Truly chiral phonons in $\alpha$-HgS

Chirality is a manifestation of the asymmetry inherent in nature. It has been defined as the symmetry breaking of the parity of static objects, and the definition was extended to dynamic motion such that true and false chiralities were distinguished. Recently, rotating, yet not propagating, atomic motions were predicted and observed in two-dimensional materials, and they were referred to as ‘chiral phonons’. A natural development would be the discovery of truly chiral phonons that propagate while rotating in three-dimensional materials. Here we used circularly polarized Raman scattering and first-principles calculations to identify truly chiral phonons in chiral bulk crystals. This approach enabled us to determine the chirality of a crystal in a non-contact and non-destructive manner. In addition, we demonstrated that the law of the conservation of pseudo-angular momentum holds between circularly polarized photons and chiral phonons. These findings are expected to help develop ways for transferring the pseudo-angular momentum from photons to electron spins via propagating chiral phonons in opto-phononic-spintronic devices.
focused on examining the phonon symmetry without considering PAM and AM.

Here we used circularly polarized Raman spectroscopy (Methods) to observe the phonon modes and their splitting in chiral crystals of α-HgS. Moreover, we performed first-principles calculations (Methods) to compute the dispersion, PAM and AM of phonons in α-HgS. A comparison between the experiment and calculation shows that the split phonons were indeed truly chiral phonons. We also confirmed that the conservation law of PAM holds in circularly polarized Raman scattering by taking into account the three-fold rotational symmetry. Trigonal α-HgS crystals contain two enantiomeric cinnabar structures with right- and left-handed helices (R- and L-HgS), which belong to the space groups $P3_21$ (translation by $c/3$ in three-fold rotation) and $P3_21$ (translation by $2c/3$ in three-fold rotation), respectively. This crystal has a three-fold helical axis along the $c$ direction (Fig. 1a), with large optical activity. Our samples were single crystals of naturally grown α-HgS with lateral dimensions of 3 mm. We selected a $c$-axis-oriented as-grown surface of R-HgS, which was confirmed by X-ray analysis.

The phonon modes at the centre of the Brillouin zone ($Γ$ point) of α-HgS are classified into two $Γ^{(1,2)}$ singlets (Raman active), three $Γ^{(2,3)}$ singlets (infrared active) and five $Γ^{(2,5)}$ doublets (Raman and infrared active). Our measurement led to the observation of the $Γ^{(1,2)}$ singlets and $Γ^{(2,5)}$ doublets, which were assigned on the basis of the selection rule. For the four incident/scattered polarization configurations (RR, LL, RL and LR), where $l_{i6}^i l_{i6} l_{a6} = 1:1:0:0$ and $0:0:1:1$ for the $Γ_1$ and $Γ_3$ modes, respectively (Extended Data Fig. 1). The transverse optical (TO) phonons of the $Γ_3$ mode were generated because the incident and scattered light were propagated along the $c$ axis. A weak signal was detected for the longitudinal optical (LO) phonon at $-145 \text{ cm}^{-1}$, presumably owing to misalignment of the experimental setup.

The phonon frequencies obtained by the Raman experiment are compared with the results of the first-principles calculations and with previous results in Extended Data Table 1. The results of the Raman experiments both of our study and of a previous study are identical to within $3 \text{ cm}^{-1}$. The results of our calculations at the $Γ$ point also closely approximate those in ref. 16, and the small differences are attributed to the difference in the positions of the atoms. In our experiments, the $Γ_3$ mode was not observed because this mode is nearly degenerate with the $Γ_1$ mode, which has a much higher intensity. In Extended Data Table 1, the frequencies of the $Γ_3$ modes obtained in our Raman experiment are averaged for the RL and LR configurations, which were split as shown in the next paragraph.

The Stokes and anti-Stokes Raman spectra (Raman optical activity) of each $Γ^{(2,5)}$ mode are shown in Fig. 2a–h. All four $Γ_1$ modes were observed with the opposite circularly polarized light between the incident and scattered light (RL and LR). On the anti-Stokes spectra (Fig. 2a–d), the absolute values of the Raman shift of the $Γ_1$ and $Γ_3$ modes in the RL configuration are lower than those in the LR configuration in Fig. 2a,c. In Fig. 2b,d, the absolute values of the Raman shift of the $Γ_1$ and $Γ_3$ modes in the RL configuration are higher than those in the LR configuration. On the Stokes spectra (Fig. 2e–h), the splittings are mirror images of those on the anti-Stokes spectra (Fig. 2a–d). The $Γ_1$ modes do not split.

