Analysis of strongly coupled electronic states in diatomic molecules: Low-lying excited states of RbCs

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Analysis and assignment of spectra involving the lowest excited states of the heavier alkali-metal atom dimers are complicated by the strong spin-orbit coupling elements. Here we report an analysis of the Fourier-transform spectroscopy data from laser-induced fluorescence of the coupled $A \pm \Sigma^+$ and $b \mp \Pi$ states of RbCs, using the discrete variable representation. Fitted parameters are given and special effects due to strong coupling are discussed.

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Because alkali-metal atoms can be laser cooled and Bose-Einstein condensed, recently there has been considerable interest in exploiting the properties of alkali-metal dimers for the formation of cold molecules [1–5], possibly by coherent processes [6–8] and for photoassociation [9,10]. Many of these techniques involve optical excitation either in the formation or detection stages. For this reason, it is useful to have an adequate characterization of various excited states of the alkali-metal dimer molecules. Furthermore, it has been proposed [11] to use heteronuclear alkali-metal dimers to form addressable qubits by means of the Stark effect in a spatially varying electric field. Work in this direction is now being actively pursued with RbCs, which was selected because the constituent atoms can be efficiently cooled with diode lasers [12]. Understanding the spectrum of RbCs is vital for this effort.

For heavier alkali-metal dimers, one difficulty has been the strong spin-orbit coupling between the two low-lying excited states, (2) $\Sigma^+$ or (1) $\Sigma_u^+$ in homonuclear alkali-metal dimers [hereafter referred to as the A state] and (1) $\Pi_3/\Pi_0$ (the b state). Analysis of spectra from these two states of Li$_2$, Na$_2$, NaK, and K$_2$ has been achieved by ingenious exploitation of laser spectroscopic techniques and traditional methods of analysis [13]. For Rb$_2$, doublets in the fluorescence spectrum from the (2) $\Pi_g$ state have been modeled using the Fourier grid Hamiltonian method [14], and data have been obtained near the dissociation limit [15]. Also, there have been enlightening model calculations [16] for Cs$_2$ and Rb$_2$. However, to our knowledge, there have not been systematic quantum state assignments of spectral data on the strongly interacting $A$ and $b$ states of KRb, KCs, RbCs, Rb$_2$, and Cs$_2$.

Absorption spectroscopy applied to these molecules yields dense, unresolvable spectra. Only the technique of laser-induced fluorescence, especially combined with the Fourier-transform spectroscopy, has resulted in precision measurements of resolved transitions, as in Refs. [17,18]. Furthermore, the perturbations are sufficiently strong that traditional band-by-band methods of analyzing spectral data become problematical. Recently, alternative methods for simulating diatomic spectra and term values have been developed [13,16,19,20]. The purpose of this paper is to present laser-induced fluorescence Fourier-transform spectroscopy (LIF-FTS) data on RbCs together with the results of analysis using the discrete variable representation (DVR) [19,21].

The model Hamiltonian we employ is based on a diabatic basis of states of given $S$, $\Lambda$, and $\Omega$, where $S$ is the total spin, $\Lambda$ and $\Omega$ are the projections of total and orbital angular momentum, respectively, along the internuclear axis [22]. The Hamiltonian is the sum of several terms: $H(R) = H_K + H_V(R) + H_{od}(R) + H_{rot}(R)$, and is a function of $R$, the internuclear distance. The kinetic-energy operator $H_K = -(h^2/2\mu)\partial^2/\partial R^2$ is diagonal over the $2S_1^+\Lambda_\Omega$ basis, but is represented by a full matrix over the mesh points [19,21]. $H_V(R)$ includes nonrelativistic $R$-dependent potentials plus spin-independent relativistic effects, $H_{od}(R)$ includes diagonal and off-diagonal spin-orbit interactions, and $H_{rot}(R)$ expresses the effects of rotation. It is assumed that the diagonal potential energies can be represented by Rydberg-Klein-Rees (RKR) potentials calculated from the Dunham coefficients $Y_{ij}$. The nonzero matrix elements of $H_V(R) + H_{od}(R) + H_{rot}(R)$ are:

