Laser and Fourier transform spectroscopy of $^7\text{Li}^{88}\text{Sr}$

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Abstract

LiSr was produced in a heat-pipe oven and its thermal emission spectrum around 9300 cm$^{-1}$ was recorded by a high resolution Fourier transform spectrometer. In addition, selected lines of the spectrum of deeply bound vibrational levels of the $1^2\Sigma^+$ and $2^2\Sigma^+$ states were studied using laser excitation to facilitate the assignment of the lines. The ground state could be described for $\nu' = 0$ to 2, $N''$ up to 105 and the $2^2\Sigma^+$ state for $\nu' = 0$ up to $N'' = 68$. For both states, Dunham coefficients, spin–rotation parameters and potential energy curves were evaluated. A coupling of the $2^2\Sigma^+$ state to the $F^2\Pi$ state was observed, allowing a local description with Dunham coefficients of the $F^2\Pi$ state and an approximate evaluation of the coupling strength.

Supplementary material for this article is available online

Keywords: molecular spectroscopy, alkaline–alkaline earth dimer, potential energy curves, rovibrational spectra

(Some figures may appear in colour only in the online journal)

Introduction

Molecules consisting of one alkali–metal atom and one alkaline–earth atom have received increasing interest for their prospective value in the field of ultracold quantum gases because their ground state $1^2\Sigma^+$ with its electric and magnetic dipole moments offers advantageous properties (see, for example, [1–3]). Rb + Sr have been created in a double species quantum gas mixture with the aim of producing ultracold molecules [2]. For LiYb [3] and RbYb [4], photoassociation at the atom pair asymptote $n^2P_{1/2} + ^1S_0$ is reported showing a vibrational structure. For RbSr, initial results on the vibrational dependence of the hyperfine structure were also obtained. LiBa [5] and LiCa [6] were studied by conventional spectroscopy resolving the deeply bound level structure of the ground and excited $^5\Sigma^+$ states.

For many molecules of this class, ab initio studies for potential energy curves (PECs), transition properties and electric dipole moments of the molecules exist (for example, see [7–11]). Additional ab initio calculations for LiSr have been performed by other groups [12–14]. Figure 1 shows part of the potential energy scheme of LiSr for the atom pair asymptotes Li(2s) + Sr(5s$^2$) and Li(2p) + Sr(5s$^2$) which is almost degenerate with Li(2s) + Sr(5s5p $^3P$). The latter atom pair also leads to molecular quartet states.

In this work, we present the first spectroscopic observation of $^7\text{Li}^{88}\text{Sr}$ and its analysis from which the bottom of the potential energy curves of the ground state $1^2\Sigma^+$ and the first excited state $2^2\Sigma^+$ of $^7\text{Li}^{88}\text{Sr}$ are derived. This was achieved by creating molecular gas in a heatpipe oven and observing the thermal emission spectrum in the near infrared region, which was expected from the ab initio results shown in figure 1. The spectrum gave no indication of more than one isotopologue. Therefore, $^7\text{Li}^{88}\text{Sr}$, formed by the most abundant isotopes of Li and Sr, was most likely observed. Laser excitations of the molecule were performed and were essential for an unambiguous assignment of the dense spectrum. For the observed $2^2\Sigma^+ \leftrightarrow 1^2\Sigma^+$ system, molecular parameters...
are derived. Figure 1 shows a crossing between the excited states $^1\Sigma^+$ and $^2\Sigma^+$. Thus perturbations are expected in the spectrum and estimations for the $^1\Sigma^+$ state will be derived from the observed coupling to the $^2\Sigma^+$ state. A comparison of the results from the $ab\text{ initio}$ studies with the experimental findings of this work is presented.

1. Experimental scheme

A sample of LiSr was prepared in a heatpipe and its thermal emission spectrum was recorded with a Fourier transform spectrometer (FTS). In a second experimental step, selected transitions of the molecule were excited by a tunable external cavity diode laser and the resulting fluorescence was resolved through the FTS.

