Photoassociation of $^{85}\text{Rb}$ atoms into $0_u^+$ states near the 5S+5P atomic limits
Photoassociation of $^{85}\text{Rb}$ atoms into $0^+_u$ states near the 5S+5P atomic limits

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Abstract

New photoassociation data on the $0^+_u$ levels of Rb$_2$ below the 5S+5P$_{1/2}$ limit are combined with older data (Cline et al 1994 Phys. Rev. Lett. 73 632) in a fit to potentials and spin–orbit functions. The P$_{1/2}$ data exhibit oscillations in the $B(v)$ values due to coupling between the two 0$^+_u$ series, as modelled accurately by a coupled potentials approach. The fitted value for the $C_3$ dispersion parameter from the combined data agrees well with the value derived from the pure long-range 0$^-_g$ state.

This article has associated online supplementary data files

1. Introduction

The availability of laser-cooled atoms has made it possible to obtain high-resolution spectra from photoassociation (PA) of atoms into molecular bound states near the dissociation limit. Such data provide information on the long-range excited state molecular potentials and are useful in designing methods for producing cold molecules by photoassociation processes (Nikolov et al 1999, Nikolov et al 2000, Comparat et al 2000, Laburthe Tolra et al 2001, Wang et al 2004, Sage et al 2005). Data from photoassociation experiments locate excited state levels and also can lead to approximate potentials from which Franck–Condon factors can be calculated.

The information obtainable from PA experiments varies with the circumstances (see, for example, the review articles by Stwalley and Wang (1999) and Jones et al (2006)). For homonuclear alkali dimers, there has been interest in the pure long-range states (Stwalley et al 1978), whose inner turning point is beyond the Le Roy radius inside which the atomic wavefunctions begin to overlap. Cold atom PA techniques have provided data on the bound
vibrational levels of the $1_u$ states associated with the $P_{3/2}$ limit of $K_2$ (Wang et al 1998) and $Cs_2$ (Comparat et al 2000), and for $0_g$ states associated with the $P_{3/2}$ limit of $Na_2$ (Ratcliffe et al 1994), $K_2$ (Wang et al 1997), $Rb_2$ (Cline et al 1994, Fioretti et al 2001, Gutterres et al 2002) and $Cs_2$ (Fioretti et al 1999, Pichler et al 2004), yielding reliable potential curves for these states. For more deeply bound states, it has been possible to determine the dispersion parameters for the long-range part of the potential, typically using the Le Roy–Bernstein (Le Roy and Bernstein 1970) asymptotic expansion. This has been done for the $P_{3/2}1_g$ states of $K_2$ (Pichler et al 2003), $Rb_2$ (Cline et al 1994, Amiot 1995) and $Cs_2$ (Comparat et al 1999, Pichler et al 2004b), for the $P_{3/2} 0_u^c$ state of $Cs_2$ (Comparat et al 1999, Pichler et al 2004b), for the $Na_2 P_{1/2} 0_u^c$ state (Tiemann et al 1996), the $Rb_2 P_{1/2} 0_u^c$ (Jelassi et al 2006a) and $0_u^c$ (Jelassi et al 2006b) states, as well as for the $0_g^c$ (Drag et al 2000, Pichler et al 2004a), $0_u^c$ (Pichler et al 2004a) and $1_g$ (Pichler et al 2004a) states of $Cs_2$ below the $6P_{1/2}$ limit.

In this study, we present new experimental data on the photoassociation of $^{85}Rb$ atoms to $0_u^c$ resonances below the $5S+5P_{1/2}$ limit and present an analysis of the new data together with previously reported data (Cline et al 1994) on PA of $Rb$ atoms below the $5S+5P_{3/2}$ limits. The two $0_u^c$ states are coupled by a spin–orbit function and can interestingly be considered together. In contrast with the elegant asymptotic quantum defect analysis of Jelassi et al (2006b), the data presented here raise new issues and challenges for two reasons: (1) the data extend far enough below the $Rb 5S+5P_{1/2}$ limit that the asymptotic expansion becomes invalid and a coupled potentials model is required; (2) including also the earlier data from below the $Rb 5S+5P_{3/2}$ limit in the model raises questions of consistency in the optimization process, but does provide a reconciliation between the earlier value (Cline et al 1994) for the $C_3$ coefficient for the $Rb(5S+5P)$ atomic limit and the value obtained more recently from the pure long-range $0_g^c$ state (Gutterres et al 2002).