The properties of phonons are discussed here on the basis of our first-principles calculations. Figure 3a displays the phonon dispersion curve calculated along the path $Δ$ from the $Γ$ to $A$ point, which is parallel to the $c$ axis (Fig. 1b). Linear splittings of $Γ^{(2,5)}$ modes appear around the $Γ$ point, which is consistent with previous calculations. From the conservation law of pseudo-momentum, the wavenumber $k$ of phonons observed by backscattering Raman spectroscopy is expressed as

Figure 1 | Chiral properties of α-HgS. a, Right-handed helical chain along the $c$ axis of R-HgS. Each Hg atom (red sphere) is bonded to two S atoms (blue spheres). Chemical bonds are denoted by green lines. b, Brillouin zone of α-HgS. The blue lines indicate the reciprocal lattice vectors. The green lines and dots represent the high-symmetry paths and points, respectively. c, Schematic diagram of phonon dispersion from the $Γ$ to $A$ point. Filled red, blue and black circles at the $N$ point correspond to the phonon modes of $Γ_1$, $Γ_2$ and $Γ_3$, respectively. d-f, Two-dimensional projections of schematic atomic motions (Hg, gold arrows; S, blue arrows) in R-HgS at point $N$ for a $Γ_1$ mode with $m^{PAM}_s = +1$ and $m^{AM}_s > 0$ (d), a $Γ_1$ mode with $m^{PAM}_s = -1$ and $m^{AM}_s < 0$ (e) and a $Γ_3$ mode with $m^{PAM}_s = 0$ and $m^{AM}_s = 0$ (f). The black lines indicate the lattice vectors. Counter-clockwise, clockwise circular and linear motions indicate that $m^{PAM}_s$ is positive, negative and zero, respectively. The three-fold rotation symmetry operation generates phase factors of atomic motions, namely $PAM m^{PAM}_s$. The phase difference at the position of each atom after the operation is shown.
as \( k = \frac{4\pi n}{\lambda} \), where \( \lambda \) is the wavelength of the incident or scattered light, and \( n = 2.77 \) is the absolute value of the complex refractive index of \( \alpha\)-HgS\(^{21}\). The value of \( k \) was calculated to be \( \approx 1/80 \) of the wavenumber \( \frac{\pi}{c} \) at the A point. We denoted this specific point on the path \( \Delta \) as ‘N’ in Fig. 3a. The experimental splitting values of the \( \Gamma_3 \) modes at this point (Stokes scattering) are almost consistent with the calculations (Extended Data Table 2). Therefore, we attribute the splits observed in Fig. 2 to the linear \( k \) shifts at the N point.

To understand the selection rule of the incident/scattered polarization configurations on the Raman spectra in Fig. 2, we calculated the PAM of phonons in R-HgS (Methods). As shown in Fig. 3a, the \( \Gamma_3 \) doublets have spin PAM \( m_{\text{PAM}}^s = \pm 1 \), whereas the \( \Gamma_3 \) and \( \Gamma_1 \) singlets have \( m_{\text{PAM}} = 0 \). The phonon bands with \( m_{\text{PAM}}^s = 1 \) and \( m_{\text{PAM}} = 0 \) intersect at the A point. These are the common features of the 31 (right-handed) helix\(^4,9,22\).

From Figs. 2e–h and 3a, \( \Gamma_3 \) doublets and \( \Gamma_1 \) phonons with \( m_{\text{PAM}} = 0 \) were observed in the RR and LL configurations, respectively (Extended Data Table 2). \( \Gamma_1 \) phonons with \( m_{\text{PAM}} = \pm 1 \) were observed in the LR and RL configurations. Right- and left-handed circularly polarized light possess PAM of \( \sigma = +1 \) and –1, respectively\(^{23}\). Therefore, we confirmed a conservation law to exist between the spin PAM of phonons and the PAM of the incident/scattered photons in the Stokes spectra as

\[
\sigma_s - \sigma_i = -m_{\text{PAM}}^s + 3p,
\]

where \( \sigma_i \) and \( \sigma_s \) represent the PAM of the scattered and incident photons, respectively. In addition, \( p = 0 \) and \( \pm 1 \) for the \( \Gamma_3 \) and \( \Gamma_1 \) modes, respectively. The factor 3p on the right-hand side of equation (1) can be understood by considering the three-fold rotational symmetry of \( \alpha\)-HgS and the Umklapp process in Raman scattering\(^{24-27}\).

