Radiative lifetime of the 2P state of lithium

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We determine the radial dipole moment between the $2S$ and $2P$ states of atomic lithium by analyzing the long-range vibrational eigenenergies of the singly excited diatomic molecule. The result can be expressed in terms of the $2P_{1/2}$ radiative lifetime of ^{7}Li, which is found to be 27.102(2)(7) ns. This result agrees with most current atomic-structure calculations and resolves the long-standing disagreement with previous experiment. The current level of precision is sensitive to relativistic effects in the atomic-structure calculation and to non-Born-Oppenheimer and radiation retardation effects in the molecule. [S1050-2947(96)50307-0]

Atomic radiative lifetimes are known to be sensitive tests of atomic-structure calculations. The relatively simple structure of atomic lithium makes it a viable candidate for testing the various *ab initio* techniques which, in recent years, have grown in both sophistication and accuracy [1–8]. A recent calculation of the $2S\leftrightarrow2P$ nonrelativistic oscillator strength by Yan and Drake [8] has an estimated uncertainty of only 1.0×10^{-6}. Experimentally, the most precisely stated measurement of a radiative lifetime for a multielectron atom is the measurement of the $2P$ lifetime of lithium by Gaupp *et al.* [9], with a one standard deviation uncertainty of 1.5×10^{-3}. Unfortunately, the experimental result and most calculations disagree by more than four standard deviations. Resolution of this large discrepancy is motivated by the need to apply atomic-structure calculations to more complicated atoms. In particular, atomic theory is crucial for interpreting parity violation in experiments with cesium [10]. Clearly, there is a strong need for finding alternative methods of precisely measuring this value.

Radiative dipole moments can be determined by analyzing the spectra of long-range, singly excited diatomic molecules. Photoassociative spectroscopy of ultracold atoms is a powerful tool for probing these high-lying molecular vibrational states [11]. In previous work, we used this technique to observe the highest vibrational levels of the $A\,^1\Sigma_u^+$ state of ^{6}Li$_2$ and ^{7}Li$_2$ [12]. The long-range portion of this potential arises from a resonant dipole-dipole interaction that has the functional form $V(R)=-C_3/R^3$. The coefficient C_3 is inversely proportional to the $2P$ atomic radiative lifetime, τ, by [13]

$$C_3=\frac{3\hbar}{2\tau}\left(\frac{\lambda}{2\pi}\right)^3,\qquad(1)$$

where λ is the wavelength of the atomic transition.

In a previous publication, we constructed a model potential for the $1\,^3\Sigma_g^+$ manifold from a variety of *ab initio* and experimental sources [14]. Eigenvalues from this model were calculated as a function of C_3 and fitted to the corresponding data. The estimated uncertainty of 6×10^{-3} was due to systematic uncertainties associated with parts of the model known only through *ab initio* calculation. However, since then, Linton *et al.* [15] have used Fourier transform

spectroscopy of the $A\,^1\Sigma_u^+$ state to measure a range of vibrational levels for which the highest-lying ones overlap the lower part of the range observed by us. Linton *et al.* have constructed a Rydberg-Klein-Rees (RKR) potential from their data that is far more accurate in the inner and intermediate portions of the potential than the *ab initio* potential we used in Ref. [14]. Consequently, nearly the entire interaction potential is now experimentally determined.

Improvements in the data analysis have also decreased the experimental uncertainty. We recently explained all of the observed molecular hyperfine splittings and transition strengths using a simple, first-order perturbation theory calculation [16]. This enables the location of the hyperfine center of gravity within each observed vibrational level to be precisely determined. Furthermore, additional lower-lying vibrational levels have been observed adding to the number of usable data points [12]. Together these improvements have reduced the statistical uncertainty to a level at which the current disagreement between theory and experiment can be resolved, and the effects of radiative retardation, an effect related to the Casimir-Polder effect in London–van der Waals forces [17], can be observed.

