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Analysis of the hyperfine structure of the $1^{3}\Delta_{g}$, $2^{3}\Pi_{g}$, and $3^{3}\Sigma_{g}^{+}$ states of ${}^{6}\text{Li}{}^{7}\text{Li}$



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ABSTRACT

We report on our theoretical analysis of the hyperfine splitting in the spectra of the $1^3\Delta_g$, $2^3\Pi_g$, and $3^3\Sigma_g^+$ triplet states of ⁶Li⁷Li, which were experimentally observed in 2002 (Li et al.) by means of Perturbation Facilitated Optical-Optical Double Resonance (PFOODR) spectroscopy. In our previous work, both homonuclear and heteronuclear molecules were analyzed. However, in this work, we theoretically investigate an isotope-substituted homonuclear molecule for the first time and demonstrate the application of our approach to this case. In our model, we reproduce the major stages of the excitation–deexcitation schemes by considering the mixed nature of the intermediate $A^1\Sigma_u^+ \sim b^3\Pi_{\Omega u}$ singlet–triplet states, whereby the three components of the $\Omega = 0, 1, 2$ basis states might contribute to the hyperfine splitting. We compute the contributions from all components of the mixed states. We present physical models for all triplet states under study, along with the obtained parameters of the analyzed molecular system and the simulation results. Additionally, we describe the principal steps of the computational algorithm in detail.

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1. Introduction

The study of alkali metal dimers has garnered increasing interest because these compounds are among the main candidates for prospective research on the ultracold photoassociation of atomic couples [1–3], the formation of Bose–Einstein or Fermi–Dirac condensates [4], and optical coherent control of quantum dynamics [5–8]. In addition, precision measurements of cold molecules are expected to be efficient tools for the study of the stability/variations of fundamental constants (proton-to-electron mass ratio, fine-structure constant) [9–12].

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Alkali dimers reveal a complex hyperfine structure (HFS) owing to the interactions of two non-zero nuclear spins with each other, with the rotation of the molecule, with the electronic spins, and with the orbital angular momentum. Therefore, it is necessary to obtain accurate quantitative information about their HFS and the parameters of the internuclear interactions.

In [13], Li et al. observed the HFS of the $1^3\Delta_g$, $2^3\Pi_g$, and $3^3\Sigma_g^+$ triplet states of ⁶Li⁷Li by means of the sub-Doppler Perturbation Facilitated Optical-Optical Double Resonance (PFOODR) excitation technique through mixed $A^1\Sigma_u^+$ ($v'_A = 5, J' = 24$) $\sim b^3\Pi_u(v'_b = 12, N' = 23, J' = 24$) window levels. The authors inferred that the Fermi contact interaction between the ⁷Li nucleus and the electron spin is primarily responsible for the HFS of the $3^3\Sigma_g^+$ and $1^3\Delta_g$ states, and that the Fermi contact constants are 110 MHz (367×10^{-5} cm⁻¹) and 107 MHz (357×10^{-5} cm⁻¹), respectively. Additional splittings due to spin-spin, spin-rotation, Fermi contact interactions were not resolved. It was found that the $3^3\Sigma_g^+$ and $1^3\Delta_g$ states

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Fig. 1. ⁶Li⁷Li triplet states' excitation scheme.

follow the case $(b_{\beta S})$ coupling scheme. The $2^{3}\Pi_{g}$ state reveals another coupling scheme and a smaller Fermi contact constant value. They concluded that the different results might be due to the doubly excited nature of the $2^{3}\Pi_{g}$ state.

