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RKRV Potential Energy Curves, Dissociation Energies, r-Centroids and Franck-Condon Factors of H_2 and N_2+ Astrophysical Important Molecules

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Abstract

The potential energy curves for the ground state of diatomic H_2 and N_2^+ molecules are constructed techniques using the five-parameter H-H function. The estimated dissociation energies are 4.61 ± 0.1 eV and 8.70 ± 0.20 eV for H_2 and N_2^+ respectively. The estimated D_0 values are in good agreement with literature values. The r-Centroids and Franck-Condon factors for the bands of $C^1\prod_u \rightarrow X^1\Sigma^+g$ of H_2 and $A^2\prod_{u1} \rightarrow {}^4\Sigma_u^+ X$ of N_2^+ molecules have been determined. The Franck-Condon factors are evaluated by the approximate analytical method of Jarmain and Fraser. The absence of the bands in these systems is explained.

Introduction

The detailed knowledge of atomic and molecular structure has been obtained from spectroscopic studies of the emission, absorption and scattering of electromagnetic radiation accompanying transitions among atomic or molecular energy levels. Whereas atomic spectra involve only electronic transitions, the spectroscopy of molecules is more intricate because vibrational and rotational degrees of freedom come into play as well. Early observations of absorption or emission by molecules were characterized as band spectra in contrast to the line spectra exhibited by atoms. It is now understood that these bands reflect closely-spaced vibrational and rotational energies augmenting the electronic states of a molecule. With improvements in spectroscopic techniques over the years, it has becomes possible to resolve individual vibrational and rotational transitions. This has provided a rich source of information on molecular geometry, energetic and dynamics. Molecular spectroscopy has also contributed significantly to analytical chemistry, environmental science, astrophysics, biophysics and biochemistry.

The hydrogen molecule plays a central role in a variety of processes that significantly influence the chemical and physical state of the interstellar medium. Because of the great importance of the molecules to an eventual understanding of diffuse and dense interstellar clouds, the Copernicus satellite was used to survey the column densities of atomic and molecular hydrogen toward a large sample of early-type stars [1-5]. Wolniewicz and Staszewska [6] have been reported born-oppheimer energies and electronic transitions moments for the $^1\Sigma^+_u \rightarrow X\ ^1\Sigma_g$ transitions in molecular hydrogen [7]. Continuous spectrum of molecular hydrogen plays an important role in many astrophysical situations. The $a^3\Sigma^+_g$- $b^3\Sigma_u^+$ transition that leads to continuum in the region 1700-5000Å given an important contributions to the opacity in stellar atmospheres.

Spectra of ion N_2^+ play a significant role in atmospheric and astrophysical phenomena. For example, the Meinel ($A^2\Pi_{1,\mu}{}^{-}X\,^4\Sigma_u^+$) and the first negative($B^2\Sigma_\mu$+-X $^4\Sigma_u^+$) band systems of $^{14}N_2^+$ were observed in the auroral emission. The first negative system of $^{14}N_2^+$ was also found in the spectra of comet tails [8]. The laboratory data on the spectra of $^{14}N_2^+$, and $^{15}N_2^+$ would be very useful in the study of their spectra resulting from the atmospheric and astrophysical phenomena mentioned above [9]. The spectra of the $A^2\Pi_\mu$-X $^4\Sigma_u$+ and $B^2\Sigma_\mu$+-X $^4\Sigma_u^+$ transitions of N_2^+ have been studied intensively since the 1920's using various spectroscopic techniques [10]. Recently, Shenghai et al [11] re-measured the rovibronic spectrum of N_2^+ in the visible region from 16800-17573cm-1 using optical heterodyne magnetic rotation enhanced velocity modulation spectroscopy. Some new lines of the (12,6) and (11,5) bands of the $A^2\Pi_\mu$-X $^4\Sigma_u^+$ transitions and the (1,5) band of the $B^2\Sigma_\mu^+$-X $^4\Sigma_u^+$ transition were observed, and the molecular constants of these three bands [12] were redefined. Coe.et al [12] observed the spectra of N_2^+ in the (0,0) band of the $B^2\Sigma_\mu^+$-X $^4\Sigma_u^+$ system from a free-jet expansion of N_2 excited by a fast electron beam. In 1932, Childs [13] predicted that a lower lying Π state was causing the observed perturbations in the B-X system of N_2^+. The perturbing state was found 18 years later, in 1950, when Meinel observed a new spectrum in an auroral emission in the near infrared (2,3). The $A^2\Pi_\mu$-$X^4\Sigma_u^+$ system is now called the Meinel system [14]. The techniques developed by Gudeman et al [15] have been applied extensively to the $A^2\Pi_\mu$-$X^4\Sigma_u^+$ system of N_2^+.

