Born–Oppenheimer breakdown in a combined-isotopomer analysis of the $A^{1}\Sigma_{u}^{+} - X^{1}\Sigma_{q}^{+}$ system of Li₂

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New high resolution polarization data have been obtained for the A-X band system of ${}^{6,7}\text{Li}_2$, and new Fourier transform data for the homonuclear lithium dimers. They are combined with earlier data for ${}^{6,6}\text{Li}_2$ and ${}^{7,7}\text{Li}_2$ in the first systematic combined-isotopomer analysis of data for Li₂. This analysis of 8445 rovibrational transitions yields an improved and internally consistent set of molecular constant for the three Li₂ isotopomers, and determines the electronic isotope shift and leading vibrational and rotational Born–Oppenheimer breakdown correction terms for both electronic states. © 2002 American Institute of Physics. [DOI: 10.1063/1.1514670]

I. INTRODUCTION

Recent years have seen numerous detailed spectroscopic investigations of the Li2 molecule.¹⁻⁴ However, in spite of the availability of extensive data sets for both the ^{7,7}Li₂ and ^{6,6}Li₂ isotopomers, no proper combined-isotopomer analyses of data for this system have been reported. This is a noteworthy omission, since Born-Oppenheimer breakdown (BOB) effects are expected to be substantial for species with small reduced mass, and Li2 would seem to be one of the best nonhydride systems for studying such interactions. Moreover, in view of the prominence of Li₂ in studies of ultracold molecules formed by photoassociation,^{1,5-8} a detailed knowledge of the relative energies of the states of the different isotopomers is of considerable practical importance. The present paper takes a first step in the direction of a comprehensive combined isotopomer analysis for the observed electronic states of Li2.

The $A^{1}\Sigma_{u}^{+} - X^{1}\Sigma_{g}^{+}$ system is the most thoroughly studied and widely exploited electronic band spectrum of Li₂. Levels of the $A^{1}\Sigma_{u}^{+}$ state have been used as intermediates for double resonance experiments,⁹⁻¹² providing access to a wide range of other singlet electronic states. Particular gateway levels^{13,14} also provide access to the manifold of triplet states using perturbation-facilitated optical–optical double resonance spectroscopy.¹⁵

Modern spectroscopic studies of the A-X system of Li₂ start from the thesis work of Hsu.¹⁶ While there were some questions regarding his analysis,¹⁷ the data set of ~18000 lines are of quite high quality, and have been the cornerstone of most later work on this system. Kusch and Hessel cor-

rected and extended Hsu's original assignments, and reported a set of molecular constants for the {7,7} isotopomer which described vibrational levels v(X)=0-14 and v(A)=0-25, for *J* up to 78.¹⁷ In 1986 Barakat *et al.*¹⁸ extended the data range to v(A)=26, but poor Franck–Condon overlap made higher vibrational levels inaccessible using onephoton transitions from the ground state.

A decade later, the development of photoassociation spectroscopy allowed Abraham *et al.*¹ to measure the binding energies of numbers of levels lying between 0.37 and 150 cm⁻¹ of the dissociation limits of ^{7,7}Li₂ and ^{6,6}Li₂. A year later, Urbanski *et al.*² used triple resonance spectroscopy to observe vibrational levels v(A) = 27-62 of the {7,7} isotopomer, and combining their measurement with the results of the Kusch–Hessel analysis, determined *A*-state molecular constants for ^{7,7}Li₂ spanning the range v(A) = 0-62. That same year, Linton *et al.*³ used optical–optical double resonance to excite levels of the $E^{1}\Sigma_{g}^{+}$ and $F^{1}\Sigma_{g}^{+}$ states of ^{6,6}Li₂ whose fluorescence into the *A* state spanned levels v(A) = 1-84, the highest of which lies only ≈ 2.4 cm⁻¹ from dissociation; however, they did not report a set of molecular constants.

More recent results on the {6,6} isotopomer were obtained by Wang *et al.*,⁴ who used sub-Doppler polarization spectroscopy to perform a high resolution one-photon study of 38 bands in the A-X system spanning the range v(X)=0-8 and v(A)=0-24, essentially the same range spanned by the Kusch–Hessel analysis of the {7,7} isotopomer data of Hsu.¹⁶ However, the molecular constants they reported were for the {6,6} isotopomer alone.

The objective of the present work is to combine some of the best results from the earlier work with new measurements for all three isotopomeric forms of Li_2 in a combinedisotopomer analysis which will yield a compact and inter-

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TABLE I. Summary of the data for the $A^{1}\Sigma_{u}^{+} - X^{1}\Sigma_{g}^{+}$ system of Li₂ used in the present analysis.

			$A^{1}\Sigma^{+}$	$X^{1}\Sigma_{g}^{+}$ state		Uncertainty	Source	
Isotopomer	Туре	No. lines	v range	v range	J range	(cm^{-1})	Ref.	
^{7,7} Li ₂	A - X absorption	1417	0-6	0-13	0-45	0.02	16	
	A - X absorption	1365	0-13	0-3	0-66	0.010	This work (Lyon)	
	A-X fluorescence	1085		0 - 12	2 - 40	0.006	This work (Lyon)	
^{5,6} Li ₂	A - X absorption	934	0 - 24	0 - 7	0-43	0.005	4	
	A - X absorption	2016	0-13	0 - 2	0 - 74	0.010	This work (Lyon)	
	A - X fluorescence	1403		0-13	1 - 49	0.006	This work (Lyon)	
^{5,7} Li ₂	A-X absorption	225	0-5	0-3	0-39	0.005	This work (Temple)	

nally consistent representation of the data for all three species, and allow the first quantitative determination of BOB effects in this system.