A heatpipe 88 cm in length and 3 cm in diameter was filled with about 25 g of Sr and about 2 g of Li. As a buffer gas, 30 mbar of argon was used. A mesh was installed in the heatpipe to enable a reflux of material condensing in the cold areas to the ends. Both ends were closed with BK7 windows tilted by a few degrees against the optical axis. One end was used for imaging the emitted light to the spectrometer, and the other end opened to a beam dump for the laser beam. A 40 cm long region in the center of the heatpipe was heated to 915 °C while the ends were kept at room temperature. The thermal emission spectrum of LiSr appears at about 915 °C.

The spectrum was recorded with a Bruker FTS (IFS 120HR). Beam splitters for the near infrared and an IR-enhanced silicon avalanche photodiode (S11519-30, Hamamatsu) were installed. An optical low-pass filter (FGL850S, Thorlabs GmbH) and electronic filters in the detection circuit were applied to restrict the spectrum to the region of interest. It should be noted that the response of the detector vanishes around 8500 cm$^{-1}$, which conveniently suppresses the detection of the rise of the thermal emission for a temperature around 900 °C.

The recorded spectrum ranges from 8500 cm$^{-1}$–12500 cm$^{-1}$; an example is given in figure 2. In the range from 9000–10000 cm$^{-1}$, LiSr dominates the spectral structure. Three prominent bands can be seen from 9000 cm$^{-1}$–10000 cm$^{-1}$, tentatively assigned to the $v'v''= (0–0), (0–1)$ and $(1–0)$ bands. Beyond the $(1–0)$ band there are weaker structures seemingly following a band pattern. They cannot be assigned so far. Starting around 10500 cm$^{-1}$, a spectrum without an obvious band structure can be seen. This structure coincides roughly with the expected $^3\Sigma^+ \leftrightarrow ^1\Sigma^+$ electronic system from the $ab\text{ initio}$ calculations [12], but it is overlapped by the Li$_2$ spectrum.

Figure 3(a) shows part of the recorded emission spectrum of LiSr in detail. To resolve the rotational structure, the thermal emission spectrum was recorded with 0.03 cm$^{-1}$, which provides in the supplementary material (available online at stacks.iop.org/JPB/50/235103/mmedia). The Doppler width is expected to be 0.023 cm$^{-1}$ for $^7$Li$^{88}$Sr at 915 °C which...
justifies the selected resolution of the FTS. After averaging 1080 scans, a signal-to-noise ratio of about 250 can be achieved.

In figure 3(a), the band heads for F1 and F2 of the (0–0) band can be seen on the right side. The R branch turns at $N'' \approx 12$. Most of the higher peaks are due to more than one transition line. The decreasing intensity towards 9380 cm$^{-1}$ is due to a perturbation in the R branch. The same perturbation is reflected in the P branch around 9350 cm$^{-1}$ (see sections 2 and 3 for details on the perturbation). Starting around 9388 cm$^{-1}$ towards lower wavenumber, the R branch of the (1–1) band starts to become visible from the background of the (0–0) emission.

To observe laser-induced fluorescence (LIF), the gas was excited with laser powers up to 100 mW. A diode laser in a Littrow configuration stabilized by a wavemeter (WS-U, High Finesse GmbH) was used to access the range from 9200 cm$^{-1}$–10600 cm$^{-1}$ with an accuracy of 20 MHz. The beam was collimated to a diameter of 2 mm and aligned with the heatpipe axis. LIF in the center of the heatpipe was imaged into the FTS, minimizing stray light in the detection, as the filters could not sufficiently block the backscattered laser light. The LIF spectra were recorded with a resolution of 0.05 cm$^{-1}$, and an example is shown in figure 3(b). The fluorescence line is greatly enhanced compared to the thermal emission lines and has a signal-to-noise ratio of approximately 100 by averaging only ten scans. In the example, the corresponding emission line in the pure thermal spectrum is an overlap of the lines F1 R18, F2 R7 and F2 R14. The LIF spectrum relates undoubtedly P or R lines for an excited rotational level. This is very important for the unambiguous assignment given in section 2.