In [14], Abraham et al. observed a HFS in the photoassociative spectra of ${}^{6}\text{Li}_{2}$ and ${}^{7}\text{Li}_{2}$ in the $A^{1}\Sigma_{u}^{+}$ and $1{}^{3}\Sigma_{g}^{+}$ states. The authors reported that the HFS of the $1{}^{3}\Sigma_{g}^{+}$ state of ${}^{6}\text{Li}_{2}$ was resolved for the first time. They also estimated the Fermi contact constant for the $1{}^{3}\Sigma_{g}^{+}$ state to be $b_{7} = 92.4 \pm 0.8$ MHz (the authors defined *b* as a coefficient in formula *b***S** · **I**, which is largely due to the Fermi contact term of the $\sigma_{g}2s$ orbital; **S** is the electron spin, and $\mathbf{I} = \mathbf{i_{1}} + \mathbf{i_{2}}$ is the nuclear spin). Therefore, according to convention of our work, $\mathcal{B}_{7} = (4 \cdot (\frac{\sqrt{6}}{2})/2) \cdot 92.4 = \sqrt{6} \cdot 92.4 \approx$ 225.35 MHz. In comparison, in earlier experiments on ${}^{7}\text{Li}_{2} \ 1{}^{3}\Delta_{g}^{+}$, $2{}^{3}\Sigma_{g}^{+}$, and $3{}^{3}\Sigma_{g}^{+}$, the Fermi contact constants were determined to be 98.664 MHz (~ 242 MHz) [15], 96.262 MHz (~ 235 MHz) and 95.663 MHz (~ 234 MHz) [16], respectively.

In the present work, we used the experimental data from [13] for a theoretical analysis of the HFS of the $1^{3}\Delta_{g}$, $2^{3}\Pi_{g}$, and $3^{3}\Sigma_{g}^{+}$ triplet states of ${}^{6}\text{Li}{}^{7}\text{Li}$. Fig. 1 demonstrates a schematic diagram of the PROODR fluorescence excitation and resolved fluorescence spectroscopy of the ${}^{6}\text{Li}{}^{7}\text{Li}$ triplet states. The experimental setup and experimental details have been described thoroughly in Li et al. [13,17].

We first compare the calculated parameters of the HFS with the experimentally derived ones for the $1^3\Delta_g$ and $3^3\Sigma_g^+$ states, and then theoretically explain the hyperfine splitting of the $2^3\Pi_g$ state.

Computational algorithms and methods that were improved upon in the past few years allowed us to analyze and simulate the HFS in ultracold photoassociation spectra of the heteronuclear NaCs molecule [18–20], as well as HFS in the PFOODR spectra of the homonuclear molecules Na₂ in the 1³ Δ_g state [21] and Cs₂ in 3³ Σ_g^+ [22]. These approaches take into account the complete excitation–de–excitation scheme and the mixed nature of the intermediate levels $A^1 \Sigma_u^+ \sim b^3 \Pi_{\Omega u}$, which, to the best of our knowledge, has not been realized preciously.

In this paper, we describe the use of our pioneering computational method on an isotope-substituted diatomic molecule, namely, on the ⁶Li⁷Li molecule, which has not been investigated with our approach before. Other objectives were to receive a simulation of the HFS in the spectra, determine predominant hyperfine interactions, and analyze the fine and hyperfine interaction parameters.

2. Theoretical model

In this section, we present the effective Hamiltonian with the corresponding equations for its terms and matrix elements used in our calculations and computational codes. Overall, the entire model is similar to our previous model, with which we considered and analyzed the HFS of the $3^3 \Sigma_g^+$ state of the homonuclear Cs₂ molecule [22]. In the presented computations, we neglected several interactions (such as spin orbit, nuclear spin–electron spin, nuclear spin–electron orbit, nuclear spin–rotation interactions) because their contributions to the hyperfine splitting were found to be insignificant. For this reason, we do not present their formulas in this paper (a more complete model can be found in our previous works [18,19,21]). Within this paragraph, we use the standard spectroscopic designations from [23], similar to [18,19,21]; terms associated with the entire molecule and individual electrons are tagged with uppercase and lowercase letters, respectively.