2. Experimental procedure and data

The experimental $^{85}Rb_2$ photoassociation (PA) spectra from Storrs are obtained using trap loss in two distinct diode-laser-based magneto-optical traps (MOTs) which are continuously loaded from background $Rb$ vapour (Huang et al 2006, Lozeille et al 2006, Wang et al 2004a). The loading times for the MOTs range from 3 to 5 s. The trapped samples, at densities and temperatures of $10^{10}$ to $10^{11}$ cm$^{-3}$ and $<200$ µK, respectively, are illuminated with $\approx 500$ mW of light from a tunable single-frequency Ti-sapphire laser. When this light is tuned to a PA resonance, pairs of free atoms are promoted to an excited molecular state and subsequently decay, either back into free atoms with increased kinetic energy or into a bound molecule. In either case, the loss of atoms from the trap results in a dip in the MOT fluorescence.

Some regions of the trap-loss spectrum have been measured using a normal MOT, while others have utilized a dark SPOT (SPontaneous force Optical Trap) (Ketterle et al 1993) which generally yields higher densities. The PA spectra from the dark SPOT are shifted relative to the spectra from the normal MOT by the 3.036 GHz $^{85}Rb$ ground-state hyperfine splitting, since the atoms in the dark region reside predominantly in the lower ($F = 2$) hyperfine level. The absolute frequencies of the PA resonances are calibrated to within 0.02 cm$^{-1}$ using I$_2$ spectroscopy.

The data scans include transitions to $0_g^c$ and $1_g$ as well as to $0_u^c$ PA resonances. Here we focus on just the $0_u^c$ series. Rotationally resolved data from 60 $0_u^c$ bands below the $5S+5P_{1/2}$ limit were obtained. Examples are shown in figure 1. Note that the relative intensity of the rotational lines varies, especially near the dissociation limit. Values for the band origins, $G(v)$, and rotational parameters, $B(v)$, are given in table 2.
The Rb$_2$ $0_u^+$ data below 5S+5P$_{3/2}$ were obtained at the University of Texas, as previously reported (Cline et al 1994). The Texas data were obtained with a far-off resonance trap (FORT) employing one fixed frequency laser, plus a second laser with 1 MHz bandwidth, to scan over the PA resonances. The two lasers were modulated alternately at 200 kHz to eliminate power broadening and shifts. Resonances were detected by reductions in the atomic fluorescence (trap loss). These resonances are broadened by pre-dissociation, and thus are more extensively overlapped than the PA resonances below 5P$_{1/2}$. PA signals for $0_u^+$ resonances that are not strongly overlapped with $0_g^-$ and $1_g$ resonances are shown in figure 2. Table 3 lists the $0_u^+$ resonance line positions together with residuals from a fit from a coupled potentials model discussed below.

3. Analysis of the data

To provide a perspective on the regime of energy and internuclear distance relevant here, we give in figure 3 approximate potentials for the Rb$_2$ A and b states and for the region near the 5S+5P atomic limit.

3.1. Results from fits to Le Roy–Bernstein expressions

In analysing the data, we consider as a first approximation the Le Roy–Bernstein semiclassical method (Le Roy and Bernstein 1970). According to Marinescu and Dalgarno (1995), for...
Figure 2. Experimental data scans over resonances below the 5S+5P_{1/2} limit, which is nominally at 12816.603 cm$^{-1}$ (Barwood et al. 1991). The 0$^+_u$ resonances are denoted by filled-in areas. Between 12789 and 12800 cm$^{-1}$ and between 12807 and 12809 cm$^{-1}$, the 0$^+_u$ bands are strongly overlapped by 0$^+_g$ bands, while beyond 12813 cm$^{-1}$, the 0$^+_u$ bands are overlapped with 1$^+_g$ bands.

Figure 3. Potentials as obtained from the final fitted parameters and ab initio results of Edvardsson et al. (2003). Energies are relative to the minimum of the X state, and thus include the X state dissociation energy of 3993.53(6) cm$^{-1}$ (Tsai et al. 1997). Part (a) gives an overall view of the potentials for the A$^1\Sigma_u^+$ and the $\Omega = 0$ component of the b$^3\Pi_u$ states. Part (b) shows more details of the region near the 5S+5P dissociation limit. The diabatic potentials (dashed line) are purely non-relativistic. The adiabatic potentials are obtained by diagonalizing the 2 × 2 matrix containing the diabatic potentials and the spin–orbit coupling function, as in (1).

alkali molecules tending to the lowest S+P atomic limit, there are two $C_3$ quantities differing by a factor of $-2$ if one neglects relativistic effects: $C_3(\sigma) = -2C_3(\pi)$. The effect of spin–orbit coupling between 0$^+_u$ states tending to P$_{3/2}$ and P$_{1/2}$ atomic limits has been discussed by
Marinescu and Dalgarno (1996) and by Aubert-Frécon et al (1998). The following is a brief summary and application to the 0_u states of Rb_2.

