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General analytical form for the long-range potential of the $(ns+np_J)$ 0_u^+ states of alkali dimers applied to $^6\mathrm{Li}_2$

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The pooling of high-resolution laser-induced fluorescence measurements with photoassociation binding energies in $^6\mathrm{Li}_2$ has provided a strict test of models proposed for extrapolation of long-range molecular potential functions. An analytical expression is given for the long-range part of the 0_u^+ molecular states originating from $M(ns\ ^2S)+M(np\ ^2P)$ alkali-metal atoms, replacing earlier expressions which assumed negligible spin-orbit coupling. The success of this model is illustrated by the excellent agreement between the experimentally determined dissociation energy $D_e=9352.032(8)\ \mathrm{cm}^{-1}$, and the value $9352.032(12)\ \mathrm{cm}^{-1}$ obtained by extrapolation of $E(R)$ values of a Rydberg-Klein-Rees potential for the $A\ ^1\Sigma_u^+$ state of $^6\mathrm{Li}_2$. The lifetime of the $^2P_{1/2}$ atomic level is 27.13(2) ns. [S1050-2947(97)04205-4]

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I. INTRODUCTION

The spectacular developments in ultracold atom trapping experiments, which have led to the observation of Bose-Einstein condensation in Li, Na, and Rb vapors [1–3] are also at the root of photoassociation spectroscopy [4–14], whereby dimers are formed in excited long-range molecular states which are almost inaccessible to standard spectroscopic methods. Traditional molecular spectroscopy has relied on extrapolation of data pertaining to the lower part of a potential-energy curve to derive accurate bond dissociation energies. The simple extrapolation of vibrational energy intervals proposed by Birge and Sponer [15] was superseded by the theory laid out by LeRoy and Bernstein [16]. An extension of this formalism, given by LeRoy [17], based on a long-range interaction of the form

$$E=D+\sum_n \frac{C_n}{R^n} \tag{1}$$

is in widespread use today for the determination of dissociation energies (D), and multipolar expansion coefficients (C_n) from potential-energy curves $E(R)$. This provides a convenient analytical form for the long-range part of the curve, but many authors have established that it is insufficient. The treatment proposed by Movre and Pichler [18] corrects the leading term in this expansion, for spin-orbit interaction between 0_u^+ states, and we develop this approach further in this paper.

Recent photoassociation data and results from multiphoton laser experiments give direct measurements of the energies of very weakly bound rotational and vibrational states, and potential curves derived from methods such as Rydberg-Klein-Rees (RKR) [19] or inverted perturbation approach (IPA) [20], can now provide a stringent test of the models for long-range interactions. Dissociation energies obtained by extrapolation can be compared with values obtained directly from binding energies and known spectral term values. Small discrepancies reveal changes in the relative importance of the different terms contributing to the potential-energy curve. Merging data $0\leqslant v\leqslant 75$ on the $A\ ^1\Sigma_u^+$ state of $^6\mathrm{Li}_2$ from an optical-optical double-resonance experiment [21], with binding energies for $62\leqslant v\leqslant 88$ measured by photoassociation of lithium atoms [11], we found that Eq. (1) does not extrapolate well to the dissociation limit D. We give the form of the full analytical expression for the long-range part of the 0_u^+ molecular states originating from $M(ns\ ^2S)+M(np\ ^2P)$ alkali-metal atoms. The validity of this expression is demonstrated by detailed examination of the potential curve for the $A\ ^1\Sigma_u^+$ state of the $^6\mathrm{Li}_2$ molecule.

II. DETAILS OF THE FITTING PROCEDURE

In a previous paper [21], using optical-optical double-resonance to excite $F\ ^1\Sigma_g^+ \sim E\ ^1\Sigma_g^+$ levels and detecting fluorescence at high resolution in the infrared region, we have been able to assign transitions covering the whole range of the A state levels from $v=0$ to $v=84$, about $2.5\ \mathrm{cm}^{-1}$ below the dissociation limit. The vibrational levels $62\leqslant v\leqslant 88$ in the vicinity of the dissociation limit have also been observed in experiments involving photoassociation of ultracold $^6\mathrm{Li}$ atoms [11]. Since several levels were observed by both techniques, we have been able to merge the two sets of results in such a way that we retained the advantages of each. The photoassociation data are more precise than the fluorescence measurements, and give accurate binding energies of the lowest rotational levels $(J\leqslant 2)$ relative to the A state dissociation limit. The fluorescence data cover a wider range of J $(3\leqslant J\leqslant 14)$ and give energies relative to a known energy origin, $v=0$ of the $X\ ^1\Sigma_g^+$ state. Combining fluorescence lines and photoassociation binding energies in a global fit, we determined an experimental value of the dissociation energy of the A state relative to $X\ ^1\Sigma_g^+$, $v=0$, $J=0$, without resorting to extrapolation procedures. Fluorescence measurements for $v>75$ were eliminated because the weak and broadened $F\rightarrow A$ transitions were much less precise than the information available from photoassociation. The lowest vibrational levels of $A\ ^1\Sigma_u^+$ are characterized by the same fluorescence data set as in Ref. [21], and the ''global'' fit presented here covers the range $56\leqslant v\leqslant 88$. The photoassociation binding energies are treated as ''transitions'' from the dissociation limit $2s+2p_{1/2}$ to high-lying rovibrational levels of the A state.

