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Observation of quasibound energy levels in the $B^1\Pi_u$ state of $^7\text{Li}_2$

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Abstract.

Double resonance excitation of $^7\text{Li}_2$ vapour with two tunable single mode lasers (Ti-sapphire and R6G dye) have been used to study levels of the $B^1\Pi_u$ state close to the potential maximum of this state ($500 \pm 3 \text{ cm}^{-1}$ above the dissociation limit). A potential energy curve has been constructed, and measured linewidths are consistent with those calculated from the potential energy curve.

Introduction.

A systematic investigation of the valence states of the lithium dimer has been pursued over the past few years by recording laser induced fluorescence by Fourier transform spectrometry. The technique probes many vibrational levels of the lower electronic state observed in fluorescence in a single spectrum, and this has made it possible to describe the potential energy curves of some electronic states almost to their dissociation limits (1,2).

Part of this experimental investigation has involved the use of double resonance excitation to populate the $F^1\Sigma_g^+$ state, which dissociates to $\text{Li}(2p) + \text{Li}(2p)$ atoms, giving access to the lower-lying $A^1\Sigma_u^+$ and $B^1\Pi_u$ states by direct fluorescence which are observed as the $F \rightarrow A$ and $F \rightarrow B$ systems. Collisional processes also populate states lying close to $F^1\Sigma_g^+$, and a few bands of the $(1)^1\Delta_g \rightarrow B^1\Pi_u$ and $(1)^3\Delta_g \rightarrow b^3\Pi_u$ systems have been observed in the same spectra (3,4).

In recording the infrared emission following excitation of the $F^1\Sigma_g^+$ state with a krypton ion laser and ring dye laser (DCM and pyridine), we noticed that the progression of PQR triplets corresponding to the F-B transition extended beyond previously observed range of vibrational levels in $B^1\Pi_u$ (Fig 1a), and sometimes terminated in bound-free oscillations. This suggested that the F-B system could be used to investigate the complete potential curve of the $B^1\Pi_u$ state, which has been calculated by ab initio methods (5) and has a potential barrier to dissociation at about 5.9 \AA because the repulsive term arising from dipole-dipole interactions between $\text{Li}(2p)$ and $\text{Li}(2s)$ atoms competes with the attractive exchange energy between the valence electrons. When the molecule rotates, a centrifugal term increases the effective barrier height. The quasibound rovibrational levels of the $B^1\Pi_u$ state are broadened by the tunnel effect: the closer a level lies to the top of the energy barrier, the broader the energy level will be. This phenomenon can be monitored on the fluorescence spectra by measuring the

width of the spectral lines : the linewidth is inversely proportional to the lifetime of the state, and the lifetime is reduced by the extent to which tunneling occurs through this potential barrier.

Experimental.

Although the $F \rightarrow B$ system of $^7\text{Li}_2$ has been observed in fluorescence after double resonance excitation using a krypton laser for one transition and a dye laser for the other, and also -by chance- with a single dye laser frequency, the systematic investigation of the $B\ ^1\Pi_u$ state became possible when two tunable lasers were employed to excite the F state. Lithium vapour was produced in a heatpipe oven at about 800°C . This temperature results in significant Boltzmann population of several vibrational levels of the ground state. A single mode Ti-sapphire laser was used to excite the $A \leftarrow X$ transition in the 4-4 band, chosen by compromise between laser power, wavelength availability and Franck-Condon factors. A counterpropagating beam from a single mode ring dye laser (R6G) then excited the $F \leftarrow A$ transition. A Fizeau wavemeter was used to monitor the two laser beams alternately. The $A \leftarrow X$ excitation could be predicted accurately from constants available in the literature (6). The $F \leftarrow A$ transition was less accurately predicted, and had to be optimised by detecting the strong blue $B \rightarrow X$ cascade emission which was a useful visual signature of the double resonance. Different vibrational levels of the F state were accessed in order to observe all the vibrational levels of $B\ ^1\Pi_u$. Fluorescence was collected on a pierced mirror, and focused on to the entrance aperture of a Bomem Fourier transform spectrometer via an optical fibre. Infrared spectra were recorded at 0.05 cm^{-1} resolution, each recording lasted about 30 minutes. Some corresponding $F \leftarrow A$ spectra were also recorded to locate the $F\ ^1\Sigma_g^+$ energy levels in energy with respect to the well established $A\ ^1\Sigma_u^+$ state. By tuning the two lasers to successive rotational lines of the $F \rightarrow A$ and $A \rightarrow X$ transitions, we measured the broadening of lines as a function of J and v in the $B\ ^1\Pi_u$ state.