II. EXPERIMENTAL DATA

The data utilized in the present combined-isotopomer "parameter fit" analysis of the A-X system of Li₂ are summarized in Table I. We were fortunate to obtain a listing of the original ^{7,7}Li₂ absorption data of Hsu,¹⁶ and since our interest here is focused on the delineation of BOB effects, we selected from that data set 45 bands consisting of 1417 lines with v(A)=0-6 and v(X)=0-13, and with J' and J'' <46. However, since the uncertainties in these data were estimated to be about four times larger than those for the more recent ^{6,6}Li₂ measurements of Ref. 4, supplementary data were clearly required. The present paper therefore analyzes the published ${}^{6,6}Li_2 A - X$ data of Ref. 4 and the ${}^{7,7}Li_2$ lines from Ref. 16 together with new measurements from three types of experiment: (i) high resolution sub-Doppler polarization spectroscopy of ^{6,7}Li₂, (ii) Doppler-limited Fourier transform absorption spectra of ^{6,6}Li₂ and ^{7,7}Li₂, and (iii) resolved A - X fluorescence spectra of ^{6,6}Li₂ and ^{7,7}Li₂, also recorded by Fourier transform spectrometry.

The new excitation spectrum of $^{\bar{6},7}Li_2$ was obtained using the sub-Doppler polarization experiment described in Ref. 4. With careful calibration against iodine lines, the uncertainties in the line frequencies are estimated to be $\approx 0.005 \,\mathrm{cm}^{-1}$, much of which is due to the Doppler broadened iodine reference lines. Some 225 rovibrational transitions were measured for ${}^{6,7}Li_2$, with v(A) ranging from 0 to 5 and v(X) from 0 to 3 (see Table I). Figure 1 compares a segment of this polarization spectrum (lower trace) with the Doppler broadened Fourier transform absorption spectrum of ^{6,6}Li₂ described below (upper trace). Both spectra were obtained using samples 95% enriched in ⁶Li, and the weak ^{6,7}Li₂ lines in the polarization spectrum are indicated by asterisks. The analogous ^{6,6}Li₂ results from Ref. 4, consisting of 934 transitions in 32 bands with v(A) ranging from 0 to 24 and v(X) from 0 to 7, are also utilized in the present combined-isotopomer analysis.

The vibrational and rotational assignment of the ${}^{6,6}\text{Li}_2$ and ${}^{6,7}\text{Li}_2$ polarization data was quite straightforward. Using the published molecular constants for the {7,7} isotopomer,¹⁷ the normal first-order semiclassical mass-scaling relationship¹⁹ can predict most transitions to within 0.2 cm⁻¹. Spectral congestion was not a problem, since the subDoppler polarization spectra had typical linewidths (full widths at half maximum) of 0.006 cm^{-1} , and the small reduced mass of lithium dimers gives rise to a relatively sparse distribution of rovibrational levels at this resolution. Moreover, perturbations between states are very rare for the lower levels of the *A* state,^{20,21} and the associated coupling is weak due to the weakness of the spin–orbit interaction. Therefore, overlapping or perturbed spectral lines were not an impediment to rovibrational assignments, although occasional duplicate assignments appear. Another property which helps confirm the spectral assignments is the band intensity profile. Based on these considerations, our assignments are believed to be unambiguous.

The new absorption and fluorescence spectra were recorded using heatpipe sources containing either naturally occurring lithium metal or a sample of 95% enriched ⁶Li. The heatpipes were operated at about 750 °C, using argon as a buffer gas. The absorption spectra from 610 to 790 nm were recorded on a Fourier transform (FT) spectrometer using a quartz halogen lamp as a light source, and appropriate optical filters. The instrumental resolution was 0.07 cm⁻¹, but measured (Doppler limited) linewidths were nearer to 0.1 cm⁻¹. The uncertainty in the line peak positions is taken as one tenth of the linewidth. However, many lines were not



FIG. 1. Comparison of Fourier transform absorption spectrum of ${}^{6.6}Li_2$ (upper trace) with sub-Doppler polarization measurements (lower trace). Lines labeled with an asterisk are ${}^{6.7}Li_2$ transitions, which are discernable only at high resolution and sensitivity.

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measured to the expected accuracy because of overlap, and obvious blends were removed from the data set. Absorption lines were assigned to transitions between vibrational levels 0-3 in the ground state and 0-13 in the *A* state for each isotopomer (2016 lines for ^{6,6}Li₂ and 1365 lines for ^{7,7}Li₂).

The problem of line overlap was partially compensated for by measuring laser-induced fluorescence spectra. A single-mode cw dye laser (SP 380D) operating with DCM dye was used to excited a chosen A - X transition $(0 \le v')$ \leq 5). Backwards fluorescence along the heatpipe axis was collected on a pierced mirror, and focused on to the entrance aperture of the FT spectrometer. Spectra were recorded using a near-infrared sensitive Si avalanche detector, and transitions were observed involving levels v''=0-12 of the X state. The measured linewidths were around 0.06 cm^{-1} . However, the absolute calibration of the fluorescence spectra not only relies on the performance of the FT spectrometer, but also requires the laser excitation to occur at the peak of the Doppler profile. Since the dye laser was sometimes off the peak maxima, the fluorescence lines were shifted with respect to the (calibrated) absorption lines. The fluorescence data thus give accurate energy spacings for the ground state (estimated uncertainties 0.006 cm^{-1}), but are not reliable for the characterization of the A state. Some 1403 such fluorescence lines were measured for ${}^{6,6}\mathrm{Li}_2$ and 1085 lines for 7,7 Li₂.