In crystals with discrete rotational symmetry, a clear distinction should be made between the PAM and AM of the phonons. The AM of phonons arises from the circular vibration of atoms in the real space, as shown in Fig. 1d–f (see also Supplementary Videos 1 and 2). The AM of phonons along the c axis is displayed in Fig. 3b along with the

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**Fig. 2 | Raman spectra of R-HgS.** a–h. Anti-Stokes (a–d) and Stokes (e–h) spectra of the \( \Gamma_3 \) (a,e), \( \Gamma_3 \) (b,f), \( \Gamma_3 \) (c,g) and \( \Gamma_3 \) (d,h) modes, along with the \( \Gamma_3 \) modes observed experimentally with RL- (blue line) and LR polarized (red line) configurations and the \( \Gamma_3 \) doublet splittings (dashed vertical lines) in a–h. The error values take into account that multiple splitting measurements were conducted in the experiment, owing to the roughness of the sample surface.
modes at the N point are calculated by the positive and negative AM, respectively. The wavenumbers at the N and A points are in the ratio of 1:80.

The labels of the irreducible representations are Δ from Γ to A, three irreducible representations are known to exist: Δ₁, Δ₂ and Δ₃. This means that the splitting of the Γ₃ modes is a characteristic feature of chiral systems. In other words, spin PAM mᵢ (RH) = 0, +1 and −1 correspond to Δ₃, Δ₂ and Δ₁, respectively, because the phase change by three-fold rotation is the index of each irreducible representation. For L-HgS, mᵢ (LH) = 0, +1 and −1 correspond to Δ₁, Δ₂ and Δ₃, respectively.

Finally, we discuss the propagation of the chiral phonons. From Fig. 3, the group velocities of the {Δ₁, Δ₂} modes at the N point are calculated to be approximately ±(0.4–2) × 10³ m s⁻¹, which is comparable to the sound velocity of acoustic phonons. Note that the nonreciprocal propagation of chiral phonons can be controlled by the PAM of the photon. This implies the possibility of transferring the PAM from phonons to electron spins via propagating chiral phonons in opto-phononic spintronic devices. For example, taking advantage of the long coherence of long-wavelength phonons, transferring the PAM from phonon to electron spins may be realized on the macroscopic scale.

Weyl phonons can exist widely in chiral crystals, as has been predicted by the first-principles calculations and verified by inelastic X-ray scattering. Note that the circularly polarized Raman spectroscopy presented in this paper may open the possibility to detect phonons carrying a non-zero Chern number by measuring the phonon PAM, instead of detecting the eigenvalue and eigenvectors of the topological bands.

We observed chiral phonons in a three-dimensional chiral system using circularly polarized Raman spectroscopy and first-principles calculations. The chiral phonons were labelled with spin PAM of {+1, −1} corresponding to {Δ₃, Δ₂} and {Δ₂, Δ₃} for R- and L-HgS, respectively, with opposite group velocities of ~1 km s⁻¹. The parity and time-reversal symmetries of the phonons satisfy the definition of truly chiral phonons, which propagate while rotating along the c axis. This is distinct from the chiral phonons observed in two-dimensional hexagonal systems. Our work also provides an optical method to identify the handedness of chiral materials using PAM, and we demonstrated that spatial imaging of chiral domains can be achieved in a non-contact and non-destructive manner.

Online content
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Methods
Raman scattering
We used a custom-built Raman spectroscopy system equipped with a monochromator, charge-coupled device camera and optical elements. Details of the setup can be found in Supplementary Fig. 2. The excitation light was generated by a diode laser with a wavelength of $\lambda = 785$ nm. The incident and scattered light were propagated along the c axis of the crystal. All the measurements were performed at room temperature.