We locate the energy levels with respect to the ($v=13$, $J=5$) level of the $F\ ^1\Sigma_g^+$ state excited by double resonance. This energy reference is calculated relative to the $v=0$, $J=0$ of the $X\ ^1\Sigma_g^+$ ground state from analysis of several A-X bands (involving the $v=3$, 4, and 6 levels of the A state and $v=0-3$ of the X state) to calculate the ($v=6$, $J=4$) energy level of the A state, one of the intermediate levels in the first excitation step. Then we added the measured wave number of the $F(v=13,\ J=5)-A(v=6,\ J=4)$ fluorescence transition. We obtained: $T(F,\ v=13,\ J=5)=32\,698.48(2)\ \mathrm{cm}^{-1}$. In the fit, the A levels are generally represented by three parameters (T'',B'',D'') or by two (T'',B''). When just one transition appears—for example, for the four last binding energies corresponding to $J=0$, $v=85,86,87,88$—only one parameter is used (T'').

In addition to the parameters generated by this initial fit of 240 lines of the $E,F\ ^1\Sigma_g^+\rightarrow A\ ^1\Sigma_u^+$ transitions and 35 binding energies, we calculated missing B'' rotational constants by interpolation or extrapolation of the known values using the method developed by Tromp and LeRoy [22].

This procedure gave the vibrational energy and rotational constants of each level of the A state between 56 and 88 and a direct determination of the dissociation energy with respect to the energy of $J=0$, $v=0$ in the $X\ ^1\Sigma_g^+$ state. We found $D=23\,231.110(4)(20)\ \mathrm{cm}^{-1}$. The statistical uncertainty is shown in the first set of parentheses and corresponds to two standard deviations, the second uncertainty is an estimate of our systematic errors.

III. THE $A\ ^1\Sigma_u^+$ STATE POTENTIAL CURVE

The RKR method was used to calculate the turning points of the A state potential-energy curve. This method requires well-behaved continuous representation of the G_v and B_v functions. As described in [21], two polynomials were required to correctly describe these two functions over the harmonic part and the long-range part of the potential. For levels $v\leqslant 56$, we have used the polynomial defined in the previous paper [21]. The second polynomial was determined from eigenvalues and rotational constants of levels between 57 and 88 determined in the preceding section. We have checked that for $v=57$, the two polynomials joined with the same energy and a difference in B_v values less than $10^{-4}\ \mathrm{cm}^{-1}$, which is of the order of magnitude of the statistical uncertainty.

The vibrational energies G_v were obtained by subtracting the energy of the potential minimum from the energy relative to $X\ ^1\Sigma_g^+$, $v=0$, $J=0$. After the RKR potential had been calculated, minor corrections were made to remove oscillations in the left-hand wall of the curve for $v>70$. The inner turning points from $v=55-88$ were fitted to an expression of the form $V(R)=A+B/R^N$ and the resulting values of A, N, and B were then used to ajust the values of R_{inner} to give a smooth function for the inner wall. The outer turning points were then corrected to conserve the difference $R_{\mathrm{outer}}-R_{\mathrm{inner}}$. The potential was refined by using the method of Hutson [23] to recalculate the eigenvalues and spectroscopic constants $(B_v,D_v,H_v$, etc.) of each vibrational level from the potential function. Using the calculated rotational and distortion constants for $57\leqslant v\leqslant 88$, improved G_v and B_v values were obtained in the global fit and a new RKR curve was constructed.

The final potential energy is given in Table I. The outer turning point of the highest vibrational level. $v=88$, corresponds to $R_{\max}=74.03$ Å which extends the range beyond the previous potential determined for $^6\mathrm{Li}_2$ [21] which covered up to $v=84$ and $R=51.5$ Å. The eigenvalues and constants generated from this potential curve by the Hutson method [23] agree with those used in the construction of the RKR potential curve to within one standard deviation.

IV. R DEPENDENCE OF THE LONG-RANGE ENERGY

In the region close to the dissociation limit, the C_3 term in Eq. (1) is dominant and the energy can be approximated by

$$E=D+\frac{C_3}{R^3}. \tag{2}$$

A fit of the outer turning points with $29.7\leqslant R_{\max}\leqslant 74.0$ Å to Eq. (2) gives $D_e=9352.229(39)\ \mathrm{cm}^{-1}$ for the $A\ ^1\Sigma_u^+$ state. This value is close to the value given in [21] though the potential curve was less precise and less extended. Nevertheless, it is significantly removed from the new experimental value of $9352.032(8)\ \mathrm{cm}^{-1}$, obtained from D-$13\,879.078\ \mathrm{cm}^{-1}$, where $13\,879.078\ \mathrm{cm}^{-1}$ is the energy of the minimum of the $A\ ^1\Sigma_u^+$ potential-energy curve with respect to our energy origin, $v=0$, $J=0$ of the $X\ ^1\Sigma_g^+$ state. This reveals that the traditional ''extrapolation'' used in [21] was inappropriate, even though the fitted parameters D_e and C_3 reproduced all the observed data points adequately.