The observed LIF shows PR-doublets in bands ($v'-(v'' \pm 1)$) directly neighbouring the excited band ($v'-v''$). Rotational satellites from collisional relaxation were sometimes recorded but never spanned more than about five rotational levels. Long vibrational progressions were not observed, as expected from the PECs in figure 1. Laser excitations in the structure from 10500 cm$^{-1}$–12000 cm$^{-1}$ have so far revealed PR-doublets that could be attributed to Li$_2$ [15].

The line position was determined by fitting one or multiple Gaussian curves to a spectral line. The average frequency uncertainty given by the fit is close to the Doppler width. Where this method was not successful due to too many overlapping lines, the center of the spectral line was used as frequency and the FWHM was used as uncertainty. In further analysis, the uncertainty was adjusted to be at least 0.02 cm$^{-1}$.

2. Line assignment

Based on the $ab$ initio calculations from [14], the observed band structure can be expected to be composed of $2 \Sigma^+ \leftrightarrow 1 \Sigma^+$ transitions (see figure 1). LIF experiments with the laser tuned to lines of the most intense band showed associated P and R lines only in the next visible band of lower frequency. Therefore, these bands can be tentatively assigned as the (0–0) and (0–1) bands of this electronic system.

A $2 \Sigma^+$ state can be adequately described in Hund’s coupling case (b) with basis vector $|\Lambda, (N, S, J)\rangle$, where $\Lambda$ is the quantum number of the projection on the molecular axis of the orbital angular momentum (here, zero), $\hat{N}$ is the total angular momentum without spins and $\hat{S}$ is the electron spin. $J = \hat{N} + \hat{S}$ is the total angular momentum of the molecule excluding nuclear spins. The energies of the rovibrational states can be expressed with the conventional Dunham expansion [16]

$$E(v, N) = \sum_{m,n} Y_{m,n}(v + 1/2)^m [N(N + 1)]^n. \quad (1)$$

For a doublet state, levels with $J = N + 1/2$ or $J = N - 1/2$ are labeled by $F_1$ or $F_2$, respectively. The energy differences between the $F_1$ and $F_2$ components are then attributed to the spin–rotation coupling, given by the Hamiltonian $\gamma \hat{S} \cdot \hat{N}$ [16], which is added to the rovibrational energies. $\gamma$ is the coupling constant. The energy of a $J$ level thus evaluates to

$$E_1(v, J) = E(v, N) + \gamma/2 \times N \quad \text{for } F_1 \quad (2a)$$

$$E_2(v, J) = E(v, N) - \gamma/2 \times (N + 1) \quad \text{for } F_2 \quad (2b)$$

for the vibrational and rotational quantum numbers $v$ and $N$ and $E(v, N)$ given by the Dunham expression. The strength of the spin–rotation coupling can change with the internuclear separation and thus a slight dependence on $v$ and $N$ was observed. For mnemonic reasons, this dependence is modeled in analogy to the Dunham expansion:

$$\gamma(v, N) = \sum_{m,n} \gamma_{m,n}(v + 1/2)^m [N(N + 1)]^n. \quad (3)$$

Many lines of the (0–0) band could be assigned to rotational transitions using frequency differences from fluorescence PR-doublets near the band head and the value for the rotational constant given in [14] as a first approximation. The corresponding fluorescence lines in the (0–1) band were assigned accordingly. Lines of both spin components $F_1$ and $F_2$ were assigned up to $N'' = 104$. Figure 4 summarizes the levels of the state $2 \Sigma^+$ that were addressed in the LIF experiments. Because the experimental procedure provides no information regarding the sign of the spin–rotation constant $\gamma$, a definite assignment of spectral lines to $F_1$ or $F_2$ could not be
intensities from the emission spectrum for the perturbed range of quantum numbers identified above. For values of \( N \) around 40 with large perturbation, the intensities reduce significantly, resulting in reduced or vanishing fluorescence from the most perturbed levels. For this reason, the lines from perturbing states, the so-called extra lines, could not be identified because the LIF experiments yielded no identifiable response. This observation is in agreement with the expectation that the perturbation comes from the coupling to the \( ^2\Sigma^+ \) state, which has a low electronic transition moment to the ground state and unfavorable Franck–Condon factors, according to \textit{ab initio} calculations [14] (see also figure 1).

