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Precise experimental test of models for the breakdown of the Born-Oppenheimer separation: The rotational spectra of isotopic variants of lithium hydride

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The frequencies of 22 rotational transitions in the four naturally occurring isotopic variants of lithium hydride have been measured to an unprecedented accuracy of a few parts in 10^8 with a tunable far-infrared spectrometer. The values of the vibrational and rotational quantum numbers v and J involved range up to 2 and 12, respectively. The measurements have been fitted with already existing data on the vibration-rotation energy levels of lithium hydride in its ground $^1\Sigma^+$ state to a single model based on the Dunham expansion. This model has been modified to take into account the Dunham and nonadiabatic corrections and their effects on the reduced mass dependence of the energy levels in the way first described by Watson [J. Mol. Spectrosc. **80**, 411 (1980)]. The data are fitted to experimental accuracy to give an improved set of reduced Dunham parameters, U_{kl}, and an improved value for the Born-Oppenheimer equilibrium bond length for LiH, $r_e^{\mathrm{BO}}=0.159\,490\,811(16)$ nm. The fit constitutes a stringent test of this type of model for the breakdown of the Born-Oppenheimer approximation.

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I. INTRODUCTION

Lithium hydride is one of the simplest heteronuclear diatomic molecules and, as such, has been the subject of many experimental [1–7] and theoretical [8–17] studies. Since the molecule contains only four electrons, it is possible to perform very accurate *ab initio* calculations of its energy levels and physical properties. It therefore provides an excellent prototype to test theoretical models and assumptions such as the Born-Oppenheimer approximation [18]. Lithium hydride is also of interest in astrophysics [19]. For example, the detection of lines in its vibration-rotation spectrum in highly red-shifted objects has recently been reported [20]. For these reasons, we have undertaken a study of the pure rotational spectrum of lithium hydride at a high accuracy, encompassing all possible naturally occurring isotopomers (from H, D, ^{6}Li, and ^{7}Li).

The rotational spectrum of this molecule, which falls at submillimeter and far-infrared wavelengths, was first reported by Pearson and Gordy [3], who detected the $J=1\leftarrow 0$ transitions of ^{6}LiD and ^{7}LiD in the $v=0$ and 1 levels. This work was later extended by Plummer, Herbst, and De Lucia [4] to include the hydride in $v=0$ and 1 levels and the $J=2\leftarrow 1$ transition of LiD isotopomers.[1] Higher J rotational transition frequencies have been measured less accurately (with an uncertainty of 12 MHz) by Fourier-transform spectroscopy by Maki, Olson, and Thompson [7]. In all these experimental studies, LiH was formed in the vapor phase by heating lithium metal or lithium hydride in the presence of hydrogen gas. The development of tunable, coherent radiation sources at far-infrared wavelengths [21,22] makes it possible to measure the higher J rotational transition frequencies much more accurately. The results of these measurements constitute the present paper. After we had made most of our measurements, we learned of similar experiments being carried out by Matsushima and co-workers in Japan. On this realization, Matsushima *et al.* ceased working on the problem and published the measurements that they had made on ^{6}LiH and ^{7}LiH [23]. A preliminary account of our observations, more concerned with their astrophysical implications, has been published elsewhere [24].

Lithium hydride has provided a good test case for the modeling of vibration-rotation energy levels and their dependence on isotopic form. In particular, because it is a light molecule, deviations from Born-Oppenheimer behavior are expected to be quite large for LiH. There have been several attempts to fit the spectroscopic data of lithium hydride in its ground electronic state to investi-

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[1] An isotopomer is a single isotopic form of a particular molecular species.