If D_e is constrained to the new value and only C_3 is treated as an adjustable parameter, the resulting fit is very bad. This reflects the gradual change in the molecular potential away from a Hund's case a limit, in which spin-orbit interactions can be ignored, towards Hund's case c situation, in which the ^2P atomic limit is recognized to have two separate levels, each of which leads to a molecular state of 0_u^+ symmetry. The 0_u^+ state associated with the $^2P_{1/2}$ limit corresponds to the $A\ ^1\Sigma_u^+$ state, and the 0_u^+ state associated with the $^2P_{3/2}$ limit corresponds to the $b^3\Pi_u$ substate. These two 0_u^+ states interact appreciably at large internuclear separations, where they become close in energy. This situation has been described completely from a theoretical point of view, for example by Movre and Pichler [18], and by Bussery and Aubert-Frécon [24]. We now require an analytical expression equivalent to these calculations which goes beyond the first-

TABLE I. RKR potential for the $A\,^1\Sigma_u^+$ state of $^6\mathrm{Li}_2$. $R_e=3.1080$ Å.

v	G_v (cm^{-1})	B_v (cm^{-1})	R_{min} (Å)	R_{max} (Å)	v	G_v (cm^{-1})	B_v (cm^{-1})	R_{min} (Å)	R_{max} (Å)
−0.25	68.950		2.9713	3.2570	44	8473.415	0.233 07	2.0300	7.8508
0	137.578	0.576 77	2.9185	3.3229	45	8555.013	0.221 17	2.0264	8.0526
1	409.805	0.569 86	2.7944	3.4987	46	8630.631	0.209 25	2.0230	8.2695
2	678.376	0.563 16	2.7152	3.6294	47	8700.412	0.197 42	2.0200	8.5028
3	943.309	0.556 47	2.6543	3.7422	48	8764.551	0.185 78	2.0172	8.7534
4	1204.627	0.549 77	2.6042	3.8448	49	8823.296	0.174 41	2.0147	9.0224
5	1462.346	0.543 08	2.5613	3.9408	50	8876.936	0.163 40	2.0124	9.3106
6	1716.483	0.536 44	2.5237	4.0321	51	8925.790	0.152 81	2.0103	9.6188
7	1967.048	0.529 85	2.4900	4.1199	52	8970.195	0.142 70	2.0084	9.9477
8	2214.052	0.523 33	2.4596	4.2050	53	9010.491	0.133 08	2.0067	10.2979
9	2457.504	0.516 86	2.4317	4.2881	54	9047.008	0.123 97	2.0051	10.6704
10	2697.410	0.510 42	2.4061	4.3695	55	9080.058	0.115 36	2.0037	11.0663
11	2933.774	0.503 98	2.3823	4.4498	56	9109.932	0.107 25	2.0024	11.4868
12	3166.595	0.497 53	2.3602	4.5291	57	9136.904	0.099 53	2.0013	11.9326
13	3395.869	0.491 05	2.3395	4.6077	58	9161.249	0.092 30	2.0003	12.4063
14	3621.588	0.484 54	2.3201	4.6859	59	9183.176	0.085 49	1.9994	12.9096
15	3843.739	0.478 00	2.3018	4.7638	60	9202.901	0.079 09	1.9986	13.4445
16	4062.303	0.471 43	2.2846	4.8416	61	9220.620	0.073 06	1.9979	14.0135
17	4277.258	0.464 84	2.2684	4.9195	62	9236.513	0.067 39	1.9972	14.6193
18	4488.578	0.458 22	2.2530	4.9976	63	9250.741	0.062 05	1.9966	15.2651
19	4696.231	0.451 57	2.2384	5.0760	64	9263.457	0.057 04	1.9961	15.9544
20	4900.181	0.444 89	2.2244	5.1549	65	9274.796	0.052 34	1.9956	16.6913
21	5100.386	0.438 17	2.2112	5.2344	66	9284.886	0.047 92	1.9952	17.4802
22	5296.798	0.431 38	2.1985	5.3146	67	9293.843	0.043 79	1.9949	18.3261
23	5489.365	0.424 53	2.1864	5.3958	68	9301.774	0.039 93	1.9939	19.2340
24	5678.025	0.417 57	2.1748	5.4781	69	9308.777	0.036 32	1.9936	20.2114
25	5862.711	0.410 50	2.1638	5.5617	70	9314.945	0.032 96	1.9933	21.2650
26	6043.348	0.403 30	2.1532	5.6467	71	9320.359	0.029 83	1.9931	22.4027
27	6219.852	0.395 94	2.1431	5.7334	72	9325.098	0.026 93	1.9929	23.6336
28	6392.131	0.388 41	2.1334	5.8221	73	9329.231	0.024 24	1.9927	24.9683
29	6560.087	0.380 69	2.1242	5.9130	74	9332.824	0.021 76	1.9926	26.4185
30	6723.612	0.372 77	2.1154	6.0063	75	9335.934	0.019 47	1.9924	27.9981
31	6882.591	0.364 63	2.1070	6.1024	76	9338.617	0.017 36	1.9923	29.7229
32	7036.898	0.356 27	2.0989	6.2017	77	9340.921	0.015 43	1.9922	31.6114
33	7186.403	0.347 65	2.0913	6.3046	78	9342.890	0.013 65	1.9922	33.6853
34	7330.967	0.338 77	2.0840	6.4114	79	9344.564	0.012 04	1.9921	35.9703
35	7470.444	0.329 60	2.0771	6.5228	80	9345.980	0.010 56	1.9920	38.4967
36	7604.684	0.320 14	2.0705	6.6392	81	9347.171	0.009 22	1.9920	41.3008
37	7733.535	0.310 35	2.0643	6.7614	82	9348.166	0.008 01	1.9919	44.4263
38	7856.846	0.300 23	2.0584	6.8901	83	9348.991	0.006 91	1.9919	47.9260
39	7974.471	0.289 78	2.0529	7.0261	84	9349.670	0.005 92	1.9919	51.8641
40	8086.277	0.278 99	2.0476	7.1703	85	9350.225	0.005 05	1.9919	56.3208
41	8192.147	0.267 89	2.0427	7.3238	86	9350.673	0.004 27	1.9918	61.3978
42	8291.991	0.256 50	2.0382	7.4876	87	9351.031	0.003 60	1.9918	67.2329
43	8385.752	0.244 87	2.0339	7.6629	88	9351.312	0.003 03	1.9918	74.0297

