Assignment of Resonance Fluorescence Series in Molecular Iodine through Circular Polarisation of Emission

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Summary We report the circular polarisation of the resonance fluorescence of iodine vapour excited by circularly polarised 5017 Å argon laser radiation; the high polarisation ratios indicate that the features are all coincidentally excited and this enables the identification of the levels lying under the gain curve of the 5017 Å line.

THE laser-induced resonance fluorescence of iodine vapour is of considerable current interest[1,2]. We demonstrate here the value of measurements of circular polarisation of emission in assigning the molecular levels excited by a particular line.

TABLE

Assignment of levels excited by 5017 Å line

Vibronic level	Molecular excitation	Fluorescence peak	
61	$P(12)$	$R(10)$	
61	$R(13)$	$P(15)$	
62	$P(25)$	$R(23)$	
62	$R(26)$	$P(28)$	
64	$R(39)$	$P(41)$	
67	$R(49)$	$P(51)$	Not resolved
70	$R(54)$	$P(56)$	
71	$R(55)$	$P(57)$	
77	$R(75)$	$P(75 \pm 1?)$	

Rotational quantum numbers are of the ground state in all cases. Vibrational quantum numbers indicate excited state values.

We have recently[3] shown that the resonance fluorescence of iodine excited by circularly polarised light consists generally of P,R doublets separated by $4B_v''(J'' + \frac{1}{2})$ with mutually opposite circular polarisations. It is therefore straightforward to identify the components of a complex emission spectrum from the signs of their circular polarisation and these may be assigned using molecular constants obtained from the rotational analysis of the $^1\Sigma_g^+$, $^3\Pi_{0_u}^+$ ground and excited states.[4]

The figure shows the emission ($I_+ + I_-$) and circular polarisation spectra ($I_+ - I_-$) of the first Stokes band of iodine at 230 mTorr pressure excited by the 5017 Å line of an argon ion laser. The sign of circular polarisation of the laser radiation is indicated in the Figure. At this pressure the resonance fluorescence process dominates the Stokes emission, though some contribution from a resonance Raman effect may be present.[5] The circular polarisation ratio c [$=(I_+ - I_-)/(I_+ + I_-)$] is *ca.* ±0·7 for all bands shown and strongly indicates a fluorescence process. The fact that *all* lines show approximately this value for c means that these are all coincidentally excited by the 5017 Å line and do not arise from states populated by inelastic collisions. Lines originating from collisionally populated levels are less strongly polarised.[6]

The strongest spectral line in the Figure is the superposition of fluorescence from those levels excited directly, each returning to the ground level. This retains the sign of input circular polarisation. The remaining lines arise from transitions according to the selection rule $\Delta J = \pm 1$ and their varying separations from the true resonance line reflect the molecular constants for the particular levels involved. These lines have opposite circular polarisation to the exciting radiation. Using the spectroscopic constants of Barrow and Yee[4] we have calculated the spectrum of I_2 in the region of 5017 Å and a number of coincidences are likely. These are shown in the Table. The two prominent lines $P(28)$, $P(41)$ are well characterised[2] and $P(51)$ has been recognised recently.[7] The remainder are reported here for what appears to be the first time.

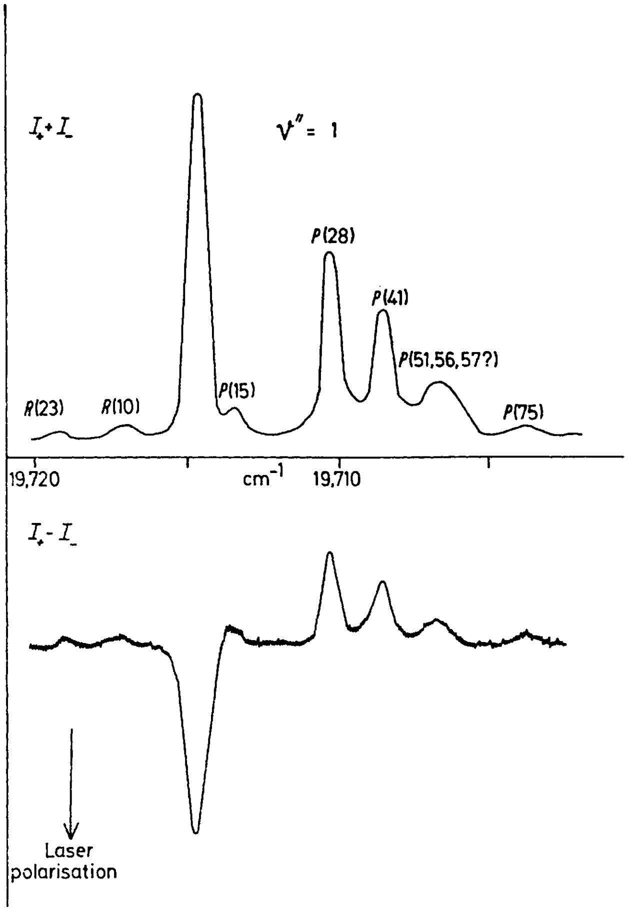

FIGURE. Emission spectrum ($I_+ + I_-$) and circular polarisation ($I_+ - I_-$) of iodine vapour at 230 mTorr pressure excited by the 5017 Å line of Ar$^+$.

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