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Analyse de la bande (0,1) de la transition $d^3\pi_g$<--- $a^3\pi_u$ du système Swan de la molécule C_2

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ABSTRACT

Analysis of the (0,1) band of the Swan system of the $d^3\pi_g$←$a^3\pi_u$ system of the C_2 molecule

A study of the C_2 radical using optical heterodyne magnetic rotation enhanced concentration modulation spectroscopy (OH-MR-CMS) technique in the visible region has been carried out. The C_2 radical was produced in an AC glow discharge of acetylene (C_2H_2) buffered with argon (Ar) gas. The vibrational (0,1) band of the C_2 molecule Swan $d^3\pi_g$←$a^3\pi$ electronic transition in the visible region between 17730-17900 cm-1 was scanned and rotationally analyzed. Molecular constants of the C_2 Swan system in the lower vibration state (0,1) transition were derived. Compared to the latest data from the literature, rotational constants are in good agreement, whereas band constants relatives to Λ-doubling splitting of ³π states display discrepencies.

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INTRODUCTION

Carbon radical is preeminent in molecules of great astrophysical significance. The swan $d^3\pi_g$←$a^3\pi_u$ system of the C_2 molecule is responsible of very intense visible bands observed in the heads of some comets [MAYER et al., 1968; LAMBERT et al., 1983; GREDEL et al., 1989]; in the spectra of the sun [BROULT et al., 1982] and in stellar atmosphere [QUERCY et al., 1971; GOEBEL et al.,1983]. The state is believed to be the ground electronic state and the energy difference between the and the states was determined as 720.0087(21) cm^{-1} for the potential minima [CHEN et al., 2015] and 613.650 (3) cm^{-1} for the $\nu=0$ level with MERER and BROWN's Hamiltonian for states [MERER AND BROWN, 1979, BRAZIER et al.,1986]

Experimental spectroscopy of the C_2 molecule emission lines began as early as two centuries ago; a historically survey of the works on this molecule has been provided [TITE et al., 1967; HUBER AND HERZBERG, 1979], and 35 bands of the Swan system have been recorded [PHILIPS AND DAVIS, 1968].

Recently, due to great improvements in performances of laboratory equipment in sensitivity, and detectivity, the C_2 molecule has been restudied in high resolution. As a result, more complete and accurate data are now available. Fourier transform emission spectroscopy (FTS) has been used intensively [AMIOT, 1983; PRASAD AND BERNATH, 1994; LLOYD AND EWART,1999; TANABASHI AND AMANO, 2002,BROCKHINE et al., 2006;TANABASHI et al., 2007; BROOKE et al.,2013; RAM et al., 2014]; for very high resolution studies, laser spectroscopy techniques have also been utilized [KANIKI et al.,2003; ZHANG et al., 2004; TULY et al.,2010; BORNHAUSER et al., 2010; FURTENBACHER et al., 2016]. Many news bands of the molecule are discovered as time passed [NAKAJIMA et al., 2009; NAKAJIMA et al., 2013]. Furthermore, an electronic database of diatomic molecules has been

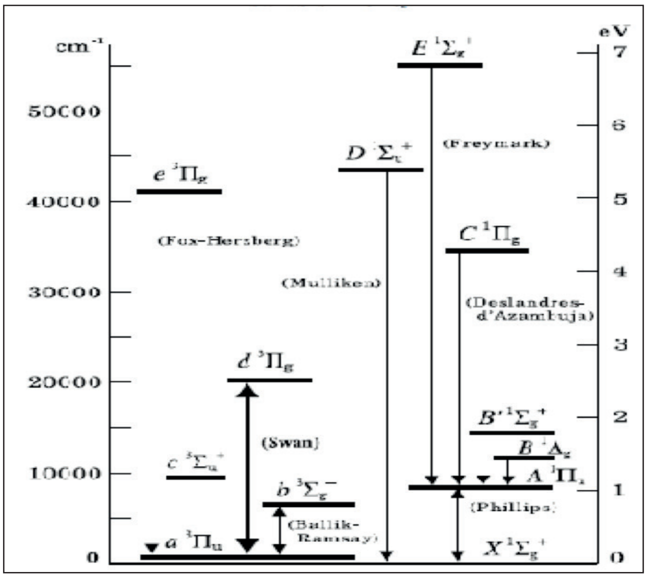

Figure 1| Low-laying electronic states of below 30.000 Cm^{-1}. [TANABASHI et al., 2007]

compiled, providing a very abundant set of literature on the C_2 molecule [BERNARTH AND MCLEAD, 2001]. Currently, the C_2 molecule plays an increasing role in understanding combustion processes.