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gate these effects. Plummer, Herbst, and De Lucia [4] were perhaps the first to do this seriously but restricted themselves to relatively few pure rotational transitions. Less precise but more extensive data from the electronic spectrum have been used by Vidal and co-workers [5]. Maki, Olson, and Thompson [7] extended the data set by incorporating measurements of the higher J rotational transitions in the far infrared and of vibration-rotation transitions, both recorded by Fourier-transform interferometric techniques. However, they were only partially successful in fitting all the data with a single model. The same data set has since been fitted satisfactorily by Coxon [25] and by Tiemann and Ogilvie [26]. There have been two approaches to fitting the data for lithium hydride, both of which have a common root in the theoretical development by Van Vleck [27], Herman and Asgharian [28], and Watson [29,30]. As these authors have shown, it is possible to formulate an effective vibration-rotation Hamiltonian that takes account of the nonadiabatic terms that are responsible for the breakdown of the Born-Oppenheimer separation. From this Hamiltonian, one can derive an expression for the vibration-rotation energy levels in the style of Dunham's original expansion [31]:

$$E(v,J)/hc=\sum_{k,l} Y_{kl}(v+\tfrac{1}{2})^k[J(J+1)]^l \qquad (1)$$

by writing

$$Y_{kl}=U_{kl}\mu^{-(k/2+l)}\left[1+\Delta_{kl}^{\mathrm{H}}\frac{m_e}{m_{\mathrm{H}}}+\Delta_{kl}^{\mathrm{Li}}\frac{m_e}{m_{\mathrm{Li}}}\right] . \qquad (2)$$

In this expression U_{kl}, Δ_{kl}^{H}, and $\Delta_{kl}^{\mathrm{Li}}$ are isotopically invariant parameters, μ is the reduced mass of the diatomic molecule

$$\mu=m_{\mathrm{H}}m_{\mathrm{Li}}/(m_{\mathrm{H}}+m_{\mathrm{Li}}) , \qquad (3)$$

and m_{H} and m_{Li} are the atomic masses of the two atoms. In particular, the dependence of the energy levels on the reduced masses of the different isotopic forms is modified from Dunham's expressions in a small but significant manner by the introduction of the two parameters Δ_{kl}^{H} and $\Delta_{kl}^{\mathrm{Li}}$ for each Dunham parameter Y_{kl}. It was this model, first given in this form by Watson [29], that was used successfully to fit the various lithium hydride data sets by Plummer, Herbst, and De Lucia [4]; Chan *et al.* [5]; and Maki, Olson, and Thompson [7]. The alternative approach utilizes the same basic theoretical model but differs at an early stage of its development, fitting the data directly with an adjustable form of the vibrational potential-energy function. This procedure should work equally well because, as Dunham [31] first showed, the parameters Y_{kl} can be expressed in terms of the coefficients of the potential-energy function. However, Maki, Olson, and Thompson [7] found that such a fit was about four times poorer than that achieved with the Watson model, Eqs. (1) and (2). Coxon [25] showed that the reason for this failure was their inadequate treatment of the J-dependent nonadiabatic mixing terms and produced a direct fit of much better quality. Very recently, Tiemann and Ogilvie [26] have made a direct algebraic connection between the U_{kl} and Δ_{kl} parameters and the coefficients in the effective potential-energy function. They have also fitted the lithium hydride data set to experimental precision with what is effectively the Watson model. We have followed the Tiemann-Ogilvie procedure in fitting the more accurate rotational frequencies measured in the present work. The model works equally well and results in a more accurate determination of certain key parameters. In particular, it provides the most stringent test of this model of the Born-Oppenheimer breakdown to date.

II. EXPERIMENTAL DETAILS

The tunable far-infrared spectrometer at the European Laboratory for Non-Linear Spectroscopy (LENS) in Florence, Italy, was used to make the measurements on lithium hydride. Coherent far-infrared (FIR) radiation is generated by nonlinear mixing of radiation from three sources, two frequency-stabilized ($\Delta\nu/\nu \sim 10^{-9}$) carbon dioxide lasers and a microwave synthesizer, in a metal-insulator-metal diode. By selecting emission from different laser lines and sweeping the microwave frequency, the spectrometer can be continuously tuned over quite a wide range (several GHz) within the region from 300 to 5500 GHz. The final uncertainty of about 35 kHz in the FIR frequency is set mainly by the accuracy of the CO_2 laser lock to the center of the line.