Potential Energy Curves

The RKRV method is a Wentzel – Kramers – Brillouin approximation with which one obtains reliable potential energy curves from the measured vibrational and rotational constants of the diatomic molecules. Experimentally determined vibrational levels are used to construct the potential energy curve. The RKRV method [16] and [17] has been used for obtaining the classical turning points, r_{max}, r_{min} of the vibrational motion. The turning points are given in terms of functions f and g as follows:

$$r_{\max} = \left[\frac{f}{g} + f^2\right]^{\frac{1}{2}} + f\,, \quad r_{\min} = \left[\frac{f}{g} + f^2\right]^{\frac{1}{2}} - f$$

$$f = \left(\frac{8\pi^2 \mu c}{h} \right)^{1\frac{1}{2}} \sum_{i=1}^{n} (\omega x)_i^{-\frac{1}{2}} \, \mathrm{h} \; W_i$$

$$g = \left(\frac{2\pi^2 \mu c}{h} \right)^{\frac{1}{2}} \sum_{i=1}^{n} \{ 2\alpha_i (\omega x)_i^{-1} [\, U_n - U_{i-1})^{\frac{1}{2}} - (U_n - U_i)^{\frac{1}{2}}] + (\omega x)_i^{-1/2} [2B_i - \alpha_i (\omega x)_i^{-1} w_i] l\, n W_i \}$$

and

$$W_i = \left[\frac{[\omega_i^2 - 4(\omega x)_i U_i]^{½} - 2(\omega x)_i^{1/2} [U_n - U_i]^{1/2}}{[\omega_i^2 - 4(\omega x)_i U_{i-1}]^{1/2} - 2(\omega x)_i^{1/2} [U_n - U_{i-1}]^{1/2}} \right]$$

The symbols have their usual significance. Using the least-square method as described by Vanderslice et al.,[17], the values of ωi, (ωx)i, Bi and αI are determined and used in the construction of the potential energy curve. The molecular constants required for the present study have been presented in Table 1.

Table 1. Spectroscopic constants of different electronic states of diatomic molecules which are considered in the present investigation

Mole-cule	μ	State	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	r_e (Å)	D_e eV
H_2	0.5039	$X^1\Sigma^+g$ $B^1\Sigma^+u$ $C^1\Pi_u2$	0 91697.2 100097.2	4401.28 1362.68 2443.96	121.59 20.68 69.04	60.80 20.23 31.30	3.025 1.120 1.615	0.7417 1.2860 1.0338	4.59
N_2^+	7.0014	$X\,^4\Sigma_u^+$ $A^2\Pi_u$ $B^2\Sigma^+$	0 9166.9 25461.1 2207 1903 2421.14	2207 1903 2421.14	16.1 15.02 24.07	1.931 1.744 2.085	0.0188 0.0188 0.0212	1.1164 1.1749 1.0742	8.71

μ = Reduced mass
T_e= Electronic energy above ground state (cm^{-1})
ω_e = Vibrational spacing (cm^{-1})
$\omega_e x_e$ = Anharmonic correction to vibrational spacing (cm-^{1})
B_e = Rigid rotator rotational spacing (cm-^{1})
α_e = Non rigid rotator correction to Be (cm-^{1})
r_e = Equilibrium inter nuclear distance (Å)