$$\langle 1\Sigma^+|H|1\Sigma^+\rangle = V(1\Sigma^+) + (x + 2)B,$$

$$\langle 3\Pi_0|H|3\Pi_0\rangle = V(3\Pi) + (\Omega - 1)\Delta_d + (x + 2)B,$$

$$\langle 1\Sigma^+|H|3\Pi_0\rangle = -\Delta_{od},$$

$$\langle 3\Pi_0|H|3\Pi_1\rangle = -\sqrt{2}xB,$$

$$\langle 3\Pi_1|H|3\Pi_2\rangle = -\sqrt{2}(x - 2)B,$$  \hspace{1cm} (1)

where $x = J(J + 1)$, $\epsilon = 1$ for $\Omega = 0$ and 1, and $-1$ for $\Omega = 2$, and $H = H_0$. In the above, $V(1\Sigma^+)$, $V(3\Pi)$, $\Delta_d$, $\Delta_{od}$, and $B = h^2/2\mu R^2$ are the functions of $R$.

In the traditional band-by-band analysis of diatomic spectra, expectation values of $H_V(R)$ are obtained over vibronic wave functions such that the Hamiltonian parameters to be fitted are the vibronic energies $G(v)$, rotational parameters...
$B(v)$, centrifugal distortion parameters, and diagonal and off-diagonal spin-orbit terms $A(v)$ and $\alpha(v,v')$. For strongly coupled electronic states, this approach would require many vibronic functions in large matrices for each vibrational level analyzed (as well as second-order perturbation sums), and would require many more fitted parameters than used in the present work. The DVR method is similar to the Fourier grid Hamiltonian method [16] in that it produces an accurate representation of the kinetic energy and takes into account interactions among all coupled vibronic levels. Trigonometric basis functions result in equidistant mesh points [21]. A scaling function [19] $R = r_0/y^2 - r_e$ was used here to increase the density of mesh points at the potential minimum relative to the long-range regime. Simple analytic expressions are available for the second derivative minimum relative to the long-range regime. Simple analytic expressions are available for the second derivative

Eigenvalues and eigenfunctions are obtained by matrix diagonalization over the mesh points.

The present analysis utilizes 427 (perturbed) levels of the $A$ state, which were measured by LIF-FTS in connection with a study of the ground state [18]. In order to fit the $X$-state parameters from the LIF-FT spectra, emission was observed from each of these excited-state levels to several ground-state levels, so that the rotational quantum number $J$ and isotopomer species ($^{85}\text{Rb}^{133}\text{Cs}$ or $^{87}\text{Rb}^{133}\text{Cs}$) could be assigned. Previously it had not been possible to characterize the upper levels, but these quantum assignments provide a major first step.

Because spin-orbit coupling is so important, the form of the spin-orbit functions $\Delta_J = \Delta_d, \Delta_{od}$ needs to be considered. For other alkali-metal dimers, including Cs$_2$ [16], K$_2$ [13], and NaK [23,24], it has been found that both the diagonal and off-diagonal spin-orbit functions $\Delta_d$ and $\Delta_{od}$ exhibit significant dips as a function of $R$. From the $ab\text{ initio}$ calculations by Fahs et al. [25] of the adiabatic relativistic potentials, it is not clear whether this is the case for RbCs. Nevertheless, in view of the trend in other homologous species, we have introduced $\Delta_J$ functions with such a dip, and have varied the depth, location, and harmonic variation of the dip. Lacking further information, we have assumed a Morse function form for each of the spin-orbit functions: $\Delta_J = P(1,i) + [P(2,i) - P(1,i)][1 - \exp(P(3,i)(P(4,i) - R))]^2$. In the fitting process, various values were assumed for $P(2,i), P(3,i), P(4,i)$ based on previous $ab\text{ initio}$ calculations of $\Delta_d$ and $\Delta_{od}$ for homologous species, and then $P(1,i)$ was varied in the least-squares-fitting procedure.