In this paper, we present the laser based absorption spectral analysis of the (0,1) vibrational band of the Swan system of the C_2 molecule forming band head at 17739.749 cm^{-1}. The optical heterodyne magnetic rotation concentration modulation spectroscopy (OH-MR-CMS), a well-known high sensitive spectroscopic technique for detecting transient species [MING et al.,2001], is used to successfully observe the spectra.

The $d^3\pi_g \leftarrow a^3\pi_t$ transition was rotationally analyzed by using the matrix elements of the effective Hamiltonian [AMIOT et al.,1978; MERER AND BROWN, 1979; BRAZIER et al.., 1986] and a set of molecular constants for the $b^3\pi_g$ and $a^3\pi_u$ states is determined.

EXPERIMENTAL DETAILS

The OH-MR-CMS spectrometry has been described with details [WANG et al.,1999; MING et al., 2001; WU et al., 2005, WU et al., 2014; WANG et al., 1999, WU et al., 2001], only aspects relevant to the study of the C_2 radical will be described. The C_2 radical was generated in a 37 KHz AC glow discharging absorption cell by a series of reactions resulting from the electric discharge through a mixture of acetylene (C_2H_2) and Argon (Ar) gas. The cell was cooled by running water and an electrical current up to 200 mA with peak to peak of 37 KHz was used.

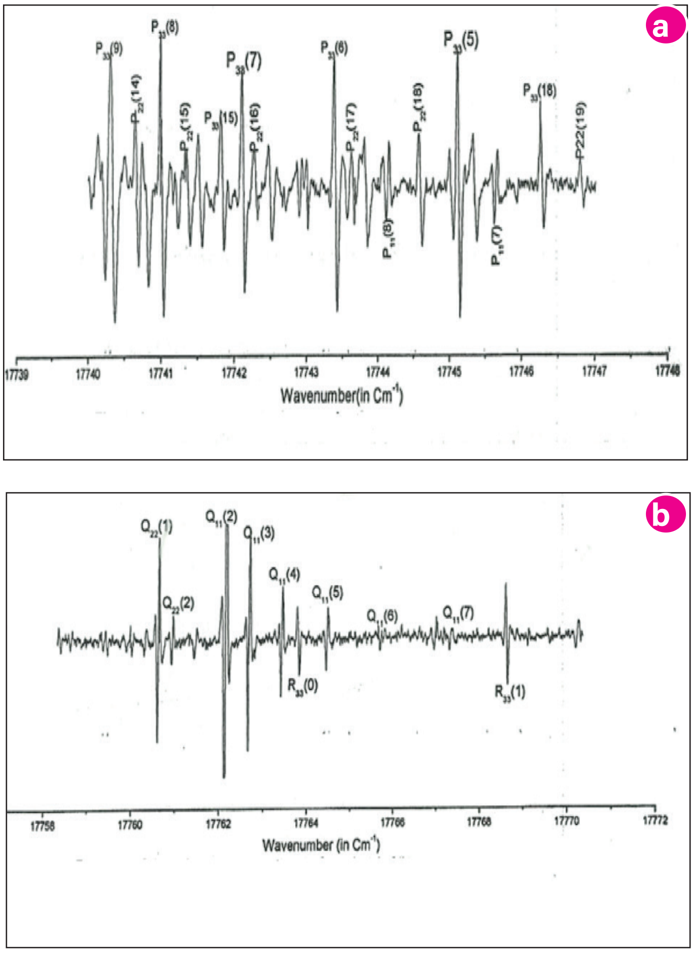

Figure 2| The relative branches of C_2 molecule Swan system: the *P* branch **(a)** and the *Q* branch **(b)**

