LABORATORY STUDIES ON COMETARY MOLECULES

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Abstract. We show results for some new bands of C_2, CN, N_2^+, CO^+, NH, OH, and CH hitherto unidentified, but expected to be present in the spectrum of comets by the analysis of Franck-Condon factors. Vibrational transition probabilities, Franck-Condon factors have been evaluated by an approxximate analytical method for the A–X system of C_2, A–X, and B–X systems of CN, B–X system of N_2^+, A–X, and B–A systems of CO^+, A–X system of NH and A–X system of OH.

1. Introduction

One of the most exciting recent developments in astronomy has been the discovery of cometary molecules. They were detected by searching for spectral lines at appropriate wavelengths.

The importance of the laboratory molecular spectra in view of its relevance to many astrophysical problems involving the estimation of the physical conditions (viz. temperature, pressure, density and abundance) of the emitter in the various cosmic sources (i.e., stellar atmosphere, aurora, night sky and compact objects such pulsars, neutron stars and black holes) from the relative intensities of the bands of a molecule and radical, it is necessary to have a theoretical knowledge of the corresponding vibrational transition probabilities for the respective band heads in a band system. The data available in the literature of C_2, CN, N_2^+, CO^+, NH, OH, and CH has been given by Singh and Chaturvedi (1986).

The vibrational bands at appropriate wavelengths of C_2, CN, N_2^+, CO^+, NH, OH, and CH were observed in the spectrum of comet by Sivaraman (1973) are listed in Table I.

We present an analysis of vibrational transition probabilities of the (A–X) system of C_2, (A–X) and (B–X) systems of CN, (B–X) system of N_2^+, (A–X) and (B–A) systems of CO^+, (A–X) system of NH, (A–X) system of OH and (A–X) and (B–X) systems of CH.

2. Excitation Process

The cometary spectra in the visible and ultraviolet regions are dominated by emission lines (Swings and Haser, 1956; Smith *et al.*, 1980; Feldman and Brune, 1976). The observed intensity pattern in comet depends upon the Sun-Comet distance. It was also found that the details of the intensity pattern observed in two

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comets are quite different in that certain lines were almost absent in one comet while it is strong in the other comet. The emission lines observed arise mostly from the ground electronic state of the molecule, which involve much energy for the excitation of the emission line. This indicates that the excitation of the bands and lines has to be related to the absorption of solar radiation.

All the observed characteristics of the emission lines can be explained by a simple physical process, called the resonance fluorescence process, as was shown in detail by Swings (1941). The absorption of solar radiation in their resonance transitions populates the upper levels, which then trickle down, giving rise to the emission lines. The population in the upper levels depends on the energy available at the wavelength under consideration. The emission bands and lines of molecule and radical depends on the corresponding transition probabilities within a band system (Singh and Chaturvedi, 1986b).

TABLE I

Vibrational bands in the comet from Sivaraman (1973)

Molecule	Transition	Wavelength (Å)	Band
C_2	$A^3\Pi_g \rightarrow X^3\Pi_u$	6677	(0, 3)
		6191	(0, 2)
		5635	(0, 1)
		5165	(0, 0)
		4737	(1, 0)
		4383	(2, 0)
CN	$A^2\Pi \rightarrow X^2\Sigma$	8106	(3, 1)
		7906	(2, 0)
	$B^2\Sigma \rightarrow X^2\Sigma$	4216	(0, 1)
		3883	(0, 0)
		3590	(1, 0)
N_2^+	$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$	3914	(0, 0)
CO^+	$A^2\Pi \rightarrow X^2\Sigma$	4543–4568	(1, 0)
		4250–4270	(2, 0)
		4000–4024	(3, 0)
		3781–3800	(4, 0)
	$B^2\Sigma \rightarrow A^2\Pi$	3951–3983	(0, 0)
		3726	(1, 0)
NH	$A^3\Pi - X^3\Sigma$	3360	(0, 0)
OH	$A^2\Sigma^+ - X^2\Pi$	3140	(1, 1)
		3090	(0, 0)
CH	$A^2 - X^2\Pi$	4310	(0, 0)
	$B^2\Sigma^- - X^2\Pi$	3920	(0, 0)

3. Franck-Condon Factors

Franck-Codon factors play a major role in determining the intensities of electronic transitions of molecules and radicals. The relative intensities of the vibrational bands within a band system of a diatomic molecule are mainly controlled by the population distribution over the vibrational levels and by the Franck-Codon factor

$$q_{v',v''} = \left| \int \Psi_{v'} \Psi_{v''} \, dr \right|^2,$$

where v' and v'' are the vibrational quantum numbers of the upper and lower electronic states, respectively, $\Psi_{v'}$ and $\Psi_{v''}$ are the vibrational eigenfunctions, and r is the internuclear distance. FCF have been calculated for a Morse (1929) model by using a method of Fraser and Jarmain (1953). We have determined FCF for band systems for which data on relative intensities of band heads were available from Pearse and Gaydon (1963). The FCF for different bands of molecules are shown in Tables II, III, IV, V, VI, VII, VIII, and IX. The FCF for the (A–X) system of CH

