

Phosphorus-Bearing Diatomic Molecules in Comet Atmosphere: A Spectroscopic Investigation

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Abstract: In the solar system comets are the most frequent entities. The identification of the bands of comets is one of the active regions of study. In the present investigations the experimental potential energy curves for the electronic ground states of diatomic molecules PH and P₂ are constructed by using Rydberg-Klein-Rees method as altered by Vanderslice *et al.* Using the Hulbert-Hirschfelder (H-H) five parameters potential function the low lying electronic ground state dissociation energy of P₂ is calculated by curve fitting technique. The estimated dissociation energy of diatomic molecule P₂ is 4.98±0.11 eV. This value is in good agreement with the literature values. Estimated dissociation energy of P₂, is used in the relation specified by Gaydon and ionization potential is evaluated for P₂ molecule. The estimated ionization potential of P₂ is 11.76 eV. The Franck-Condon factors and r-centroids for the band system of a³Σ_u⁺ - X¹Σ_g⁺, ³Δ_u - X¹Σ_g⁺, b³π_g - X¹Σ_g⁺, ¹Σ_u⁻ - X¹Σ_g⁺, ¹Δ_u⁻ - X¹Σ_g⁺ and A¹π_g - X¹Σ_g⁺ of P₂ molecule have been calculated using an approximate analytical methods of Jarman and Fraser and Nicholls and Jarman. The non-appearance of the bands in this system is explained.

Key words: Comet diatomic molecules • Potential energy curves • Franck-Condon factors • R-centroids
• Dissociation energy

INTRODUCTION

Comets are frequently considered as the last witness of the formation of our solar system. A comet is a generally nebulous celestial body of small mass revolving around the Sun [1-5]. Its appearance and brightness vary markedly with its distance from the Sun. One of the key points to study and understand, in the search of comets, is how much ice and dust specks, accreted in comets, have been changed in the solar nebula before, during and later the formation of the Sun, planets and small bodies such as asteroids and comets. Phosphorus has been detected as part of the dust component in comet Halley [6-8]. It is an important element in all known forms of life and phosphorus-bearing compounds have been observed in space [9-10]. Phosphorus being a biogenic element, the study of the various forms in which it is present in the different astronomical environments is a matter of great interest, although still poorly understood [11]. Phosphine ice is also a plausible major phosphorus constituent of

comets, although recent searches in the gaseous coma of a few comets turned out unsuccessful, providing upper limits not significant enough to conclude whether or not PH₃ locks most of phosphorus in these solar system bodies [12-13]. An emission feature attributable to the J=1-0 line of PH₃ was also observed independently in the spectra of IRC+10216 and the carbon rich envelope CRL 2688 from observations of an emission line at 266.9 GHz [14]. The scale length of PH₃ in the coma is about 13,000-16,000 km. Other P-bearing species likely to be found in the coma include: PH₂, PC, PN and HCP [15-16]. Phosphorus is a [17] relatively rich element cosmically, with P/H ~ 3 × 10⁻⁷. Two rotational transitions of PO were observed toward VY CANIS MAJORIS: the J= 5.5 → 4.5 at 239.9-240.2 GHz [10] and the J= 6.5 → 5.5 at 283.6 – 283.8 GHz.

The first phosphorous species found in the diffuse clouds was the P=N molecule [18-19]. Mean while PN is detected only in active star-forming regions one must study the prospect of this molecule was formed by

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processes like high temperature gas phase reaction or particle disruption. In contrast, it would also be conceivable that the PN molecule was initially synthesized in the increasing atmospheres of evolving stars, then reducing in the nearby interstellar medium. The second phosphorous [20] compound detected in the interstellar medium was the C=P radical, found in the circumstellar region around IRC 10216, a late type evolved star [21]. High quality UV observations have confirmed that phosphorous is depleted by approximately a factor of 3 relative to its solar-system abundance in sightlines containing both warm, diffuse clouds and denser cold clouds [22-23]. Therefore, a significant fraction of interstellar phosphorous must be trapped in the grain phase. Based on its adequate cosmic richness (eighteenth most rich element, $[P] / [N] = 4 \times 10^{-3}$) and the positive identification of P-bearing species in the interstellar medium (such as, PN, PC, HCP and PO), would expect simple molecules, diatomic (like PH, PO, PC, PS, P₂) to exist in Cometary ices and hence be released into gas phase upon ice sublimation. Bright bands that are produced by gases jet glowing by the Sun's radiation characterize the spectrum of a comet. Three types of emission are found in optical spectra of comets: continuous emission, emissions from neutral molecules and atoms and emissions due to molecular and atomic ions [24].