The complete data set used in the present analysis may be obtained either from the corresponding author's dataarchive web site (http://www.temple.edu/molecular_optics), or from the Journal's supplementary material archive.²²

III. METHOD OF ANALYSIS

The present analysis of data for the A-X system of Li₂ was based on use of the combined-isotopomer level energy expression introduced in Ref. 23. For isotopomer " α " of a general diatomic molecule A–B in a ¹ Σ electronic state formed from atoms of mass M_A^{α} and M_B^{α} , the energy of vibration–rotation level (v, J) is written as²⁴

$$E^{\alpha}(v,J) = \sum_{m=0}^{m_{\max}} \sum_{l=0}^{l_{\max}(m)} Y_{l,m}^{\alpha} (v + \frac{1}{2})^{l} [J(J+1)]^{m}$$
$$= \sum_{m=0}^{m_{\max}} \sum_{l=0}^{l_{\max}(m)} \left(\frac{\mu_{1}}{\mu_{\alpha}}\right)^{m+l/2} (v + \frac{1}{2})^{l} [J(J+1)]^{m}$$
$$\times \left\{ Y_{l,m}^{1} + \frac{\Delta M_{A}^{\alpha}}{M_{A}^{\alpha}} \delta_{l,m}^{A} + \frac{\Delta M_{B}^{\alpha}}{M_{B}^{\alpha}} \delta_{l,m}^{B} \right\}, \qquad (1)$$

where $\alpha = 1$ (as in $Y_{l,m}^{1} \equiv Y_{l,m}^{\alpha=1}$) labels the selected reference isotopomer, $\Delta M_{\rm A}^{\alpha} = M_{\rm A}^{\alpha} - M_{\rm A}^{1}$ is the difference between the mass of atom A in isotopomer α and its mass in the reference isotopomer, $\mu_{\alpha} = M_{\rm A}^{\alpha} M_{\rm B}^{\alpha} / (M_{\rm A}^{\alpha} + M_{\rm B}^{\alpha})$ is the usual reduced mass of isotopomer α , and $Y_{0,0}^{1} \equiv 0$. Use of this expansion means that in a combined-isotopomer data analysis, independent $\{Y_{l,m}\}$ expansion parameters only need be determined for the reference isotopomer $\alpha = 1$, with those for other isotopomers being defined by a combination of the usual firstorder semiclassical mass scaling with additive BOB correction terms:

$$Y_{l,m}^{\alpha} = \left\{ Y_{l,m}^{1} + \frac{\Delta M_{A}^{\alpha}}{M_{A}^{\alpha}} \delta_{l,m}^{A} + \frac{\Delta M_{B}^{\alpha}}{M_{B}^{\alpha}} \delta_{l,m}^{B} \right\} \left(\frac{\mu_{1}}{\mu_{\alpha}} \right)^{m+l/2}.$$
 (2)

As for any homonuclear diatomic, for Li₂ A=B, so $\delta_{l,m}^{A} = \delta_{l,m}^{B} \equiv \delta_{l,m}^{Li}$ and there is only one set of BOB correction term coefficients to be determined.

For the reference isotopomer ($\alpha = 1$), $\mu_{\alpha} = \mu_1$ and $\Delta M_{\rm A}^{\alpha} = \Delta M_{\rm B}^{\alpha} = 0$, so Eq. (1) collapses to the familiar Dunham expansion for the levels of a vibrating rotor.^{19,25} Similarly, if $\alpha \neq 1$ and all of the $\{\delta_{l,m}\}$ are identically zero, Eq. (1) becomes the level-energy expression which would be appropriate if all isotopomers of the given molecular species had *exactly* the same potential energy function, *and* the firstorder semiclassical (or Jeffreys-Weentzel-Kramers-Brillouin or Bohr-Sommerfeld) quantization condition were exact for this species. The fact that neither of those conditions is ever exactly true gives rise to a need for the atomicmass-dependent corrections terms associated with the parameters $\{\delta_{l,m}^{A}\}$. While the relative magnitudes of these two types of contributions cannot be determined in an empirical "parameter-fit" analysis based on a fit to level energy expressions such as Eq. (1), and both are generally present, it has become customary to refer to terms of this type collectively as "BOB corrections."

The expansion of Eq. (1) is formally exactly equivalent to an expression introduced some years earlier by Ross, Eng, and Kildal,²⁶ for which Bunker²⁷ and Watson²⁸ had provided theoretical justification, and the expansion parameters of the two forms can be readily interrelated.²³ However, in Eq. (1) the BOB energy corrections are additive rather than multiplicative, and the reference species whose parameters are directly determined by the fit is an actual molecular species, rather than a hypothetical model system in which the firstorder semiclassical quantization condition is exact and the intermolecular potential energy function is exactly the same for all isotopomers. Other advantages of the combinedisotopomer level energy expression of Eq. (1) are discussed in Ref. 23.