Evaluation of the Dissociation Energy

In the construction of RKRV potential curves, the energies U(r) are calculated with the empirical potential functions by varying the De value. An average percentage deviation is determined between the calculated U(r) and the experimental G(V) values. The dissociation energy from any function is that value of De which gives the smallest deviation. The corresponding function determined the dissociation energy of the molecule. A critical evaluation of the more important of these functions was given by Steele et al., [18], and they have shown that the potential function of Hulburt-Hirschfelder (H-H) fits well with the RKRV curves of a large number of diatomic molecules [19-20]. In the present investigation, it is noted that H-H function fits best and reproduce the experimental energy values (Table 4 & 5). Different D_e values are used in the H-H function and the D_e values for which the best fit of the energy values U(r) is observed, is taken as the dissociation energy (D_e) of the molecule.

r-Centroids and Franck- Condon factors

The Franck-Condon factors are depends mainly on the shape and relative separation in the internuclear distance between the upper and lower potentials involved. These factors control the form of the wave function $\psi_{\upsilon'}$, $\psi_{\upsilon''}$ and their overlap. In order to calculate Franck-Condon factors, one has to evaluate the $\int \psi_{v'}\psi_{v''}\,d\,r$. In the absence of exact expressions for ψ_υ one may use the eigen functions derived from same approximate potential functions. Therefore the methods for calculating Franck-Condon factors depend on the choice of approximate eigen functions ψ_υ obtained by solving Schrodinger equations with approximate potential functions.

Fraser and Jarmain [21] introduced the method of average 'a' Morse constant, which allows analytic integration of the integral

$$q_{v'v''} = \int_0^\infty \psi_{v'} r^n \psi_{v''} d\,r$$

where n = 0,1,2.

The above integral becomes Franck-Condon factor when n=0. The method successfully replaces cumbersome numerical integration for many band systems. The details of the method are described elsewhere [21-25]. The method yields accurate Franck-Condon factor especially when vibrational quantum numbers are low.

The r-Centroids r_υ', r_υ'' represented the characteristic internuclear separation of a υ'-υ'' transition in a diatomic molecular band system and are defined by

$$r_{v',v''} = \frac{\int \psi_{v'} r \psi_{v''} d\,r}{\int \psi_{v'}\psi_{v''} d\,r}$$

By use of the quadratic equation method of Nicholls and Jarmain [25], the r-centroids and Franck-Condon factors for B-X of the ScS and C-X of the TiCl systems have been evaluated. Chakraborthy and Pen [24] mentioned that this method is valid for $\Delta r_e = r_{e1}-r_{e2}$ in the range of 0.01-0.25 Å. The details of the said methods were reported in the literature [21], [24-25] only the results of the present work given in Tables (6-10).

Results and Discussion

Potential Energy Curve of H_2 and N_2^+ Molecules

In the present study, the experimental true potential energy curves for $X^1\Sigma^+_g$, $B^1\Sigma^+_u$ and $C^1\prod_u^2$ states of H_2 molecule using RKRV method are constructed, and as shown in Fig. 1. The spectroscopic constants required for the evaluations of turning points are presented in Table 1. The maximum and minimum internuclear distances for eight vibrational levels of ground state $X^2\Sigma^+$ and the excited states $B^1\Sigma^+$ and $_uC^1\prod_u^2$ are calculated by using the formula of Vanderslice et al method [26]. The values obtained by this method are presented in Table [2 & 3]. The graphical forms of these curves are shown in Fig. 1.

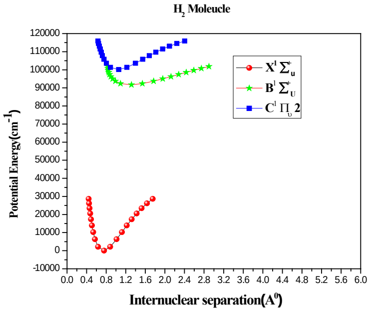

Fig. 1. Potential Energy curve of H_2 molecule

The potential energy curves have been constructed for eight vibration levels belong to the ground state and the results are presented in Table [2&3]. The r_{min} and r_{max} values have been calculated for eight vibration levels in B state and six levels for C state and the results are presented in table [2&3]. The most prominent feature of their curves is that these are not narrow well type potentials which indicate that the molecule behaves like anharmonic oscillator. The shapes of the curves represent the conventional from of potential energy curves with a smooth asymptotic rise to the dissociation limit with increasing separation (r) between the nuclei–which indicate that the molecule behaves like an anharmonic oscillator.