2.1. Model Hamiltonian

The effective Hamiltonian for the isotope-substituted ⁶Li⁷Li molecule can be written in the form:

$$\mathbf{H}^{(\text{ef})} = (\mathbf{H}^{\text{R}} + \mathbf{H}^{\text{CD}}) + \mathbf{H}^{\text{SS}} + \mathbf{H}^{\text{SR}} + \mathbf{H}^{\text{hfs}}.$$
 (1)

The parenthesis distinguishes the rotational part which consists of the rotational term \mathbf{H}^{R} and the centrifugal distortion term \mathbf{H}^{CD} .

$$\mathbf{H}^{\mathbf{R}} = \left\langle \nu \left| \frac{\hbar^2}{2\mu r^2} \right| \nu \right\rangle \mathbf{R}^2 = B_{\nu} (\mathbf{J} - \mathbf{L} - \mathbf{S})^2.$$
(2)

$$\mathbf{H}^{\rm CD} = -D_{\nu} (\mathbf{R}^2)^2. \tag{3}$$

The simplified form of the spin-spin (SS) interaction is:

$$\mathbf{H}^{\rm SS} = \frac{2}{3}\lambda \left(3\mathbf{S}_z^2 - \mathbf{S}^2\right). \tag{4}$$

The spin-rotation (SR) interaction is given by:

$$\mathbf{H}^{\mathrm{SR}} = \gamma \, \mathbf{R} \cdot \mathbf{S} = \gamma \left[\mathbf{J} \cdot \mathbf{S} - \mathbf{L} \cdot \mathbf{S} - \mathbf{S}^2 \right]. \tag{5}$$

The Hamiltonian of the hyperfine interaction for ⁶Li⁷Li comprises the Fermi contact interaction, the electric quadrupole interaction, and the nuclear SS interaction, and can be defined as:

$$\mathbf{H}^{\rm hfs} = \mathbf{H}^{\rm hfs,7} + \mathbf{H}^{\rm hfs,6} + \mathbf{H}^{\rm II},\tag{6}$$

where

$$\mathbf{H}^{\mathrm{II}} = d_{I}(\mathbf{I}_{1} \cdot \mathbf{I}_{2} - 3\mathbf{I}_{1z} \cdot \mathbf{I}_{2z}) \approx d_{I}'\mathbf{I}_{1} \cdot \mathbf{I}_{2}, \tag{7}$$

$$\mathbf{H}^{\mathrm{hfs},\mathrm{i}} = \mathbf{H}^{\mathrm{FC},\mathrm{i}} + \mathbf{H}^{\mathrm{EQ},\mathrm{i}} \tag{8}$$

$$= b_F^i \mathbf{I}_i \cdot \mathbf{S} + \mathbf{T}^2 (\nabla \mathbf{E}_i) \cdot \mathbf{T}^2 (\mathbf{Q}_i)$$

with index i = 6,7, corresponding to ⁶Li and ⁷Li, **H**^{II} – nuclear spin interaction (II), **H**^{FC,i} – Fermi contact interaction (FC), **H**^{EQ,i} – electric quadrupole interaction (EQ).

2.2. Interaction matrix elements for Hund's case (a_{β}) basis

An isotope-substituted molecule has several features that must be taken into account when constructing a model. First, there are no changes for the form of the main equations. The Hamiltonian of the electrons in our case is invariant under the inversion of the electron coordinates of the molecule; thus, the g/u-parity is considered. However, there is no permutation symmetry for identical nuclei and, therefore, the selection of states associated with it. Additionally, the relationship with the atomic parameters at large internuclear distances changes, which is described in more detail in Section "Results and Discussion". The present model is similar to the one we used for the simulation of HFS in our previous works. Therefore, all equations for the interaction matrix elements can be found in Liu et al. [18], Sovkov et al. [21], Onishchenko et al. [22]. However, the nuclear SS interaction was included in our model for the first time, and the equation for its matrix element is as follows:

$$\langle n\Lambda S\Sigma J\Omega IFM_F | d_{I'} \mathbf{I}_1 \cdot \mathbf{I}_2 | n'\Lambda' S'\Sigma' J'\Omega' I'FM_F \rangle$$

$$= \frac{1}{2} \delta_{SS'} \delta_{\Sigma\Sigma'} \delta_{\Lambda\Lambda'} \delta_{JJ'} \delta_{II'} \langle n\Lambda | d_{I'} | n'\Lambda \rangle$$

$$\times [I(I+1) - I_1(I_1+1) - I_2(I_2+1)]$$

$$(9)$$

Furthermore, in this study, the designations of the parameters used in the original works of Refs. [18,19,21] are utilized.