Table 1| Observed transition wavenumbers [a,b] of the P branch of the (0,1) band (in cm^{-1})

J	P_{11}	P_{22}	P_{33}
1			
2			
3	17753.846(2)		
4	17751.349(-8)	17749.336(11)	17747.083(2)
5	17749.349(1)	17747.263(-7)	17745.121(-2)
6	17747.386(-8)	17745.344(2)	17743.398(1)
7	17745.633(4)	17743.827(-11)	17742.119(-4)
8	17744.126(1)	17742.486(-1)	17741.012(1)
9	17742.385(-4)	17741.530(-7)	17740.337(-3)
10	17741.884(1)	17740.76(3)	17739.809(3)
11	17741.711(3)	17740.761(-5)	17739.708(0)
12	17740.711(-3)	17740.363(-5)	17739.727(20)
13	17740.559(-10)	17740.313(-5)	17740.215(-4)
14	17740.532(-1)	17740.667(0)	17740.810(-3)
15	17741.013(15)	17741.367(0)	17741.832(1)
16	17741.662(-5)	17742.286(4)	17742.991(-9)
17		17743.537(-3)	17744.569(-9)
18		17745.026(-5)	17746.269(0)
19	17745.321(-2)	17746.803(12)	17748.422(0)
20	17747.049(-10)	17748.858(5)	17750.673(-8)
21	17749.137(-2)		17753.272(6)
22	17751.409(-3)		
23			
24	17756.874(1)		

[a] In P-branch, the spectral lines with odd J values represent e-e transition and those with even J values represent f-f transitions.
[b] The numbers in parentheses indicate (obs.-calc.)x10^{-3} in cm^{-1}.

The detection of the laser absorption signal was performed with an avalanche photodiode (APD) demodulated by a double balance mixer (DBM) at 480 MKz and amplified by a digital display lock-in amplifier (Model Stanford Research System (SRS) 850). The signal was processed by a computer system using coherent autoscan software associated to the laser system. The laser system used was a ring dye laser (coherent 899-29 autoscan) using Rhodamin-6G as a gain medium pumped by 6~7 W of 532 nm light from a CW compact diode laser head (coherent Verdi-10). The laser system was equipped with a computer controlled wavelength-meter that was able to be turned to any desired wavelength within the dye range frequency. The visible region between 17730-17900 cm^{-1} was scanned and a rich spectra was assigned to the vibrational (0,1) band of the swan system of the C_2 molecule. Many unidentified lines were also recorded. The spectral lines were calibrated using laser absorption lines of iodine (I_2) [GESTENKORN AND LUC, 1978] which were simultaneously recorded with the C_2 lines. The absolute accuracy of the C_2 lines was estimated to ± 0.007 cm^{-1} for strong unblended lines, this accuracy was degraded for blended lines and weak's ones. Portions of the recorded spectra are shown in **Figures 1** and **2**. It can be confirmed that the spectrum is from neutrals species. Indeed, signals are observed when demodulated at 2f and line profile is of the 3rd derivative of Gaussian profile. For the , only symmetric states obtained on interchange of the equivalent nuclei are allowed. As a result, only e-levels are possible for even-J and f-levels for odd-J in the state, and vice-versa in the state [HERZBERG, 1950].

Furthermore, the relative spectral phase of R branches is the opposite of that of P branches due to the Faraday Effect. Once manually selected, this lead to a clear pattern represented in **Figures 2**.

ANALYSIS AND ASSIGNMENT

The AC glow discharge in the C_2H_2 buffered by Ar gas could lead to different species of molecules such as C_2, H_2, CH; even to ionic molecules such as C^{2+}, H^{2+},all of which are candidate molecules and could explain the congested spectra obtained. In spite of this fact, strong and clear 3rd derivative Gaussian profiles were distinctive and could be picked manually. Parts of these spectra are shown in **Figure 2**.