Table 2 Turning points of the potential energy curves for different states of H2 molecule

V	U (cm^{-1})	R min (Å)	R max (Å)
$X^1\Sigma^+_g$	State $T_e = 0$		
0	2170.24	0.633	0.882
1	6328.34	0.571	1.013
2	10243.26	0.535	1.121
3	13915.00	0.509	1.222
4	17343.56	0.490	1.321
5	20528.94	0.474	1.422
6	23471.14	0.461	1.525
7	26170.16	0.450	1.634
8	28626.00	0.441	1.751
$B^1\Sigma^+_u$	State $T_e = 91697.2$		
0	676.17	1.094	1.540
1	1997.49	0.988	1.771
2	3277.45	0.931	1.955
3	4516.05	0.894	2.123
4	5713.29	0.869	2.282
5	6869.17	0.852	2.437
6	7983.69	0.841	2.590

7	9056.85	0.836	2.744
8	10088.65	0.835	2.899
$C^1\Pi_u$	State T_e = 100097.2		
0	1204.72	0.888	1.223
1	3501.60	0.805	1.399
2	5678.40	0.757	1.545
3	7708.11	0.723	1.681
4	9599.76	0.697	1.816
5	11353.32	0.676	1.953
6	12968.80	0.660	2.095

In the present study the experimental potential energy curves for the X ${}^4\Sigma_u^+$, $A^2\Pi_\mu$ and $B^2\Sigma^+$ of N_2^+ molecule using RKRV method [26] is constructed as shown in Fig 2. The spectroscopic constants required in the present study for the evaluation of the r_{max} and r_{min} points are taken from Scholl et a1 [27] are presented in Table 1.

The maximum and minimum internuclear separations for nine vibrational levels of the ground state $X^4\Sigma_u$+ state, seven vibrational levels of $A^2\Pi_\mu$ state and six vibrational levels of $B^2\Sigma^+$ state have been determined by using Vanderslice et al [26] method. The values obtained by this method are presented in Table 3. From Fig. 2 it is interesting to note that there are crossings of potential curves of $X^4\Sigma_u^+$ and $A^2\Pi_\mu$ states. The possibility of crossing is expected in between the curves $X^4\Sigma_u^+$ of the vibrational levels of 6-7 and $A^2\Pi_\mu$ of the 2-3 vibrational levels. These crossings indicate the possible perturbations and pre-dissociations. The $r_\pm$ values for the ground state $X^4\Sigma_u^+$ and the excited state $A^2\Pi_\mu$ almost the same. So, the important feature of the potential curves is that they are lying approximately one above the other, indicating that the structure of the molecule in the ground state and the excited state should be nearly the same.

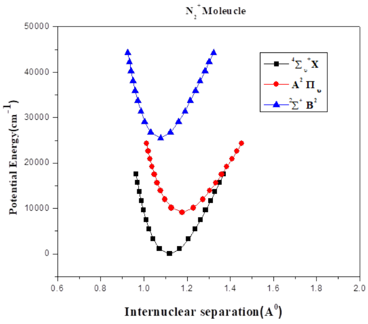

Fig. 2. Potential energy curve of N_2^+ molecule

Table 3: Turning points of the potential energy curve for different states of molecule N_2^+

v	U (cm-^{1})	R min (Å)	R max (Å)
$X^4\Sigma_u^+$	State T_e = 0		
0	1099.47	1.072	1.166
1	3274.27	1.043	1.206
2	5416.87	1.024	1.236
3	7527.27	1.010	1.262
4	9605.47	0.998	1.286

5	11651.48	0.987	1.308
6	13665.25	0.978	1.329
7	15646.88	0.970	1.350
8	17596.28	0.963	1.370
$A^2\prod_u^1$	State T_e= 9166.9		
0	947.74	1.127	1.228
1	2820.70	1.096	1.272
2	4663.62	1.076	1.305
3	6476.50	1.061	1.334
4	8259.34	1.048	1.360
5	10012.14	1.038	1.384
6	11734.90	1.028	1.407
$B^2\Sigma^+$ state	StateT_e= 25461.1 cm-^{1}		
0	1204.5	1.032	1.122
1	3577.5	1.004	1.160
2	5902.4	0.986	1.190
3	8179.1	0.972	1.215
4	10407.7	0.960	1.238
5	12588.1	0.951	1.260

