
Investigation of the Spin–Orbit Perturbation of the $6^1\Pi$ State in KLi Molecule

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Strong perturbation in the $6^1\Pi$ state of the $^{39}\text{K}^7\text{Li}$ molecule is analysed. The perturbing state is identified as $3^3\Delta$ on the basis of experimental observations aided by comparison with recent theoretical calculations. Possibilities of accessing triplet states of KLi via the $6^1\Pi \sim 3^3\Delta$ perturbation are discussed.

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1. Introduction

Interactions between molecular states manifesting themselves as perturbations in the spectra have always been a nuisance for spectroscopists because they result in positions of energy levels no longer following regular patterns. On the other hand, when studied in detail and fully understood, perturbations can provide a wealth of information about molecular states inaccessible for direct excitation. Diatomic alkali molecules provide a good example. Their electronic ground states are $^1\Sigma^+$ (or $^1\Sigma_g^+$ for homonuclear dimers) and only singlet states can be reached from there by an optical transition. However, interactions of excited states resulting in mixing of wave functions of singlet and triplet characters open windows to the triplet manifold of states, which can be explored further in multistep excitation or fluorescence experiments. The heteronuclear diatomics are particularly suitable for such studies because the lower symmetry of these molecules enlarges the possibilities of interaction between molecular states beyond those present in

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the homonuclear dimers. Indeed, several techniques of perturbation facilitated laser spectroscopy have been demonstrated on alkali molecules (see e.g. [1–5]). A special interest in the lowest triplet state in alkali dimers, $a^3\Sigma_{(u)}^+$, should be noted since the precise knowledge of its potential energy curve is crucial in various applications, including formation of ultracold molecules [6], Bose–Einstein condensation [7] and ultracold atomic collisions [8]. For the reasons stated above precise localisation of strong singlet–triplet perturbations in molecular spectra is of primary importance.

This paper reports the experimental observation of perturbation of the $6^1\Pi$ state in $^{39}\text{K}^{7}\text{Li}$ molecule by some directly unobservable (“dark”) electronic state. The strongest perturbation observed at $v = 10$ level of $6^1\Pi$ is analysed in detail, resulting in assignment of the perturber as the $3^3\Delta$ state. A possibility of using the $6^1\Pi \sim 3^3\Delta$ perturbation as a convenient gateway to the triplet states of KLi is considered.

2. Experimental

The experiment was performed by the polarisation labelling spectroscopy technique in a V-type optical-optical double resonance excitation scheme [9]. Since the experimental arrangement is the same as described in our recent papers [10, 11] only the necessary minimum information will be given here. We observed excitation spectra in the $6^1\Pi \leftarrow X^1\Sigma^+$ band system of KLi induced by a beam of light from an optical parametric oscillator/amplifier system equipped with a frequency doubler. The exciting light had a spectral width of 0.16 cm^{-1} and for the purpose of the present experiment was tuned between 29300 and 32000 cm^{-1} . By simultaneous recording of optogalvanic spectrum of argon and transmission fringes of a Fabry–Pérot etalon we achieved accuracy in determination of absolute transition wave numbers better than 0.1 cm^{-1} . The observed molecular transitions originated from altogether 17 rovibrational levels labelled in the ground $X^1\Sigma^+$ state with light of a dye laser and terminated on all levels of the $6^1\Pi$ state accessible due to selection rules and non-negligible Franck–Condon factors. Thus our measurements in the main isotopologue $^{39}\text{K}^{7}\text{Li}$ spanned levels with vibrational quantum numbers v ranging between 0 and 15 and rotational numbers $J = 10\text{--}64$. A few weak transitions assigned to the $^{41}\text{K}^{7}\text{Li}$ isotopologue allowed to verify the vibrational numbering in the $6^1\Pi$ state. The energies of the $6^1\Pi$ state levels were obtained from wave numbers of the identified lines by adding highly accurate term values of the $X^1\Sigma^+$ state [12]. All the experimental data (positions of the observed lines) are available on request from the authors.