The basis of the lifetime extraction involves the construction of an accurate model for the $A\,^1\Sigma_u^+$ adiabatic potential from which vibrational eigenenergies can be computed as a function of various parameters, including the C_3 coefficient. The RKR potential by Linton *et al.* of the $A\,^1\Sigma_u^+$ manifold covers the range of internuclear separation of $R=3.8a_0$ to $R=97.3a_0$, where a_0 is the Bohr radius [15]. In constructing the model, we elected to use only those RKR points up to $R=25.4a_0$, which encompass the energy range from the bottom of the potential well up to our lowest-lying observed vibrational level. Two *ab initio* points at $R=3.25a_0$ and $R=3.50a_0$ were used for the top of the inner wall [18]. The RKR points are assumed to be the best possible representation of the inner portion of the potential with the only parameter being D_e, the dissociation energy, which locates the bottom of the RKR well with respect to the asymptotic $2S_{1/2}+2P_{1/2}$ limit.

The analytic form for large R can be described as

$$V(R)=-\frac{C_3}{R^3}-\frac{C_6}{R^6}-\frac{C_8}{R^8}+\frac{N(N+1)}{2\mu R^2}+\langle T_{nuc}\rangle,\qquad(2)$$

where the C_3 term is dominant and is related to the atomic dipole transition moment, C_6 and C_8 are higher-order dispersion terms [19], the rotational energy is described by the quantum number N, and the expectation value of the nuclear kinetic energy, $\langle T_{nuc} \rangle$, represents first-order corrections to the Born-Oppenheimer approximation [20]. Due to the ultracold temperatures of the lithium vapor (a few mK), the spectrum [12] is rotationally uncomplicated with the dominant feature being $N=1$, corresponding to s-wave collisions. At very long range, where fine structure of the P state is significant, the Hund's case (b) $A\,^1\Sigma_u^+$ potential correlates to a Hund's case (c) 0_u^+ potential, which depends on C_3 and the $2P$ state fine-structure interval [21]. The analytic form for the 0_u^+ potential given in Ref. [21] is used to correct the C_3 term in Eq. (2) for fine-structure effects.

At the current level of precision, radiation retardation effects in the long-range portion of the potential become important and must be accounted for. An exact quantum electrodynamic expression for this effect has been obtained for the case of a $S+P$ resonance without spin [22]. This treatment can be incorporated into the analysis since the data are predominantly in Hund's case (b) where the electron spin is decoupled from the molecular interaction. The C_3 term is multiplied by an R-dependent term, $C_3 \to C_3 \alpha(R)$, where

$$\alpha(R) = \cos\left(\frac{2\pi R}{\lambda}\right) + \left(\frac{2\pi R}{\lambda}\right)\sin\left(\frac{2\pi R}{\lambda}\right), \quad (3)$$

and λ is the wavelength of the $2S \leftrightarrow 2P$ transition.

Sensitivity to non-Born-Oppenheimer effects must also be considered. To first order, corrections to the Born-Oppenheimer potential may be calculated by taking the expectation value of the nuclear kinetic operator in the molecular electronic wave-function basis, $\langle T_{nuc} \rangle$. For the case of a homonuclear diatomic molecule, $\langle T_{nuc} \rangle$ reduces to three separate terms [20,23]:

$$\langle T_{nuc} \rangle = Q(R) + P(R) + S(R), \quad (4)$$

where

$$Q(R) = -\frac{\hbar^2}{2\mu}\left\langle \frac{\partial^2}{\partial R^2} \right\rangle, \quad (5)$$

$$P(R) = \frac{\hbar^2}{2\mu R^2}\langle L_x^2 + L_y^2 \rangle, \quad (6)$$

$$S(R) = -\frac{\hbar^2}{8\mu}\left[\left\langle \sum_i \nabla_i^2 \right\rangle + \left\langle \sum_{i \neq j} \nabla_i \nabla_j \right\rangle\right]. \quad (7)$$

The internuclear axis defines the z axis, L_x and L_y are the corresponding projections of the total electronic orbital angular momentum, the individual electrons making up the molecule are indexed by i and j, and the reduced mass of the system is given by μ. The $\langle\ \rangle$ brackets indicate expectation values taken over the electronic wave functions. The expectation value of electronic angular momentum, $P(R)$, is ex-

pected to dominate the other two terms in the case where the united molecule has nonzero $\vec{L}$ [23]. $P(R)$ can be evaluated in the long-range (Heitler-London) basis, where electron overlap is zero, by

$$P(R) \approx \frac{\hbar^2}{2\mu R^2}[l_s(l_s+1) + l_p(l_p+1)] = \frac{2\hbar^2}{2\mu R^2}, \quad (8)$$