First-principles calculations
First-principles calculations were performed using the ABINIT package, which implements density functional perturbation theory. An anaddb code was used to obtain the phonon dispersion curve. For the calculation of the phonon dispersion, the exchange-correlation energy of electrons is described in the generalized gradient approximation with norm-conserving pseudo-potentials, and spin–orbit coupling was not considered. We set the kinetic energy cut-off to 60 Ha, which was necessary to obtain a well-converged result, and the wave vector $k$ of the phonon dispersion curve. In addition, we increased the precision of the $k$ grids to 8 x 8 x 8 to obtain the converged phonon frequencies at the $\Gamma$ point. The following lattice parameters of $\alpha$-HgS were used: cell volume of $V_0 = 160.02 \AA^3$, cell lengths of $a = 4.11 \AA$, $b = 4.11 \AA$ and $c = 9.40 \AA$, and cell angles of $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 120^\circ$. HgS is composed of three Hg atoms at $(0.699, 0.699, 0.000)$, $(0.000, 0.301, 0.23)$ and $(0.301, 0.000, 1/3)$ and three S atoms at $(0.509, 0.509, 1/2)$, $(0.000, 0.491, 1/6)$ and $(0.491, 0.000, 5/6)$, whereas L-HgS is composed of three Hg atoms at $(0.699, 0.699, 0.000)$, $(0.301, 0.000, 2/3)$ and $(0.000, 0.301, 1/3)$ and three S atoms at $(0.509, 0.509, 1/2)$, $(0.491, 0.000, 1/6)$ and $(0.000, 0.491, 5/6)$, of which the bases are the a, b and c components. The essential part of the ABINIT results was confirmed using the VASP package.

Calculation of PAM
In a material with three-fold rotational symmetry, PAM is defined as

$$\{C_3 | 0\} u(k) = \exp[-\frac{2\pi i}{3} m_p^{\text{PAM}}(k)] u(k),$$

where $m_{pam}(k)$ is the PAM of phonons, $u(k)$ is the displacement vector and $\{C_3 | 0\}$ is the three-fold rotation around the c axis. However, $\alpha$-HgS has a three-fold helical rotational symmetry instead of a three-fold rotational symmetry. Therefore, we defined the PAM of phonons in R- and L-HgS as

$$\{C_3 | c/3\} u(RH, k) = \exp[-\frac{2\pi i}{3} m_p^{\text{PAM}}(RH, k)] u(RH, k),$$

$$\{C_3 | 2c/3\} u(LH, k) = \exp[-\frac{2\pi i}{3} m_p^{\text{PAM}}(LH, k)] u(LH, k),$$

where $\{C_3 | c/3\}$ and $\{C_3 | 2c/3\}$ are combinations of the three-fold rotation around the c axis and the c/3 and 2c/3 translations along the c axis, respectively.

The displacement vector of phonons can be expressed as

$$u_k(l, j) = m_s^{-1} e_0(k, j) \exp[\{i |k \cdot R_j - \omega(k, j)t\}],$$

where $j$ is the number of phonon modes, $m_s$ is the mass of the $j$th atom in the $l$th unit cell, $e_0(k, j)$ is the eigenvector of the dynamical matrix and $R_j$ is the position of the $l$th unit cell. The use of equation (5) indicates that the phase of the eigenvector consists of two parts: $e_0(k, j)$ and $\exp[|k \cdot R_j|]$ both of which contribute to the calculation of the PAM. In the former, the phase difference of $e_0(k, j)$ leads to the spin PAM $m_{pam}^s$ which is quantized as an integer. The latter factor, $\exp[|k \cdot R_j|]$ provides the orbital PAM $m_{pam}^o$ which is therefore equal to $\frac{1}{2}k \cdot c$ under a three-fold helical rotation. Consequently, for each wavenumber $k$, the total PAM is

$$m_{pam} = m_{pam}^s + m_{pam}^o.$$  

Here we considered only the spin PAM in the phonon dispersion, as shown in Fig. 3a.

Calculation of AM
The AM of phonons at wavenumber $k$ of mode number $j$ is defined as

$$m_{am}(k, j) = (e(k, j)^{\dagger} M(k, j) e(k, j)) \hbar,$$

where $M = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$, which is the position of the $\Gamma$ point.