In principle there are no restrictions regarding which isotopomer is selected as the reference species whose parameters $\{Y_{l,m}^1\}$ explicitly appear in Eq. (1). If no rounding is performed, exactly the same quality of fit and exactly the same set of single-isotopomer $\{Y_{l,m}^{\alpha}\}$ parameters are obtained from Eqs. (1) and (2) for *any* choice of reference isotopomer.²⁹ Thus, although the data for ^{6,6}Li₂ used in the present analysis span a wider range of levels (v(A)=0-24and v(X)=0-14) than those for ^{7,7}Li₂ (v(A)=0-13 and v(X)=0-13), we adopted the convention²³ of using the most abundant isotopomer, ^{7,7}Li₂, as the reference species.

In the fits reported herein, each of the *N* experimental data $y_{obs}(i)$ was weighted by the inverse square of its estimated uncertainty u(i), and the overall quality of fit is characterized by the value of dimensionless standard error³⁰

$$\bar{\sigma}_{f} = \left\{ \frac{1}{N - M} \sum_{i=1}^{N} \left[\frac{y_{\text{calc}}(i) - y_{\text{obs}}(i)}{u(i)} \right]^{2} \right\}^{1/2},$$
(3)

where $y_{calc}(i)$ is the value of datum *i* predicted by the *M* parameter model being fitted to. The parameter uncertainties

	Ground $X^{1}\Sigma_{g}^{+}$ state			$A^{1}\Sigma_{u}^{+}$ state				
Case	Vib-rot levels	$10^3 \times \delta_{1,0}^{\mathrm{Li}}$	$10^5 imes \delta_{0,1}^{\mathrm{Li}}$	Vib-rot levels	$\delta^{\mathrm{Li}}_{0,0}$	$10^3 \times \delta_{1,0}^{\mathrm{Li}}$	$10^5 imes \delta_{0,1}^{\mathrm{Li}}$	$ar{\sigma}_{\! f}$
(i)	Band constants	а	а	Dunham{7,5,3,1}	а	0.0	0.0	1.188
(ii)	Band constants	а	а	Dunham{7,5,3,1}	а	0.0	$9.6(\pm 2.2)$	1.184
(iii)	Band constants	а	а	Dunham{7,5,3,1}	а	$9.1(\pm 0.6)$	0.0	1.130
(iv)	Band constants	а	а	Dunham{7,5,3,1}	а	9.1(±0.6)	8.8(±2.1)	1.125
(v)	Dunham{5,4,3,2,0}	0.0	0.0	Band constants	а	а	а	1.089
(vi)	Dunham{5,4,3,2,0}	0.0	$1.0(\pm 2.0)$	Band constants	а	а	а	1.089
(vii)	Dunham{5,4,3,2,0}	$5.9(\pm 0.5)$	0.0	Band constants	а	а	а	1.049
(viii)	Dunham{5,4,3,2,0}	$5.9(\pm 0.5)$	$1.5(\pm 2.0)$	Band constants	а	а	а	1.049
(ix)	Dunham{5,4,3,2,0}	0.0	0.0	Dunham{7,5,3,1}	0.0	0.0	0.0	5.352
(x)	Dunham{5,4,3,2,0}	0.0	0.0	Dunham{7,5,3,1}	$0.438(\pm 0.003)$	0.0	0.0	1.415
(xi)	Dunham{5,4,3,2,0}	$5.8(\pm 0.6)$	0.0	Dunham{7,5,3,1}	$0.450(\pm 0.003)$	0.0	0.0	1.385
(xii)	Dunham{5,4,3,2,0}	0.0	0.0	Dunham{7,5,3,1}	$0.409(\pm 0.004)$	$6.1(\pm 0.7)$	0.0	1.391
(xiii)	Dunham{5,4,3,2,0}	$6.0(\pm 0.6)$	0.0	Dunham{7,5,3,1}	$0.420(\pm 0.004)$	$6.4(\pm 0.7)$	0.0	1.357
(xiv)	Dunham{5,4,3,2,0}	0.0	$-7.1(\pm 0.3)$	Dunham{7,5,3,1}	$0.375(\pm 0.003)$	0.0	0.0	1.229
(xv)	Dunham{5,4,3,2,0}	0.0	0.0	Dunham{7,5,3,1}	$0.375(\pm 0.003)$	0.0	$7.1(\pm 0.3)$	1.225
(xvi)	Dunham{5,4,3,2,0}	0.0	$1.7(\pm 2.3)$	Dunham{7,5,3,1}	$0.375(\pm 0.003)$	0.0	8.8(±2.3)	1.225
(xvii)	Dunham{5,4,3,2,0}	$5.6(\pm 0.5)$	$-7.5(\pm 0.3)$	Dunham{7,5,3,1}	$0.341(\pm 0.004)$	$8.9(\pm 0.6)$	0.0	1.138
(xviii)	Dunham{5,4,3,2,0}	$5.6(\pm 0.5)$	0.0	Dunham{7,5,3,1}	$0.341(\pm 0.004)$	$8.9(\pm 0.6)$	$7.5(\pm 0.3)$	1.134
(xix)	Dunham{5,4,3,2,0}	5.6(±0.5)	0.9(±2.1)	Dunham{7,5,3,1}	$0.341(\pm 0.004)$	8.9(±0.6)	8.4(±2.1)	1.134

^aSets of band constants are used for each vibrational level of each isotopomer of one state, so BOB parameters are not relevant for this case.