The FIR radiation emitted by the diode is collimated by an off-axis parabolic mirror and detected by a liquid helium-cooled Si-composite bolometer after passing through the absorption cell. A moving rooftop mirror is inserted in the beam path in order to modulate the optical path length traveled by the FIR radiation and so to eradicate interference effects that might otherwise degrade the recordings. A more detailed description of the apparatus has been given elsewhere [32].

The absorption heat-pipe cell that was used for the present measurements is made from a stainless steel tube, 1.2 m long and 25 mm internal diameter. An electric current was passed through heating wire using a variable voltage controller to heat the central 0.9 m of the cell. The temperatures used were in the range 780–953 K and were measured by a chromel-alumel thermocouple placed near the middle of the cell. The values obtained were nicely consistent with the fitted Doppler linewidths of the observed lines. The end sections of the cell were water-cooled and closed with high-density polyethylene windows.

Two different procedures were used in the production of lithium hydride. In the first, commercially available LiH powder was simply heated in the cell to generate sufficient vapor pressure. In the second, lithium wire was heated in a stream of H_2 or D_2 to form LiH. Only the second method was used to form LiD. In neither case was the lithium sample isotopically enriched, so that ^{6}Li was present only in natural abundance (7.5%).

Temperature was found to be the most convenient parameter to control the sample density. Measurements involving the ^{7}Li isotope in the ground vibrational level were made with temperatures between 780 and 828 K,

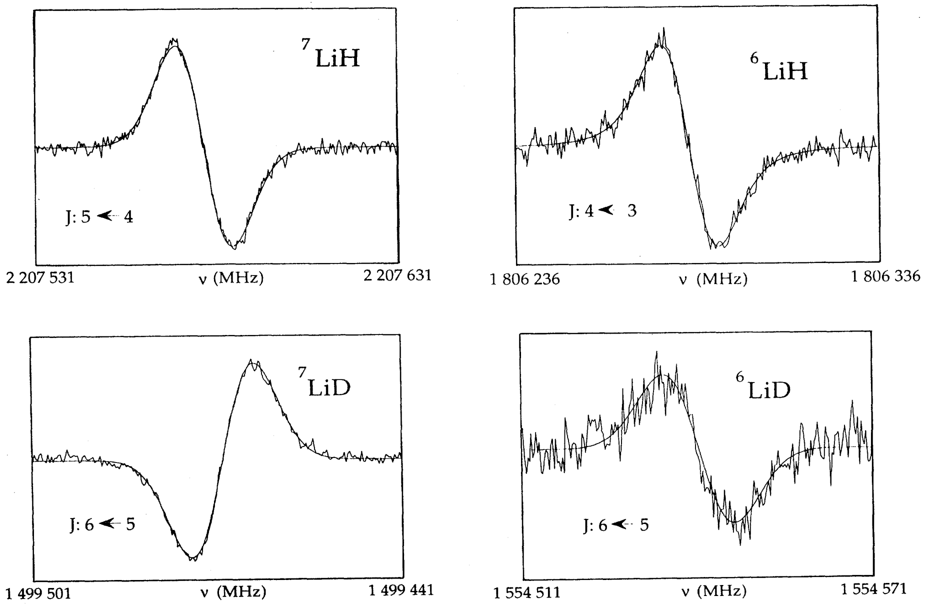

FIG. 1. Examples of experimental recordings of lines in the rotational spectrum of the four naturally occurring isotopomers of lithium hydride in the $v=0$ level of the ground electronic state. The line shape is the first derivative of an absorption profile because the signal is detected at the modulation frequency (780 Hz) of the FIR radiation. The phase of the signal depends on the sideband of the carrier in which it occurred. The continuous line in each figure is the fitted Voigt profile. Note the poorer signal-to-noise ratio for the lines involving the ^{6}Li isotope, present only in natural abundance (7.5%).