The origin of spin and orbital PAMs
Here we provide an explicit form of the spin and orbital PAMs associated with the non-primitive translation. The atomic displacement vector field $u_k(r)$ associated with the phonon propagation may be generally written as

$$u_k(r) = e(k) \exp[i(k \cdot r)].$$

Then, $u_k(r)$ is transformed in accordance with a general rule

$$[C_3 | c/3] u_k(r) = [C_3 e(k)] \exp[i(k \cdot [C_3 | c/3]^{-1} r)].$$

Note that $[C_3 | c/3]^{-1} = [C_3^{-1} | c^{-1} c/3]$.

where $C_j e(k) = \exp(-\frac{2\pi i}{3} m_p^{\text{PAM}})$, thus we have

$$[C_3 | c/3] u_k(r) = \exp[-\frac{2\pi i}{3} (m_p^{\text{PAM}} + m_p^{\text{o}})] u_k(r),$$

where the respective spin and orbital PAMs are introduced as

$$m_{pam} = m, $$

and

$$m_{pam}^o = \frac{3}{2\pi} [\{(k, k) \cdot \hat{r} + \frac{1}{\sqrt{2}} (C_3 k) \cdot c \}],$$

which yield the total PAM, $m_{pam} = m_{pam}^s + m_{pam}^o$.

In this study, we consider the path $A$ from $\Gamma$ to $A$, where $C_3 k = k$ denotes the modulo reciprocal lattice vectors. Thus, $m_{pam}^o = \frac{1}{2\pi} k \cdot c$. The same symmetry properties apply to the photons propagating along the helical axis. Then, we obtain the selection rule in equation (1), which includes only $m_{pam}^o$ by cancelling out the $m_{pam}^s$ terms because of the law of conservation of momentum.

Data availability
Source data are provided with this paper.

Code availability
All custom codes used for the data processing and numerical simulations are available from the corresponding author upon reasonable request.
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Author contributions
T.S. and J.K. conceived the study. K.I. and H.M. performed the Raman experiments. Y.K., Y.T. and S.I. conducted the X-ray analyses. K.I., H.M., T.Z. and S.M. performed the first-principles calculations. K.I., H.M., J.K. and T.S. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

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Extended Data Fig. 1 | Full Raman spectra of R-HgS. Full Raman spectra were recorded at room temperature using various polarized configurations. The black, green, red and blue spectra represent the LL-, RR-, LR- and RL-polarized configurations, respectively. R and L represent the right- and left-handed helicities of circularly polarized light, respectively.
Extended Data Fig. 2 | Dispersion of L-HgS along the left-handed helical axis. (a) Phonon dispersion curves for spin PAM $m_{\text{PAM}}^s = 0$ (black), +1 (red) and −1 (blue). (b) Phonon AM along the helical axis, denoted by the colour gradient. Red and blue curves correspond to the positive and negative AM, respectively.
Extended Data Fig. 3 | Raman spectra of α-HgS with unknown chirality. (a–h), Anti-Stokes (a–d) and Stokes (e–h) spectra of the $\Gamma_3^{(2)}$ (a,e), $\Gamma_3^{(3)}$ (b,f), $\Gamma_3^{(4)}$ (c,g) and $\Gamma_3^{(5)}$ (d,h) modes, along with the $\Gamma_3$ modes observed experimentally with RL- (blue line) and LR-polarized (red line) configurations and the $\Gamma_3$ doublet splittings (dashed vertical lines) in (a–h). The error values take into account that multiple splitting measurements were conducted in the experiment, owing to the roughness of the sample surface.
Extended Data Table 1 | Phonon frequencies in α-HgS. The experimental values in cm⁻¹ were obtained at room temperature. The calculated values in cm⁻¹ are at the Γ point.

| Symmetry | Our experiments | Experiments | Our calculations | Calculations |
|----------|-----------------|-------------|------------------|--------------|
| Γ₂₁𝐿Ｏ   | Inactive        |             | 40.2             | 44.1         |
| Γ₁      | 42              | 45          | 41.0             | 39.1         |
| Γ₃₁𝑇Ｏ   | 43.5            |             |                  | 42.0         |
| Γ₂₂𝑇Ｏ   | 85              | 88          | 84.4             | 83.1         |
| Γ₃₂𝑇Ｏ   | 103             | 106         | 114.4            | 121.4        |
| Γ₄₀     | Inactive        |             | 149.4            | 159.6        |
| Γ₂₀     | 254             | 256         | 237.5            | 232.1        |
| Γ₃₁     | 282             | 283         | 263.0            | 259.3        |
| Γ₃₂     | 344             | 345         | 320.2            | 319.2        |
| Γ₅₀     | Inactive        |             | 339.4            | 337.7        |
Extended Data Table 2 | Chiral properties of phonons in R-HgS along the right-handed helical axis. Owing to the roughness of the sample surface, multiple splitting measurements were conducted, with the deviation indicated by the error values.