reported herein are 95% confidence limit ($\approx 2\sigma$) uncertainties, and the atomic masses used in the combined-isotopomer mass scaling, $M(^{7}\text{Li}) = 7.016\,004\,1\,\text{u}$ and $M(^{6}\text{Li}) = 6.015\,122\,3\,\text{u}$, were taken from the 1993 mass table.³¹ In a fit which yields $\bar{\sigma}_{f} \lesssim 1$, on average all data are represented within their respective experimental uncertainties.³²

The present analysis was performed using program DSPARFIT,³³ which can simultaneously fit any combination of microwave, infrared, electronic band, or fluorescence series data, for one or multiple isotopomers, and involving one or more electronic states, to band-constant or Dunham-expansion or near-dissociation expansion level-energy expressions. If desired, it can also determine Born–Oppenheimer breakdown and/or Λ -doubling correction terms. It can also utilize the "sequential rounding and refitting" procedure of Ref. 30 to obtain a final parameter set involving the smallest possible number of significant digits, while ensuring no significant loss of accuracy in predictions generated from those parameters.

IV. RESULTS AND DISCUSSION

The initial stage of the analysis involved the determination of which orders to use in the double polymonial expansion of Eq. (1) for each electronic state. From a series of trial fits it was quickly determined that an optimum representation of the data set of Table I was obtained using $m_{\text{max}}=4$ and $l_{\text{max}}(m)=5, 4, 3, 2, \text{ and 0 for } m=0-4$ respectively, to define the $\{Y_{l,m}\}$ expansions for the $X^{1}\Sigma_{g}^{+}$ state, and $m_{\text{max}}=3$ with $l_{\text{max}}(m)=7, 5, 3, \text{ and 1 for } m=0-3$ to define those for the $A^{1}\Sigma_{u}^{+}$ state. Note that, as shown by Eq. (2), the constant contribution to the isotope shift for levels of isotopomer α of Li₂ in a given electronic state is given by

$$Y_{0,0}^{\alpha} = \left\{ \frac{\Delta M_{\rm A}^{\alpha}}{M_{\rm A}^{\alpha}} + \frac{\Delta M_{\rm B}^{\alpha}}{M_{\rm B}^{\alpha}} \right\} \delta_{0,0}^{\rm Li},\tag{4}$$

where the two terms in parentheses allow the isotopic identity of either one or both atoms to change. As discussed in Ref. 34, unless one has data which allow a precise determination of the *differences* between the dissociation energies \mathfrak{D}_e of different isotopomers, one cannot determine independent values of this leading BOB correction for the individual electronic states considered in the analysis. As a result, the quantity actually determined from our analysis is the difference between the individual values of $\delta_{0,0}^{\text{Li}}$ for the two electronic states:

$$\tilde{\delta}_{0,0}^{\text{Li}}(A) \equiv \delta_{0,0}^{\text{Li}}(A) - \delta_{0,0}^{\text{Li}}(X)$$
(5)

The remaining question was then: How many BOB correction parameters $\delta_{l,m}^{\text{Li}}$ could be determined for each state? The results of a series of fits addressing this question are summarized in Table II. The first eight rows of Table II show the results of fits in which the vibration-rotation energies of levels in either the $X^{1}\Sigma_{g}^{+}$ or the $A^{1}\Sigma_{u}^{+}$ state were represented by sets of band constants $\{G_v, B_v, D_v, ...\}$ for each vibrational level of each isotopomer, while those for the other state were represented by the combined-isotopomer expression of Eq. (1). Use of Eq. (1) means that vibrational and rotational BOB correction parameters may in principle be determined for that state, but since the other state is represented by independent sets of band constants for each isotopomer, the electronic isotope shift parameter $\tilde{\delta}_{0,0}^{\text{Li}}(A)$ is not defined in such fits. However, this type of fit reduces the effects of interstate correlation and facilitates the delineation of which vibrational and rotational BOB correction terms may be determined from these data.

The results in the first four rows of Table II show that inclusion of the $\delta_{1,0}^{\text{Li}}(A)$ parameter in the analysis yields a significant ($\approx 5\%$) improvement in the overall quality of fit, and the modest uncertainty (of $\approx 7\%$) in the resulting $\delta_{1,0}^{\text{Li}}(A)$ value gives further assurance of its physical significance. The

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situation is not so clear for the leading BOB correction to the inertial rotation constant $\delta_{0,1}^{\text{Li}}(A)$ which determines the isotopic shift of the equilibrium bond length, since allowing it to vary yields only a marginal improvement in the quality of fit. On the other hand, the associated parameter uncertainty is only a small fraction of the parameter value itself. Moreover, within the uncertainties, these values of $\delta_{0,1}^{\text{Li}}(A)$ are essentially the same as those determined in all of the other Table II fits in which it was a free parameter. This model independence provides some assurance that a meaningful value of $\delta_{0,1}^{\text{Li}}(A)$ may also be determined in the present study.

Rows (v)-(viii) of Table II summarize the results of fits in which band constants were used for the $A^{1}\Sigma_{u}^{+}$ state and Dunham expansions with BOB corrections for the $X^{1}\Sigma_{q}^{+}$ state. The fact that the values of $\bar{\sigma}_{f}$ for these cases are smaller than those for cases (i)-(iv) merely reflects the fact that the data set spans a wider range of v values for the A state than for the X state, so the additional flexibility associated with use of band constants for each level of each isotopomer, rather than smooth Dunham expressions, makes a larger difference here. In this case we again see that allowing the leading vibrational BOB parameter $\delta_{1,0}^{\text{Li}}(X)$ to vary yields a distinct improvement in $\overline{\sigma}_{f}$ (this time by 4%) and a parameter value with a fairly small uncertainty of 8%. In contrast, freeing the leading rotational BOB parameter $\delta_{0,1}^{L1}(X)$ yields no significant improvement in $\overline{\sigma}_{f}$, and in this case [rows (vi) and (viii)] the predicted parameter uncertainty is larger than the parameter value itself. On the other hand, the fact that very similar values of $\delta_{0,1}^{\text{Li}}(X)$ are obtained in cases (vi) and (viii) suggests that these estimates of $\delta_{0,1}^{\text{Li}}(X)$ may in fact be physically significant. This question is considered further in the following.