and data for ^{6}Li and for excited vibrational levels were recorded at temperatures up to 953 K to compensate for the lower populations. The pressure in the sample cell was measured with a MKS Baratron 120 capacitance gauge and was usually kept low enough (50 to 100 Pa) so that the collisional broadening of the observed lines was barely perceptible. Studies in our laboratory have indicated that pressure shifts of the frequencies were small (always less than 1 kHz/Pa) [33]. Nevertheless, where a frequency was measured over a range of pressures, the value extrapolated to zero pressure was adopted in our analysis.

TABLE I. Pure rotational frequencies of isotopomers of LiH in the ground $^1\Sigma^+$ electronic state, measured in this work.

Isotope	v	J	ν (MHz)	Observed-calculated (MHz)
^{7}LiH	0	1-0	443 952.930(120)[a]	−0.019
		3-2	1 329 415.425(50)	0.017
		4-3	1 769 711.222(84)	−0.076
		5-4	2 207 584.583(55)	0.085
		7-6	3 073 719.689(46)	−0.065
	1	5-4	2 144 133.660(140)	−0.027
		6-5	2 566 428.764(70)	−0.035
	2	3-2	1 253 771.890(180)	0.024
		6-5	2 491 759.620(140)	0.298
^{6}LiH	0	4-3	1 806 284.250(130)	0.112
		5-4	2 253 109.840(150)	0.371
		6-5	2 696 797.930(120)	0.172
	1	3-2	1 317 579.780(300)	−0.404
		6-5	2 618 408.030(150)	0.042
^{7}LiD	0	6-5	1 499 472.047(69)	0.038
		10-9	2 478 645.131(64)	0.072
	1	6-5	1 467 117.962(85)	0.063
		12-11	2 893 542.680(160)	0.287
	2	8-7	1 906 609.320(190)	−0.178
		12-11	2 830 280.940(300)	−0.419
^{6}LiD	0	6-5	1 554 541.660(190)	0.079
		11-10	2 817 913.720(130)	−0.280

[a] The numbers in parentheses are the estimates of experimental error (1σ), in units of the last quoted decimal place.

TABLE II. Values of the isotopically invariant parameters for LiH in its ground $^1\Sigma^+$ state, determined in the least-squares fit. The units of the parameters are as follows: $U_{kl}^{(1)}, U_{kl}$, $\mathrm{cm}^{-1}\,\mathrm{u}^{(k/2+l)}$; $U_{kl}^{(2)}$, $\mathrm{cm}^{-1}\,\mathrm{u}^{(k/2+l+1)}$; Δ_{kl}^{a}, Δ_{kl}^{b}, dimensionless. The atomic masses used in these calculations are $m_{\mathrm{H}} = 1.007\,825\,035$ u, $m_{\mathrm{D}} = 2.014\,101\,779$ u; $m_{^6\mathrm{Li}} = 6.015\,101\,4$ u, $m_{^7\mathrm{Li}} = 7.016\,003\,0$ u; where u is the unified atomic mass unit.