The identification of the lines in the bands of a comet is quite a complex and challenging task. The normal procedure is to look for the coincidences between the laboratory wavelength of lines and the experimental wavelengths in the spectra of a comet, which have been rectified for the velocity effect. Using this technique, several well-known atoms and molecules that are seen in other astronomical entities have been recognized in the spectra of comets. Laboratory information is not obtainable for each and every transition for all the atoms and molecules identified in comets. It is interest to note that several transitions were observed first in the cometary spectra before being studied in the laboratory. Reliable atomic and molecular information on cometary materials are essential for models of photon-driven chemical and physical process and the models of the steady state properties of astrophysical objects that absorb or emit photons.

The study of electronic spectra of the molecules PH and P₂ allow we to know the chemical and physical processes that take place in the comet atmosphere. The detection of molecular lines in emission suggests that the vibrational and rotational states of molecules can be

excited by radiative or collisional means in the comet atmosphere. The measurements of the strengths of lines from different rotational/vibrational states can therefore serve as effective probes of the temperature, density and radiation background of the comet atmosphere. In order to interpret dissociation equilibria and ionization process and to estimate molecular abundances in stellar and in any other astrophysical atmospheres, accurate dissociation energies and ionization potentials of Cometary molecules are essential. Recent molecular spectroscopic studies inspire the author to evaluate dissociation and ionization energy of P₂ and to construct potential energy curves of PH and P₂. Newly stated data on PH and P₂ also encouraged the author to accept the current investigation.

Potential Energy Curves and Dissociation Energies:

The electronic and vibrational energy levels of a diatomic molecule in a given electronic state are often described by a potential energy (Y-axis) – inter-nuclear distance (X-axis) diagram or simply called potential energy curve. Each electronic state of a molecule has its own potential energy curve. So, for any molecule, a number of such curves representing the corresponding electronic states are possible. Experimentally observed vibrational levels are used to construct the potential energy curve. The Rydberg-Klein-Rees (RKR) method gives the turning points for the known vibrational levels by.

$$r_{\pm} = \left(\frac{f_v}{g_v} + f_v^2 \right)^{1/2} \pm f_v$$

where r_{\pm} and g_v are calculated by the procedure of RKR method.

The Rydberg –Klein –Rees –Vanderslice (RKRv) method is an enriched form of Rydberg –Klein –Rees (RKR) method, which makes usage of Wentzel-Kramers-Brillouin (WKB) approximation from which one get consistent potential energy curves by the observed vibrational and rotational constants. Several authors employed this method and built the potential energy curves [25-31]. Its reliability and performance is quite appreciable. In the current study [32-33] the molecular constants used are recorded in Table 1. The calculated values of the turning points are specified in Table 2, used for the molecular vibrations in different electronic states of PH and P₂. The Rydberg –Klein –Rees –Vanderslice (RKRv) turning points are presented in the [34-35] Hulburt –Hirschfelder's five parameter potential function, the energies $U(r)$ is calculated by varying the D_e values. Among the calculated $U(r)$ and the experimental $G(v)$ values, an average percentage deviation is determined.

Table 1: Molecular constants of PH and P₂ comet molecules for different electronic states

Molecule	μ	State	T _e (cm ⁻¹)	ω _e (cm ⁻¹)	ω _e x _e (cm ⁻¹)	B _e (cm ⁻¹)	α _e (cm ⁻¹)	r _e (Å ⁰)
PH	0.97606	X ³ Σ ⁻	0	2368.47	44.86	8.5187	0.2548	1.4239
P ₂	15.49221	X ¹ Σ _g ⁺	0	782	2.9	0.299	0.0014	1.9066
		a ³ Σ _u ⁺	17990.3	505	4.6	0.241	0.0014	2.1234
		³ Δ _u	22446.0	562	0.4	0.249	0.0012	2.0898
		b ³ Π _g	26675.0	632	3.3	0.276	0.0018	1.9864
		b' ¹ Σ _u ⁻	26148.2	579	2.2	0.251	0.0014	2.0810
		¹ Σ _u ⁻	26165.8	575	2.0	0.251	0.0014	2.0808
		¹ Δ _u ⁻	29269.1	582	2.2	0.253	0.0014	2.0753
		A ¹ Π _g	33327.2	591	2.7	0.269	0.0019	2.0100