TABLE II

Franck-Codon factors for the ($A^3\Pi_g \rightarrow X^3\Pi_u$) system of C_2

Wavelength (Å)	Band	Franck-Condon Factors	Additional band in comet
6677.3	(2, 5)	0.0404	–
6599.2	(3, 6)	0.0404	–
6533.7	(4, 7)	0.0807	Yes
6480.5	(5, 8)	0.0807	Yes
6442.3	(6, 9)	0.0807	Yes
6191.2	(0, 2)	0.1211	–
6122.1	(1, 3)	0.1614	Yes
6059.7	(2, 4)	0.1211	Yes
6004.9	(3, 5)	0.1211	Yes
5958.7	(4, 6)	0.0807	Yes
5923.4	(5, 7)	0.0404	–
5635.5	(0, 1)	0.3228	–
5585.5	(1, 2)	0.3228	Yes
5540.7	(2, 3)	0.2421	Yes
5501.9	(3, 4)	0.1614	Yes
5470.3	(4, 5)	0.0807	Yes
5165.2	(0, 0)	0.4036	–
5129.3	(1, 1)	0.2421	Yes
5097.7	(2, 2)	0.0404	–
4737.1	(1, 0)	0.3632	–
4715.2	(2, 1)	0.3228	Yes
4697.6	(3, 2)	0.2825	Yes
4684.8	(4, 3)	0.1614	Yes
4678.6	(5, 4)	0.0807	Yes
4668.7	(6, 5)	0.0404	–
4382.5	(2, 0)	0.0807	–
4371.4	(3, 1)	0.1614	Yes
4365.2	(4, 2)	0.2018	Yes

have been calculated by Pathak (1967) and Garland and Crosley (1985) and FCF for the (B–X) system of CH has been calculated by Garland and Crosley (1985) are shown in Tables X and XI.

4. Discussion

The difference between wavelengths observed by Sivaraman (1973) and laboratory wavelengths for (A–X) system of C_2, (B–X) system of CN, (B–X) system of N_2^+ and (A–X) system of NH are not large; the difference in wavelengths for (A–X) system of CN, (A–X) and (B–A) systems of CO^+, (A–X) system of OH and (A–X) and (B–X) systems of CH occasionally have relatively large values.

Our results are presented in last column of Tables II to XI indicate that the respective band heads could also be present, since the corresponding transition probabilities are appreciable.

TABLE III
Franck-Condon factors for the ($A^2\Pi \rightarrow X^2\Sigma$) system of CN

Wavelength (Å)	Band	Frank-Condon factors	Additional band in comet
14610	(1, 2)	0.1659	Yes
14201	(0, 1)	0.3317	Yes
11247	(1, 1)	0.0829	–
11009	(0, 0)	0.8293	Yes
9392.5	(2, 1)	0.3317	Yes
9198.1	(1, 0)	0.5805	Yes
8067	(3, 1)	0.6635	–
7915.3	(2, 0)	0.8293	–
6961.0	(9, 5)	0.0829	–
6954.3	(3, 0)	0.1659	Yes
6817.6	(8, 4)	0.1659	Yes
6656.6	(7, 3)	0.7464	Yes
6502.3	(6, 2)	0.8293	Yes
6456.4	(11, 6)	0.0829	–
6355.1	(5, 1)	0.7464	Yes
6301.2	(10, 5)	0.0829	–
6213.8	(4, 0)	0.3317	Yes
6153.5	(9, 4)	0.2488	Yes
6012.5	(8, 3)	0.4976	Yes
5877.6	(7, 2)	0.7464	Yes
5748.7	(6, 1)	0.5805	Yes
5728.5	(11, 5)	0.0829	–
5625.0	(5, 0)	0.1659	Yes
5615.7	(10, 4)	0.2488	Yes
5490.2	(9, 3)	0.4147	Yes
5365.0	(8, 2)	0.3317	Yes
5254.9	(7, 1)	0.2488	Yes
5129.7	(6, 0)	0.0829	–
5043.1	(10, 3)	0.0829	–
4949.1	(9, 2)	0.1659	Yes