The remaining entries in Table II correspond to fits in which the energy levels of both electronic states were represented by Eq. (1). The very large value of $\overline{\sigma}_f$ associated with the first of these fits, case (ix), shows that complete neglect of BOB effects yields an unacceptably poor representation of the data. The fact that the values of $\overline{\sigma}_f$ for all of the subsequent cases (x)–(xix) are four to five times smaller shows that the electronic isotope shift term $\delta_{0,0}^{\text{Li}}(A)$ is by far the most important BOB correction for this system. The results summarized in rows (xi)–(xiii) also clearly confirm our conclusion that physically significant values of the leading vibrational BOB parameter may be determined for both electronic states.

For the leading rotational BOB parameters $\delta_{0,1}^{\text{Li}}$, the results for cases (xiv)–(xvi) and cases (xvii)–(xix) of Table II show that the data are quite sensitive to the difference

$$\widetilde{\delta}_{0,1}^{\text{Li}}(A) \equiv \delta_{0,1}^{\text{Li}}(A) - \delta_{0,1}^{\text{Li}}(X)$$

\$\approx 7.5(\pm 0.26)\times 10^{-5} cm^{-1}, (6)

which is determined with a predicted uncertainty of only 3%, and that this term yields a significant ($\approx 15\% - 20\%$) reduction in $\overline{\sigma}_f$. However, they also show that the separate values for the two electronic states are highly correlated parameters whose individual values have much larger uncertainties ($\approx 25\%$ for $\delta_{0,1}^{\text{Li}}(A)$ and $\geq 100\%$ for $\delta_{0,1}^{\text{Li}}(X)$). On the other

hand, within the uncertainties, the individual values for the two states are the same as those yielded by the individualstate BOB analyses of rows (iv) and (viii). Indeed, except for the four cases in which all of the BOB corrections to $Y_{0,1}^{\alpha}$ were attributed to only one state or the other [cases (xiv) and (xv), and (xvii) and (xviii)], all of the fitted values of $\delta_{0,1}^{\text{Li}}(A)$ and $\delta_{0,1}^{\text{Li}}(X)$ yielded by the various models are essentially the same.

The model independence of the $\delta_{0,1}^{\text{Li}}(X)$ values associated with cases (vi), (viii), (xvi), and (xix) suggests that in spite of their large predicted uncertainties, the fact that $\delta_{0,1}^{\text{Li}}(X)$ has a non-negligible positive value of magnitude $\approx 10^{-5} \text{ cm}^{-1}$ is probably correct. On the other hand, it is difficult to justify recommending a set of parameters in which one of the fitted values has an uncertainty greater than 200%. Thus, we select model (xviii) (second to last row of Table II) as our optimum representation of the information contained in the data set considered here. At the same time, to take account of the probable small positive value of $\delta_{0,1}^{\text{Li}}(X)$, our final estimated uncertainty in $\delta_{0,1}^{\text{Li}}(A)$ is based on the results of cases (xvi) and (xix).

The resulting recommended molecular constants are listed in Table III. The parameters actually determined by the fits are those associated with the chosen reference isotopomer ^{7,7}Li₂, while those for the "minority" isotopomers in the second and third columns of Table III were generated from those in the first column using Eq. (2), and the values of $\bar{\sigma}_f$ at the bottom of columns two and three are the dimensionless rms discrepancies for that one isotopomer obtained on fixing its molecular constants at the rounded values determined from the combined-isotopomer analysis. Relatively more significant digits are required to represent these (derived) minority-isotopomer parameters, since the compensating changes associated with the sequential rounding and refitting procedure do not come into play, and they can only be rounded at the first digit of the "parameter sensitivity."^{23,30}

In the present work the electronic state energy for isotopomer α is represented by the value of T_0^{α} , rather than by the estimated energy of the potential energy minimum T_e^{α} . This choice is based on the fact that T_0^{α} is an actual experimental observable, while in a "parameter-fit" analysis T_e^{α} is at best an extrapolated quantity.^{23,33} In a "potential-fit" analysis involving fits to exact quantal eigenvalue-difference simulations of the observed transition frequencies, 3^{5-37} the electronic energy at the potential minimum T_e^{α} would be a natural parameter of the fit, and its differences for different isotopomers would directly reflect the atomic-massdependent "adiabatic" correction to the potential energy function. However, in the present type of analysis those shifts are combined with contributions from breakdown of the first-order semiclassical quantization condition. While estimates of the latter can be generated from standard formulas,^{19,25} it does not seem desirable to mix such an afterthe-fact interpretation with the actual data analysis. Hence, $T_0^1 = T_0^{\alpha = 1}$ is one of the parameters determined by the fit, while values of T_0^{α} for the minority ($\alpha > 1$) isotopomers are determined by taking account of isotopic zero-point energy differences and the BOB terms.

