

OBSERVATION OF AN UNGERADE RYDBERG STATE OF $^7\text{Li}_2$

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Some weak, collisionally induced transitions have been observed following excitation of the two lowest vibrational levels of the 5d $^1\Pi_g$ state of $^7\text{Li}_2$ (produced in a heatpipe source). The transitions were recorded in Fourier transform resolved fluorescence spectra in the near infrared (7900 - 8800 cm^{-1}), at an instrumental resolution of 0.08 cm^{-1} , and they have been assigned as transitions from a Rydberg $^1\Pi_u$ state to $v = 0, 1$ and 2 of the $^1\Delta_g$ electronic state. It seems highly likely that the two upper state levels populated through the collisions are $v = 0$ and $v = 1$ of a $^1\Pi_u$ state which lies very close in energy to the 5d $^1\Pi_g$ state. The energy transfer occurs to $v = 0$ of the $^1\Pi_u$ state from $v = 0$ of the 5d $^1\Pi_g$ state, and (at low J only) to $v = 1$ of the $^1\Pi_u$ state from $v = 1$ of 5d $^1\Pi_g$. Six bands were analysed: 0-0, 0-1, 0-2, 1-0, 1-1 and 1-2.

The rotational constants of this $^1\Pi_u$ state are too large to be high levels of the other ungerade Rydberg state of Li_2 documented in the literature, namely the D $^1\Pi_u$ state studied by Theiss and co-workers^b. They are however sufficiently close to those of the 5d $^1\Pi_g$ state ($T_e = 37257.7 \text{ cm}^{-1}$, $B_e = 0.48 \text{ cm}^{-1}$, $\omega_e = 237.4 \text{ cm}^{-1}$) given in earlier work^c, that we suggest the Rydberg state is most likely to correlate at long range with $\text{Li}(2s) + \text{Li}(5p)$ atoms.

Principal spectroscopic constants are $T_0 = 37390.198(5) \text{ cm}^{-1}$, $B_0 = 0.50627(12) \text{ cm}^{-1}$, $\Delta G_v = 262.4 \text{ cm}^{-1}$.

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