TABLE IV

Franck-Condon factors for the ($B^2\Sigma \rightarrow X^2\Sigma$) system of CN

Wavelength (Å)	Band	Franck-Condon factors	Additional band in comet
4606.1	(0, 2)	0.0094	–
4578.0	(1, 3)	0.0187	–
4553.1	(2, 4)	0.0187	–
4531.9	(3, 5)	0.0187	–
4514.8	(4, 6)	0.0187	–
4502.2	(5, 7)	0.0187	–
4216.0	(0, 1)	0.0843	–
4197.2	(1, 2)	0.0750	Yes
4181.0	(2, 3)	0.0656	Yes
4167.8	(3, 4)	0.0562	Yes
4158.1	(4, 5)	0.0469	–
4152.4	(5, 6)	0.0375	–
3883.4	(0, 0)	0.0937	–
3871.4	(1, 1)	0.0843	Yes
3861.9	(2, 2)	0.0750	Yes
3854.7	(3, 3)	0.0562	Yes
3850.9	(4, 4)	0.0375	–
3590.4	(1, 0)	0.0750	–
3585.9	(2, 1)	0.0656	Yes
3583.9	(3, 2)	0.0562	Yes

TABLE V

Franck-Condon factors for the ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) System of N_2^+

Wavelength (Å)	Band	Franck-Condon Factors		Additional Band in comet
		FCF (I_{he})	FCF (I_n)	
5864.7	(0, 4)	0.1612	0.0000	Yes
5653.1	(2, 6)	0.1612	0.0403	Yes
5564.1	(3, 7)	0.0403	0.0000	–
5485.5	(4, 8)	0.2014	0.0000	Yes
5228.3	(0, 3)	0.2820	0.0806	Yes
5148.8	(1, 4)	0.1612	0.1209	Yes
5076.6	(2, 5)	0.2820	0.0403	Yes
5012.7	(3, 6)	0.1209	0.0403	Yes
4957.9	(4, 7)	0.2014	0.0403	Yes
4709.2	(0, 2)	0.1612	0.0806	Yes
4651.8	(1, 3)	0.1612	0.0103	Yes
4599.7	(2, 4)	0.2417	0.0806	Yes
4554.1	(3, 5)	0.1612	0.0000	Yes
4515.9	(4, 6)	0.2417	0.0000	Yes
4490.3	(5, 7)	0.0806	0.0403	–
4278.1	(0, 1)	0.3223	0.2417	Yes
4236.5	(1, 2)	0.2820	0.2014	Yes
4199.1	(2, 3)	0.1612	0.0806	Yes

Table V (continued)

Wavelength (Å)	Band	Franck-Condon Factors		Additional band in comet
		FCF (I_{he})	FCF (I_n)	
4166.8	(3, 4)	0.1209	0.0000	Yes
4140.5	(4, 5)	0.0806	–	–
3914.4	(0, 0)	0.2417	0.2417	–
3884.3	(1, 1)	0.1209	0.0403	Yes
3857.9	(2, 2)	0.0806	0.0806	–
3835.4	(3, 3)	0.0403	0.0403	–
3818.1	(4, 4)	0.0403	0.0000	–
3582.1	(1, 0)	0.1612	0.1209	Yes
3563.9	(2, 1)	0.1612	0.0000	Yes
3548.9	(3, 2)	0.1209	–	Yes
3538.3	(4, 3)	0.0806	–	–
3532.6	(5, 4)	0.0403	0.0000	–
3308.0	(2, 0)	0.0806	0.0403	–
3298.7	(3, 1)	0.1209	0.0403	Yes
3293.4	(4, 2)	0.1209	0.0000	Yes

TABLE VI

Franck-Condon factors for the ($A^2\pi \rightarrow X^2\Sigma$) system of CO^+

Wavelength (Å)	Band	Franck-Condon Factors	Additional band in comet
6238.7	(0, 2)	0.3700	Yes
5900.4	(2, 3)	0.0529	–
5693.6	(1, 2)	0.1586	Yes
5499.9	(0, 1)	0.3171	Yes
5072.1	(1, 1)	0.2643	Yes
4910.9	(0, 0)	0.1586	Yes
4865.8	(3, 2)	0.0529	–
4711.2	(2, 1)	0.2643	Yes
4565.8	(1, 0)	0.4228	–
4518.0	(4, 2)	0.1586	Yes
4403.3	(3, 1)	0.1057	Yes
4274.3	(2, 0)	0.5285	–
4244.1	(5, 2)	0.0529	–
4151.9	(7, 3)	0.0529	–
4138.9	(4, 1)	0.1057	Yes
4019.7	(3, 0)	0.4757	–
3908.0	(5, 1)	0.1057	Yes
3795.8	(4, 0)	0.4228	–
3705.3	(6, 1)	0.2114	Yes
3600.8	(5, 0)	0.3171	Yes
3525.6	(7, 1)	0.1057	Yes
3427.9	(6, 0)	0.2114	Yes

Table VI (continued)