3. Analysis

A global analysis of the $6^1\Pi$ state is presented elsewhere [11]. It provided molecular constants describing energies of unperturbed levels with a standard deviation $\sigma = 0.08\text{ cm}^{-1}$. However, experimental positions of some levels deviated

from the calculated ones by more than 2σ . Particularly large discrepancies were noted for $v = 10$, $J \approx 10$ – 30 levels, exceeding 1 cm^{-1} . Inspection of the spectra corresponding to transitions to these levels revealed a presence of strong companion (extra) lines (Fig. 1), forming a picture characteristic of perturbation of two electronic states.

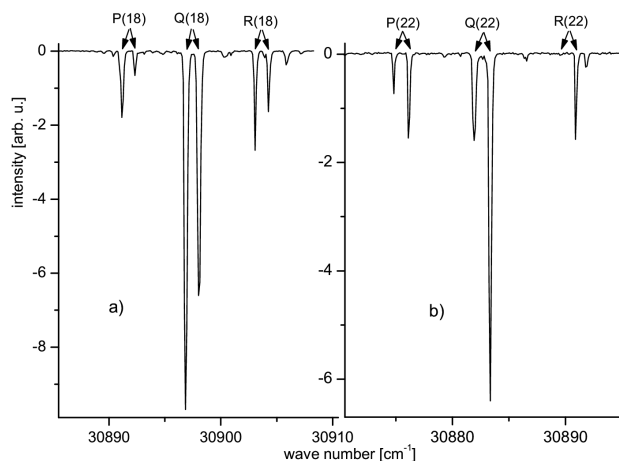


Fig. 1. Fragments of the $6^1\Pi \leftarrow X^1\Sigma^+$ excitation spectrum of KLi illustrating main line/extra line pairs in transitions to $v' = 10$. The labelled lines correspond to transitions from the ground state levels $v'' = 1$, $J'' = 18$ (a) and $v'' = 1$, $J'' = 22$ (b).

The perturbation can be visualised in two different ways. In one of them the displacements ΔE of rotational levels are drawn separately for e and f parity. The corresponding Figs. 2a and b reveal that the perturbation is homogeneous, as the deviations due to interaction of states do not become zero for $J = 0$ while $\Delta E \rightarrow 0$ beyond the perturbation region. This occurs when the perturbation matrix element H_{AB} between the interacting states is J -independent. The displacements of levels may be related to their unperturbed positions E_A , E_B , and H_{AB} by [13]:

$$\Delta E = \frac{E_B - E_A}{2} \pm \sqrt{\left(\frac{E_B - E_A}{2}\right)^2 + H_{AB}^2}. \quad (1)$$

With $H_{AB} = \text{const}(J)$ and a simple dependence of rotational level energies on J neglecting rotational constants higher than B_v , the formula (1) was fitted to the experimental data, providing $H_{AB} = 0.60 \pm 0.02 \text{ cm}^{-1}$ and the rotational constants of the perturbing state $B_{\text{pert},f} = 0.1633 \pm 0.0005 \text{ cm}^{-1}$ and $B_{\text{pert},e} = 0.1618 \pm 0.0005 \text{ cm}^{-1}$ for e and f parity levels, respectively.

The alternative way to analyse perturbations has been introduced by Gerö [14]. The following expressions are formed, basing on experimental positions of rotational lines in the spectra

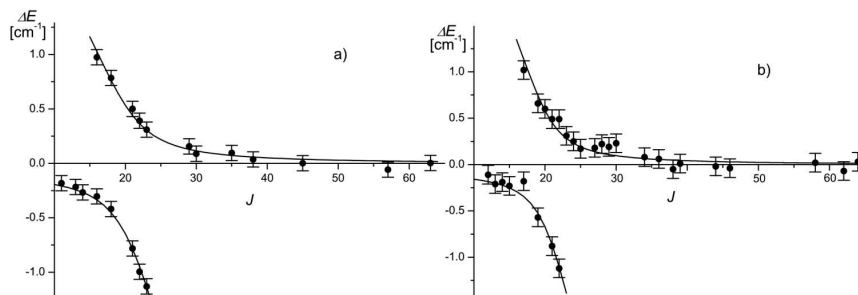


Fig. 2. Differences between the measured and expected term values (circles) for rotational levels of f parity (a) and e parity (b) in the $v' = 10$ level of the $6^1\Pi$ state, fitted under assumption of a constant value of the perturbation matrix element between $6^1\Pi$ and its perturber. The error bars represent the experimental uncertainties.