k	l	$U_{kl}^{(1)}$	$U_{kl}^{(2)}$	U_{kl}[b]	Δ_{kl}^{H}	$\Delta_{kl}^{\mathrm{Li}}$
1	0	1 319.949 5(11)[a]	−0.034 70	1 319.910 2(11)	−0.674 58(80)	−0.1290(57)
2	0	−20.433 01(95)	0.000 229	−20.432 75(95)	−0.470(15)	
3	0	0.146 35(35)		0.146 35(35)		
4	0	−0.002 365(43)		−0.002 365(43)		
0	1	6.627 125 6(13)	−0.000 021 58	6.627 101 0(13)[c]	−1.556 97(22)	−0.1623(22)
1	1	−0.179 128 7(17)	$-0.952\,0\times10^{-5}$	−0.179 139 5(17)	−0.883 1(68)	
2	1	0.001 610 1(13)	$0.621\,4\times10^{-6}$	0.001 610 8(13)		
3	1	−0.000 030 62(28)		−0.000 030 62(28)		
0	2	$-0.668\,222\,3\times10^{-3}$	$-0.599\,3\times10^{-7}$	$-0.668\,290\,3\times10^{-3}$	−3.995(18)	−1.183(98)
1	2	$0.116\,071\times10^{-4}$	$0.528\,3\times10^{-8}$	$0.116\,131\times10^{-4}$		
2	2	$-0.854\,263\times10^{-7}$		$-0.854\,263\times10^{-7}$		
3	2	$-0.438\,740\times10^{-8}$		$-0.438\,740\times10^{-8}$		
0	3	$0.742\,998\times10^{-7}$	$0.178\,0\times10^{-10}$	$0.743\,200\times10^{-7}$	−6.05(36)	−8.7(20)
1	3	$-0.407\,193\times10^{-9}$	$-0.110\,5\times10^{-11}$	$0.408\,447\times10^{-9}$		
2	3	$-0.547\,206\times10^{-10}$		$-0.547\,206\times10^{-10}$		
3	3	$0.210\,992\times10^{-11}$		$0.210\,992\times10^{-11}$		
0	4	$-0.107\,323\times10^{-10}$	$-0.465\,6\times10^{-14}$	$-0.107\,376\times10^{-10}$		
1	4	$-0.203\,120\times10^{-12}$		$-0.203\,120\times10^{-12}$		
2	4	$0.166\,689\times10^{-13}$		$0.166\,689\times10^{-13}$		
0	5	$0.181\,506\times10^{-14}$	$0.132\,4\times10^{-17}$	$0.181\,656\times10^{-14}$		
1	5	$0.773\,273\times10^{-16}$		$0.773\,273\times10^{-16}$		
2	5	$-0.373\,986\times10^{-17}$		$-0.373\,986\times10^{-17}$		
0	6	$-0.345\,088\times10^{-18}$		$-0.345\,088\times10^{-18}$		
1	6	$-0.231\,595\times10^{-19}$		$-0.231\,595\times10^{-19}$		
0	7	$0.702\,832\times10^{-22}$		$0.702\,832\times10^{-22}$		
1	7	$0.653\,429\times10^{-23}$		$0.653\,429\times10^{-23}$		
0	8	$-0.150\,517\times10^{-25}$		$-0.150\,517\times10^{-25}$		
0	9	$0.334\,672\times10^{-29}$		$0.334\,672\times10^{-29}$		

[a] The numbers quoted in parentheses are the 1σ standard deviations of the least-squares fit, in units of the last quoted decimal place.

[b] The parameter U_{kl} includes the Dunham corrections and is determined by using Eq. (4), strictly speaking for the ^{7}LiH isotopomer.

[c] The parameter U_{01} also includes a contribution from the third-order parameter $U_{01}^{(3)} = -0.892\,26\times10^{-7}\ \mathrm{cm}^{-1}\,\mathrm{u}^3$.

III. RESULTS

We have recorded rotational lines for all four naturally occurring isotopomers of lithium hydride in the manner described in the previous section. Examples of typical recordings for each species in the $v = 0$ level are shown in Fig. 1. The line shape is the first derivative of an absorption profile because the FIR radiation is frequency modulated and the signal is detected at this modulation frequency. The line shapes of the lithium hydride spectra were fitted with a Voigt profile by least squares, using a computer program developed by Chance *et al.* [34]. The transition frequencies obtained in this way are given in Table I; the estimated uncertainties, which are also given, are determined predominantly by the accuracy of fit to the line shape, that is, by the signal-to-noise ratio. About five measurements were made of each transition.