Also with LIF, a system of three connected bands was discovered which are identified as the \((1-0), (1-1)\) and \((1-2)\) bands by inserting the vibrational spacing of the ground state obtained from the fluorescence progressions. LIF experiments in the less intense spectral structure seen between the \((1-0)\) band and 10000 cm\(^{-1}\) in figure 2 were unsuccessful, possibly due to insufficient laser intensity. For the \((1-0)\) band, lines in the range of \( N^\prime = 40 \)– 60 were assigned using the already derived rotational energies of the ground state (see upper part in figure 4) but the excited state could not be described by the Dunham model. For this reason, only the \( \nu' \) = 0 state with rotational levels up to \( N^\prime \) = 68 is considered in this work.

Four hundred and sixty-eight measured transition frequencies and 821 frequency differences of the PR-doublets, along with their assigned quantum numbers, were used for a linear fit of the Dunham coefficients for both \( ^2\Sigma^+ \) states, as given in (1) and spin–rotation parameters in (3). The transitions associated with an upper level that was recognized as perturbed were excluded from this fit.

### 3. Perturbation

A substantial number of observed transition lines suggest perturbations in the \( ^2\Sigma^+ \) state (see figure 5(a)). For the lines with significant deviation from the Dunham model, the LIF experiments proved highly important in ascertaining the quantum number assignment since the PR-differences are exclusively governed by the involved (unperturbed) \( ^2\Sigma^+ \) levels.

According to [14], the \( ^1\Pi_{1/2} \) and \( ^1\Pi_{3/2} \) states are energetically closest to the state under study, \( ^2\Sigma^+ \) and \( ^2\Pi \) states are coupled by the spin–orbit and rotational interaction. Following [17], the matrix representation of the Hamiltonian in Hund’s coupling case (a) with state vector \([\Lambda, \Sigma, \Sigma, J] \) for a total angular momentum \( J \) is derived, where \( \Sigma \) is the quantum number of the projection of \( S \) and \( \Omega = \Lambda + \Sigma \) is the quantum number of the projection of \( J \) to the molecular axis. Hyperfine interaction has not been considered. No effects of the hyperfine structure by additional splitting or on line shapes were observed, and hence it can be assumed that its effects on the line positions are negligible. The matrix is given in table 1. The upper and lower signs correspond to the \( F_1 \) and \( F_2 \) states of a given total angular momentum \( J \).

The diagonal entries describe the energies of the \( ^2\Sigma^+ \) and \( ^2\Pi \) states without coupling. \( E_{\text{Dun}} \) for the \( ^2\Sigma^+ \) state is the

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Figure 5. (a) Deviation of actual transition frequencies in the \((0-0, 1)\) bands from frequencies calculated with the Dunham model. Circles represent transitions in the \((0-0)\) band and triangles represent transitions in the \((0-1)\) band. (b) Deviations considering coupling between electronic states. The grey area depicts the experimental uncertainty.

Figure 6. Intensities of thermal emission lines of the \((0-0)\) band. Line intensities were always determined on a local scale subtracting the background. Overlapping lines were left out if their respective intensities could not be determined. Thermal populations calculated with \( E(\nu' = 0, N^\prime) \approx Y_{01} \times N^\prime(N^\prime + 1) \) are shown for comparison (black circles).
Table 1. Interaction between the $2^3\Sigma^+$ and $1^2\Pi$ states in Hund’s coupling case (a) for a set of vibrational levels $\nu_{\Sigma^+}$, $\nu_{\Pi}$. $E_{\text{Dum}}$ is the energy calculated from Dunham parameters, $\gamma$ is the spin–rotation constant, $A$ is the spin–orbit coupling constant, $B$ is the rotational constant for a given vibrational state. $T_{ij}$ is the electronic energy and $G_{ij}(\nu)$ is the vibrational energy of $1^2\Pi$. The factor $p$ represents the expectation value $\langle\nu_2|L^2|\nu_1\rangle$. Subscripts on the constants indicate a value for the $\Sigma$ or $\Pi$ state or a mixture thereof. Upper signs are for $F_1$ and lower signs for $F_2$.