Wavelength (Å)	Band	Franck-Condon factors	Additional band in comet
3366.1	(8, 1)	0.1057	Yes
3314.2	(10, 2)	0.0529	–
3273.9	(7, 0)	0.1057	Yes
3222.4	(9, 1)	0.0529	–
3180.3	(11, 2)	0.0529	–
3135.5	(8, 0)	0.0529	–
3093.3	(10, 1)	0.0000	–

TABLE VII

Franck-Condon factors for the ($B^2\Sigma - A^2\Pi$) system of CO^+

Wavelength (Å)	Band	Franck-Condon factors	Additional band in comet
4236.2	(0, 1)	0.0181	Yes
4231.6	(0, 1)	0.0482	Yes
4212.9	(0, 1)	0.0422	Yes
4209.1	(0, 1)	0.0482	Yes
4201.5	(1, 2)	0.0060	–
4182.6	(1, 2)	0.0060	–
4179.1	(1, 2)	0.0060	–
3977.7	(0, 0)	0.0241	Yes
3973.5	(0, 0)	0.0542	Yes
3957.0	(0, 0)	0.0422	Yes
3953.6	(0, 0)	0.0603	Yes
3729.7	(1, 0)	0.0181	Yes
3724.9	(1, 0)	0.0482	Yes
3711.2	(1, 0)	0.0542	Yes
3707.4	(1, 0)	0.0542	Yes
3515.8	(2, 0)	0.0121	–
3511.7	(2, 0)	0.0422	Yes
3500.4	(2, 0)	0.0181	Yes
3496.7	(2, 0)	0.0241	Yes
3331.9	(3, 0)	0.0060	–
3329.0	(3, 0)	0.0060	–
3317.9	(3, 0)	0.0060	–
3314.8	(3, 0)	0.0060	–

TABLE VIII

Franck-Condon factors for the ($A^3\Pi - X^3\Sigma$) system of NH

Wavelength (Å)	Band	Franck-Condon factors	Additional band in comet
3676.3	(0, 1)	0.0893	–
3637.7	(0, 1)	0.2679	–
3370.0	(1, 1)	0.8038	Yes
3360.0	(0, 0)	0.8931	–
3336.0	(2, 2)	0.1786	Yes
3317.0	(1, 1)	0.2679	Yes
3302.5	(0, 0)	0.3572	–
3635.0	(1, 2)	0.1786	Yes
3272.8	(2, 2)	0.2679	Yes
3137.0	(2, 1)	0.1786	Yes
3119.5	(2, 1)	0.1786	Yes
3050.3	(1, 0)	0.0893	–
3047.2	(1, 0)	0.0000	–
3023.0	(1, 0)	0.0000	–

TABLE IX

Franck-Condon factors for the ($A^2\Sigma^+ - X^2\Pi$) system of OH

Wavelength (Å)	Band	Franck-Condon Factors	Additional band in comet
3447.7	(0, 1)	0.1851	Yes
3194.9	(2, 2)	0.0926	Yes
3124.05	(1, 1)	0.0926	–
3063.8	(0, 0)	0.9256	–
2952.5	(3, 2)	0.0926	Yes
2882.725	(2, 1)	0.2777	Yes
2818.85	(1, 0)	0.5554	Yes
2683.325	(3, 1)	0.1851	Yes
2614.35	(2, 0)	0.2777	Yes
2444.0	(3, 0)	0.0000	–

TABLE X

Franck-Condon factors for the ($A^2\Delta - X^2\Pi$) system of CH

Franck-Codon factors From (Garland and Crosley, 1985)		Band	Franck-Condon factors from (Pathak, 1967)	Additional band in comet
FCF	Wavelength (Å)			
0.0072	4890	(0, 1)	0.00692	–
0.0056	4859	(1, 2)	0.00823	–
0.9920	4315	(0, 0)	0.99093	–
0.9860	4314	(1, 1)	0.98306	Yes

Table X (continued)

Franck-Codon factors From (Garland and Crosley, 1985)		Band	Franck-Condon factors from (Pathak, 1967)	Additional band in comet
FCF	Wavelength (Å)			
0.0074	3859	(1, 0)	0.00721	–
–	–	(0, 2)	0.00018	–
–	–	(0, 3)	0.00000	–
–	–	(1, 3)	0.00018	–
–	–	(2, 0)	0.00004	–
–	–	(2, 1)	0.00867	–
–	–	(2, 2)	0.98386	Yes
–	–	(2, 3)	0.00672	–

TABLE XI

Franck-Condon factors for the ($B^2\Sigma^- - X^2\Pi$) system of CH

Wavelength (Å)	Band	Franck-Condon factors from Garland and Crosley (1985)	Additional band in comet
4504	(1, 2)	0.1710	Yes
4353	(0, 1)	0.1140	Yes
4034	(1, 1)	0.5690	Yes
3886	(0, 0)	0.8650	–
3633	(1, 0)	0.1180	Yes

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