INTERCOMBINATION TRANSITIONS BETWEEN LEVELS $X^1\Sigma_g^+$ AND A $^3\Pi_u$ IN C_2.

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ABSTRACT. We present a new calculation of intercombination transition probabilities between levels $X^1\Sigma_g^+$ and a $^3\Pi_u$ of the C_2 molecule. Starting from experimental energy levels, we calculate RKR potential curves using Leroy's Near Dissociation Expansion (NDE) method ; these curves give us wave functions for all levels of interest. We then compute the energy matrix for the four lowest states of C_2, taking into account Spin-Orbit coupling between a $^3\Pi_u$ and A $^1\Pi_u$ on the one hand and X $^1\Sigma_g^+$ and b $^3\Sigma_g^-$ on the other. First order wave functions are then derived by diagonalization. Einstein emission transition probabilities of the Intercombination lines are finally obtained.

Electric dipole transitions between levels $X^1\Sigma_g^+$ and a $^3\Pi_u$ of C_2 can occur through spin-orbit coupling of a $^3\Pi_u$ with A $^1\Pi_u$ and of $X^1\Sigma_g^+$ with b $^3\Sigma_g^-$. The A $\leftrightarrow$ a coupling had already been considered in the literature at least qualitatively (see for exemple Van Dishoeck and Black 1982 or Lambert and Danks 1983) but not the X $\leftrightarrow$ b coupling which is nonetheless of the same order of magnitude as the other.
The Einstein emission transition probability is given by the usual formula :

$$A_{v'J',v''J''} = \frac{(64\pi^4)}{3h} . \sigma^3 . \left(\frac{1}{2J'+1}\right)$$

$$\left| <^1\Sigma_{g\,0}^+ ;J';v';e\right| \, D \left|^3\Pi_{u,|\Omega|};J'';v'';{}^e_f> \right|^2 \; , \qquad (14)$$

here σ is the wave number of the transition in cm^{-1}, and D stands for the electric dipole moment operator of either the singlets or the triplets. Due to the homonuclear nature of the molecule, $^1\Sigma_g^+$ has only even values of J (e states), and so the transition occurs with an e state of $^3\Pi$ when $\Delta J = 0$ and an f state when $\Delta J = \pm 1$.
Each first-order wave-function for X $^1\Sigma_g^+$ or a $^3\Pi_u$ is a linear combination of both singlet and triplet zero-order wave-functions of different Ω values. And hence the rotational factors do not factorise

TABLE 1 : $X\ ^1\Sigma_g^+ \rightarrow a\ ^3\Pi_{u,1}$ transitions. Radiative lifetimes (s).

Author v'		1	2	3	4
V.D. & B.		33	5,9	2,4	1,3
L. & D.		2300	330	130	75
P.	J'=0	1075	175	77	45
	J'≠0	714	116	50	30
L.B. & R.	J'=0	725	133	63	41
(a)	<J'≠0>	684	130	62	43
L.B. & R.	J'=0	565	559	6,7	5,8
(b)	<J'≠0>	530	557	6,1	5,7

TABLE 2 : $a\ ^3\Pi_{u,1} \rightarrow X\ ^1\Sigma_g^+$ transitions. Radiative lifetimes (s).

Author v'		0	1	2	3	4	5
V.D. & B.		3.3 (5)−0.5	1000−16,7	333−5,9	167−3,3		
L. & D.	(Ω'=1)	1.8(5)	460	160	75	60	30
P.	(Ω=0) <J>	7.4(5)	1890	663	373		
	(Ω=1) <J>	1.6(5)	368	125	71		
	(Ω=2) <J>	11.4(5)	2500	870	479		
L.B. & R.	Ω=0	6.4(5)	1910	733	423	361	404
(a)	Ω=1	1.4(5)	372	139	78	66	72
	Ω=2	10.0(5)	2570	966	554	470	524
L.B. & R.	Ω=0	7.0(5)	1510	1550	227	317	793
(b)	Ω=1	1.5(5)	293	295	37	58	142
	Ω=2	11.1(5)	2020	2070	260	414	1040

as usual and we cannot use classical Hönl-London formulae. We must know the sign of each rotational factor before performing the summation and only after that can we take the square of the integral (which is not at all the same as a sum of squares).

Tables 1 and 2 compare our results (L.B. & R. |(a) : $^3\Sigma_g^-$ neglected (b) : full interaction) with those of Van Dishoeck and Black (V.D. & B.), Lambert and Danks (L. & D.) and Pouilly (P.).

Pouilly's computation neglects the effect of the b state ; with the same approximation, we get results compatible to within 10 to 20% to her's (which is quite good, since we did not have the same potentials). She explains the factor of 20 (for the $X \to a$ transition) between her results and V.D. & B.'s by the fact that her computation leads to an equivalent $|\Sigma R_e|^2$ of 10^{-6} au when V.D. & B. choose 2.10^{-15} au. As we reproduce her results, the argument holds for us also. We can see that L. & D.'s results are remarkably near ours, without $b^3\Sigma_g^-$, for the $a \to X$ transition while there is a discrepancy of a factor of 2 for the $X \to a$ transition.

In comets, the equilibrium is governed by the fluorescence led by the solar radiation field. Since quadrupole transitions inside the $X^1\Sigma_g^-$ state can be neglected (V.D. & B.), we expect that intercombination transitions, which depopulate high v levels, will lower the excitation temperature.

References

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