3. Computational algorithm

Transitions from the ground $X^1 \Sigma_g^+$ state to the intermediate $A^1 \Sigma_u^+ \sim b^3 \Pi_u$ states were excited by a pump laser, whereas the upper triplet states were detected by scanning the probe laser frequency and monitoring the $3^3 \Sigma_g^+ / 1^3 \Delta_g / 2^3 \Pi_g \rightarrow a^3 \Sigma_u^+ / b^3 \Pi_u$ fluorescence. The corresponding excitation schemes and diagrams (Fig. 1) demonstrating the excitation of the triplet states are given below:

- $3^{3}\Sigma_{g}^{+}(v = 6, N = 23)$ $\leftarrow b^{3}\Pi_{u}(v'_{b} = 12, N' = 23, J' = 24) \sim A^{1}\Sigma_{u}^{+}$ $\leftarrow X^{1}\Sigma_{g}^{+}(v_{X}, N_{X})$
- $2^{3} \prod_{g} (v = 4, N = 22, 24)$ $\leftarrow b^{3} \prod_{u} (v'_{b} = 12, N' = 23, J' = 24) \sim A^{1} \Sigma_{u}^{+}$ $\leftarrow X^{1} \Sigma_{g}^{+} (v_{X}, N_{X})$
- $1^{3}\Delta_{g}(v = 4, N = 22, 23, 24)$ $\leftarrow b^{3}\Pi_{u}(v'_{b} = 12, N' = 23, J' = 24) \sim A^{1}\Sigma_{u}^{+}$ $\leftarrow X^{1}\Sigma_{g}^{+}(v_{X}, N_{X})$

Similarly to our previous study on the HFS analysis of the $3^3 \Sigma_g^+$ state of Cs₂ [22], we have no information on the value of the vibrational and rotational quantum numbers v_X and N_X of the initial ground state ⁶Li⁷Li X¹ Σ_g^+ in the excitation schemes. However, this characteristic is inconsequential when calculating the relative intensities: the HFS patterns do not change regardless of whether the excitation scheme starts with the $N_X = J - 1$ or $N_X = J + 1$ level and do not depend on v_X .

In [13,24], the levels of the intermediate states were described for Hund's coupling case (*b*) (the levels $A^1 \Sigma_u^+ \sim b^3 \Pi_u$ were identified by the rotational quantum number N', and, in most cases, by the vibrational quantum number v_b , although in some cases by v_A).

The equations and computational programs used in the present work employed a Hund's case (a_{β}) basis; thus, the vectors of the triplet $b^{3}\Pi_{u}$ state assigned to Hund's coupling case (*b*) should be expanded on the basis functions of Hund's case (*a*).

Both Hund's case (*a*) and (*b*) basis functions equivalently span the same multiplet of the electronic spin and can be easily transformed into each other. The transformation matrix is well known and can be found in Brown and Howard [25].

The major steps of the simulation process of the HFS of the ${}^{6}\text{Li}{}^{7}\text{Li}$ molecule are similar to those used for the HFS of the Cs₂ molecule in our previous work [22]. We obtained the eigenenergies and eigenvectors of the HF components for fixed vibrational states ($\nu = 6$; 4; 4) for the $3^{3}\Sigma_{g}^{+}$, $2^{3}\Pi_{g}$, and $1^{3}\Delta_{g}$ states, respectively. To achieve this, the Hamiltonian matrix was constructed for a Hund's case (a_{β}) basis and diagonalized. Next, to predict the populations of the *I*, *F* sublevels of the $A^{1}\Sigma_{u}^{+} \sim b^{3}\Pi_{u}$ states, we calculated the optical transition probabilities for the initial stage of the excitation scheme. It was presumed that the rovibrational levels of the

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$$3^{3}\Sigma_{a}^{+}(v=6, N=23) \leftarrow b^{3}\Pi_{u}(v_{b}=12, N_{b}=23, J=24)$$



Fig. 2. HFS spectrum ⁶Li⁷Li $3^{3}\Sigma_{g}^{+}(v = 6, N = 23) \leftarrow b^{3}\Pi_{u}(v'_{b} = 12, N' = 23, J' = 24) \sim A^{1}\Sigma_{u}^{+}$: experiment [13], simulation.