$$f_Q(J) = \frac{Q(J-1) - Q(J)}{2J} \approx B'' - B'_f, \quad (2)$$

$$f_{PR}(J) = \frac{R(J-2) - R(J-1) + P(J) - P(J+1)}{4J} \approx B'' - B'_e, \quad (3)$$

where B'' relates to the ground state and B'_e , B'_f to the upper state (higher rotational terms were neglected on the right side of both equations again). If these expressions are plotted against J (Fig. 3a,b), for unperturbed regions horizontal lines are obtained, whereas near the upper state perturbation the apparent B' value is affected and the deviation from the straight line occurs. Since we have observed several extra lines, the plots show points of intersection at the ordinate equal to $(B' + B_{\text{pert}})/2 - B''$. Our experimental values provide in this way $B_{\text{pert},f} = 0.1640 \text{ cm}^{-1}$ and $B_{\text{pert},e} = 0.1624 \text{ cm}^{-1}$. Although the accuracy of these values cannot be determined in a straightforward way, they agree reasonably with the numbers quoted before.

The nature of the perturbing electronic state can be identified by an analysis of the perturbation pattern together with the results of the recent theoretical calculations on excited states of KLi [15, 16]. The $6^1\Pi$ state dissociates into $\text{K}(4^2P) + \text{Li}(2^2P)$ atoms. This asymptote gives rise to a multitude of states capable of interacting with the $6^1\Pi$ state: two $^1\Sigma^+$, $^1\Sigma^-$, another $^1\Pi$, $^1\Delta$, two $^3\Sigma^+$, $^3\Sigma^-$, two $^3\Pi$ and $^3\Delta$. A $^1\Pi \sim ^1\Sigma^{+(-)}$ rotational perturbation (caused by the L -uncoupling interaction) influences only $e(f)$ components of the $^1\Pi$ state as the $^1\Sigma^{+(-)}$ state contains solely $e(f)$ -parity levels and is therefore excluded from further consideration. At a $^1\Pi \sim ^3\Sigma^+$ spin-orbit perturbation two of three $^3\Sigma^+$ components interact with the e parity levels of $^1\Pi$, while the third $^3\Sigma^+$ component interacts with f levels of $^1\Pi$. Thus we have two perturbations in the P , R branches at different J values and one perturbation in the Q branch at a J value about halfway between the other two, contrary to the experimental observation. The same argument relates to a $^1\Pi \sim ^3\Sigma^-$ perturbation except that e/f parity levels

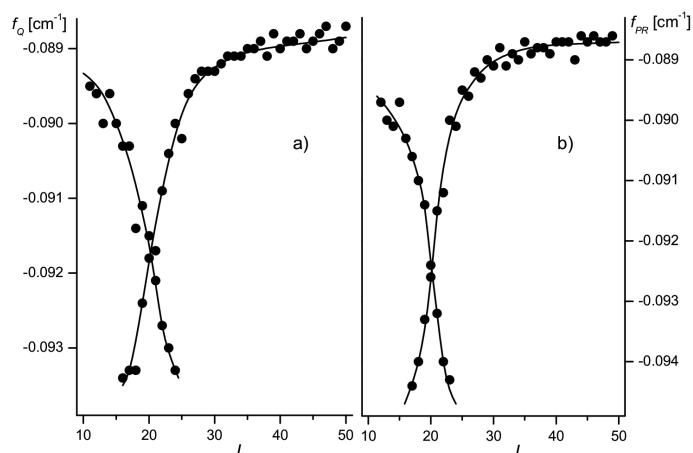


Fig. 3. The perturbation in the $v' = 10$ level of the $6^1\Pi$ state in KLi illustrated by Gerö's method: values of $B' - B''$ are plotted as a function of the rotational quantum number for f and e parity levels (f_Q and f_{PR} , respectively, in parts (a) and (b)).