| $2^3\Sigma^+_{1/2}$ | $1^2\Pi_{1/2}$ | $1^2\Pi_{3/2}$ |
|-------------------|----------------|----------------|
| $E_{\text{Dum}}(v, N = J \mp 1/2)$ | $p/2 [A_{\Sigma^+} - \gamma_{\Sigma^+} + 2 B_{\Sigma^+} (J \mp 1/2)]$ | $-p [A_{\Pi} - \gamma_{\Pi} + 2 B_{\Pi} (J \mp 1/2)]$ |
| $-\gamma_{\Sigma^+}/2 \times [J \mp 1/2]$ | $T_{\Pi} + B_{\Pi} [J (J + 1) + 1/4]$ | $\sqrt{J (J + 1) - 3/4}$ |
| $p/2 [A_{\Sigma^+} - \gamma_{\Sigma^+} + 2 B_{\Sigma^+} (J \mp 1/2)]$ | $G_{\Pi}(\nu) (A_{\Pi} + \gamma_{\Pi})/2$ | $T_{\Pi} + B_{\Pi} [J (J + 1) - 7/4]$ |
| $2 B_{\Sigma^+} (J \mp 1/2)$ | $G_{\Pi}(\nu) (A_{\Pi} - \gamma_{\Pi})/2$ | $G_{\Pi}(\nu) (A_{\Pi} - \gamma_{\Pi})/2$ |

Table 2. Reduced interaction matrix between the $2^3\Sigma^+$ and $2^3\Pi_{1/2}$ state. $d_{\Sigma\Pi} = A_{\Sigma^+} - \gamma_{\Sigma^+}$ and $A = A_{\Pi} \pm \gamma_{\Pi} \approx A_{\Pi}$. The $2^3\Pi_{3/2}$ state is ignored.

| $2^3\Sigma^+_{1/2}$ | $2^3\Pi_{1/2}$ |
|-------------------|----------------|
| $E_{\text{Dum}}(v, N = J \mp 1/2)$ | $p/2 [d_{\Sigma\Pi} + g_{\Pi}(\nu)]$ |
| $-\gamma_{\Sigma^+}/2 \times [J \mp 1/2]$ | $T_{\Pi} - A_{\Pi}/2 + G_{\Pi}(\nu)$ |
| $p/2 [d_{\Sigma\Pi} + g_{\Pi}(\nu)]$ | $+ B_{\Pi} [J (J + 1) - 1]$ |

Figure 7. Rotational energies of the $\nu' = 0$ level of the $2^3\Sigma^+$ state and the three closest vibrational levels of the $1^2\Pi_{1/2}$ state.

required. For the $1^2\Pi$ state we start with parameters taken from [14]. In order to come close to the observed resonant perturbation, $T_{\Pi}$ and $B_{\Pi}$ were adjusted to move the crossing points of the rotational ladders of one vibrational level of $1^2\Pi_{1/2}$ and $\nu_2 = 0$ into the range of maximal deviation (see figure 7). The variation of the sign of the deviation shows that the rotational constant of the perturbing state must be larger than that of state $2^3\Sigma^+$ to obtain repelling levels in the observed direction. Taking this initial choice of parameters for the $1^2\Pi_{1/2}$ state, only $p$, $d_{\Sigma\Pi}$ and $B_{\Pi}$ are unknown for a fit.