Note: μ = reduced mass, T_e = electronic energy above ground state (cm⁻¹), ω_e = vibrational spacing (cm⁻¹), ω_ex_e = anharmonic correction to vibrational spacing (cm⁻¹), B_e = rigid rotator rotational spacing (cm⁻¹), α_e = Non rigid rotator correction to B_e(cm⁻¹), r_e = equilibrium inter nuclear distance (Å⁰)

Table 2: Turning points of the potential energy curve for the electronic groundstate of PH Comet molecule

v	U (cm ⁻¹)	r _{min} (Å ⁰)	r _{max} (Å ⁰)	v	U (cm ⁻¹)	r _{min} (Å ⁰)	r _{max} (Å ⁰)
PH molecule				Te = 0 (cm ⁻¹)			
Te = 0 (cm ⁻¹)				X ³ Σ ⁻			
0	1173.0	1.314	1.557	8	16890.3	1.086	2.252
1	3451.7	1.247	1.675	9	18451.1	1.074	2.335
2	5640.7	1.206	1.769	10	19922.3	1.064	2.421
3	7740.0	1.176	1.853	11	21303.6	1.054	2.511
4	9749.5	1.152	1.934	12	22595.3	1.045	2.605
5	11669.3	1.132	2.013	13	23797.2	1.036	2.704
6	13499.4	1.114	2.092	14	24909.4	1.028	2.809
7	15239.7	1.099	2.171	15	25931.8	1.020	2.922

A precise assessment of the dissociation energy (D₀) needs an empirical potential function, which gives the best replica of the experimental energy values. Steele *et al.* [34] presented a critical assessment of these functions and they have been revealed that the five parameter potential function of Hulbert –Hirschfelder [34-35] fits well with the Rydberg-Klein-Rees-Vanderslice (RKR) curves of a enormous number of diatomic molecules. In the current study, from Table 3, it is noticed that the [34-35] Hulbert –Hirschfelder (H-H) potential energy function fits best and replicate the experimental energy values. Unlike D_e values are used in the Hulbert-Hirschfelder potential function, for which the best suitable D_e value of the energy values U(r) is identified and is taken as the dissociation energy (D_e) of the diatomic molecule.

Franck –Condon factors and r-Centroids: Franck-Condon factors play a very significant role in the calculation of vibrational transition probabilities of diatomic molecules. These factors arrays are the basic molecular data, which are needed in interpretation of intensities of molecular spectra. The relative vibrational transition probability or band strength of rotational and vibrational terms is separable may be written as the product of the square of a transition moment multiplied by a vibrational overlap integral:

$$\rho_{v',v''} = |R_e^2 (\bar{r}_{v',v''})| q_{v',v''}$$

where R_e is the electronic transition moment, $\bar{r}_{v',v''}$ is the r - Centroid of the band and q_{v',v''} is the Franck – Condon factor given by

$$q_{v',v''} = \left| \int_0^w \Psi_{v'} \Psi_{v''} dr \right|^2$$

where Ψ_{v'} and Ψ_{v''} are the vibrational wave function of the molecule in the levels v' and v'' between which the transitions v' and v'' takes place. An excellent review on the methods of the evaluation of Franck-Condon factors was given by Chakraborty and Pan [36]. The details of the technique are described elsewhere [31, 34-36].

The technique yields accurate r-Centroid ($\bar{r}_{v',v''}$) of the band,

$$\bar{r}_{v',v''} = \int \Psi_{v'} r \Psi_{v''} dr / \Psi_{v'} \Psi_{v''} dr$$

By the use of the quadratic equation method of Nicholls and Jarman [37] and Chakraborty and Pan [36], r-centroids are estimated for different bands.