The present measurements of the rotational frequencies are consistent with those made previously by Fourier-transform techniques but are more than two orders of magnitude more accurate. Of all those made by Maki, Olson, and Thompson [7], only one is in common with our measurements, the $J = 7$-6 for ^{7}LiH in the $v = 0$ level. Their value is 3077 715±12 MHz, about 4.5 MHz below our value, which has an uncertainty of 46 kHz. There are also some measurements in common with those reported by Matsushima *et al.* [23] for LiH. For the most part, these agree with our measurements to better than 100 kHz.

IV. ANALYSIS

We have chosen to use the formulation of Tiemann and Ogilvie [26] to fit our measurements. Indeed, Tiemann has kindly incorporated our data in a fit with his computer program to provide the results presented in this paper. The essential model comes from Watson's paper [30] and is given in Eqs. (1)–(3). Tiemann and Ogilvie have built into their fitting procedure the constraints between successive U_{kl} parameters, which follow from the implicit form of the potential that governs the vibrational motion. In particular, the higher-order centrifugal distortion parameters can be determined in this way. The parameters U_{kl} with $l \geq 2$ are exactly determined by the values of U_{k0} and U_{k1} [30]. These higher-order parameters play an important role in modeling the isotopic dependencies of the vibration-rotational levels of LiH because the molecule is so light that the Dunham expansion in Eq. (1) converges only slowly. The models of Watson and of Tiemann and Ogilvie differ in one respect, namely, how they treat the so-called Dunham corrections, those terms that feed through from higher order in a quantum-mechanical treatment when it is forced to conform to the quantum number dependence given in Eq. (1). In Watson's treatment, the effect of these terms is absorbed into the Δ_{kl}^{a} terms in Eq. (2); in other words, these corrections take account of both the nonadiabatic and the Dunham corrections. In Tiemann and Ogilvie's treatment, which is linked all the time to a specific form of the potential-energy function, the Dunham corrections are calculated explicitly and applied to the U_{kl} parameters in the form

$$U_{kl}=U_{kl}^{(1)}+U_{kl}^{(2)}/\mu+U_{kl}^{(3)}/\mu^2+\cdots \ , \tag{4}$$

where the terms $U_{kl}^{(2)}$, $U_{kl}^{(3)}$, etc. are the Dunham corrections, and the reduced mass factor is introduced to ensure that the $U_{kl}^{(i)}$ are all mass-independent. As a result of this difference, the parameters Δ_{kl}^{a} determined in the two approaches are not exactly comparable.

The data set used for our fit is essentially the same as that used by Tiemann and Ogilvie [26], that is, the submillimeter measurements of Pearson and Gordy [3] and Plummer, Herbst, and De Lucia [4] and the Fourier-transform FIR and IR measurements of Maki, Olson, and Thompson [7], augmented by the very accurate FIR measurements given in Table I. The data were weighted inversely as the square of their experimental uncertainty. The results of the fit are given in Tables I (residuals) and II (parameter values determined). For most of the measured transitions, the residuals are smaller than the estimated experimental error. Values for 18 adjustable parameters are determined in the fit.

V. DISCUSSION

Measurements made of the rotational transition frequencies of all four naturally occurring isotopomers of lithium hydride are more than two orders of magnitude more accurate than those obtained previously by Fourier-transform interferometry [7]. The data have been fitted to within experimental error by a single model, which applies the Dunham corrections explicitly and treats the nonadiabatic corrections in the form described by Watson [30]. Because the new data depend primarily on the rotational constant, there has been most improvement in the reduced Dunham rovibrational parameters that relate most closely to it, U_{01}, U_{11}, U_{02}, and their associated correction factors Δ_{kl}^{a}. A comparison of the values for these parameters with those obtained in previous fits is given in Table III. Not only has the precision of these parameters been improved but also their accuracy; consequently their physical interpretation, where possible, is more reliable.