order terms given by Julienne and Vigué for the $M(ns\ ^2S)+M(np\ ^2P_{3/2})$ limit [25], where significant off-diagonal terms in the matrices describing the coupling between spin-orbit substates have been omitted. Such an expression can be obtained by diagonalizing the 2×2 long-range energy matrix given in [24] for the two 0_u^+ states (labeled 1 and 2) dissociating into $M(ns\ ^2S)+M(np\ ^2P_{1/2})$ and $M(ns\ ^2S)+M(np\ ^2P_{3/2})$, respectively. The elements of the matrix are obtained in a straightforward way by using molecular wave functions expressed on the basis of atomic functions described by the quantum numbers $|JM_J\rangle$. They are given by

$$E(1,1)=D+\sum_{n=3,6,8,10}\frac{C_n(^1\Sigma_u^+)+2C_n(^3\Pi_u)}{3R^n}$$

$$+\frac{E_{ex}(^1\Sigma_u^+)+2E_{ex}(^3\Pi_u)}{3}$$

$$E(1,2)=E(2.1)=-\frac{\sqrt{2}}{3}\left[\sum_{n=3,6,8,10}\frac{C_n(^1\Sigma_u^+)-C_n(^3\Pi_u)}{R^n}+E_{ex}(^1\Sigma_u^+)-E_{ex}(^3\Pi_u)\right],$$

$$E(2.2)=D+\Delta E+\sum_{n=3,6,8,10}\frac{2C_n(^1\Sigma_u^+)+C_n(^3\Pi_u)}{3R^n}+\frac{2E_{ex}(^1\Sigma_u^+)+E_{ex}(^3\Pi_u)}{3}. \tag{3}$$

The C_n terms in Eq. (3) are the usual multipolar expansion coefficients for the $^1\Sigma_u^+$ and $^3\Pi_u$ states dissociating into $M(ns)+M(np)$. Numerical values have been published recently [26] for all the alkali-metal dimers for $n=3$, 6, and 8. The quantity D represents the energy of the dissociation limit $(^2S)+(^2P_{1/2})$, and ΔE is the atomic fine structure splitting $E[^2P_{3/2}]-E[^2P_{1/2}]$. The exchange terms $E_{ex}(^{2S+1}\Lambda_u)$ are readily evaluated for each alkali dimer using the asymptotic form of the surface integral method [27–30], i.e.,

$$E_{ex}(^{2S+1}\Lambda_u)=(-)^S I(21\Lambda,200|21\Lambda,200)+I(21\Lambda,200|200.21\Lambda).$$

The basic integrals I represent both exchange integrals without and with excitation transfer [30]. They are evaluated from known formulas available for instance in Appendix A of Ref. [28] involving atomic energy parameters $\alpha_{nl}=\sqrt{-2\varepsilon_{nl}}$ (where ε_{nl} is the energy of the atomic alkali-metal state nl^2L) and the asymptotic parameters A_{nl} given in [29].