Since the $1^2\Pi$ state is not known well enough to assign $\nu_{\Pi}$ unambiguously and thus to calculate the desired overlap integral with the $2^3\Sigma^+$ state with satisfactory reliability, we incorporate parameter $p$ into $d_{\Sigma\Pi}$, and set $B_{\Pi}$ initially to zero. The rovibronic parameters $T_{\Pi}$, $B_{\Pi}$ and $d_{\Sigma\Pi}$ were varied in order to minimize the deviation for all data points shown in figure 5 by a non-linear least-squares fit using the energies obtained after matrix diagonalization. From this fit, unperturbed levels of the $2^3\Sigma^+$ state and corresponding transition frequencies were constructed and then applied in the linear fit with energies represented by equation (2) for the improved Dunham coefficients for the $1^2\Sigma^+$ and $2^3\Sigma^+$ states. For this, 1534 observations (transition frequencies from the thermal emission spectrum, fluorescence lines along with frequency differences from LIF spectra) were used. Such a procedure was cycled and after three iterations the Dunham coefficients

rovibronic energy according to equation (1). For the $2^3\Pi$ state, the energy levels are given by the electronic energy $T_{\Pi}$, vibrational energy $G_{\Pi}(\nu)$ and rotational constant for a vibrational level $B_{\Pi}$. Three additional parameters appear in the matrix: the coupling constants of the spin–rotation interaction and the spin–orbit interaction, $\gamma$ and $A$, and the factor $p = \langle\nu_2|L^2|\nu_1\rangle$, which will be approximated as the product of an overlap integral $\langle\nu_2|\Pi|\nu_1\rangle$ of the coupled vibrational states and the expectation value $\langle\Pi|L^2|\Sigma\rangle$ over the electronic space.

Assuming the electronic states belong to $L = 1$, $\langle L^2 \rangle$ evaluates to $\sqrt{2}$. For all parameters, a subscript indicates the corresponding electronic state. The non-diagonal terms for $\Delta \Omega = 0$ come from spin–orbit interaction and those for $\Delta \Omega = \pm 1$ are rotational interactions; the latter ones also couple $2^3\Sigma^+_{3/2}$ and $1^2\Pi_{1/2}$.

To keep the number of fit parameters low, some simplifications had to be made because we only have data for state $2^3\Sigma^+$, which couples strongly through spin–orbit interaction to the component $\Omega = 1/2$ of $1^2\Pi$ but only weakly by rotation to $\Omega = 3/2$. Thus we reduce the $3 \times 3$-matrix to a $2 \times 2$ case. The coupling constants $A_{\Sigma^+}$ and $\gamma_{\Sigma^+}$ cannot be separated by fitting experimental data. They are combined into the constant $d_{\Sigma\Pi}$. For the same reason, we combine $A_{\Pi}$ and $\gamma_{\Pi}$ to the effective constant $A$. From the difference of the $1^2\Pi_{1/2}$ and $1^2\Pi_{3/2}$ PECs given in the supplement of [14], $A_{\Pi}$ can be estimated to be 118 cm$^{-1}$. The approximate interaction matrix is shown in table 2.

To characterize the perturbation seen in figure 5(a), knowledge about the crossing of the rotational states of the $2^3\Sigma^+$ and $1^2\Pi$ states and the various coupling strengths is
changed by less than the estimated standard deviation from the linear fit. Thus we obtained convergence of the iterative fitting procedure. Finally, the stability of this solution was checked by fitting the parameters for the \( 2^3\Sigma^+ \) and \( 1^2\Pi_{1/2} \) states along with \( d_{3\Pi} \) simultaneously in the non-linear fit step. Additionally, we allowed the variation of the \( J \)-dependent off-diagonal term by \( B_{3\Pi} \). It turned out that this contribution is insignificant in the range of observations. The final coefficients are listed in table 3 together with estimated standard deviations from the linear fit. The standard deviation of the fit was 0.492.

Figure 5(b) shows that the perturbation is well described because most deviations lie within the grey area, which represents the experimental uncertainty. For the \( F_2 \) states closest to the perturbation, no ideal description could be achieved. To improve the modeling, we would like to obtain the \( 1^2\Pi \) data, especially the observation of the extralines expected around the perturbed lines of \( 2^2\Sigma^+ \), but we have so far been unsuccessful in our efforts.