As seen in Table III, the overall zero-point level isotope

TABLE III. Properties of the $X^{1}\Sigma_{g}^{+}$ and $A^{1}\Sigma_{u}^{+}$ states of Li₂ determined from a simultaneous fit of 8445 data for three isotopomers to level energy differences defined by Eq. (1); the numbers in parentheses are 95% confidence limit uncertainties.

		All-isotopomerfit	From ^{7,7} Li ₂ Cons	ants and Eq. (2)	
		^{7,7} Li ₂	^{6,7} Li ₂	^{6,6} Li ₂	
		$X^{1}\Sigma^{+}$ state	constants		
	T_0	0.0	7.108 688	13.947 141	
	$Y_{1,0}$	351.406 64 (200)	365.731 663 9	379.516 224	
	$Y_{20}^{1,0}$	-2.583 24 (82)	-2.798 158 15	-3.013 076 3	
	$Y_{3,0}^{2,0}$	-0.005832(140)	-0.006 574 743	-0.007 346 586	
10^{4}	Y_{40}	-1.3(1)	-1.525 311	$-1.768\ 618$	
10^{4}	Y 5.0	-0.0617(33)	-0.075 344 9	-0.0906564	
	$Y_{0,1}$	0.672 529 7 (99)	0.728 482 24	0.784 434 779	
10^{4}	Y _{1.1}	-70.461 (31)	-79.434 62	-88.759 912	
10^{4}	Y _{2.1}	-0.3068 (70)	-0.359 973 4	-0.417 394	
10^{4}	Y _{3.1}	-0.007 5 (7)	$-0.009\ 158\ 62$	$-0.011\ 019\ 8$	
10^{4}	$Y_{4,1}$	-0.000 546 (24)	-0.000693929	$-0.000\ 866\ 421$	
10^{7}	Y _{0.2}	-97.928 (60)	-114.90049	-133.228 65	
10^{7}	Y _{1.2}	-0.419 (17)	-0.511 662	-0.615 641	
107	Y _{2,2}	-0.007 (3)	$-0.008\ 896\ 5$	$-0.011\ 108$	
107	Y _{3,2}	-0.001 44 (12)	$-0.001\ 904\ 75$	$-0.002\ 467\ 86$	
10^{10}	Y _{0,3}	1.318 (12)	1.675 089	2.091 469	
10^{10}	Y _{1,3}	0.017 (3)	0.022 487	0.029 135	
10^{10}	Y _{2,3}	-0.004 (3)	-0.001 927 3	-0.002 591 3	
10^{16}	$Y_{0,4}$	-7.9 (9)	-10.876	-14.622	
	$\delta^{ m Li}_{1,0}$	0.0056 (5)			
		$A^{1}\Sigma_{u}^{+}$ state	constants		
	T_0	14 020.586 3 (15)	14 025.703 532	14 030.624 272	
	$\delta \widetilde{Y}_{0,0}$	0.0	-0.05674	-0.113481	
	Y _{1.0}	255.476 68 (260)	265.890 301 3	275.910 936 3	
	$Y_{2,0}$	-1.580 147 (1200)	-1.711 610 69	$-1.843\ 074\ 38$	
	Y _{3,0}	0.001 6 (2)	0.001 803 77	0.002 015 524	
	$Y_{4,0}$	0.000 199 2 (240)	0.000 233 724 55	0.000 271 006 73	
10^{7}	$Y_{5,0}$	-160.681 (13000)	-196.215 48	-236.0902	
10^{7}	$Y_{6,0}$	4.372 (370)	5.556 517	6.937 712	
10^{7}	$Y_{7,0}$	-0.049(4)	$-0.064\ 814\ 52$	-0.08397594	
	$Y_{0,1}$	0.497 454 9 (93)	0.538 828 201	0.580 199 426	
10^{4}	$Y_{1,1}$	-54.828 3 (160)	-61.811 037	-69.067 357	
10^{4}	$Y_{2,1}$	0.234 75 (370)	0.275 435 9	0.319 371 6	
107	Y _{3,1}	-5.55 (40)	-6.777 38	-8.15467	
107	$Y_{4,1}$	0.06 (2)	0.076 256	0.095 211	
107	$Y_{5,1}$	-0.002 64 (34)	$-0.003\ 492\ 05$	-0.00452442	
107	$Y_{0,2}$	-75.008 (49)	$-88.00\ 809$	-102.04655	
107	$Y_{1,2}$	0.6114 (40)	0.746 611	0.898 336	
10/	Y _{2,2}	-0.006 6 (4)	$-0.008\ 388\ 2$	-0.010 473 2	
10'	Y _{3,2}	-0.00022(2)	-0.000291	$-0.000\ 377\ 03$	
1010	$Y_{0,3}$	1.031 (7)	1.310 331	1.636 043	
10^{10}	$Y_{1,3}$	-0.010 6 (4)	-0.014 021 1	-0.018166	
	$\widetilde{\delta}^{\mathrm{Li}}_{0,0}$	0.341 (4)			
	$\delta^{ m Li}_{1,0}$	0.008 9 (6)			
10^{4}	$\delta^{ m Li}_{0,1}$	0.75 (20)			
No. of da	ta	8445	225	4353	
No. paran	neters	212^{a}	0	96^{b}	
$ar{\sigma}_{\! f}$		1.134	1.343	1.167	

^aIn addition to the 4 BOB correction and 38 Dunham expansion parameters, the fit determined 170 independent initial-state term values for the upper states of the F-A fluorescence series and of A-X emission excited by lines of indeterminate accuracy.