It should be noted that the C_3 coefficient given by Julienne and Vigué [25] for the attractive 0_u^+ state corresponding to $^2P_{3/2}$ is just the term in R^{-3} in the diagonal matrix element $E(2,2)$. The off-diagonal term $E(1,2)$ is responsible for the fact that the long-range energy does not in reality follow $1/R^3$ behavior.

For the two 0_u^+ states dissociating into $M(ns)+M(np)$, we have

$$C_3(^1\Sigma_u^+)=-\frac{2M^2}{3},\quad C_3(^3\Pi_u)=-\frac{M^2}{3},$$

$$C_6(^1\Sigma_u^+)=-\frac{20R_{01}+22R_{12}}{45},\quad C_6(^3\Pi_u)=-\frac{5R_{01}+19R_{12}}{45}, \tag{4}$$

where M^2 is the square of the radial part of the atomic dipole matrix element $M^2=[\langle ns|r|np\rangle]^2$. The term M^2 is related to the square of the dipole matrix element d^2 of Julienne and Vigué [25] by $M^2e^2=3d^2$. The atomic parameters R_{ij} are to be found in Eq. (18) of Ref. [24]: $R_{01}\equiv R_{01}^{1111}$ and $R_{12}\equiv R_{12}^{1111}$.

Analytical diagonalization of the 2×2 energy matrix given in Eq. (3) yields a general expression for the energy of the two 0_u^+ states dissociating into $M(ns)+M(np)$

$$\begin{aligned}E(0_u^+)={}&D+\frac{\Delta E}{2}-\frac{M^2}{2R^3}-\frac{1}{2R^6}\left[\frac{5R_{01}}{9}+\frac{82R_{12}}{90}\right]+\frac{C_8(^1\Sigma_u^+)+C_8(^3\Pi_u)}{2R^8}+\frac{C_{10}(^1\Sigma_u^+)+C_{10}(^3\Pi_u)}{2R^{10}}+\frac{E_{ex}(^1\Sigma_u^+)+E_{ex}(^3\Pi_u)}{2}\\&\pm\frac{1}{2}\left\{\left(\frac{M^2}{9R^3}+\frac{1}{3R^6}\left[\frac{R_{01}}{3}+\frac{R_{12}}{15}\right]+\frac{C_8(^3\Pi_u)-C_8(^1\Sigma_u^+)}{3R^8}+\frac{C_{10}(^3\Pi_u)-C_{10}(^1\Sigma_u^+)}{3R^{10}}+\frac{E_{ex}(^3\Pi_u)-E_{ex}(^1\Sigma_u^+)}{3}-\Delta E\right)^2\right.\\&\left.+\frac{8}{9}\left(\frac{M^2}{3R^3}+\frac{1}{R^6}\left[\frac{R_{01}}{3}+\frac{R_{12}}{15}\right]+\frac{C_8(^3\Pi_u)-C_8(^1\Sigma_u^+)}{R^8}+\frac{C_{10}(^3\Pi_u)-C_{10}(^1\Sigma_u^+)}{R^{10}}+E_{ex}(^3\Pi_u)-E_{ex}(^1\Sigma_u^+)\right)^2\right\}^{1/2}. \end{aligned}\tag{5}$$

The + sign in front of the square root corresponds to the upper 0_u^+ substate, associated with $b\ ^3\Pi_u$ in this instance, and the − sign corresponds to the lower $A\ ^1\Sigma_u^+$ state.

The next step was to establish the region for which this expression remains valid, and to discover whether it can be applied correctly to a small portion of a potential-energy curve and extrapolate correctly to the true dissociation limit. The $A\ ^1\Sigma_u^+$ state of $^6\mathrm{Li}_2$ was used as a test. The outer part of the RKR potential curve obtained in this way was first compared directly with a theoretical 0_u^+ state curve obtained by using Eq. (5) with our experimental value of D_e, and the values of parameters M^2, R_{01}, R_{12}, and C_8 deduced from quantities given in [26], and C_{10} recalculated from expressions given in [24] using model potential atomic orbitals. In order to evaluate exchange terms, the quantities α_{2s},α_{2p} have been obtained from the experimental atomic energies ε_{2s} and ε_{2p}, i.e., $\alpha_{2s}=0.630$, $\alpha_{2p}=0.510$, while the tabulated value $A_{2s}=0.82$ [29] of the asymptotic parameter has been used. For the excited orbital $2p$ the value $A_{2p}=0.219$ used was derived from the formula [30]

$$A_{2p}=\frac{2^{1/\beta}\beta^{1+(1/\beta)}}{\left[\Gamma\left(\frac{1}{\beta}+2\right)\Gamma\left(\frac{1}{\beta}-1\right)\right]^{1/2}}$$

with $\beta\equiv\alpha_{2p}$ and $\Gamma(x)$ is the gamma function.