Results.

Our complete data set has enabled us to investigate the sequence of last quasibound levels in the $B\ ^1\Pi_u$ state, occurring at increasing J for decreasing v values. The widths of the fluorescence lines observed in transitions to these levels are tabulated in Table I. Some typical $F\ ^1\Sigma_g^+ \rightarrow B\ ^1\Pi_u$ laser induced fluorescence spectra are illustrated in Figure 1 below.

Figure 1: Examples of Fourier transform spectra of the F-B laser induced fluorescence.

Fig. 1a) F-B fluorescence from $v'=9, J'=10$.

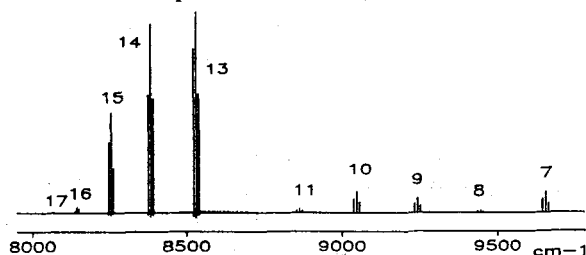


Fig 1b) Fluorescence to $v''=16$ and 17 in $B\ ^1\Pi_u$ from $v'=14, J'=7$, showing broadening of the last three rotational lines.

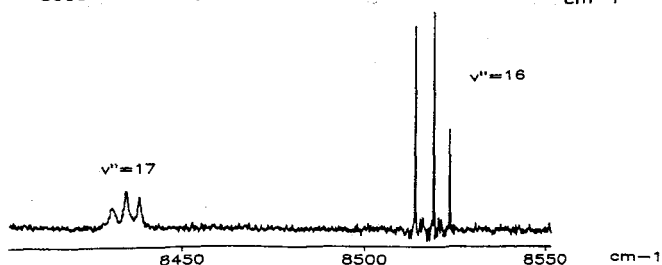


Fig. 1c) In fluorescence excited at $J'=20$, the last observed vibrational level of $B^1\Pi_u$ is $v=16$.

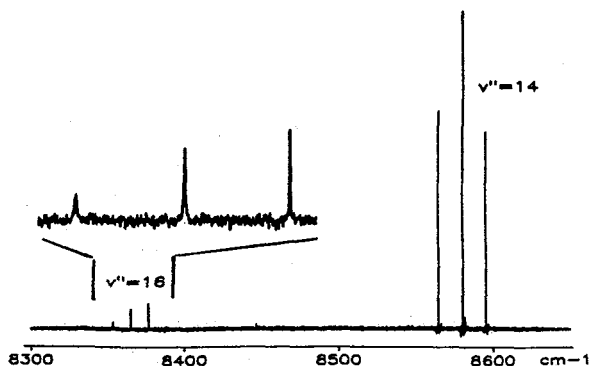


Table I : Observation of the quasibound energy levels of the $B^1\Pi_u$ state.

v	J	$T_{v,J}$	FWHM (obs) (cm^{-1})	FWHM (calc) (cm^{-1})
17	2	3463.72	0.91	0.61
17	3	3465.24	0.85	0.66
17	4	3467.35	1.10	0.74
17	5	3469.58	1.14	0.81
17	6	3472.58	1.23	0.94
17	7	3476.18	1.32	1.12
17	8	3480.10	1.9	1.33
17	9	3484.70	1.9	1.63
17	10	3489.46	1.7	1.97
17	11	3495.06	4	2.51
16	22	3523.96	0.28	0.33
16	23	3536.27	0.70	0.66
16	24	3548.81	1.29	1.26
16	25	3561.26	2.55	2.17