Dissociation Energies of H_2 and N_2^+ Molecules

The hydrogen molecule plays a central role in a variety of processes that significantly influence the chemical and physical state of the interstellar medium. Because of the great importance of the molecules to an eventual understanding of diffuse and dense interstellar clouds, the Copernicus satellite was used to survey the column densities of atomic and molecular hydrogen toward a large sample of early-type stars [28-31]. Employing the latest molecular spectroscopic constants, the dissociation energy of H2 molecule is determined. Dissociation energy of diatomic molecules is of great interest in thermo chemistry, combustion physics and astrophysics. The quantitative problems of valance, statistical calculations of equilibrium at high temperature, in chemical bonding and in many other problems the dissociation energy plays a fundamental rule. The author has taken up this investigation to find the dissociation energy of H_2 molecule as it has astrophysical importance and its spectra were observed in early type stars.

In the chosen empirical Potential function, the turning Points evaluated from the true potential energy curves are substituted for different values of D_e. The energy values U(r) are then calculated for various vibrational levels. These values may be compared with those obtained from experimental data and vice versa. The value of De for which the best fit is obtained, is taken to be the value of dissociation energy for the given state of the molecule.

In the present investigation, H-H function [32] has chosen for H2 molecule because this function is often superior to other functions. The deviation of the calculated energy from the experimentally observed value is found to be a minimum for the selected potential function (Table 4). The function leading to the smallest deviation determines the dissociation energy of the molecule. The De obtained for H2 molecule is found to be 4.61$\pm$0.1 eV and are very close to the values given by Suchard [33] (4.47 eV) and Huber and Herzberg [34] 5.27 eV.

Table 4 Energy values obtained from Hulburt–Hirschfelder (H-H) function for the $X^1\Sigma^+_g$ electronic state of H_2 molecule

rO (A^o)	U (cm^{-1})	U(r) cm^{-1}		
		D_e=4.59 eV	D_e =4.61 eV	D_e =4.64 eV
0.882	2170.24	2170.46	2182.18	2193.89
1.013	6328.34	6313.52	6347.59	6381.65
1.121	10243.26	10187.82	10242.81	10297.78
0.222	13915.00	13795.35	13869.82	13944.24
1.321	17343.56	17142.17	17234.69	17327.17
1.422	20528.94	20237.21	20346.44	20455.62
1.525	23471.14	23091.63	23216.27	23340.85
1.634	26170.16	25718.76	25857.57	25996.33
1.751	28626.00	28134.69	28286.55	28438.34
0.633	2170.24	2172.92	2184.65	2184.65
0.571	6328.34	6345.54	6379.79	6414.03
0.535	10243.26	10282.66	10338.16	10393.64
0.509	13915.00	13972.66	14048.07	14123.46
0.490	17343.56	17402.12	17496.05	17589.93
0.474	20528.94	20558.16	20669.13	20781.04
0.461	23471.14	23429.68	23556.14	23682.54
0.450	26170.16	26008.41	26148.79	26289.11
0.441	28626.00	28289.58	28442.28	28594.90
Average percentage deviation		0.71	0.70	0.78

Molecular spectra of nitrogen N_2^+ play a significant role in atmospheric and astrophysical phenomenon. The laboratory data on the spectra of $^{14}N^+$ $^{15}N^+$ would be very useful in the study of their spectra. Gilmore [35] has compiled and extended early work on N_2 potential energy curves the spectra of the $A^2\Pi_\mu$-$X^2\Sigma_g^+$ and $B^2\Sigma_\mu^+$-$X^2\Sigma_g^+$ transitions of N_2^+ have been studied intensively since the 1920 using various spectroscopic techniques [36]. Recently, Shenghai et al [37] remeasured the rovibronic spectrum of N_2^+ in the visible region from 16800-17573cm^{-1} using optical heterodyne magnetic rotation enhanced velocity modulation spectroscopy. Employing the Hulburt-Hirschfelder's [32] potential function the D_e value for the ground state of N_2^+ molecule has been evaluated. The relevant U(r) values for the selected D_e values are given in the Table 5.