The predicted curve [Eq. (5) with theoretical parameters] and the RKR outer turning points are comparable to $12\leqslant R\leqslant75$ Å. Because the differences between the two are tiny (the largest difference is 0.14 cm^{-1} at $R_{\max}=11.93$ Å), the broken curve in Fig. 1 shows the difference $\Delta V(R)$ as a function of internuclear distance, rather than the curves themselves. Agreement is very good. We then studied the

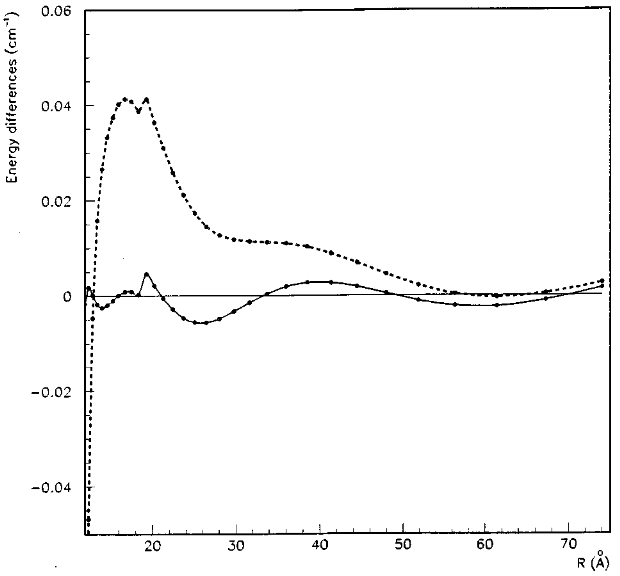

FIG. 1. Differences between RKR and calculated $V(R)$ curves for the long-range part of the $A\ {}^1\Sigma_u^+$ state of ${}^6\mathrm{Li}_2$. Broken line: calculation with Eq. (5) and theoretically predicted parameters [26]. Solid line: calculation with Eq. (5) and the fitted parameters of Table III (without retardation effects). Dots indicate the RKR outer turning points.

contribution of each of the terms in Eq. (5) as a function of R (again using theoretical parameters), to establish each point beyond which higher-order terms could be neglected. The results of this investigation are illustrated in Fig. 2, where energy differences are drawn which correspond to successive omission of exchange, R^{-10}, R^{-8}, and R^{-6} terms in formula (5). For example, considering a threshold of 0.025 cm^{-1}, exchange contributions must be considered for $v \leqslant 58$, R^{-10} contributes significantly for $v \leqslant 61$, R^{-8} contributes significantly for $v \leqslant 67$, and R^{-6} terms must be included for $v \leqslant 74$. For $v > 75$, only R^{-3} terms are non-negligible.

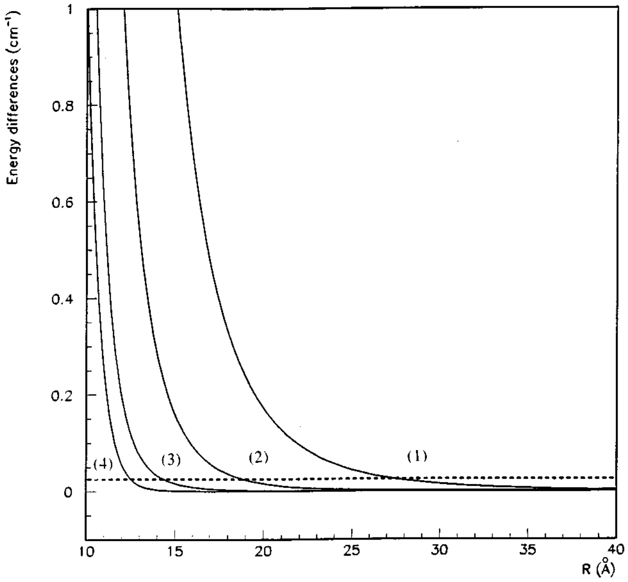

FIG. 2. Energy differences between the total energy [Eq. (5)] and (1) exchange R^{-10}, R^{-8}, and R^{-6} terms, (2) exchange R^{-10} and R^{-8} terms, (3) exchange and R^{-10} terms, (4) exchange terms. The dashed line represents a threshold of 0.025 cm^{-1}.