^bThese 96 parameters are the initial-state term values for the upper states of the F-A fluorescence series and of A-X emission excited by lines of indeterminate accuracy.

shift parameter is $\tilde{\delta}_{0,0}^{\text{Li}}(A) = 0.341 (\pm 0.004) \text{ cm}^{-1}$. Thus, the total effective isotopic shift from ^{7,7}Li₂ to ^{6,6}Li₂ in the $A^{1}\Sigma_{u}^{+}$ state is $\delta \tilde{Y}_{0,0}({}^{6,6}\text{Li}_{2}) = -0.1135(\pm 0.0015) \text{ cm}^{-1}$, while that between ^{7,7}Li₂ and ^{6,7}Li₂ is exactly half that value [see Eq. (4)]. As in Eqs. (5) and (6), the "tilde" in the symbol $\tilde{Y}_{0,0}$

indicates that this is the difference between the total zeropoint isotope corrections in the upper and lower electronic states.

While combined under the general label of "BOB corrections," the terms associated with the parameters $\{\delta_{l,m}^{Li}\}$

contain two different types of contributions. The first are those associated with breakdown of the first-order semiclassical quantization condition which was the basis for the conventional isotopic vibrational parameter scaling by powers of $(\mu_1/\mu_{\alpha})^{1/2}$, while the second are those due to the small "adiabatic correction" differences between the electronic potential energy function for different isotopomers. The former are labeled "sc" and the latter "el:"

$$\delta_{l,m}^{\text{Li}} = \delta_{l,m}^{\text{Li,sc}} + \delta_{l,m}^{\text{Li,el}}.$$
(7)

As they have the same functional dependence on the atomic masses, these two types of contributions cannot be distinguished from one another in "parameter-fit" analyses such as that reported here.

Substituting the expansion coefficients of Table III into the usual expression for the semiclassical contribution to the zero-point energy generated from Dunham theory^{19,25}

$$Y_{0,0}^{\rm sc} = \frac{Y_{0,1} + Y_{2,0}}{4} - \frac{Y_{1,0}Y_{1,1}}{12Y_{0,1}} + \frac{(Y_{1,0}Y_{1,1})^2}{144(Y_{0,1})^3}$$
(8)

yields the differences $\tilde{Y}_{0,0}^{\rm sc}(A) \equiv Y_{0,0}^{\rm sc}(A) - Y_{0,0}^{\rm sc}(X) = 0.1056$, 0.1144, and 0.1232 cm⁻¹ for ^{7,7}Li₂, ^{6,7}Li₂, and ^{6,6}Li₂, respectively. Combining these results with the overall differences $\delta \tilde{Y}_{0,0}^{\alpha}$ from Table III yields estimates for the ^{6,7}Li₂ and ^{6,6}Li₂ A - X electronic isotope shifts of $\delta T_e = -0.066$ (±0.001) and -0.131 (±0.002) cm⁻¹, respectively. We believe that this is the first experimental determination of an electronic isotope shift for any Li₂ system.

Note that this estimate of the electronic isotope shift has the same sign, but is significantly smaller than the -0.351cm⁻¹ difference between the spacings of the $A^{1}\Sigma_{u}^{+}$ (²S +²P) and $X^{1}\Sigma_{g}^{+}$ (²S+²S) potential asymptotes for ^{7,7}Li₂ and ^{6,6}Li₂.³⁸ This provides further evidence that the BOB corrections to the vibrational level energy expressions for these states are not negligible, since they must cumulatively account for the difference between these values.³⁹

V. CONCLUSIONS

New high resolution polarization A - X transition data for ^{6,7}Li₂ and absorption and dispersed fluorescence data for ^{7,7}Li₂ and ^{6,6}Li₂, augmented with previous ^{6,6}Li₂ and ^{7,7}Li₂ A-X transition data, comprise a set of 8445 rovibrational transition lines for the three Li2 isotopomers. Our use of these data in the first combined-isotopomer analysis performed for Li₂ has yielded improved and internally consistent values of the molecular constants for the three isotopomers in the two states. Only 38 Dunham coefficients and four BOB correction parameters are required to represent all of these data within the experimental uncertainties. This analysis yields a value of $\delta T_e = -0.131 (\pm 0.002) \text{ cm}^{-1}$ for the A-X electronic isotope shift from ^{7,7}Li₂ to ^{6,6}Li₂, and good estimates of the leading vibrational BOB correction parameters for both states and of the leading BOB rotational correction parameter for the $A^{1}\Sigma_{u}^{+}$ state. Note, however, that the difference between the A- and X-state rotational BOB correction terms $\tilde{\delta}_{0,1}^{\text{Li}}(A) = \delta_{0,1}^{\text{Li}}(A) - \delta_{0,1}^{\text{Li}}(X) = 7.5(\pm 0.3) \times 10^{-5} \text{ cm}^{-1}$ is much more accurately determined than the values for the individual states.

Since $\delta_{0,1}^{\text{Li}}(A)$ is positive and the mass difference ΔM_{Li} is negative going from ⁷Li to ⁶Li, the BOB corrections to the leading inertial rotational constants (B_e) for ^{6,6}Li₂ is negative. Thus, although the uncertainties are fairly large, the present analysis predicts that the equilibrium $A^{1}\Sigma_{u}^{+}$ -state bond length implied by this constant increases from the heavier to the lighter isotopomers.

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