical studies of these neighboring members of the $A=4 n+3$ series of the $T=3 / 2$ quartets. Isospin mixing has been discussed for $A=35[20,57]$ but no clear explanation for the breakdown has been given so far. Isospin mixing is plausible also for


FIG. 3. Cubic coefficients for the known (lowest) $T=3 / 2$ isobaric quartets. The value for $A=31$ (red square) is from this work, for $A=21$ from Ref. [17], and the rest have been adopted from Ref. [13]. The lower panel shows the significance of the deviation from zero.
the $A=31$ quartet because there are candidates for the $T=1 / 2,3 / 2^{+}$states $[58,59]$ close to the $T=3 / 2$ IAS.

The breakdown of the IMME at $A=31$ is a crucial finding since the proton separation energy $S_{p}=282.8(44) \mathrm{keV}$ based on the quadratic IMME prediction from Ref. [1] has been used in Ref. [60] to determine the adopted level energies in ${ }^{31} \mathrm{Cl}$ from the beta-delayed proton data of ${ }^{31} \mathrm{Ar}$ [26-29]. The new mass value of ${ }^{31} \mathrm{Cl}$ shows it is less bound than previously expected. The proton separation energy $S_{p}=264.6(34) \mathrm{keV}$ is 31 keV lower and $\approx 15$ times more precise than the AME12 value [ $S_{p}=296(50) \mathrm{keV}$ [6] ]. The new mass measurement shifts all levels based on beta-delayed proton data [26-29] 18 keV lower in energy and reduces the inherent systematic uncertainties from 50 keV to 3.4 keV . The revised energy for the $J^{\pi}=$ $5 / 2^{+}, T=5 / 2$ IAS in ${ }^{31} \mathrm{Cl}$, the member of the $T=5 / 2$ sextet at $A=31$, is $12292.2(23) \mathrm{keV}$ based on Refs. [26,28] and the $S_{p}$ and $S_{2 p}$ values from this work.

The two lowest excited states in ${ }^{31} \mathrm{Cl}$ are relevant for the radiative resonant proton captures in the $r p$ process. By combining the new $S_{p}$ value with the beta-delayed proton data of Refs. [26,28], excitation energies of 726(16) and $1728(4) \mathrm{keV}$ are obtained for the $1 / 2^{+}$and $5 / 2^{+}$states, respectively. The excitation energy for the first-excited state agrees well with the USDB shell-model value of 724 keV [30]. However, the excitation energies are lower than the presently recommended values [740(50) and $1746(5) \mathrm{keV}$ [60] ] and the recent results from $\mathrm{R}^{3} \mathrm{~B}$ [782(32) and 1793(26) keV [30] ]. The weighted mean for the resonance energies was calculated from Refs. [26,28,30] by using the $S_{p}$ value from this work for Ref. [30]. The resulting resonance energies, $E_{r}=472(14) \mathrm{keV}$ and $1464(2) \mathrm{keV}$, are very close to the beta-delayed proton data $[26,28]\left[E_{r}=461(16) \mathrm{keV}\right.$ and $\left.1464(2) \mathrm{keV}\right]$. The resonant proton capture rate to the first-excited state is slightly lower with the new resonance energy but, because the


FIG. 4. The ratio of $(\gamma, p)$ to $(p, \gamma)$ rates for typical XRB conditions. The uncertainties related to the JYFLTRAP $Q$ value are shown by the blue lines and to the AME12 value by the gray-shaded area. The dashed lines indicate the temperatures where $\lambda_{\gamma, p}$ is equal to $\lambda_{p, \gamma}$.
resonance energies agree within the error bars, the calculated proton-capture rates do not change significantly from Ref. [31].

The new $S_{p}$ value was used to compute the ratio of photodisintegration rate on ${ }^{31} \mathrm{Cl}$ to the proton capture rate on ${ }^{30} \mathrm{~S}$ according to Eq. (1) and using $\lambda_{p, \gamma}=N_{A}\langle\sigma v\rangle_{r} \rho \frac{X_{i}}{m_{H}}$ for typical XRB conditions with density $\rho=10^{6} \mathrm{~g} / \mathrm{cm}^{3}$ and hydrogen mass fraction of $X_{H}=0.73$. The uncertainty related to the $Q$ value has been significantly reduced and the photodisintegration rate takes over at lower temperatures compared to the ratio calculated with the AME12 $Q$ value (see Fig. 4). Above 0.44(1) GK, at least $20 \%$ of the reaction and decay flow has to wait for $\beta^{+}$decay of ${ }^{30} \mathrm{~S}$ and it becomes a waiting point. The upper-temperature limit for the ${ }^{30} \mathrm{~S}$ waiting point, $1.0(3) \mathrm{GK}$, comes from the rate of the unmeasured ${ }^{30} \mathrm{~S}(\alpha, p){ }^{33} \mathrm{Cl}$ reaction [31].

The JYFLTRAP Penning-trap mass measurement of ${ }^{31} \mathrm{Cl}$ has shown that the quadratic IMME fails at $A=31$ and the cubic term is nonzero. Theoretical calculations are anticipated
to explain the deviation from the quadratic form and to explore possible underlying reasons for similarities in the cubic coefficients for $A=31$ and $A=35$. Isospin mixing between $T=1 / 2$ and $T=3 / 2$ states is plausible because there are candidates for $3 / 2^{+}$states lying nearby the IAS. The improved precision in the proton separation energy of ${ }^{31} \mathrm{Cl}$ has reduced the uncertainties related to excitation energies in ${ }^{31} \mathrm{Cl}$ and the photodisintegration rate of ${ }^{31} \mathrm{Cl}$. Photodisintegration starts to dominate at lower temperatures than previously thought. The improved rate will be useful for future XRB model calculations helping to interpret the observed double-peaked structure in the luminosity curves.

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