RESULTS AND DISCUSSIONS

The inherent error in the H-H function specified by Steele *et al.* [34] is 2%. The error involved in evaluation of D_e is the minimum average percentage deviation plus the

Table 2 (continued): Turning points of the potential energy curves for the different electronic states of P₂ comet molecule

v	U (cm ⁻¹)	r _{min} (Å°)	r _{max} (Å°)	v	U (cm ⁻¹)	r _{min} (Å°)	r _{max} (Å°)
P ₂ molecule T _e = 0 (cm ⁻¹)				Te = 17990 1.3(cm ⁻¹)			
X ¹ Σg ⁺				a ³ Σ _u ⁺			
0	390.2	1.856	1.961	0	251.3	2.060	2.192
1	1166.4	1.821	2.005	1	747.1	2.017	2.247
2	1936.8	1.798	2.036	2	1233.7	1.989	2.288
3	2701.4	1.781	2.063	3	1711.1	1.967	2.323
4	3460.2	1.766	2.087	4	2179.3	1.947	2.355
5	4213.2	1.753	2.109	5	2638.3	1.931	2.385
6	4960.4	1.741	2.130	6	3088.1	1.915	2.414
7	5701.8	1.731	2.149	7	3528.7	1.901	2.441
T _e =22446.0 (cm ⁻¹)				T _e =26675.0 (cm ⁻¹)			
³ Δ _u				b ³ Π _g			
0	280.9	2.030	2.154	0	315.1	1.930	2.048
1	842.1	1.989	2.205	1	940.5	1.893	2.097
2	1402.5	1.963	2.242	2	1559.3	1.868	2.134
3	1962.1	1.943	2.273	3	2171.5	1.850	2.165
4	2520.9	1.926	2.300	4	2777.1	1.834	2.193
5	3078.9	1.911	2.325	5	3376.1	1.820	2.220
6	3636.1	1.898	2.349	6	3968.5	1.808	2.244
7	4192.5	1.887	2.371	7	4554.3	1.808	2.268
P ₂ molecule T _e = 26165.(cm ⁻¹)				P ₂ molecule T _e = 26148.2 (cm ⁻¹)			
b ¹ ³ Σ _u ⁻				¹ Σ _u ⁻			
0	288.9	2.022	2.145	0	287	2.022	2.145
1	863.5	1.982	2.196	1	858	1.982	2.196
2	1433.7	1.957	2.233	2	1425	1.956	2.233
3	1999.5	1.937	2.265	3	1988	1.936	2.265
4	2560.9	1.920	2.293	4	2547	1.919	2.293
5	3117.9	1.905	2.319	5	3102	1.905	2.319
6	3670.5	1.893	2.344	6	3653	1.892	2.344
7	4218.7	1.881	2.367	7	4200	1.881	2.367
P ₂ molecule T _e =26269.1 (cm ⁻¹)				P ₂ molecule T _e =33327.2 (cm ⁻¹)			
¹ Δ _u ⁻				A ¹ Π _g			
0	290.4	2.016	2.139	0	294.8	1.952	2.074
1	868.0	1.977	2.190	1	880.4	1.914	2.125
2	1441.2	1.951	2.227	2	1460.6	1.889	2.163
3	2010.0	1.931	2.258	3	2035.4	1.870	2.195
4	2574.4	1.914	2.287	4	2604.8	1.854	2.225
5	3134.4	1.900	2.313	5	3168.8	1.841	2.252
6	3690.0	1.887	2.338	6	3727.4	1.829	2.278
7	4241.2	1.875	2.361	7	4280.6	1.818	2.302

inherent error in the potential function. The D₀ value of P₂ is found to be 4.984±0.112eV. Here D₀=D_e - G (0). The turning points obtained from the RKR method for the electronic ground state X ³Σ⁻ of PH and X ¹Σg⁺, a ³Σ_u⁺, ³Δ_u, b ³Π_g, b¹ ³ Σ_u⁻, ¹Σ_u⁻, ¹Δ_u⁻ and A¹Πg states of P₂ are presented in Table 2. The relevant U(r) values for the selected D_e values are given in the Table 3. Careful analysis of the Table 3, reveals that average percentage deviation for P₂ molecule is 0.230 and D₀=4.984±0.112eV (i.e. [(0.23+2) (5.03)/100]=0.112eV) for P₂. Hence the

dissociation energy for the electronic ground state of P₂ is 4.984±0.112 eV. The D₀ value quoted by Darwent [38] is 5.02 eV and by Huber and Herzberg [39, 40] is 5.033eV. The dissociation energy recommended by Sandoval *et al* [40] for P₂ is 4.90 eV and Gingerich *et al* [41] quoted value is 4.84 eV. The estimated D₀ value of P₂= 4.98±0.112eV is in good agreement with the value suggested by [40] Sandoval et.alis 4.90 eV, Vendeneyev *et al.* [42] recommended value is 5.06 eV, Huber and Herzberg [39] is 5.033 eV and Gingerich *et al.* [41] quoted value is 4.84 eV