Table 5 Energy values obtained from Hulburt–Hirschfelder (H-H) function for the $^4\Sigma_u^+X$ electronic state of N_2^+ molecule

r (A^o)	U (cm^{-1})	U(r)cm^{-1}		
		D_e =8.69eV	D_e =8.70eV	D_e =8.72eV
1.166	1099.47	1095.84	1098.97	1102.10
1.206	3274.27	3264.83	3274.15	3283.48
1.236	5416.87	5405.27	5420.71	5436.15
1.262	7527.27	7519.19	7539.67	7561.14

1.286	9605.47	9604.96	9632.40	9659.83
1.308	11651.48	11666.55	11699.88	11733.20
1.329	13665.28	13703.83	13742.99	13782.12
1.350	15646.88	15718.16	15763.06	15807.95
1.370	17596.28	17710.36	17760.95	17811.53
1.072	1099.47	1905.43	1098.55	1101.68
1.043	3274.27	3261.15	3270.46	3279.78
1.024	5416.87	5392.10	5407.50	5422.90
1.010	7527.27	7487.93	7509.32	7530.71
0.998	9605.47	9547.97	9575.24	9602.52
0.987	11651.48	11571.90	11604.95	11638.00
0.978	13665.28	13559.60	13598.33	13637.06
0.970	15646.88	15510.58	15554.88	15599.19
0.963	17596.28	17424.78	17474.55	17524.32
Average percentage deviation		0.45	0.35	0.40

For the molecule N_2^+ it is obvious from Table 5 that the best fitting of the energy value is achieved for D_e = 8.70 eV. Since the average percentage deviation in this case is minimum 0.35. The inherent error in the H-H function given by Steele et al [38] is 2%. The error involved in the evaluation of D_e is the average percentage deviation plus the inherent error in the potential function. Hence, the dissociation energy for the ground state of N_2^+ is 8.73eV and the value as measured from the lowest vibration levels is D_0 =8.70 ± 0.20 eV. The estimated D_0 value for N_2^+ (8.70 ± 0.20 eV) is in good agreement with the value recommended by Gaydon [39] obtained from extrapolation method (8.73 eV) and also with Huber and Herzberg [34] quoted value 8.71 eV.

r – Centroids of H_2 and N_2^+ Molecules

To understand the physical conditions of the emitter from the relative intensities of the bands of a molecules. One must have a theoretical knowledge of the corresponding r-Centroids and vibrational transition probabilities for the respective band heads in a band system. The values of r-Centroids of H_2 molecule are estimated by the quadratic equation method of Nicholls and Jarmain [40]. Molecular hydrogen is undoubtedly the most abundant molecule in the interstellar medium. Nevertheless, its abundance has been directly measured only in diffuse clouds, which can be probed by ultraviolet absorption lines. The reason for this is well known; the absence of dipole rotational or vibrational transitions makes the opacities of H_2 lines very small, even through dense molecular clouds. In addition, the small moment of inertia of H_2 results in widely spaced rotational levels which can be excited to emit only under unusual conditions [2-4].The results are presented in the Table. 6 The value of $r_{v'v''}$ (r-Centroids) was found to increase with the increase of the λv', v'' value has been observed by Nicholls and Jarmain [40]. The internuclear distance of the upper state is greater than the ground state ($r_{e1}>r_{e2}$) in all cases, r-Centriods estimates are expected to increase with wavelengths which is the trend observed in red-degraded band systems of H_2 molecule. The sequence difference Δr = r v'+1, v" +1 -rv', v" for this system is found to be a constant (~0.005A0). It is seen that Δr is greater than 0.01A0 for this system suggesting that the potentials are wide. In the case of $C^1\prod_{u2}\rightarrow X\ ^1\Sigma^+_g$ system of, H_2, r_0, 0 is found to be slightly greater than $(r_{e1}+r_{e2})/2$ indicating there by that the potentials are not very anharmonic.