 $X^1 \Sigma_g^+$ state, from which excitation starts, exhibit evenly populated *I*, *F* components. Then, we calculated the hyperfine component *I*, *F* populations of the $3^3 \Sigma_g^+$, $2^3 \Pi_g$, and $1^3 \Delta_g$ triplet states (second step of the excitation scheme), taking into account the already calculated populations of the *I*, *F* components of the *A* ~ *b* blended state.

However, we could not find any model in literature that would characterize an interaction between $A^1 \Sigma_u^+ \sim b^3 \Pi_u$ intermediate levels for the isotope-substituted lithium molecule (unlike for Cs₂ [22]); therefore, we adopted the algorithm that we utilized for the analysis of the blended $A^1 \Sigma_u^+ \sim b^3 \Pi_u$ states of Na₂ [21]. We assumed that the coordinate wave functions are of the same shape, and that contributions of the Ω components are determined by their amplitudes.

In the final step, the intensity distributions of the experimental HFS were simulated. For this, we computed the probabilities of the optical transitions from the upper triplet states $2^{3}\Pi_{g}$ and $3^{3}\Sigma_{g}^{+}$ to the $a^3 \Sigma_u^+$ effective vibrational level and from the $1^3 \Delta_g$ to the $b^3 \Pi_u$ vibrational level (in accordance with the selection rules). One of the major advantages of the experimental technique in work [13] is that laser beams counter-propagate, resulting in sub-Doppler resolution. Therefore, Doppler line-broadening might be neglected in the experimental spectra. The line-broadening is mainly due to finite lifetimes and collisions of lithium molecules with each other and with a buffer gas. Both of these mechanisms give Lorentzian contours. Therefore, the calculated probabilities ("discrete spectra") were convolved with Lorentzian functions, approximating the line profiles. During the optimization, the Lorentzian widths were fitted along with the interaction parameters. A more detailed description of the simulation procedure can be found in Onishchenko et al. [22].

4. Results and discussion

4.1. Simulation of the experimental spectra

Theoretical models were constructed separately for the $3^{3}\Sigma_{g}^{+}$, $2^{3}\Pi_{g}$, and $1^{3}\Delta_{g}$ triplet states. The numerical values of the molecular constants B_{v} and D_{v} were adopted from [26].

The simulation results of the ⁶Li⁷Li $3^{3}\Sigma_{g}^{+}$, $2^{3}\Pi_{g}$, and $1^{3}\Delta_{g}$ excitation spectra with HFS [13] are presented in Figs. 2–7.



Fig. 3. HFS spectrum ⁶Li⁷Li $2^{3}\Pi_{g}$ ($\nu = 4$, N = 24) $\leftarrow b^{3}\Pi_{u}(\nu'_{b} = 12, N' = 23, J' = 24$) $\sim A^{1}\Sigma_{u}^{+}$: experiment [13], simulation.

GHz



Fig. 4. HFS spectrum ⁶Li⁷Li $2^{3}\Pi_{g}$ (v = 4, N = 24) $\leftarrow b^{3}\Pi_{u}$ ($v'_{b} = 12$, N' = 23, J' = 24) $\sim A^{1}\Sigma_{u}^{+}$: experiment [13], simulation.



Fig. 5. HFS spectrum ⁶Li⁷Li $1^{3}\Delta_{g}$ (v = 4, N = 22) $\leftarrow b^{3}\Pi_{u}(v'_{b} = 12, N' = 23, J' = 24) \sim A^{1}\Sigma_{u}^{+}$: experiment [13], simulation.

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Fig. 6. HFS spectrum ⁶Li⁷Li $1^{3}\Delta_{g}$ (v = 4, N = 23) $\leftarrow b^{3}\Pi_{u}(v'_{b} = 12, N' = 23, J' = 24) \sim A^{1}\Sigma_{u}^{+}$: experiment [13], simulation.



Fig. 7. HFS spectrum ⁶Li⁷Li $1^{3}\Delta_{g}$ ($\nu = 4$, N = 24) $\leftarrow b^{3}\Pi_{u}(\nu'_{b} = 12, N' = 23, J' = 24) \sim A^{1}\Sigma_{u}^{+}$: experiment [13], simulation.