For transitions from the $X$ state, $b$-state levels are observable only by acquiring singlet character by mixing with the $A$-state levels. Hence in the present dataset, there is no information on the $b$-state levels below the minimum of the $A$ state. We have fixed the value for the excitation energy of the $b$ state, $T_e(b)$, at a value close to that obtained from $ab\text{ initio}$ calculations [26], but slightly higher so that fitted value for $Y_{10} = \omega_e(b)$ is also close to the theoretical values. The true value of $T_e(b)$ could deviate from this assumed value by as much as 5 cm$^{-1}$, although the $v = 0$ level of $b \ ^3\Pi_0$ (in contrast to $^3\Pi_1$) is less certain than this. In fitting the data, we have optimized the values of $T_e(A)$. Dunham coefficients $Y_{ij}$ for the $A$ and the $b$ state, and the minimum value of the functions $\Delta_d$ and $\Delta_{od}$, as given in Table I for $^{85}\text{Rb}^{133}\text{Cs}$.

<table>
<thead>
<tr>
<th>$A \ ^1\Sigma^+$</th>
<th>$b \ ^3\Pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_e$</td>
<td>10065.0</td>
</tr>
<tr>
<td>$Y_{10}(\omega_e)$</td>
<td>37.73</td>
</tr>
</tbody>
</table>

This work

| $T_e$            | 10037.829(230)   | 8852.0*          |
| $Y_{10}$         | 36.650(40)       | 55.85(20)        |
| $Y_{60}$         | 1.23742(48)[−2]  | −1.77349(42)[−2] |

Spin-orbit parameters

$\Delta_d(R)$ $\Delta_{od}(R)$

| $P(1)$             | 135.49(28)       | 130.77(37)       |
| $P(2)$             | 184.70*          | 261.2*           |
| $P(3) (\text{Å}^{-1})$ | 0.24*            | 0.23*            |
| $P(4) (\text{Å})$  | 5.82*            | 5.85*            |

Parameters for $^{87}\text{Rb}^{133}\text{Cs}$ may be obtained by the usual scaling relations, as in [18]. Vibrational numbering of the two states is aided by data on the two isotopomers. Also, the perturbation interactions depend on vibrational overlaps which are quite sensitive to vibration numbering, so that data on just one isotopomer gave a strong indication of the vibrational quantum numbers. Potentials calculated from the fitted parameters are shown in Fig. 1.

The 427 experimental term values have been fit to an rms residual of about 0.25 cm$^{-1}$ as compared with experimental errors estimated to be about 0.02 cm$^{-1}$ [27]. Figure 2 shows the experimental $^{85}\text{Rb}^{133}\text{Cs}$ term values (dots) and calculated term values (solid lines connecting values for integral $J$) over the two regions of energy and rotation. It was important to have sufficient data, as shown in the lower part of Fig. 2, to fit the low-order $Y_{ij}$ parameters. However, for higher-energy regions such as that shown in the top part of Fig. 2, the DVR approach could work with quite sparse data that
would be difficult to fit with band-by-band approaches. The fit residuals are far smaller than the vibrational intervals, but large enough to suggest that a significant effect may be omitted in our Hamiltonian, possibly associated with spin-orbit couplings with other electronic states shown in Fig. 1. Attempts to introduce such coupling elements have not reduced the rms residual, however.

The estimated spin-orbit functions are roughly comparable to the average of the theoretical functions for Rb$_2$ and Cs$_2$ given in Ref. [16]. However, the value obtained here for the $^3\Pi_1$-$^3\Pi_0$ interval is 71% of this interval in the \textit{ab initio} calculations of Fahs et al. [25] on RbCs, while the minimum splitting between the two adiabatic $\Delta_v=0$ potentials (near 5.34 Å), which we obtain, is just 50% of the theoretical value in Ref. [25]. Two avoided crossings with $b^3\Pi_1$ levels suggest that the $\Delta_J$ function in Table I may be incorrect by 3–5 cm$^{-1}$, but there is insufficient information for a better empirical estimate.