and P , R/Q branches should be interchanged in the above description. The only other state of $^1\Pi$ symmetry located in the energy range of interest, $7^1\Pi$, has been investigated in our previous experiment [11] and is definitely not interacting with the $6^1\Pi$ state. A $^1\Pi \sim ^1\Delta$ rotational interaction is a heterogeneous one and as such is also ruled out. This leaves us with only two possibilities, homogeneous spin–orbit perturbations $^1\Pi \sim ^3\Pi_{\Omega=1}$ and $^1\Pi \sim ^3\Delta_{\Omega=1}$. Inspection of the theoretical potential energy curves shows that the candidates for the perturber are $7^3\Pi$ and $3^3\Delta$ states (Fig. 4), differing much in the shape of their potentials. The $7^3\Pi$ state is characterised by a double minimum well resulting from a prominent anticrossing with a higher state of the same symmetry, $8^3\Pi$ (see Fig. 4). As a consequence its potential well is unusually broad, corresponding to rotational constant for levels above the inner barrier (the levels close to the energy of $v = 10$ in the $6^1\Pi$) $B \leq 0.153 \text{ cm}^{-1}$ and low values of overlap integrals $|\langle v_{7^3\Pi} | v_{6^1\Pi} \rangle| < 0.05$. On the contrary, the curve for the $3^3\Delta$ state is Morse-like. It is worth noting that the calculations predict the energy of the most strongly perturbed level, $6^1\Pi(v = 10, J = 20)$, nearly equal to the energy of $3^3\Delta(v = 10, J = 20)$. Taking into account the accuracy of the theoretical calculations, which provide the electronic term value T_e for the $6^1\Pi$ state too high by 42 cm^{-1} [11], this coincidence may be fortuitous, but the values of the rotational constant ($B \approx 0.169 \text{ cm}^{-1}$) and the overlap integral ($|\langle v_{3^3\Delta} | v_{6^1\Pi} \rangle| \approx 0.5$) make the $3^3\Delta$ state a much more plausible candidate for the perturber. (Let us note that our previous tentative assignment of the perturber as $7^3\Pi$ [11] was done before the recent calculations on Δ states [16] became available to us.)

It is common to relate the electronic part of the perturbation matrix element, $\xi_{el} = H_{AB}/\langle v | v_{\text{pert}} \rangle$, to the atomic spin–orbit parameters, here equal to

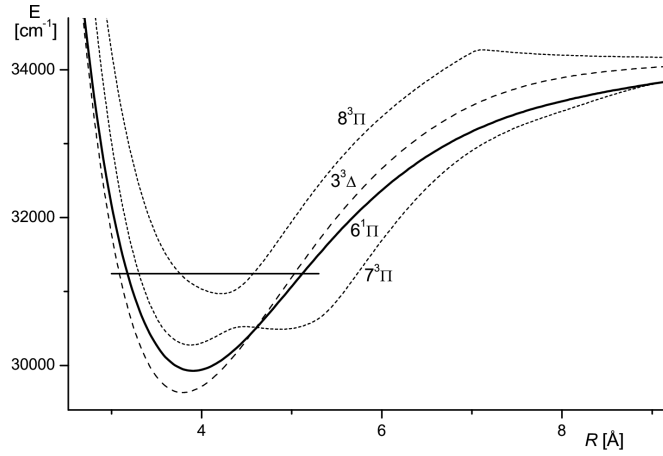


Fig. 4. Selected potential energy curves of KLi [16] relevant to perturbation of the $6^1\Pi$ state. Position of the strongly perturbed $v' = 10$ level in $6^1\Pi$ is indicated.

$\zeta_K = (2/3)[E(4^2P_{3/2}) - E(4^2P_{1/2})] = 38.5 \text{ cm}^{-1}$ and $\zeta_{Li} = (2/3)[E(2^2P_{3/2}) - E(2^2P_{1/2})] = 0.22 \text{ cm}^{-1}$ [17]. However, the relation is straightforward only for molecular states arising from a single molecular orbital configuration. This is the case for the $3^3\Delta$ state which corresponds to the configuration $(\pi 4p_K)(\pi 2p_{Li})$. The molecular orbital for the $6^1\Pi$ state can actually be constructed as a mixture of $(\sigma 4p_K)(\pi 2p_{Li})$ and $(\sigma 2p_{Li})(\pi 4p_K)$. Nevertheless, we may get some insight into the possible range of ξ_{el} by taking into account each of these configurations separately. Let us consider the configuration $(\sigma 4p_K)(\pi 2p_{Li})$. The corresponding electronic wave functions are combinations of the Slater determinants, e.g.