The RKR outer turning points were then used as input data for a nonlinear least-squares fit to Eq. (5), to see whether we were able to determine all the parameters, and to see whether the dissociation energy D_e, determined from the potential curve, was closer to the experimental value than the D_e value obtained from the LeRoy formula Eq. (2). As there are only seven turning points with $12 \leqslant R_{\max} \leqslant 16$ Å, the C_8, C_{10} and exchange parameters could not all be determined directly. We chose to fix the $C_{10}({}^1\Sigma_u^+)$ and $C_{10}({}^3\Pi_u)$ parameters at their theoretical values, and to impose $C_8({}^3\Pi_u) = 0.175\,970\,4 \times C_8({}^1\Sigma_u^+)$; this ratio in the C_8 parameters is also taken from the results of Marinescu and Dalgarno [26]. The parameter $C_8({}^1\Sigma_u^+)$ was treated as an adjustable parameter. We found that D_e and M^2 are almost invariant with the number of points included in the fit, but that R_{01} and R_{12} were more sensitive to the data base. This can be seen from a selection of results presented in Table II. Table III gives the parameters determined from the full data set ($R > 12$ Å). These parameters reproduce the RKR curve very well, as shown by the solid curve of $\Delta V(R)$ in Fig. 1. From the fitted value of M^2 (see Table III) we determine the lifetime of the ${}^2P_{1/2}$ atomic level to be 27.13(2) ns where the uncertainty corresponds to two statistical standard deviations. This matches both the value 27.102(2)(7) ns given by McAlexander, Abraham, and Hulet [31] for ^{7}Li and various calculated values quoted in Ref. [31] which are close to 27.08 ns.

The formula energy [Eq. (5)] was also tested by using a smaller data base to see whether it remains reliable in extrapolation and to see whether the parameters obtained match

TABLE II. Dissociation energy with respect to the minimum of the $A\ {}^1\Sigma_u^+$ state [including $Y_{00} = 0.093(5)$ cm^{-1}], and long-range parameters obtained with different ranges of $R_{\max}$. Quantities in parentheses are two standard deviations in units of last digit.

D_e (cm^{-1})	M^2 ($e^2\ a_0^2$)	R_{01} ($e^2\ a_0^5$)	R_{12} ($e^2\ a_0^5$)	$10^{-6}C_8({}^1\Sigma_u^+)$ ($e^2\ a_0^7$)	$10^{-8}C_{10}({}^1\Sigma_u^+)$ ($e^2\ a_0^9$)	rms error (cm^{-1})	Method
9352.032(8)[a]						0.006	fit of energies (direct)
9352.032(6)	16.493(20)	0.0	0.0	0.0	0.0	0.003	Eq. (5), $R \geqslant 36$ Å
9352.031(9)	16.484(12)	2146(570)	3541(663)	0.0	0.0	0.005	Eq. (5), $R \geqslant 16$ Å
9352.033(7)	16.492(8)	1610(236)	3055(579)	−0.327(133)	0.0	0.004	Eq. (5), $R \geqslant 14$ Å
9352.033(7)	16.491(6)	1684(465)	3121(444)	−0.255(80)	−0.226 fixed	0.004	Eq. (5), $R > 13$ Å

[a] This uncertainty contains the statistical error (4.10^{-3} cm^{-1}) plus the uncertainty in the position of the minimum of the potential curve with respect to $v = 0$ of the ground state.

TABLE III. Parameters describing the long-range interaction $0_u^+(\mathrm{Li}\,2s+\mathrm{Li}\,2p)$ derived from the $A\ {}^1\Sigma_u^+$ potential curve. Quantities in parentheses are two standard deviations in units of last digit. $C_n(\mathrm{cm}^{-1}\ \text{Å}^n)=C_n(\mathrm{a.u.})\times 219\,474.63\times 0.529\,177^n$.

Parameters	From RKR curve (12 Å$<R<$75 Å) without retardation effects	From RKR curve (12 Å$<R<$75 Å) including retardation effects	Theory [26]
D_e (cm^{-1})	9352.032(8)[b]	9352.035(7)	
M^2 (a.u.)	16.488(7)	16.484(7)	16.513
$C_3(^1\Sigma_u^+)$ (a.u.)[a]	$-10.992(5)$	$-10.989(5)$	-11.01
$C_3(^3\Pi_u)$ (a.u.)[a]	$-5.496(2)$	$-5.495(2)$	-5.503
R_{01} (a.u.)	1900(312)	1967(240)	1405
R_{12} (a.u.)	3318(417)	3379(310)	2948
$C_6(^1\Sigma_u^+)$ (a.u.)[a]	$-2467(247)$	$-2526(185)$	-2066
$C_6(^3\Pi_u)$ (a.u.)[a]	$-1612(179)$	$-1645(134)$	-1401
$C_8(^1\Sigma_u^+)$ (a.u.)	$-0.135(80)\times 10^6$	$-0.111(70)\times 10^6$	-0.2705×10^6
$C_8(^3\Pi_u)$ (a.u.)	$-2.4(1.4)\times 10^4$[c]	$-2.0(1.2)\times 10^4$[b]	-4.76×10^4
$C_{10}(^1\Sigma_u^+)$ (a.u.)	-0.226×10^8(fixed)[d]	-0.226×10^8(fixed)[c]	
$C_{10}(^3\Pi_u)$ (a.u.)	-0.165×10^8(fixed)[d]	-0.165×10^8(fixed)[c]	
A_{np} (asymptotic parameter)	0.439(90)	0.447(87)	
rms error (cm^{-1})	0.002	0.002	

[a] Deduced from the fitted values of M^2, R_{01}, and R_{12} using Eq. (4).