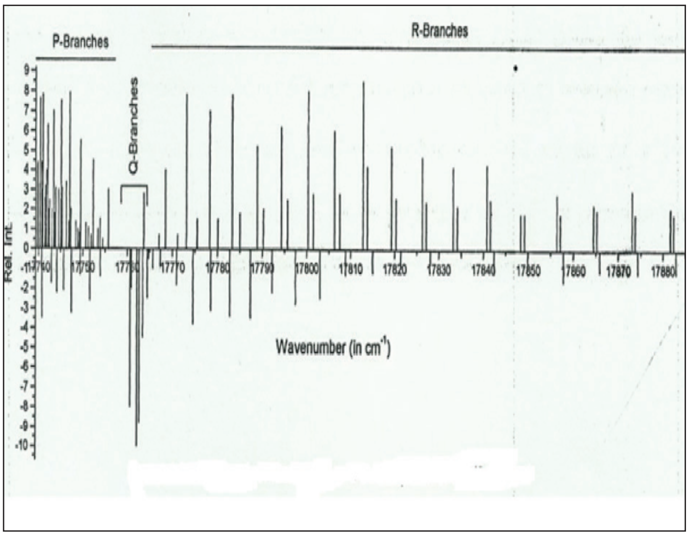

Figure 3| Bar graph of the C_2 molecule Swan system (0,1) band

The Swan system of the C_2 molecule is a $\mathbf{b^3\pi_g \leftarrow a^3\pi_e}$ electronic transition with each state obeying Hund's case (b) coupling at high J-values, but Hund's case (a) still a good approximation at low J-values. It is predicted that in such $\mathbf{a^3\pi - {}^3\pi}$ transition, six strong rotational branches three P and three R branches arising from transitions with $\mathbf{\Delta J = \pm 1}$ between $\mathbf{3\pi - 3\pi}$[F3], ${}^3\pi - {}^3\pi$[F2] appear and ${}^3\pi - {}^3\pi$[F1] substrates labeled as F3, F2 and F1(in brackets), also two weak rotational Q branches are expected [HERZBERG, 1950].

These predictions matched well the spectrum in **Figure 2** and enabled the assignment as P, Q and R branches. The whole spectrum is shown in **Figure 3**.

The branch head position, the line spacing and the phase characteristic made it simple to identify the P and R branches and confirm the rotational assignment for each bands. The assignments and transition wavelengths agree well with those from the literature [PHILIPS AND DAVIS, 1986; T. AMANO et al., 2007; BROOKE et al., 2013].

Table 2| Transition wavenumbers[a,b] of Q-branch of the (0,1) Band (in cm^{-1})

J	Q11	Q22
0		
1		17760.644(6)
2	17762.144(5)	17760.951(-2)
3	17762.686(-1)	
4	17763.433(0)	17762.686(6)
5	17764.471(4)	
6	17765.718(-1)	
7	17767.338(-3)	
8		
9		
10		
11		

[a] In the R-branch, the spectral lines with odd j-values represent e—e transitions and those with even J values represent f—f transitions.
[b] The numbers in parentheses indicate (obs.-calc.)x 10^{-3} in cm^{-1}

Table 3| Transition wavenumbers[a,b] of R-branch of the (0,1) Band (in cm^{-1})

J	R11	R22	R33
0			17763.813(4)
1			17768.623(-6)
2	17770.985(1)		17773.213(3)
3	17774.607(-1)		17778.433(4)
4	17778.555(2)		17783.418(-1)
5	17782.818(-5)	17785.085(-4)	17789.014(-1)
6	17787.415(1)	17790.347(4)	17894.451(2)
7	17792.325(-3)	17795.802(-3)	17800.467(15)
8	17797.552(1)	17801.580(-1)	17810.642(5)
9	17803.089(-1)	17807.564(13)	17812.931(0)
10	17808.914(3)	17813.879(-2)	17819.394(0)
11	17815.064(-4)	17820.413(-1)	17826.411(-4)
12	17821.459(3)	17827.246(-1)	17833.399(-2)
13	17828.202(-4)	17834.316(-2)	17840.936(-4)
14	17835.157(1)	17841.695(-5)	17848.457(-4)
15	17842.478(-1)	17849.292(6)	17856.519(1)
16	17849.983(1)	17857.226(-9)	17864.575(-3)
17	17857.878(1)	17865.350(6)	17873.181(-4)
18	17865.918(7)	17873.845(-19)	17881.769(-10)
19	17874.382(10)	17882.483(12)	17890.891(17)
20		17891.526(-9)	