Table 3: Calculated Energy values using Hulburt – Hirschfelder’s five parameter potential function

X ¹ Σ _g ⁺ (P ₂ molecule)		Calculated U (r) in (cm ⁻¹)		
r (Å)	U (cm ⁻¹)	D _e = 5.0330 eV	D _e = 5.0082eV	D _e = 5.0578 eV
1.961	390.2	390.3	388.4	392.2
2.005	1166.4	1167.0	1161.3	1172.8
2.036	1936.8	1938.9	1929.3	1948.4
2.063	2701.4	2705.9	2692.5	2719.2
2.087	3460.2	3468.6	3451.5	3485.6
2.109	4213.2	4226.9	4206.1	4247.8
2.130	4960.4	4981.3	4956.7	5005.8
2.149	5701.8	5731.7	5703.5	5759.9
1.856	390.2	390.1	388.2	392.1
1.821	1166.4	1165.9	1160.1	1171.6
1.798	1936.8	1934.8	1925.3	1944.3
1.781	2701.4	2697.0	2683.7	2710.3
1.766	3460.2	3451.9	3434.9	3468.9
1.753	4213.2	4199.6	4178.9	4220.3
1.741	4960.4	4939.7	4915.3	4964.0
1.731	5701.8	5672.2	5644.2	5700.1
Average percentage deviation		0.23	0.49	0.49

as dissociation energy of P₂. After careful observation of dissociation energies given by different authors [35] for P₂, is 4.98±0.11 eV considered as best dissociation energy in the present study. The dissociation energies and ionization potentials of ionized and non –ionized molecules can be linked by the cycle [35] as:

$$I(AB) = D(AB) + I(A) - D(AB^+)$$

A and B are the respective elements in the molecule. B⁺ is the ionized element. I and D refer to ionization potential and dissociation energy. The molecules considered in the present study are concern with phosphorus. Ionization potential of phosphorus is 10.48e V given by Gaydon [35] is considered in the above cycle to estimate ionization potentials of I(AB) molecule [43].

Ionization potential of P₂ can be estimated from the following.

$$I(P_2) = D(P_2) + I(P) - D(P_2^+)$$

The estimated dissociation energy of P₂ from curve fitting procedure is 4.98± 0.11e V. Herzberg [42, 43] quoted D₀ (P₂⁺) value 3.7e V is substituted in the above cycle, then

$$I(P_2) = 4.98 + 10.48 - 3.7 = 11.76 \text{ eV}$$

The calculated value of I (P₂) =11.76e V is in good agreement with the value 11.8e V given by Wilkinson [44].

One must have a theoretical knowledge of Franck – Condon factors, r-centroids and the consistent potential energy curves to know the physical conditions of the emitter for the corresponding band heads in a band system. The sequence difference, $\Delta r = r_{v'+1, v''+1} - r_{v', v''}$, for the systems a³Σ_u⁺ - X¹Σ_g⁺, ³Δ_u - X¹Σ_g⁺, b³π_g - X¹Σ_g⁺, ¹Σ_u⁻ - X¹Σ_g⁺, ¹Δ_u⁻ - X¹Σ_g⁺ and A¹π_g - X¹Σ_g⁺ are found to be constant. It is seen in the Tables from 4a to 4f that Δr is less than 0.01 Å for these systems suggesting that the potentials are not very wide. It has been observed by Nicholls and Jarman [37], that the value of r_{v', v''} (r-centroids) was found to increase with the increase of the r_{v', v''} (wavelength). The internuclear distance of the ground state is less than (r_{e1}>r_{e2}) the upper state in all cases, r-centroids evaluations are likely to increase with wavelength, which is the tendency detected in a red-degraded band system. In the case of a³Σ_u⁺ - X¹Σ_g⁺ system of P₂, r₀₀ is slightly greater than (r_{e1}+ r_{e2})/2 value, indicating that the potentials are not very much an harmonic and it is interest to note that r₀₀ is slightly less than (r_{e1}+ r_{e2})/2 value for the systems ³Δ_u - X¹Σ_g⁺, b³π_g - X¹Σ_g⁺, ¹Σ_u⁻ - X¹Σ_g⁺, ¹Δ_u⁻ - X¹Σ_g⁺ and A¹π_g - X¹Σ_g⁺ of P₂, suggesting that the potential functions are an harmonic in nature.