[b] In addition to the statistical error on D_e, one can also consider the uncertainty in the position of the minimum of the $A\ {}^1\sigma_u^+$ potential curve with respect to $v=0$ of the ground state, estimated at 0.004 cm^{-1}. The long-range analysis then leads to $D_e=9352.032(12)$ cm^{-1}.

[c] Deduced from the fitted value of $C_8(^1\Sigma_u^+)$ using $[C_8(^3\Pi_u)]/[C_8(^1\Sigma_u^+)]=0.175\,970\,4$.

[d] Calculated from expressions in [24] using model potential atomic functions.

those found using the complete data set. The results presented in Table IV are convincing, and suggest that it should be possible to get closer to the true dissociation energy even when extrapolating from data which do not extend to very large R by replacing Eq. (2) by Eq. (5).

From an identical set of observed data, McAlexander, Abraham, and Hulet [31] have recently analyzed the long-range part of the $A\ {}^1\Sigma_u^+$ state of Li$_2$ using an energy expression in

$$\sum_n \frac{C_n(^1\Sigma_u^+)}{R^n}$$

where the $C_3(^1\Sigma_u^+)$ was corrected for fine-structure effects as well as retardation effects. Adiabatic corrections were also included.

Our analysis has concentrated heavily on contributions from the off-diagonal terms in R^{-3} and R^{-6}, and we wanted to ensure that neglect of the retardation effects deemed to be important around 75 Å in ^{6}Li$_2$ [31] but negligible in the $A\ {}^1\Sigma_u^+$ state of Na$_2$ [32] at 250 Å did not affect the numerical results of our fit to any great extent. We thus added supplementary terms to Eq. (5) to incorporate retardation effects, in the way suggested by Meath [33], so that $C_3(^1\Sigma_u^+)$ is multiplied by $[1+(\gamma^2/2)]$ and $C_3(^3\Pi_u)$ is multiplied by $[1-(\gamma^2/2)]$, where $\gamma=(2\pi R)/\lambda$, where λ is the wavelength of the $^2S\rightarrow{}^2P$ transition.

The three terms varying as R^{-3}, which appear in the general expression [Eq. (5)] for the energy, are then corrected in the following way:

$$-\frac{M^2}{2R^3}\rightarrow-\frac{M^2}{6R^3}\left(3+\frac{\gamma^2}{2}\right),$$

$$\frac{M^2}{9R^3}\rightarrow\frac{M^2}{9R^3}\left(1+\frac{3\gamma^2}{2}\right)\quad\text{and}\quad\frac{M^2}{3R^3}\rightarrow\frac{M^2}{3R^2}\left(1+\frac{3\gamma^2}{2}\right).$$

TABLE IV. Extrapolation with Eq. (5) to the dissociation limit for different ranges of R_{max}. Quantities in parentheses are two standard deviations in units of last digit.

D_e (cm^{-1})	M^2 ($e^2a_0^2$)	R_{01} ($e^2a_0^5$)	R_{12} ($e^2a_0^5$)	Range of R_{max} (Å)	rms error (cm^{-1})
9352.039(13)	16.517(31)	0.0	0.0	26–52	0.004
9352.029(18)	16.483(17)	2170(708)	3563(547)	16–36	0.003
9352.032(10)	16.485(13)	2144(913)	3540(794)	16–52	0.003
9352.242(25)	16.493(59)	0.0	0.0	26–52	0.007
					Eq. (1), cf. [17]

From the full data set ($R>12$ Å) a fit has been performed with the corrected energy expression and the parameters obtained are given in Table III. As can be seen the variations due to the retardation effects are of the same order as statistical errors so that these effects are found to be negligible.

Following the scheme described by McAlexander, Abraham, and Hulet [31], we have estimated adiabatic corrections at large R and have performed a fit including these corrections for the data base $R>15$ Å. The new values for the parameters remain within the statistical errors given in Table III, and in contrast to Ref. [31], we find D_e increases by only 0.003 cm^{-1}.

V. CONCLUSION

Pooling high-resolution laser-induced fluorescence measurements and photoassociation data, we have determined an ''experimental'' dissociation energy for the $^6\mathrm{Li}_2$ molecule in the $A\ ^1\Sigma_u^+$ state. A potential-energy curve has been constructed by the RKR method from these data. This curve was used to test the performance of an analytical expression for potential curve as a function of R: this expression should find applications in the study of other 0_u^+ states of alkali-metal dimers observed in photoassociation [4–14]. We find that the off-diagonal terms in $1/R^3$ are essential, and that off-diagonal terms in $1/R^6$ must also be included if one is to obtain both the $C_6(^1\Sigma_u^+)$ and $C_6(^3\Pi_u)$ parameters close to theoretical predictions. A complete presentation of the analytical form of the long-range energy dependence with R will be published shortly for the other states [34], whereupon it will be possible to predict the long-range interactions for all the molecular states.

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