Because of their accuracy, the present measurements provide the most demanding test of models of the breakdown of the Born-Oppenheimer (BO) separation to date. The extent of departure from the Born-Oppenheimer separation can be gauged from the parameters Δ_{01}^{H} and $\Delta_{01}^{\mathrm{Li}}$. This has been discussed in some detail by Tiemann and Ogilvie [26]. Estimates from the experimental value of the rotational magnetic moment show that the rotational contribution to the nonadiabatic mixing for LiH is almost, but not quite, negligible. The smallness of this contribution to the breakdown can be attributed to the remoteness of the excited electronic Π states of LiH, which lie at least 34 900 cm^{-1} above the ground state [35]. For lithium hydride, therefore, the Born-Oppenheimer breakdown revealed by the Δ_{01}^{H} and $\Delta_{01}^{\mathrm{Li}}$ parameters arises predominantly from the vibrational momentum term [29,30].

Because the present measurements lead to a refinement of the rotational constant of lithium hydride, a corresponding improvement in knowledge of the equilibrium bond length is also expected. An explicit form for the

TABLE III. A comparison of certain reduced Dunham parameters for lithium hydride obtained in this work with those obtained by previous workers.

Parameter	This work	Maki, Olson, and Thompson [7]	Tiemann and Ogilvie [26]
$U_{01}/\mathrm{cm}^{-1}\,\mathrm{u}^{1}$	6.627 101 0(13)[a]	6.627 104 7(92)	6.627 124 7(41)
Δ_{01}^{H}	−1.556 97(22)	−1.563 4(11)[b]	−1.557 60(48)
$\Delta_{01}^{\mathrm{Li}}$	−0.162 3(22)	−0.117(15)[b]	−0.160 0(68)
$U_{11}/\mathrm{cm}^{-1}\,\mathrm{u}^{3/2}$	−0.179 139 5(17)	−0.179 142 5(69)	−0.179 129 7(25)
Δ_{11}^{H}	−0.883 1(68)	−0.761(41)[b]	−0.868(17)
$10^3 U_{02}/\mathrm{cm}^{-1}\,\mathrm{u}^{2}$	−0.668 290 2[c]	−0.668 149(69)	−0.668 222 1[c]
Δ_{02}^{H}	−3.995(18)	−3.429(53)[b]	−4.080(30)
$\Delta_{02}^{\mathrm{Li}}$	−1.183(98)	d	−0.60(11)

[a] The figures in parentheses give one standard deviation of the least-squares fit, in units of the last quoted decimal place.

[b] The Δ_{kl}^{a} parameters in this fit are not exactly comparable with the others because they contain an additional contribution from the Dunham corrections [31].

[c] The parameter U_{02} is determined from U_{01} and U_{10}($U_{02}=-4U_{01}^{3}/U_{10}^{2}$) and constrained to this value in these fits.

[d] Parameter not determined.

TABLE IV. Values for the pure rotational transition frequencies (in MHz) of the isotopomers of lithium hydride in the $v=0$ level of the $X\,^1\Sigma^+$ state, calculated by using the parameters as determined in the least-squares fit.

