MAGNETIC ROTATION STUDY OF THE $A^3\Pi_{1u}$–$X^1\Sigma_g^+$ SYSTEM OF $^{79}Br_2$

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The magnetic rotation spectrum of $^{79}Br_2$ has been measured from 14,988 to 15,488 cm^{-1} using a tunable, cw dye laser (effective linewidth $\sim$ 2 MHz) with DCM dye. The study was carried out using a cell filled to $\sim$6.5 Torr with 99.4% isotopically pure $^{79}Br_2$. Over 5000 transitions (with Doppler width of about 450 MHz) were measured, the majority of which ($>$ 4500) belong to the $A^3\Pi_{1u}$–$X^1\Sigma_g^+$ system of the molecule. The range of upper-state vibrational levels observed ($v' = 13$ to 38) extended very close to the dissociation limit of the A state. With more standard techniques such as absorption or fluorescence, transitions in the A–X system are typically difficult to detect because of much stronger transitions in the same region from the $B^3\Pi_{0^+_u}$–$X^1\Sigma_g^+$ system; the opposite is true for magnetic rotation, due to magnetic activity of the $A^3\Pi_{1u}$ electronic state.

Magnetic rotation signals normally get weaker with increasing J, since the effective g-factor, g_J, decreases as J increases. As a result, magnetic rotation spectra usually give strong signals only for low-J transitions. For the A–X system of Br_2, however, an interference effect between spin-uncoupling and magnetic mixing to other electronic states—primarily the $A'^3\Pi_{2u}$ state—led to the measurement of rotational transitions right up to the breaking-off point (e.g. J = 82 for $v' = 25$). These high-J transitions were comparable in strength with those at low-J. The interference effect manifests itself as the addition to g_J of a term that increases with J.

Structure observed in low-J transitions has been attributed to hyperfine effects in the A state. Transitions to quasi-bound levels above the dissociation limit of the A state appear to suffer from strong, systematic perturbations, likely due to interaction with a dissociative state. Perhaps the most interesting feature of the spectrum is a series of extra lines tentatively identified as belonging to the $A'^3\Pi_{2u}$–$X^1\Sigma_g^+$ system, the result of intensity-borrowing from near-resonant perturbations with the A state $v' = 27$ rotational levels $2 \leq J \leq 31$.

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