The sets of HFS parameters for the triplet states derived during the optimization are listed in Table 1. The table shows the factually fitted parameters, which correspond to the matrix elements, spanning the electronic spatial and spin degrees of freedom (see Refs. [18,21,22]).

To estimate the influence of various terms of the hyperfine Hamiltonian, definite interactions were turned off during the simulation process. From these auxiliary computations, we concluded that the FC interaction has the main impact on the HFS profiles, followed by the impact of the SS interaction. The remaining parameters, such as SR (for the Σ and Δ states), EQ (for all states), and II (for the Π state) interactions make additional contributions that are, however, less noticeable.

The other interactions, which are unaccounted terms of the Hamiltonian (for instance, dipole interactions, taking into account the orientations of each electron and nucleus, and the distance between them) and possible processes affecting modeling, which are listed in Section 4.3, might influence some weaker features of the simulated profiles.

Table 1

Parameters of the fine and hyperfine interactions obtained from a simulation of the experimental HFS of the ⁶Li⁷Li 3³ Σ_{g}^{+} , 2³ Π_{g} , and $1^{3}\Delta_{g}$ states. All values are expressed in MHz; estimated standard deviations are given in parentheses and refer to the last reported digits, and "e" sets the decimal order. The strict definitions of the parameters \mathcal{B}_k and \mathcal{Q}_k can be found in Liu et al. [18].

	$\mathcal{B}_{F7}(FC)$	$\mathcal{B}_{F6}(FC)$	$\gamma(SR)$	$\lambda(SS)$	$Q_7(EQ)$	$\mathcal{Q}_6(\text{EQ})$
$3^3\Sigma_g^+ \ 1^3\Delta_g$	255.0(1.5)	85.5(3.6)	30.0(1.5)e-2	427.5(5.4)	63(12)	283.5(9.6)
	229.92(1.05)	91.89(0.64)	44.63(1.96)e-2	139.2(1.8)	309(6)	8.4(2.1)
$2^3 \Pi_g$	B _{F7} (FC)	B _{F6} (FC)	<i>d</i> ′(II)	λ (SS)	Q ₇ (EQ)	Q ₆ (EQ)
	138.70(0.75)	46.0(1.4)	33.4(0.4)	156.0(2.1)	-215.7(7.5)	215.0(5.7)

4.2. Asymptotic properties

We estimate the asymptotic behavior of diatomic molecular systems at large internuclear distances, for which all molecular equations reproduce the energy structure of two independent atoms. The dominant source of the hyperfine splitting is the FC interaction; thus, our reasoning is aimed at assessing the asymptotic value of the molecular electronic spatial diagonal matrix element of this term.

In our previous work [18], we derived expressions connecting the asymptotic matrix elements with the atomic matrix elements, which significantly simplified the overall analysis.

These formulae are as follows:

$$\langle n^{1}\Lambda | \mathbf{h}_{ik} | n^{1}\Lambda \rangle \rightarrow \frac{1}{2} \delta_{\psi_{\bar{k}}, \psi_{\bar{k}}'} \langle \psi_{k}(\mathbf{q}_{k}) | \mathbf{h}_{kk} | \psi_{k}'(\mathbf{q}_{k}),$$
 (10)

$$\begin{split} \langle n^{3}\Lambda | \mathbf{h}_{ik} | n^{3}\Lambda \rangle &\to \frac{1}{2} \delta_{\psi_{\widetilde{k}}, \psi_{\widetilde{k}}'} \langle \psi_{k}(\mathbf{q}_{k}) | \mathbf{h}_{kk} | \psi_{k}'(\mathbf{q}_{k}), \\ \langle n^{1}\Lambda | \mathbf{h}_{ik} | n^{3}\Lambda \rangle &\to \frac{(-1)^{k+i}}{2} \delta_{\psi_{\widetilde{k}}, \psi_{\widetilde{k}}'} \langle \psi_{k}(\mathbf{q}_{k}) | \mathbf{h}_{kk} | \psi_{k}'(\mathbf{q}_{k}), \end{split}$$