Additionally, a local deviation around \( N'' = 53 \) for \( F_2 \) and \( N'' = 57 \) for \( F_3 \) can be seen in figure 5. These might indicate a crossing of \( 2^2\Sigma^+ \) with \( 1^2\Pi_{1/2} \). That state was ignored in the simplified interaction model and therefore the aforementioned lines were ignored in the fitting process. A manual adjustment of the spin–orbit coupling parameter \( A_{3\Pi} \) to shift the \( 1^2\Pi_{1/2} \) state to the corresponding energies gives a value of \( A_{3\Pi} = 88(2) \text{ cm}^{-1} \), which is still close to the \( ab \) initio value, but we believe that this single observation is not yet conclusive.

### 4. Results and discussion

The deeply bound rovibrational levels of the \( 1^2\Sigma^+ \) and \( 2^2\Sigma^+ \) states of \( ^7\text{Li}^{88}\text{Sr} \) were modeled using thermal emission and LIF spectra. The \( \nu'' = 0 \), 1 levels of the ground state \( 1^2\Sigma^+ \) could be described up to \( N'' = 105 \) and the \( \nu'' = 2 \) level with \( N'' \) ranging from 41–64 by the Dunham parameters, including spin–rotation. Transitions in this system were found to take place mainly between states with the same or a directly neighbouring vibrational quantum number. This restricts the study of the molecule via LIF experiments and becomes a time consuming work because only short progressions were observed. To investigate higher vibrational states for a more complete ground state potential, other studies, including higher lying electronic states, need to be employed.

With the perturbation model from section 3, molecular parameters for the \( \nu' = 0 \) level of the \( 2^2\Sigma^+ \) state with \( N'' < 69 \) were derived. Including higher rotational states in the evaluation has not yet proved successful due to the complex perturbation structure. The isolated perturbation of the rovibrational levels for \( N'' < 69 \) provided an opportunity to gauge the strength of the \( 1^2\Pi — 2^2\Sigma^+ \) coupling and to gain insight into the \( 1^2\Pi \) state. Since the \( 1^2\Pi \) state could not be observed directly with the applied method, this knowledge will be the initial ingredient when incorporating transition lines of higher \( 2^2\Sigma^+ \) levels into the analysis of the spectrum.

The derived molecular parameters are given in table 3. Since only a finite number of parameters were fitted, the given parameters are not the true Dunham parameters; they are significantly affected by the truncation of the power expansion. For example, \( Y_{10} \) of \( 2^2\Sigma^+ \) is the rotational constant \( B_{3\Pi} \) of the evaluated vibrational level. Utilizing the observed perturbation, a parametrization of the energy levels of the \( 1^2\Pi_{1/2} \) state in the neighbourhood of \( \nu_2 = 0 \) of the \( 2^2\Sigma^+ \) state was possible. The effective coupling parameter, \( p/2 \times d_{3\Pi} \) is 2.644 cm\(^{-1}\) is fairly low compared to the estimated spin–orbit parameter around 100 cm\(^{-1}\), indicating the weak overlap of the involved vibrational levels of the \( 1^2\Pi \) and \( 2^2\Sigma^+ \) states. A fit with the \( J \)-dependent coupling parameter \( B_{3\Pi} \) (see table 2) did not provide any significant improvement and showed variations in the value of \( \gamma_{00} \) of \( 2^2\Sigma^+ \) of less than 1%. Thus the effective spin–rotation interaction of \( 2^2\Sigma^+ \) does not originate from the investigated local perturbation but will be the

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### Table 3. Dunham and spin–rotation parameters for the first two \( ^2\Sigma^+ \) states and the first \( ^2\Pi_{1/2} \) state of \( ^7\text{Li}^{88}\text{Sr} \). The parameters give an accurate description for levels with \( N'' < 105 \), \( \nu'' = 0 \), 1 and \( 40 \leq N'' \leq 60 \), \( \nu'' = 2 \) in the \( 1^2\Sigma^+ \) state, \( N'' < 69 \), \( \nu'' = 0 \) in the \( 2^2\Sigma^+ \) state and for \( J'' < 70 \), \( \nu'' \approx 15 \) in the \( 1^2\Pi \) state. All values are given in cm\(^{-1}\).