Franck- Condon factors are determined [45] for twenty eight bands of a³Σ_u⁺ - X¹Σ_g⁺ system of P₂ Molecule and the results are presented it is seen from Table 4. In the case of a³Σ_u⁺ - X¹Σ_g⁺ system, the difference in the equilibrium inter nuclear distances of the upper and lower

Table 4: Franck–Condon factor and r-centroids values for the $a^3\Sigma_u^+ - X^1\Sigma_g^+$, $^3\Delta_u - X^1\Sigma_g^+$ and $b^3\Pi_g - X^1\Sigma_g^+$ systems of P_2 molecule

(v', v'')	$a^3\Sigma_u^+ - X^1\Sigma_g^+$		$^3\Delta_u - X^1\Sigma_g^+$		$b^3\Pi_g - X^1\Sigma_g^+$	
	FC-factor	r-Centroids	FC-factor	r-Centroids	FC-factor	r-Centroids
(0,0)	0.001	2.005	0.005	1.99	0.352	1.989
(0, 1)	0.008	2.025	0.031	2.011	0.375	2.01
(0, 2)	0.032	2.044	0.08	2.031	0.192	2.032
(0, 3)	0.077	2.065	0.139	2.052	0.062	2.054
(0, 4)	0.134	2.085	0.178	2.072	0.013	2.077
(0, 5)	0.18	2.107	0.234	2.092	0.003	2.1
(1 0)	0.005	1.993	0.028	1.975	0.353	1.973
(1 1)	0.034	2.012	0.098	1.996	0	1.994
(1 2)	0.089	2.032	0.146	2.017	0.177	2.016
(1 3)	0.13	2.051	0.177	2.037	0.257	2.038
(1 4)	0.109	2.072	0.06	2.058	0.229	2.06
(1 5)	0.069	2.092	0.017	2.078	0.631	2.082
(2, 0)	0.017	1.981	0.07	1.96	0.19	1.958
(2 1)	0.071	2	0.142	1.981	0.147	1.979
(2 2)	0.116	2.019	0.089	2.002	0.109	2
(2 3)	----	2.039	--	2.022	---	2.021
(2, 4)	0.015	2.058	0.769	2.043	---	2.043
(2 5)	0.15	2.079	---	2.063	---	2.065
(3 0)	0.034	1.97	0.119	1.945	0.073	1.943
(3 1)	0.099	1.988	0.119	1.966	0.228	1.964
(3 2)	0.087	2.007	0.001	1.987	0.013	1.985
(3 3)	0.008	2.026	0.007	2.008	0.004	2.006
(3 4)	----	2.046	----	2.028	---	2.027
(3 5)	----	2.065	----	2.048	---	2.049
(4 0)	0.056	1.959	0.154	1.931	0.021	1.929
(4 1)	0.103	1.977	0.046	1.952	0.149	1.949
(4 2)	0.042	1.995	0.394	1.973	0.064	1.969
(4 3)	0.005	2.014	---	1.993	---	1.99
(4 4)	----	2.033	---	2.014	---	2.011
(4 5)	-----	2.053	---	2.034	---	2.033
(5 0)	0.078	1.948	0.159	1.916	0.001	1.915
(5 1)	0.085	1.966	0.001	1.937	---	1.935
(5 2)	0.006	1.984	0.319	1.958	0.91	1.955
(5 3)	----	2.002	----	1.979	---	1.975
(5 4)	-----	2.021	----	1.999	---	1.996
(5 5)	-----	2.04	----	2.019	---	2.017

states are comparatively large $0.2168A^0$. So, the Condon parabola is open. In this case, more number of bands appears in a band system. This conclusion is true from the various low values of the F-C factors of different bands. The order of the magnitude of the F-C factors of the $a^3\Sigma_u^+ - X^1\Sigma_g^+$ system of P_2 for the bands (0,0) (0,1) (1,0) (3,3) and (5,2) are small and they may not probably be observed experimentally. It is noticed from the Table (4a) that for the bands of v' and v'' progressions observed, the vibrational sum rule is not fulfilled. Therefore, it would definitely yields more new bands, if more investigational work is done on the band spectrum of the P_2 molecule on this system. Reported FC factors (0,4) (0,5) (1,3) (1,4) (2,2) (2,5) and (4,1) bands are high and show maximum intensity, compare to all other bands.