J	^{6}LiH	^{7}LiH	^{6}LiD	^{7}LiD
1-0	453 160.292(15)[a]	443 952.949(13)	260 307.014(13)	251 043.552(9)
2-1	905 683.403(29)	887 294.458(24)	520 404.703(25)	501 892.461(18)
3-2	1 356 934.619(41)	1 329 415.408(32)	780 084.205(35)	752 352.499(26)
4-3	1 806 284.138(50)	1 769 711.298(34)	1 039 137.583(44)	1 002 230.269(32)
5-4	2 253 109.469(59)	2 207 584.498(32)	1 297 358.284(50)	1 251 333.611(37)
6-5	2 696 797.758(70)	2 642 446.446(32)	1 554 541.581(55)	1 499 472.009(40)
7-6	3 136 748.032(88)	3 073 719.754(46)	1 810 485.020(57)	1 746 456.981(42)
8-7	3 572 373.327(118)	3 500 840.218(79)	2 064 988.840(60)	1 992 102.467(44)
9-8	4 003 102.689(159)	3 923 258.712(126)	2 317 856.393(66)	2 236 225.199(47)
10-9	4 428 383.045(214)	4 340 442.945(188)	2 568 894.533(78)	2 478 645.059(54)
11-10	4 847 680.897(284)	4 751 879.084(267)	2 817 914.000(98)	2 719 185.418(66)
12-11	5 260 483.875(372)	5 157 073.213(364)	3 064 729.777(125)	2 957 673.468(84)
13-12	5 666 302.091(483)	5 555 552.635(486)	3 309 161.428(161)	3 193 940.521(108)
14-13	6 064 669.335(627)	5 946 867.013(641)	3 551 033.412(204)	3 427 822.300(138)
15-14	6 455 144.069(814)	6 330 589.326(840)	3 790 175.376(257)	3 659 159.205(174)
16-15	6 837 310.25(106)	6 706 316.67(110)	4 026 422.420(322)	3 887 796.554(218)
17-16	7 210 777.96(138)	7 073 670.87(144)	4 259 615.341(402)	4 113 584.813(273)
18-17	7 575 183.87(181)	7 432 298.96(188)	4 489 600.848(501)	4 336 379.787(340)
19-18	7 930 191.51(235)	7 781 873.43(244)	4 716 231.750(627)	4 556 042.806(424)
20-19	8 275 491.40(304)	8 122 092.40(315)	4 939 367.122(786)	4 772 440.874(530)

[a] The figures in parentheses give the estimated uncertainty, in units of the last quoted decimal place.

mass-independent potential function underpins Tiemann and Ogilvie's treatment [26]. The value for r_e^{BO} for this potential obtained in the present fit is 0.159 490 811(16) nm, which is to be compared with 0.159 491 045(85) nm by Coxon [25] and 0.159 491 1(1) nm by Maki, Olson, and Thompson [7]. The present measurements on the rotational spectrum of lithium hydride, therefore, give a fivefold improvement in our knowledge of this bondlength. The previously determined values are less reliable because they are based on less accurate rotational frequencies, and in addition, the model used by Maki, Olson, and Thompson is deficient in its treatment of the nonadiabatic mixing terms.

Only certain rotational frequencies for isotopomers of lithium hydride have been measured in this work. For the sake of completeness, values for all transition frequencies up to $J=20\leftarrow19$ for LiH in the $v=0$ level have been computed from the parameters listed in Table II and are given in Table IV. Where comparison is possible, good agreement is noted with the measurements of Matsushima *et al.* [23].

Some comments on the difference between the Watson model [30] and the Tiemann-Ogilvie model [26] for isotopic scaling of Dunham coefficients are in order. The former has the virtue of simplicity because it does not make explicit reference to a potential-energy function. Data can therefore be fitted without consideration of the form of this potential. In this case, the dimensionless parameters Δ_{kl}^a absorb the effects of both the breakdown of the Born-Oppenheimer separation and the Dunham corrections. Tiemann and Ogilvie, on the other hand, link their treatment to a specific power series form for the potential energy. It is this potential function to which the bond length r_e^{BO} refers. The same function is used to determine the Dunham corrections $U_{kl}^{(2)}$, $U_{kl}^{(3)}$, . . . explicitly. In their model, therefore, the Δ_{kl}^a parameters have contributions from the Born-Oppenheimer breakdown effects only. The fact that Δ_{kl}^a parameters determined for LiH by the two different methods are so similar in value (see Table III) indicates that the Dunham corrections are almost too small to be significant.

There is much current interest in the correct description of isotopic scaling on energy levels, including the effects of the breakdown of the Born-Oppenheimer approximation. For example, calculations of the vibration-rotation energy levels of H_3^+ and D_3^+ are at the point where such effects are significant [36]. Again, there is now a large database on the vibration-rotation energy levels of diatomic metal hydrides [37]. For these molecules, it is often the case that several isotopomers exist that can be fitted with a single Hamiltonian. The present work on LiH confirms the ability of the Watson model to achieve this result.

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