| \( Y_{10} \) | \( Y_{20} \) | \( F_{2}^{2\Sigma^+} \) | \( \gamma_{10} \) | \( \gamma_{20} \) | \( \gamma_{30} \) | \( n \) |
|-------------|-------------|----------------|-------------|-------------|-------------|----|
| 0.0 | 182.9305(54) | -3.0263(26) | 8.88(46) \times 10^{-3} | -5.28(16) \times 10^{-4} | 0 |
| 2.072284(79) \times 10^{-1} | -3.3395(23) \times 10^{-3} | -1.0525(92) \times 10^{-4} | - | - | 1 |
| -1.0297(17) \times 10^{-6} | -3.662(42) \times 10^{-8} | - | - | - | 2 |
| -5.89(10) \times 10^{-12} | -2.187(32) \times 10^{-12} | - | - | - | 3 |
| 9389.2125(26) | 186.94a | - | 4.651(46) \times 10^{-2} | - | 0 |
| 1.890807(81) \times 10^{-1} | - | - | - | - | 1 |
| -7.922(18) \times 10^{-7} | - | - | - | - | 2 |
| 3.77(14) \times 10^{-12} | - | - | - | - | 3 |
| 5403.7(24)b | 285.634a | -1.91289a | - | - | 0 |
| 2.837(14) \times 10^{-1} | -2.01 \times 10^{-3}a | - | - | - | 1 |

\( a \) Value from [14].

\( b \) Disregarding an offset of \( A/2 \).
Table 4. Comparison of measured spectroscopic constants of $^7$Li$^{88}$Sr with results of various ab initio works. All values are given in cm$^{-1}$, except $R_e$ which is given in Å. Experimental data are rounded for this comparison; actual uncertainties for the underlying Dunham parameters can be found in Table 3.

| Method               | $R_e$  | $D_e$  | $\omega_0 \approx Y_{00}$ | $\omega_a \approx -Y_{20}$ | $B_e \approx Y_{01}$ | $T_e$  | Reference |
|----------------------|--------|--------|-----------------------------|-----------------------------|----------------------|--------|-----------|
| $^1\Sigma^+$         | 3.55   | 2367   | 182.2                       | –                           | –                    | 0      | [13]      |
| CCSD(T)              | 3.531  | 2226.4 | 182.1                       | 4.29                        | 0.203                | 0      | [12]      |
| SO-MS-CASPT2         | 3.579  | 2075.26| 168.62                      | –                           | 0.203                | 0      | [14]$^a$ |
| MRCI                 | 3.574  | 2483   | 179.1                       | 3.22                        | –                    | 0      | [10]      |
| Spectroscopy         | 3.545$^b$ | –    | 182.93                      | 3.03                        | 0.207                | 0      | This work |
| $^2\Sigma^+$         | 3.785  | 6860.54| 186.94                      | –                           | 0.1711               | 9488.63| [14]$^b$ |
| MRCI                 | 3.728  | 7811   | 183.0                       | 1.07                        | –                    | 9469   | [10]      |
| Spectroscopy         | 3.712$^{c,e}$ | (186.94)$^d$ | –                        | 0.18908$^e$ | 9388.31$^{f}$ | This work |

$^a$ Values have been converted to $^7$Li$^{88}$Sr.
$^b$ From RKR calculation.
$^c$ $R_0 = 3.708$ Å.
$^d$ RKR potentials were calculated with $\omega_0$ taken from [14].
$^e$ No one vibrational state was involved.

Together with data from different publications for $^7$Li$^{40}$Ca [6, 18] and $^7$Li$^{138}$Ba [5], a trend in the molecular constants seems to emerge. For the $\Sigma$ states, the product of the reduced mass and the rotational constant decreases with an increase in the reduced mass while the product of the reduced mass and the spin–rotation coupling increases with the reduced mass. This finding relates nicely to the increase of the spin–orbit interaction from Ca via Sr to Ba.

The spectrum of LiSr is fairly dense and thus difficult to analyze due to the many overlapping lines. Thus alkali–alkaline earth dimers with a larger reduced mass should have denser spectra and the LIF method would be immensely advantageous to obtain simplified spectra to help in the assignment of quantum numbers. Work on KCa is in progress in our lab and confirms this expectation.

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