In the case of $^3\Delta_u - X^1\Sigma_g^+$ system, the difference (Δr_c) in the equilibrium inter nuclear distances of the upper and lower states are comparatively large ($0.1832A^0$). So, the Condon parabolas are more open. From the magnitude of the F - C factors of the $^3\Delta_u - X^1\Sigma_g^+$ system of P_2 , it is perceived that the sum rule is not satisfied for v' and v'' progressions. The FC factors for (0, 0) and (5, 1) band is originate to be small indicating its absence. The FC factors for the bands (4, 2) (5, 2) (0, 5) and (2, 5) bands are high and show maximum intensity for these bands. Between all bands observed in this system (2, 5) band is found to be the strongest. For this system FC factors are calculated [45] for twenty five bands of P_2 Molecule and the results are presented.

Table 4 (continued): Franck–Condon factor and r-centroids values for the ${}^1\Sigma_u^- - X\ {}^1\Sigma_g^+$, ${}^1\Delta_u^- - X\ {}^1\Sigma_g^+$ and a ${}^1\pi_g^- - X\ {}^1\Sigma_g^+$ systems of P_2 molecule

(v', v'')	${}^1\Sigma_u^- - X\ {}^1\Sigma_g^+$		${}^1\Delta_u^- - X\ {}^1\Sigma_g^+$		$A\ {}^1\pi_g^- - X\ {}^1\Sigma_g^+$	
	FC-factor	r-Centroids	FC-factor	r-Centroids	FC-factor	r-Centroids
(0,0)	0.008	1.988	0.011	1.988	0.184	1.957
(0, 1)	0.046	2.01	0.057	2.008	0.315	1.992
(0, 2)	0.115	2.032	0.134	2.031	0.267	2.026
(0, 3)	0.183	2.054	0.2	2.054	0.147	2.059
(0, 4)	0.209	2.077	0.213	2.077	0.062	2.093
(0, 5)	0.175	2.1	0.174	2.101	0.013	2.126
(1 0)	0.037	1.973	0.046	1.97	0.298	1.93
(1 1)	0.121	1.994	0.136	1.992	0.088	1.966
(1 2)	0.156	2.016	0.156	2.014	0.015	2
(1 3)	0.088	2.037	0.07	2.036	0.16	2.033
(1 4)	0.015	2.06	0.001	2.059	0.207	2.067
(1 5)	0.003	2.082	0.065	2.083	0.113	2.1
(2, 0)	0.081	1.958	0.095	1.955	0.254	1.904
(2 1)	0.147	1.979	0.149	1.976	0.009	1.939
(2 2)	0.065	2	0.048	1.998	0.163	1.974
(2 3)	---	2.021	---	2.02	---	2.008
(2, 4)	0.094	2.043	0.297	2.042	0.483	2.041
(2 5)	---	2.065	---	2.065	---	2.074
(3 0)	0.125	1.943	0.137	1.939	0.151	1.876
(3 1)	0.103	1.963	0.09	1.96	0.126	1.913
(3 2)	0	1.984	0	1.982	0.028	1.948
(3 3)	0.551	2.006	0.408	2.003	---	1.983
(3 4)	---	2.027	---	2.025	---	2.016
(3 5)	---	2.049	---	2.048	---	2.049
(4 0)	0.15	1.928	0.158	1.924	0.07	1.848
(4 1)	0.037	1.949	0.02	1.945	0.172	1.886
(4 2)	0.028	1.969	0.035	1.966	---	1.922
(4 3)	---	1.99	---	1.987	---	1.957
(4 4)	---	2.011	---	2.009	---	1.991
(4 5)	---	2.033	---	2.031	---	2.024
(5 0)	0.151	1.914	0.156	1.91	0.025	1.818
(5 1)	0.006	1.934	---	1.93	0.162	1.859
(5 2)	---	1.955	0.746	1.951	---	1.896
(5 3)	---	1.975	---	1.972	---	1.932
(5 4)	---	1.996	---	1.993	---	1.966
(5 5)	---	2.017	---	2.015	---	2