For the 0_u manifold, one has a 2 by 2 Hamiltonian matrix. Neglecting rotation, it is

\[
H = \begin{pmatrix}
\Delta_{\Pi} & V(\Pi_u) - \Delta_{\Pi} \\
V(\Pi_u) & \Delta_{\Pi} + V(\Pi_u)
\end{pmatrix},
\]

(1)

where the \( V(\Pi_u) \) and \( V(\Pi_u) \) are Born–Oppenheimer potentials (possibly including relativistic mass corrections, but not spin–orbit effects), \( \Delta \) is the atomic spin–orbit splitting of the \( P \) state, and \( \Delta_{\Pi} \) and \( \Delta_{\Pi} \) are functions of the internuclear separation, \( R \), that express diagonal and off-diagonal spin–orbit effects.

Asymptotically, the (non-relativistic) potentials behave as

\[
V(\Pi_u) \to E^0 - C_3(\sigma) R^3, \quad V(\Pi_u) \to E^0 - C_3(\pi) R^3
\]

(2)

where \( E^0 \) is the centre-of-gravity of the \( P \) levels.

As discussed in Gutterres et al (2002), the \( C_3 \) parameters are related to the dipole transition moments for either \( P_J \) state,

\[
M_J^2 = |\langle 5s|\sigma|5p_J\rangle|^2 = \frac{9\hbar}{4\tau_j} \left( \frac{\lambda_j}{2\pi} \right)^3
\]

(3)

where \( \tau_j \) is the radiative lifetime and \( \lambda \) is the wavelength of the 5P_\( J \to 5S \) transition. Thus,

\[
C_3(\sigma) = -\frac{M_{\frac{3}{2}}^2}{4}, \quad C_3(\pi) = \frac{M_{\frac{1}{2}}^2}{2}.
\]

(4)

As also discussed in Gutterres et al (2002), the \( \langle \sigma|\pi|p_J \rangle \) moments are not exactly identical because of relativistic effects in the wavefunctions. Estimates of the differences range from 2.3 \times 10^{-4} to 2.2 \times 10^{-3}. In this study, these effects are masked by uncertainties in the short-range potential.

Neglecting now the \( R \)-dependences of the spin–orbit functions, we substitute (2) into (1). In doing so, we assume that \( |\Delta| > 2C_3/3R^3 \), as is the case over a considerable range of \( R \) for the Rb_2 states of interest here. We obtain

\[
V(P_{\frac{1}{2}}) = E^0 - C_3(\sigma) R^3 \approx \frac{4C_3(\sigma) R^3}{3 R^3},
\]

\[
V(P_{\frac{3}{2}}) = E^0 - C_3(\pi) R^3 \approx \frac{5C_3(\pi) R^3}{3 R^3}.
\]

(5)

For the levels studied here, there are departures from these idealized expressions due to departures of the potentials from a precise \( C_3/R^3 \) form, \( R \)-dependence of the spin–orbit functions, and effects of the inner wall.

As reported in Cline et al (1994), the 0_u states near the 5S+5P_3/2 atomic limit fit quite nicely to the semiclassical expression derived by Le Roy and Bernstein (1970),

\[
v_D - v = \frac{4\alpha_3}{\hbar} \sqrt{2\mu C_3^{1/3}|D - E(v)|^{1/6}}, \quad \alpha_3 = \frac{\sqrt{\pi} \Gamma(5/6)}{2\Gamma(4/3)} = 1.120 2513,
\]

(6)

applied to a potential of the form \( V(R) = D - C_3/R^3 \). If one writes \( v_D - v = K(D - E(v))^{1/6} \), then if \( D \) and \( E(v) \) are in cm\(^{-1} \) and \( C_3 \) is in atomic units, \( K = 36.1269 C_3^{1/3} \). Row 2 of table 1 gives the fitted value of \( C_3 \) from Cline et al (1994), multiplied by 0.6 to be consistent with (5).
Figure 4. Results of a fit of the $0^+_u$ data below the $5S+5P\frac{1}{2}$ limit to the semiclassical model of (6). The full circles and left axis show $v^* = v_D - v$ versus $[\epsilon = D - E(v)]^{1/6}$, while the open circles and right axis show the residuals of this fit.

Table 1. $C_3$ values (in au) obtained from previous studies and from the present work. All values are stated in atomic units, and apply to $C_3(\pi)$. Uncertainty limits for results from the present work are not stated because of the high degree of correlation between the various fitted parameters.