where \mathbf{h}_{ik} is an operator of an interaction between the electron of the *i*th nucleus and another *k*th nucleus, $\psi_k(\mathbf{q}_k)$ is the wave function of the *k*th electron with the coordinate \mathbf{q}_k , $\psi_{\tilde{k}}$ represents the wave function of another (different from k) atom. Moreover,

$$\langle (1/2, 1/2)S || \mathbf{T}^{1}(\mathbf{s}_{i}) || (1/2, 1/2)S') \rangle$$
 (11)

$$= (-1)^{S'(2-i)+S(i-1)} [(2S+1)(2S'+1)]^{(1/2)}$$

$$\times \begin{cases} \frac{1}{2} & S & \frac{1}{2} \\ S' & \frac{1}{2} & 1 \end{cases} \sqrt{\frac{3}{2}}$$

$$= \begin{cases} 0, & S = S' = 0 \\ \sqrt{3/2}, & S = S' = 1 \\ (-1)^i \sqrt{3}/2, & S = 0, S' = 1, i = 1, 2. \\ (-1)^{i-1} \sqrt{3}/2, & S = 1, S' = 0 \end{cases}$$

 $\rightarrow (\sqrt{6}/2)b_k$

When discussing triplet states, it is sufficient to consider only the second case, for which S = S' = 1. The properties described above allow for the derivation of the asymptotic values of the molecular matrix elements in terms of the elements of the atomic matrices.

Therefore, for parameter $\widetilde{\mathcal{B}}_{Fk}$ in the matrix element for the FC interaction (see Eq. (19) in our previous work [22]), within the basis of non-symmetrized relative electron permutations (gerade/ungerade), we have:

$$\widetilde{\mathcal{B}}_{Fk} = \sum_{i} \langle {}^{3}\Lambda | b_{F}^{(ki)} | {}^{3}\Lambda \rangle \langle S = 1 | | \widetilde{\mathbf{T}}^{1}(\mathbf{s}_{i}) | | S' = 1 \rangle$$
(12)

where

$$b_k = \langle nl | b_F^{(kk)} | nl \rangle \tag{13}$$

is the diagonal electron matrix element of the *k*th atom, and $b_{r}^{(ki)}$ represents the local FC interaction between the *i*th electron and the *k*th nucleus. Factor $\sqrt{6}/2$ is the factor that connects our definition of molecular parameters at the asymptote with atomic parameters. Its nature is geometric and is not related to the correlation effects.

Therefore, the FC constants ($\tilde{\mathcal{B}}_{F6}$ and $\tilde{\mathcal{B}}_{F7}$) for ${}^{6}\text{Li}_{2}$ and ${}^{7}\text{Li}_{2}$ are given by (the values of the corresponding atomic matrix elements $(b_6 \text{ and } b_7)$ of $2S_{1/2}$ atomic states for ⁶Li and ⁷Li, and are given in Li et al. [13]):

 $\widetilde{\mathcal{B}}_{F6} = \sqrt{6}/2 \cdot 152.137 = 186.329$ MHz for ⁶Li₂; $\widetilde{\mathcal{B}}_{F7} = \sqrt{6}/2 \cdot 401.752 = 492.043$ MHz for ⁷Li₂.

Eq. (10) quoted above are matrix elements within the basis of the asymptotic electronic state functions that do not possess a definite g/u parity, which is the case for a heteronuclear molecule. However, in the case of homonuclear diatomic molecules (including isotope-substituted ones, for which the spatial configuration of the electric field also exhibits inversion symmetry), the basis functions must be symmetrized correspondingly, which results in the modification of the matrix elements as well.

The matrix element is zero if there are no identical atomic states between the two asymptotic molecular states, regardless of whether or not those atomic states are identical within every one of the molecular states.

If both molecular states are identical (the matrix element is diagonal) but comprise of different atomic states, the g/usymmetrized functions become sums or differences of the initially non-symmetrized ones, differing by the inversion of the electronic cloud, divided by $\sqrt{2}$. Consequently, an asymptotic matrix element within such functions becomes the half-sum of the matrix elements of a kind of (10) with summands dealing with one of two atomic state functions and constituting the asymptotic molecular state. If only one of these states contributes (such as for the FC interaction at the s + p asymptote), this makes the result twice as small as (10).