It is seen from the Table 4, for twenty four bands of $b^3\pi_g^- - X\ {}^1\Sigma_g^+$ system of P_2 Molecule, the Franck-Condon factors are determined employing the method of Fraser and Jarman [45]. In this system, the differences in the equilibrium internuclear distances of the lower and upper states are comparatively small $0.0798A^0$. So, the Condon parabola is less. The FC factors of (0,0) (1,1) (1,0) (1,5) (5,2) bands are found to be stronger compare to others. Of the strongest bands (5, 2) band is found to be strongest. The vibrational sum rule is satisfied for this system; further experimental work will not be helpful to observe more new bands.

Franck - Condon factors are determined [45] for twenty five bands of ${}^1\Sigma_u^- - X\ {}^1\Sigma_g^+$ system of P_2 Molecule and the results are presented in the Table 4, In the case of ${}^1\Sigma_u^- - X\ {}^1\Sigma_g^+$ system, the difference in the equilibrium

inter nuclear distances of the upper and lower states are comparatively large $0.1742A^0$. So, the Condon parabola is more open. In this case, more number of bands appears in a band system. This conclusion is true from the various low values of the FC factors of different bands. The order of the magnitude of the FC factors of the ${}^1\Sigma_u^- - X\ {}^1\Sigma_g^+$ system of P_2 for the bands (0,0) (1,5) (3,3) and (5,1) are low perhaps, they may not be detected experimentally. As for the bands are observed for v' and v'' progressions, the vibrational sum rule is not fulfilled. Therefore, if more new work is done on the band spectrum of the P_2 molecule on this system, it would definitely yields more new bands. Franck-Condon factors (0, 4) and (3, 3) bands are high and show maximum intensity, among all the bands reported.

For twenty five bands ${}^1\Delta_u^- - X\Sigma_g^+$ system of P_2 Molecule, the Franck-Condon factors are determined employing the method of Fraser and Jarman [45]. In this system, the differences in the equilibrium inter nuclear distances of the upper (r_{e1}) and lower (r_{e2}) states is comparatively large 0.1687Å. In this case, the more number of bands appears in a band system. This conclusion is true from the various low values of the FC factors of different bands.

The orders of the magnitude of the FC factors of the ${}^1\Delta_u^- - X\Sigma_g^+$ system of P_2 Molecule for the bands (1, 4) and (3, 2) are low and perhaps may not be detected experimentally. It is noticed from Table 4, that for v' and v'' progressions, the sum rule is not fulfilled for the observed bands. So this system would definitely yields more new bands, if more investigational work is done on the band spectrum of the P_2 molecule. Amongst all the bands reported Franck-Condon factors (3,3) (0,3) (2,4) (5,1) and (0,4) bands are high and indicate maximum intensity for these bands. Between all bands observed in this system (5, 2) band is found to be the strongest. It is observed from Table 4, that the vibrational sum rule is satisfied for this system; further experimental work will not be helpful to observe more new bands. Franck - Condon factors are determined [45] for twenty three bands of $A^1\Pi_g - X^1\Sigma_g^+$ system of P_2 Molecule.

In this system, the differences in the equilibrium inter nuclear distances of the upper and lower states are small 0.1034Å. So, the Condon parabola is narrow. The F-C factors of (0,1) (2,5) (1,0) (2,0) (0,2) (1,4) bands are found to be stronger compare to others. Of the strongest bands (2, 5) band is found to be strongest. The F - C factors for the bands (0, 3) (1,3) (0,0) (1,5) (1,4) (2,2) (3,1) (3,0) (4,1) and (5,1) are equal in magnitude which proposes that bands are of almost equal intensity.

CONCLUSION

The study of electronic spectra of the molecules PH and P_2 allow we to know the chemical and physical processes that take place in the comet atmosphere. The detection of molecular lines in emission suggests that the vibration and rotational states of molecules can be excited by radioactive or collision means in the comet atmosphere. The measurements of the strengths of lines from different rotational/vibration states can therefore serves effective probes of the temperature, density and radiation background of the comet atmosphere.

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