<table>
<thead>
<tr>
<th>Source</th>
<th>$C_3(\pi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory (Marinescu and Dalgarno 1995)</td>
<td>9.202</td>
</tr>
<tr>
<td>Experiment (Cline et al 1994)</td>
<td>8.784(6)</td>
</tr>
<tr>
<td>Experiment (Gutterres et al 2002)</td>
<td>8.905(26)</td>
</tr>
<tr>
<td>This work: Coupled potentials fit to $P_{1/2}$ data</td>
<td>8.948</td>
</tr>
<tr>
<td>This work: Fit to combined $P_{1/2}$ and $P_{3/2}$ data</td>
<td>8.903$^a$</td>
</tr>
</tbody>
</table>

$^a$ Preferred result from the present work.

but excluding the ‘systematic’ uncertainty of 0.4 au quoted in Cline et al (1994). As stated in Cline et al (1994), one expects that even for $0^+_u$ levels below $5P_{3/2}$, other potential terms will enter, so this value differs from values obtained from results obtained from experimental data on the pure long-range $0^-_u$ state (Gutterres et al 2002), also listed in table 1.

Levels below the $5S+5P_{1/2}$ atomic limit can also be fit to the expression given in (6), and a nearly straight-line plot of $v_D - v$ versus $[D - E(v)]^{1/6}$ results, as shown in figure 4. However, the deviations, which are plotted in this figure relative to the right axis, are large compared with the experimental uncertainty, and show systematic effects that give a nearly oscillatory behaviour.

3.2. Fitting procedure with a coupled potentials model

To understand the residuals in figure 4, we consider various approximations to the relevant potentials and spin–orbit functions. Bound state eigenvalues are calculated by the discrete variable representation (DVR) (Colbert and Miller 1992) approach, with an appropriate scaling of the $R$ coordinate to increase the density of points where the momentum is greatest (Tiesinga et al 1998). For metastable (pre-dissociating) states above the $5P_{1/2}$ limit, the use of an absorbing potential (Monnerville and Robbe 1994) used in previous work (Bergeman et al 2002) did not yield stable results as a function of the position of the imaginary potential terms, so we choose to calculate scattering phase shifts with a two-channel renormalized Numerov
method (Johnson 1973, 1978, 1985). Resonance positions are indicated by maxima of the energy derivative of these phase shifts. By comparing the eigenvalues and resonance energies with the observations, the potentials and spin–orbit functions can be adjusted to optimally fit the experimental data.

The available PA data lie within 70 cm\(^{-1}\) of the 5P\(_{1/2}\) limit, and within 30 cm\(^{-1}\) of the 5P\(_{3/2}\) limit, while the relevant potentials, for the A' \(^{1}\Sigma_{u}^{+}\) and b' \(^{3}\Pi_{du}\) state, are calculated to be 5800 and 6800 cm\(^{-1}\) deep, respectively. In contrast to lighter alkali dimer molecules (Na\(_{2}\) and K\(_{2}\)), these Rb\(_{2}\) states have not been well characterized by analysis of spectroscopic data from absorption of ground-state molecules. Clearly, the present data cannot determine the deeper parts of the potentials, so our interpretation of the 0\(^{0}\) \(^{0}\) PA resonances necessarily makes use of \textit{ab initio} potentials. We employ those calculated by Lunell and colleagues (Edvardsson \textit{et al} 2003).
Table 3. $^3\Omega$ band energy levels measured from the PA spectrum below the $^5P_{1/2}$ limit. Columns 1 and 4 give the measured laser energy, columns 2 and 5 the residuals from the fit to the coupled potentials model, and columns 3 and 6 the estimated experimental uncertainty. Many highly blended bands are excluded in this listing. All quantities are in cm$^{-1}$.

<table>
<thead>
<tr>
<th>$E_L$</th>
<th>Residual $\sigma$</th>
<th>$E_L$</th>
<th>Residual $\sigma$</th>
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<td>12.781.8041</td>
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<td>12.793.0791</td>
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<td>12.784.3310</td>
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<tr>
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<td>12.810.7310</td>
<td>-0.0261</td>
<td>0.0150</td>
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Since the $ab\ initio$ potential functions are not determined to spectroscopic accuracy, adjustments are justified. For example, the potential energy minima are undoubtedly uncertain to $\approx 50$ cm$^{-1}$ and can thus be adjusted over this range. An adjustable extrapolation for the inner walls was also used. For the long-range part, the $C_n$ parameters have been determined quite accurately, but small adjustments can be made consistent with the stated uncertainty limits. The exchange parameters, which are not accurately determined in previous studies, have also been adjusted to fit the data.