| Symmetry at \( \Gamma \) point | Experiment | | Calculation |
|---------------------------------|------------|-----------------|--------------|
|                                 | Config.    | Frequency [cm\(^{-1}\)] | Splitting [cm\(^{-1}\)] | Symmetry at N point | Frequency [cm\(^{-1}\)] | Splitting [cm\(^{-1}\)] | \( m_{\text{PAM}} \) | \( m_{\text{AM}} \) |
| \( \Gamma_3^{(2)} \)            | RL         | 84.9            | 0.3 ± 0.01    | \( \Delta_3^{(2)} \) | 84.2          | 0.4            | -1            | -           |
|                                 | LR         | 85.3            | 0.3 ± 0.01    | \( \Delta_2^{(2)} \) | 84.6          | 0.4            | +1            | +           |
| \( \Gamma_3^{(3)} \)            | LR         | 103.2           | 0.3 ± 0.16    | \( \Delta_2^{(3)} \) | 114.0         | 0.9            | +1            | -           |
|                                 | RL         | 103.5           | 0.3 ± 0.16    | \( \Delta_3^{(3)} \) | 114.9         | 0.9            | -1            | +           |
| \( \Gamma_3^{(4)} \)            | RL         | 281.9           | 0.4 ± 0.08    | \( \Delta_3^{(4)} \) | 262.7         | 0.7            | -1            | +           |
|                                 | LR         | 282.3           | 0.4 ± 0.08    | \( \Delta_2^{(4)} \) | 263.4         | 0.7            | +1            | -           |
| \( \Gamma_3^{(5)} \)            | LR         | 343.5           | 0.3 ± 0.05    | \( \Delta_2^{(5)} \) | 320.0         | 0.4            | +1            | +           |
|                                 | RL         | 343.7           | 0.3 ± 0.05    | \( \Delta_3^{(5)} \) | 320.4         | 0.4            | -1            | -           |
Extended Data Table 3 | Chiral properties of phonons in α-HgS with unknown chirality. The error values take into account that multiple splitting measurements were conducted in the experiment, owing to the roughness of the sample surface. Calculations were performed for L-HgS.

| Symmetry at Γ point | Config. | Frequency [cm\(^{-1}\)] | Splitting [cm\(^{-1}\)] | Symmetry at N point | Frequency [cm\(^{-1}\)] | Splitting [cm\(^{-1}\)] | \(m_{PAM}^s\) | \(m_{AM}^s\) |
|---------------------|---------|------------------------|------------------------|---------------------|------------------------|------------------------|--------|--------|
| \(\Gamma_3^{(2)}\)  | LR      | 84.6                   | 0.4 ± 0.04             | \(\Delta_2^{(2)}\)  | 84.2                   | 0.4                    | +1     | +      |
|                     | RL      | 85.0                   |                        | \(\Delta_2^{(2)}\)  | 84.6                   |                        |        |        |
| \(\Gamma_3^{(3)}\)  | RL      | 102.9                  | 0.4 ± 0.04             | \(\Delta_2^{(3)}\)  | 114.0                  | 0.9                    | −1     | +      |
|                     | LR      | 103.3                  |                        | \(\Delta_3^{(3)}\)  | 114.9                  |                        | +1     | −      |
| \(\Gamma_3^{(4)}\)  | LR      | 281.9                  | 0.5 ± 0.08             | \(\Delta_2^{(4)}\)  | 262.7                  | 0.7                    | +1     | −      |
|                     | RL      | 282.4                  |                        | \(\Delta_3^{(4)}\)  | 263.4                  |                        | −1     | +      |
| \(\Gamma_3^{(5)}\)  | RL      | 343.1                  | 0.4 ± 0.03             | \(\Delta_2^{(5)}\)  | 320.0                  | 0.4                    | −1     | −      |
|                     | LR      | 343.5                  |                        | \(\Delta_3^{(5)}\)  | 320.4                  |                        | +1     | +      |