$$|6^1\Pi, e\rangle = \frac{1}{2} (|\sigma_K\alpha\pi_{Li}^+\beta\rangle - |\sigma_K\beta\pi_{Li}^+\alpha\rangle + |\sigma_K\alpha\pi_{Li}^-\beta\rangle - |\sigma_K\beta\pi_{Li}^-\alpha\rangle), \quad (4)$$

$$|3^3\Delta_1, e\rangle = \frac{1}{\sqrt{2}} (|\pi_K^+\beta\pi_{Li}^+\beta\rangle - |\pi_K^-\alpha\pi_{Li}^-\alpha\rangle). \quad (5)$$

Assuming the spin-orbit operator as a sum over one electron angular momentum operators [18]:

$$H_{so} = \sum_i \zeta_i [l_{iz}s_{iz} + (1/2)(l_i^+s_i^- + l_i^-s_i^+)] \quad (6)$$

(where summation is over two valence electrons) we obtain for the electronic perturbation parameter

$$\begin{aligned} \xi_{el} = \langle 3^3\Delta_1, e | H_{so} | 6^1\Pi, e \rangle &= \frac{1}{2\sqrt{2}} [\langle \pi_K^+\beta | (1/2\zeta_K)(l^+s^- + l^-s^+) | \sigma_K\alpha \rangle \\ &+ \langle \pi_K^-\alpha | (1/2\zeta_K)(l^+s^- + l^-s^+) | \sigma_K\beta \rangle] = 1/2\zeta_K = 19.2 \text{ cm}^{-1}. \end{aligned} \quad (7)$$

Considering in a similar way the configuration $(\sigma 2p_{Li})(\pi 4p_K)$ for the $6^1\Pi$ state we arrive to the other limiting value of $\xi_{el} = 1/2\zeta_{Li} = 0.11 \text{ cm}^{-1}$. The

experimental value seems to lie safely within these limits. With the theoretical value of $|\langle v | v_{\text{pert}} \rangle| \approx 0.5$ we get $\xi_{\text{el}} = 1.2 \text{ cm}^{-1}$ which points at high contribution of $(\sigma 2p_{\text{Li}})(\pi 4p_{\text{K}})$ to the molecular orbital of the $6^1\Pi$ state. Generally, the experimental position of the perturbed levels as well as the value of the perturbation matrix element will provide a sensitive test for any theoretical calculation involving the excited states of KLi molecule.

4. Conclusion

In the conclusion we shall discuss a possibility of accessing the normally unobservable triplet states of KLi via the $6^1\Pi \sim 3^3\Delta$ mixed levels. The $v = 10$, $J = 20$ level in the $6^1\Pi$ state where the perturbation culminates can be reached from the $X^1\Sigma^+$ state by a two-photon transition, using radiation of a ring dye laser operated around 640 nm, convenient for DCM dye. Alternatively, a stepwise excitation scheme $X^1\Sigma^+ \rightarrow B^1\Pi \rightarrow 6^1\Pi$ may be employed. As an example, we find favourable Franck–Condon factors for the pathway $(v_X = 1, J_X = 18) \rightarrow (v_B = 8, J_B = 19)$ at 18107.45 cm^{-1} , $(v_B = 8, J_B = 19) \rightarrow (v_{6\Pi} = 10, J_{6\Pi} = 20)$ at 12803.40 cm^{-1} or 12802.10 cm^{-1} (for excitation of the “main” and “extra” levels, respectively), which can be realised with single mode dye (Rhodamine 110) and Ti:Sa lasers. The one photon excitation in UV, as in the present experiment, is the third possibility. Population of rovibronic levels of a mixed singlet-triplet character can be followed either by further excitation within the triplet manifold or by observation of resolved fluorescence to lower triplet states. Although the symmetry of the perturber, $^3\Delta$, narrows the range of states accessible by one photon transitions to $^3\Pi$ and $^3\Phi$, a cascade fluorescence may terminate even on the lowest triplet state, $a^3\Sigma^+$.

Acknowledgments

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