After various attempts to employ spin–orbit functions of Morse potential form, we eventually used $ab\ initio$ results obtained for analogous states of $K_2$ (Manaa et al. 2002), scaled to give the known Rb $^5\Sigma^+$ fine structure splitting. The variation of these functions about the known asymptotic (atomic) limit was adjusted in the fitting process, and the sharp change at the last calculated value was smoothed somewhat. The resulting functions are shown in figure 5.

The effect of the coupling between the $0^+_u$ states dissociating to $5S+5P_{1/2}$ and to $5S+5P_{3/2}$ is shown most dramatically in a plot of $B(v)$ values, given in figure 6. The solid line and small circles denote values obtained from a fit to only the data below the $5P_{1/2}$ limit. In this plot, the larger $B(v)$ values are associated with states that have the most $P_{3/2}$ character, which are most tightly bound in this energy region. Points for which data are missing are those for which the PA excitation amplitude is very small due to small overlap of the initial and PA resonance
wavefunctions. Very similar plots of Rb$_2$ 0$_u^+$ $B(v)$ values have been obtained by Kokouline et al (1999, 2000) from purely theoretical calculations.

Efforts to fit the combined 0$_u^+$ data sets from below the P$_{3/2}$ limit together with the data below the P$_{1/2}$ limit were not totally satisfactory. Because the rotational structure of the pre-dissociated bands was not resolved, the peak was estimated to correspond with the transition to the $J = 2$ line. Optimum adjustments of the $ab\ initio$ potentials and spin–orbit functions differed for the two data sets, so the overall best results were a compromise, in which the residuals of each showed deviations larger than experimental uncertainties. For example, the residuals for the P$_{3/2}$ data shown in figure 7(a) show significant deviations between calculated and observed resonance energies for the lowest energies, while for these same adjusted parameters and spin–orbit functions, the residuals for the P$_{1/2}$ data were larger than when these data were fit alone (figure 7(b)). We should also mention that the best fits to the data in either region were obtained by making small shifts of the energy scales (∼0.03 cm$^{-1}$) that undoubtedly compensate for deficiencies of the model potentials and spin–orbit functions. The residuals plotted in figure 7 and listed in tables 2 and 3 do include these shifts. Despite these less than desirable features in our analysis, the optimum value of $C_3(\pi)$
Figure 7. (a) Residuals from fits to the $0^+_u \frac{P_3}{2}$ data using the coupled potentials model. Experimental uncertainties are given in table 3. (b) Residuals from fits to the $0^+_u \frac{P_1}{2}$ data with only the $P_3/2$ data included (full circles) and with the combined data (open circles). Including the $P_{3/2}$ data in the fit enlarges the residuals somewhat. The rms scatter of the residuals from the fit to the $P_{1/2}$ data alone was approximately 0.006 cm$^{-1}$.

from such combined fits was indeed found to be restricted well within the uncertainty limits of the value obtained from the pure long-range $0^-$ state (Gutterres et al 2002). Our recommended value also agrees well with the value from lifetime measurements noted in this reference. Thus a primary result of the fit to the combined data is to reduce the ‘systematic uncertainty’ of 0.3 au in $C_3(\pi)$ quoted in Cline et al (1994). The model used here includes many of the additional effects, such as the effect of the short-range potential, that were not included in the asymptotic energy model used by Cline et al (1994). Hyperfine structure effects, discussed with more recent data below the $5P_{3/2}$ limit of $^{87}$Rb (Kemmann et al 2004), are not included in our model, however, and may explain some of the deviations with observations. Furthermore, there remains an undetermined amount of correlation between the $C_3(\pi)$ value obtained here and other adjustable parameters, so that meaningful uncertainty limits on this parameter cannot be given.

The fitted potentials and spin–orbit functions are given in an associated online data file (available from stacks.iop.org/JPhysB/39/S813), for use in calculating Franck–Condon factors and other properties.

In summary, we have presented new data on the photoassociation of $^{85}$Rb atoms into $0^+_u$ states below the $5S+5P_{1/2}$ limit, and have modelled these data together with previous data on $0^+_u$ levels below the $5S+5P_{3/2}$ limit, by the use of two potentials coupled by a spin–orbit function. This model confirms in detail that the $0^+_u$ series tending to these two limits are coupled in such a way as to produce maxima in the rotational parameters $B(v)$ below the $P_{1/2}$ limit where the intermixing with states tending to the $P_{3/2}$ limit is maximal. It is hoped that current work to obtain improved $ab\ initial$ potentials and spin–orbit functions, and also to obtain and analyse spectroscopic data for lower $0^+_u$ levels, will reduce the small but persistent deviations between model calculations as presented here, and experiment.

Acknowledgments

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