The entire line material was fitted to the model of the effective Hamiltonian [AMIOT et al.,1978; AMANO et al.,

Table 4| The molecular constants of the C_2 molecule swan system in the lower state (ν=1) and upper state (ν=0) in (cm^{-1})

	$a^3\pi_u(v=1)$		$d^3\pi_g(v=0)$	
Parameter	This work	Ref.[Brooke et al. 2013]	This work	Ref.[Brooke et al. 2013]
T_v	0.0	1618.02244(53)	17760.428038(18)	19378.46749(51)
A_v	17.25111(19)	-15.26986(43)	-13.99065(18)	-14.00139(63)
$A_{Dv}x10^4$	-17.02(11)	2.266(73)	5.276(20)	5.068(23)
B_v	1.60743232(81)	1.6074266(44)	1.74555145(83)	1.7455663(43)
D_vx10^6	6.5785(13)	6.4439(21)	6.9270(14)	6.8205(16)
Q_vx10^4	4.7732(39)	-5.772(42)	-6.3130(39)	-7.752(43)
P_vx10^3	-0.5020(24)	2.705(44)	1.3991(48)	3.973(43)
Q_v	0.645379(96)		0.590099(60)	
λ_v	-0.16367(97)	-0.15373(51)	0.03206(10)	0.03301(47)
$\lambda_{Dv}x10^4$	-0.4486(70)		-0.4974(64)	
Υ_v	0.011473(68)		0.00014611(94)	

Numbers in parentheses indicate one standard deviation to the last significant digits of the constants.

2007; BROOKE et al., 2013] where the matrix elements were described in detail. The molecular constants of the $\mathbf{b^3\pi_g}$ state, the most precise up to date, reported in this reference were fixed at values of the above references.

The lines in the least square were weighted in a fitting procedure which provide a set of derived precise molecular constants for the **ν=0** level of the $\mathbf{a^3\pi_u}$ state and the **ν=1** level of the $\mathbf{b^3\pi_g}$

CONCLUSION

A part of the visible spectra of the C_2 molecule between 17730-17900 cm^{-1} has been recorded in absorption from an AC glow discharge in acetylene buffered by argon gas using optical heterodyne magnetic rotation concentration modulation spectroscopy.

The spectra assigned as the Swan system $\mathbf{\nu=1, b^3\pi_g \leftarrow a^3\pi_u, \nu=0}$ of the C_2 molecule was rotationally analyzed using the matrix elements of the effective Hamiltonian of AMIOT et al. [1978].

A set of precise molecular constant for the **ν=0** level of the $\mathbf{a^3\pi_u}$ state and the **ν=1** level of the $\mathbf{b^3\pi_g}$ state were obtained and compared to the more precise one from the more recent presented in the literature. Rotational constants **Bv** and **Dv** are consistent to those from the literature. Whereas band constants relative to the **Λ**-doubling splitting parameters of the $^3\pi$ states are differents.

These high order approximation constants have been let freely floating in our fitting procedure, they introduce little error and don't impact on the quality of the fit.

Résumé

La technique « optical heterodyne magnetic rotation enhanced concentration modulation spectroscopy (OH-MR-CMS) » est utilisée pour étudier le radical C_2 dans le visible. Le radical C_2 est produit dans une décharge électrique au sein d'un tube ou l'on fait circuler simultanément l'acétylène (C_2H_2) et l'argon (Ar). La bande (0,1) de la molécule C_2 Swan système $d^3\pi_g \leftarrow a^3\pi_u$ de la transition électronique dans le visible entre 17730-17900 cm^{-1} a été scannée et analysée rotationnellement. Les constantes moléculaires du système Swan du radical C_2 dans l'état bas de la transition (0,1) ont été obtenues et comparées aux données les plus récentes de la littérature. Les constantes rotationnelles s'accordent bien; tandis que des écarts assez significatifs apparaissent pour les constantes des bandes relatives au dédoublement-Λ des états $^3\pi$...

Mots clés : *Swan system du radical C_2, OH-MR-CMS, Constantes moléculaires, dédoublement-Λ.*

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