We consider that in terms of the FC interaction, the major contribution comes from the ground state (the contribution of the excited state can be neglected) (s + p asymptote); thus, it would be sufficient to divide the estimated values in half for $\tilde{\mathcal{B}}_{F6}$ and $\tilde{\mathcal{B}}_{F7}$ to obtain ones in a properly symmetrized g/u basis:

 $B_{F6} = 186.329/2 = 93.1645$ MHz for ⁶Li₂;

 $\mathcal{B}_{F7} = 492.043/2 = 246.0215$ MHz for ⁷Li₂;

The asymptotic values are close to those given in Table 1 for the $3^{3}\Sigma_{g}^{+}$ and $1^{3}\Delta_{g}$ states.

The $2^3 \Pi_g$ state exhibits a doubly excited nature $[\sigma_u(np)]^1[\pi_u(np)]^1$. An uncompensated magnetic moment in the *p*-orbitals leads to some changes in the spatial distributions of the electrons in the s-orbitals; in other words, the s-orbital does not directly contribute to the FC interaction; thus, the constant for this term should be smaller. In our model, the FC interaction effectively includes all effects of the nuclear and electron spin

interactions (not only the contact ones, which should be zero for non-s-orbitals). Table 1 shows that the FC constants are noticeably lower in this case than those for the $3^3\Sigma_g^+$ and $1^3\Delta_g$ states. Moreover, we determined that the II interaction contributes to the hyperfine splitting for the $2^3\Pi_g$ instead of the SR interaction, which is important for the $3^3\Sigma_g^+$ and $1^3\Delta_g$ states. All these factors might be reasons for the differences in the hyperfine patterns of the $2^3\Pi_g$ state spectral lines and those of the $3^3\Sigma_g^+$ and $1^3\Delta_g$ states.

4.3. Unaccounted processes affecting the modeling

The simulation of the experimental spectra demonstrates a satisfactory result, which can be seen in Figs. 2-7. However, there are still some discrepancies between the experimental and the simulated spectra. The remaining differences might be due to the following reasons. First, accidental optical resonances with other rovibronic levels can occur. Investigated transitions can overlap with accidental resonances, which in turn can cause the distortion of line shapes. Second, we presumed that the comparatively high temperature and the buffer gas pressure destroyed the alignment of the molecules at every step of the excitation scheme; however, there could be some remaining alignment that was not taken into account in our model. Third, the relative populations of the hyperfine components in the intermediate and upper states can be altered by collisions. Fourth, it is also possible that some neighboring levels belonging to other electronic states perturb the levels engaged in the excitation scheme.

To assess the impact of these processes and possibly take them into account in our calculations, supplementary experiments as well as substantial and complicated reworking of the theoretical model, which are not currently accessible for us, are required.

5. Conclusions

We constructed a theoretical model for the HFS analysis of the homonuclear isotope-substituted ${}^{6}\text{Li}^{7}\text{Li}$ for the ${}^{3}\Sigma_{g}^{+}$, ${}^{2}{}^{3}\Pi_{g}$, and ${}^{3}\Delta_{g}$ triplet states. The main steps of the excitation–de–excitation scheme were implemented, and the mixed nature of the window levels was taken into account. We theoretically studied an isotope-substituted homonuclear molecule for the first time. The dominant source of the hyperfine splitting for the three triplet states is the Fermi contact interaction, which is in good agreement with derivations of the asymptotic value of the molecular electronic spatial diagonal matrix element of this term. We obtained satisfactory simulation results and estimated the HF parameters based on these results.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Sofiia S. Onishchenko: Investigation, Formal analysis, Writing - original draft, Writing - review & editing. Vladimir B. Sovkov: Conceptualization, Investigation, Software, Methodology, Writing - review & editing. Feng Xie: Investigation, Writing - review & editing. Sergey S. Lukashov: Investigation, Writing - review & editing. Vera V. Baturo: Investigation, Writing - review & editing. Wu: Investigation, Writing - review & editing. Jizhou Wu: Investigation, Writing - review & editing. tion, Writing - review & editing.

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