The coupling between the A and $b^3\Pi_0$ states is about 120 cm$^{-1}$ as compared with the vibrational frequencies of 36 and 56 cm$^{-1}$, respectively. This gives rise to several special effects. As shown in Fig. 3(a) for RbCs $J=0$ (hence $\Omega=0$) levels, the fraction of the A-state character of all vibronic states above $v=1$ of the A state varies between 30% and 80%. Figure 3(b) shows the composition of one particular $J=0$ level in terms of unperturbed vibronic levels of the A and $b^3\Pi_0$ states. Figure 3(c) shows the quasioscillatory variation of the A-state character as a function of $J$ for the two levels that for $J=0$ lie just above $E=12040$ cm$^{-1}$ in Fig. 2(a). The narrow dips in these curves occur when there are crossings with $|\Omega|=1$ levels of the b state, as may be seen by examining the energy curves for these two levels. Comparison of Figs. 2(a) and 3(c) also indicates that there is a narrow avoided crossing between these two levels near $J=126$, and wider avoided crossings with other nearby levels at $J=86$ and 161.

FIG. 1. Diabatic potentials for the RbCs A and b states obtained in the present work (solid lines), plus potentials for higher-lying states from Ref. [26] (dashed lines). In the inset, adiabatic potentials for the $A^1\Sigma^+$ and $b^3\Pi_0$ states are shown as dotted lines.

FIG. 2. Experimental term values (dots) plus calculated term values, shown as solid lines connecting values for integral $J$, for $^{85}$Rb$^{133}$Cs, for the two regions of energy. The vibronic identifications refer to the major component. $A(2)$ denotes $v=2$ of the A state, $b0(32)$ denotes $v=32$ of the $b^3\Pi_0$ component, etc., $|\Omega|=2$ levels of the b state interact very slightly and are omitted from these plots.

FIG. 3. (a) The fraction of the A-state character in the $J=0$ levels, showing a high degree of intermixing for all levels above $v=0$ of the A state. (b) For the $J=0$ level at $E=10921$ cm$^{-1}$, this graph shows the composition in terms of unperturbed vibronic levels of the $A^1\Sigma^+$ (positive axis) and $b^3\Pi_0$ (negative axis) states, over a range of about 150 cm$^{-1}$. (c) These curves show the fractional A-state character for the two vibronic levels that for $J=0$ lie just above $E=12040$ cm$^{-1}$ in Fig. 1.
Since the diabatic potentials evidently are far from a diagonal representation, it is tempting to consider the adiabatic correction terms in the present case can be obtained by calculating the multicomponent diabatic wave function, \( \Psi(R) = S(R)\Phi(R) \):

\[
V_{ad}(R) = S(R)^{-1}[H_V(R) + H_{\alpha}(R)]S(R),
\]

\[
S^{-1}HS\Phi = \left[ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V_{ad} \right] \Phi
\]

\[
-\frac{\hbar^2}{2\mu} S^{-1} \left[ \frac{\partial^2 S}{\partial R^2} \Phi + 2 \frac{\partial S}{\partial R} \frac{\partial \Phi}{\partial R} \right]
\]

\[= E\Phi. \quad (2)\]

The nonadiabatic correction terms in the last bracket are usually quite small except in the case of homogeneous perturbations, as discussed in Ref. [22]. An estimate for correction terms in the present case can be obtained by calculating eigenvalues with adiabatic potentials (without the correction terms) and comparing with eigenvalues from the diabatic approach used above. We find that correction terms estimated in this manner are frequently as large as 6 cm\(^{-1}\) due to the strong spin-orbit mixing.

In summary, we have shown that the DVR numerical method can be used to analyze spectral data for strongly coupled diatomic electronic states, and we have discussed some of the features that result from the strong coupling. The success of this analysis raises hopes that spectral data on analogous electronic states in related molecules can be similarly analyzed, and that additional data on RbCs can be used to resolve open questions discussed above.

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[12] D. DeMille et al. (private communication).
[27] See EPAPS Document No. E-PLRAAN-67-R09305 for a list of experimental and fitted term values. A direct link to this document may be found in the online article’s HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory/epaps/. See the EPAPS homepage for more information.