where $l_s=0$ and $l_p=1$ are the orbital angular momenta of the atomic electrons. The first term of $S(R)$ represents a change in the reduced mass of the system due to the finite mass of the electrons. The second term depends on overlap and is small in the long-range region [20]. The first term can be written as a function of the average electronic kinetic energy which, using the virial theorem [24], can be expressed as a function of the Born-Oppenheimer potential, $V_{BO}(R)$:

$$S(R) \approx \frac{m_e}{4\mu}\langle T_e \rangle = \frac{m_e}{4\mu}\left[-V_{BO}(R) - R\frac{\partial}{\partial R}V_{BO}(R)\right], \quad (9)$$

where m_e is the electron mass. In the long-range Heitler-London basis, the expectation value of the nuclear momentum, $Q(R)$, is found to be constant and can be neglected. The variation of $Q(R)$ in the intermediate and inner regions of the potential is expected to be small compared to $P(R)$ [20,23]. In the analytic outer region of the potential [Eq. (2)] the non-Born-Oppenheimer terms [Eq. (4)] are approximated by the sum of Eqs. (8) and (9). In the inner region, the non-Born-Oppenheimer terms are assumed to be already accounted for by the RKR potential, but the rotational energy, dependent on N, must be added. The inner and outer regions are joined smoothly using a cubic spline.

A Numerov-Cooley algorithm [25] is used to compute the eigenvalue spectrum of the model potential as a function of C_3, C_6, and D_e. A multiparameter simplex fitting routine is used to minimize the standard χ^2 function [26],

$$\chi^2 = \sum_v \left[\frac{E_v^{(e)} - E_v^{(t)}(C_3, C_6, D_e)}{\sigma_v^{(e)}}\right]^2, \quad (10)$$

where the sum extends over the vibrational levels v, $E_v^{(e)}$ are the experimental vibrational eigenenergies with accompanying uncertainties $\sigma_v^{(e)}$, and the model potential energies are given by $E_v^{(t)}(C_3, C_6, D_e)$. This fit was done for the $N=1$, $v=69-76, 79-97$ levels of $^7\text{Li}_2$, corresponding to an R range of $30a_0$ to $170a_0$, and for the $v=63-72, 76-88$ levels of $^6\text{Li}_2$, which correspond to $R=29a_0$ to $150a_0$ [27]. The residuals of these fits were found to be randomly scattered with no observable systematic offsets. Several vibrational levels deeper than these were excluded because the long-range expansion [Eq. (2)] becomes invalid at small R where the exchange interaction becomes significant. Including these levels made the χ^2 value unstatistical, even though the extracted C_3 was insensitive to their inclusion. The fractional difference between the Linton et al. RKR potential and the

TABLE I. Values are given for C_3, C_6, and D_e obtained by fitting to the $N=1$ $A\,^1\Sigma_u^+$ $v=63-72,76-88$ vibrational features for ^{6}Li$_2$ and $v=69-76,79-97$ for ^{7}Li$_2$. The statistical uncertainties are shown in the first set of parentheses and correspond to one standard deviation. The second uncertainty is an estimate of our systematics. The mean is calculated weighted by the statistical uncertainty, and is reported with a systematic uncertainty found by adding the systematic uncertainty of both isotopes in quadrature.

	C_3 (a.u.)	C_6 (a.u.)	D_e (cm^{-1})
^{6}Li$_2$	11.0032(10)(20)	2140(150)(40)	9352.18(8)(2)
^{7}Li$_2$	11.0022(13)(20)	2350(320)(40)	9352.10(18)(2)
Weighted mean	11.0028(8)(28)	2180(140)(57)	9352.17(8)(3)

long-range model, Eq. (2), is 1.5×10^{-3} at $R=35a_0$ and increases to 8.0×10^{-3} at $R=20a_0$, owing to the effect of exchange. The results of each fit with the corresponding uncertainties are shown in Table I. Similar fits were performed for different ranges of vibrational levels and the results were found to be insensitive within the corresponding uncertainties. The statistical uncertainty in C_3, C_6, and D_e can be found by projecting the appropriate χ^2 boundary onto the corresponding parameter axis [26]. The large uncertainty associated with C_6 reflects its relatively small contribution to the molecular interaction at the large ranges represented by the data. The high-lying data are not sensitive to the value of C_8 so its value was fixed at the current theoretical value of 2.705×10^5 atomic units (a.u.) [19].