In order to construct as complete a potential energy curve as possible for the $B^1\Pi_u$ state, we exploited data at $J=10$, which covers $v=0-17$ in $B^1\Pi_u$. The $T_{v,J=10}$ energies can be obtained directly from the $Q(10)$ lines for the f levels, which should be unperturbed by interaction with $A^1\Sigma_u^+$, and in order to confine the numerical treatment of this problem to f levels, the effective B_v values at $J=10$ were determined from Q lines from spectra containing $Q(9)$ and $Q(11)$ lines. With G_v and B_v values at $J=10$, an RKR curve at $J=10$ was calculated with the usual RKR routine. By subtracting the centrifugal energy term, $h/(8\pi^2\mu c) \cdot [J(J+1) - \Omega^2]/R^2$ from each point on the the RKR curve at $J=10$, a rotationless potential curve is obtained. The points on the curve no longer correspond to the turning points at integral v . The outermost part of the rotationless potential curve of the $B^1\Pi_u$ state can be described by a potential of the empirical form :

$$U(R, J=0) = D_e + \frac{C_3}{R^3} (1 - e^{-\alpha(R-3\beta)})^3 - \frac{C_6}{R^6} (1 - e^{-\alpha(R-6\beta)})^6 - \frac{C_8}{R^8} (1 - e^{-\alpha(R-8\beta)})^8 - Ae^{-BR} \quad (i)$$

To derive the parameters in this expression, we added the last four points of the ab initio curve from

(5) which represent internuclear distances $7.9 \leq R \leq 15.9$ Å. Our experimental observations thus relate to the inner part of the potential curve, and the additional ab initio points cover the outer part of the potential curve, at R values beyond R_{\max} (5.9 Å). A least-squares fit of points on the potential energy curve from $4.1 < R < 15.9$ Å gives the following parameters for the dispersion and exchange energy terms:

$$\begin{array}{lll} C_3 = 1.81(2) \times 10^5 \text{ cm}^{-1} \text{ Å}^3 & \alpha = 2.09(8) \text{ Å}^{-1} & A = 1.26(2) \times 10^6 \text{ cm}^{-1} \\ C_6 = 7.6(2) \times 10^6 \text{ cm}^{-1} \text{ Å}^6 & \beta = 0.528(4) \text{ Å} & B = 1.489(4) \text{ Å}^{-1} \\ C_8 = 1.8(6) \times 10^7 \text{ cm}^{-1} \text{ Å}^8 & D_e = 2984.22 \text{ cm}^{-1} & \end{array}$$

E_{hump} , the rotationless barrier height, is found to be $500 \pm 3 \text{ cm}^{-1}$. To obtain the long-range part of the potential curve of the $B^1\Pi_u$ state at any J value, the centrifugal term, $h/(8\pi^2\mu c) \cdot [J(J+1)-\Omega^2]/R^2$, must be added to the energy given by (i) at each internuclear distance R .

At a given energy and J value, we can estimate the width of the potential barrier, and also the integral P illustrated by the shaded area in Figure 2, limited by the maximum in the potential curve and the energy of the quasibound level of interest.

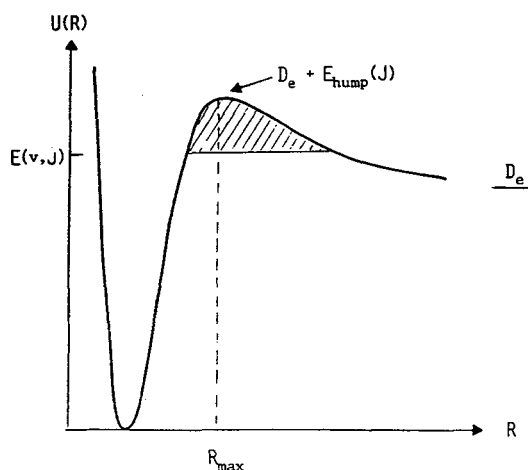


Figure 2 : Form of the potential curve of the $B^1\Pi_u$ state.

Chawla *et al* (7) have shown that the lifetime of the level is given by $1/\tau = P \cdot \partial E(v, J) / \partial v$, and that the full width at half maximum of a fluorescence line terminating on the level with lifetime τ is $2\pi\tau$, in cm^{-1} . From the analytical form of the potential curve in the region of the barrier, we can predict the full width at half maximum for the quasibound levels we have observed (see table I). The agreement is satisfactory except for levels close to the potential maximum. Work is in progress to improve our representation of this part of the curve, because very small errors in either the height of the barrier (E_{hump}) or the shape of the curve, affecting the estimated width of the barrier at a given energy, create large errors in the integral P and thus changing the calculated linewidths.

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