Including the adiabatic correction, $\langle T_{nuc}\rangle$, caused the fitted value of C_3 to increase by 0.009 a.u. and the value of D_e to increase by 0.16 cm^{-1}. $P(R)$ was found to have five times the effect on C_3 than $S(R)$. The inclusion of radiation retardation reduces the fitted value of C_3 by 0.005 a.u. Our model is expected to have some systematic uncertainty due to the neglect of spin exchange, the overlap term in $S(R)$, $Q(R)$, and spin in the calculation of the effects of retardation. The largest uncertainty is associated with the neglect of $Q(R)$. Since $Q(R)$ is comparable to $S(R)$ in the region of interest [23], we estimate a systematic uncertainty in C_3 of ±0.002 a.u., based on the observed effect of $S(R)$.

Linton et al. extract values for the long-range coefficients and the dissociation energy from their RKR analysis of their data [15]. Our values are in good agreement with their work and others [19]. Our value for C_3 is an order of magnitude more precise because of the higher precision of our photoassociation data. Also, our extracted value for C_3 should be more accurate since the effects of fine-structure, Born-Oppenheimer corrections, and radiation retardation are accounted for.

Taking a weighted mean of the results of the two isotopes for C_3, we conclude that the radiative lifetime for the $2P_{1/2}$ state of ^{7}Li is 27.102(2)(7) ns. The first uncertainty corresponds to one statistical standard deviation, while the second represents the systematic uncertainty. The values for the $2P_{3/2}$ state and for ^{6}Li are slightly different because of differences in the transition energy, but are contained within the uncertainty limits given. Figure 1 shows our result in comparison with recent experimental and theoretical values.
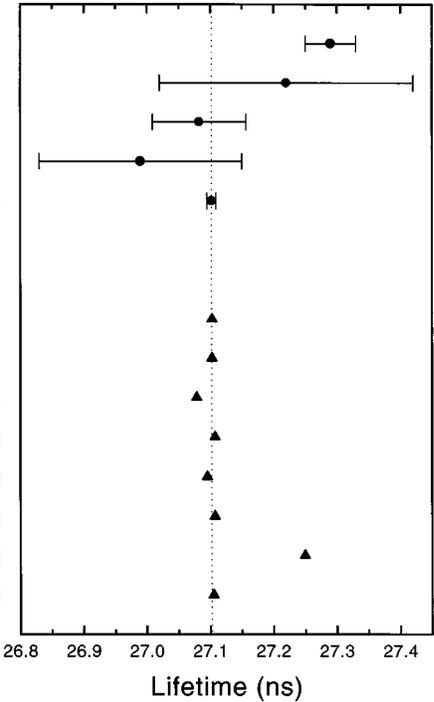
FIG. 1. Comparison of recent measurements and some theoretical calculations of the Li $2P_{1/2}$ radiative lifetime. The error bars given for Gaupp et al. and Carlsson et al. [28] correspond to one standard deviation. Linton et al. report a value for C_3 which we have converted to the lifetime value shown; the error bar represents their estimate of uncertainty taken from the quality of their fit. The error bar for our previous work represents an estimated systematic error. For the present result, the error bar is a combination of a one standard deviation statistical uncertainty and the systematic uncertainty. The conversion from oscillator strength or C_3 was done using the experimental transition energies of Ref. [29]. Reference [8] quotes a new unpublished experimental value by Volz and Schmoranzer of 27.11(6) ns.

We agree very well with all but the quantum Monte Carlo calculation of Ref. [7] and the experimental work of Gaupp et al., with which we strongly disagree. Our result is precise enough to differentiate between various theoretical results. When relativistic effects in the transition energy are taken into account [30], we agree fractionally to within 1×10^{-4} with the extremely precise work of Yan et al. [8]. At the present level of precision, we are sensitive to nonadiabatic effects, and for the first time, to the radiative retardation force between atoms. Without the radiative retardation correction, Eq. (3), the fits become unstatistical for the extracted values of C_3, C_6, and D_e.

Note added. Recently, we became aware of a similar analysis of the photoassociative spectrum of Na [31].

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