Table 6 r – Centroids for the $C^1\prod_u \rightarrow X^1\Sigma_+g$ transition of H_2 Molecule

γ'/ γ''	0	1	2	3	4	5
0	0.882(a)	0.974(a)	1.070(a) 1098.2(b)	1.175(a) 1145.4(b)	1.289(a) 1192.7(b)	1.418(a)
1	0.837(a)	0.924(a) 1028.4(b)	1.015(a)	1.112(a) 1115.8(b)	1.216(a) 1160.8(b)	1.332(a) 1206.2(b)
2	0.797(a)	0.880(a)	0.967(a) 1047.3(b)	1.058(a) 1089.4(b)	1.155(a) 1132.2(b)	1.261(a) 1175.4(b)
3	0.761(a)	0.842(a)	0.925(a)	1.012(a)	1.104(a) 1106.6(b)	1.202(a)
4	0.730(a)	0.809(a)	0.889(a)	0.973(a)	1.060(a)	1.152(a) 1123.1(b)
5	0.703(a)	0.780(a)	0.859(a)	0.939(a)	1.023(a)	1.111(a)

where (a) r-Centroids (b) Wavelength(A0)

Sequence Difference H_2

$\Delta\bar{v}$	+4	+3	+2	+1	0	-1	-2	-3	-4
$\Delta\bar{r}$	0.050	0.04	0.045	0.043	0.041	0.043	0.045	0.047	0.050

Gilmore [35] has compiled and extended early work on N_2^+ potential energy curves the spectra of the $A^2\Pi_\mu$-$X^2\Sigma_g^+$ and $B^2\Sigma_\mu^+$-$X^2\Sigma_g^+$ transitions of N_2^+ have been studied intensively since the 1920 using various spectroscopic techniques [36]. Recently, Shenghai et al [37] remeasured the rovibronic spectrum of N_2^+ in the visible region from 16800-17573cm^{-1} using optical heterodyne magnetic rotation enhanced velocity modulation spectroscopy. The nitrogen molecular ion has been widely studied experimentally [41] because of its importance as a probe of the atmosphere and comet Tailscoe et al [12] observed spectra of N_2^+ in the (0,0) bond of the $B^2\Sigma_u^+$- $X^2\Sigma_g^+$ system. Fine and hyperfine structure in $N_2^+$of $B^2\Sigma_+$- $X^2\Sigma_g^+$ system has been studied by Scholl et al [42].

The values of r-Centroids of N_2^+ molecule are estimated by the quadratic equation method of Nicholls and Jarmain [40]. The results are presented in the Table 7. As the internuclear distance in the upper state is larger than the internuclear distance in the lower state (i.e.,$r_{e1}>r_{e2}$) in $A^2\prod_{u1} \rightarrow {}^4\Sigma_u^+$ X systems the value of r-Centroid (rv',v'') increases with the increase of corresponding wavelength (λv'v'') which is the trend observed in a red-degraded band system. The sequence difference, Δr = r v'+1, v'' +1 - $\tilde{r}$ v',v'' for the system is constant in accordance with the observations of Nicholls and Jarmain [40]. Also the values for the band system of $A^2\prod_{u1} \rightarrow {}^4\Sigma_u^+$ X of N_2^+ are less than 0.01A^0 which indicates that the potentials are not wide. The value $(r_{e1}+r_{e2})/2$ is less than the r_{00} for the $A^2\prod_{u1} \rightarrow {}^4\Sigma_u^+$ X system of N_2^+ molecule, which shows that the potentials are not very much anharmonic. The sequence difference $\Delta r = r_{v'+1, v''+1} - r_{v', v''}$ has been found to be constant in accordance with the observations of Nicholls and Jarmain [40].

Table 7 r-Centroids for the $A^2\prod_{u1} \rightarrow {}^4\Sigma_u^+ X$ transition of N^+_2 molecule

γ'/ γ''	0	1	2	3	4	5
0	1.147	1.192	1.243	1.300	1.366	1.444

1	1.112	1.153	1.199	1.249	1.306	1.372
2	1.080	1.118	1.159	1.205	1.255	1.313
3	1.051	1.086	1.124	1.165	1.211	1.262
4	1.025	1.057	1.092	1.130	1.172	1.217
5	1.000	1.031	1.064	1.099	1.137	1.178

Sequence Difference N^{+}_{2}

$\Delta\bar{v}$	+4	+3	+2	+1	0	-1	-2	-3	-4
$\Delta\bar{r}$	0.006	0.007	0.006	0.006	0.006	0.006	0.006	0.007	0.006

Franck-Condon Factors of H_2 Molecule ($B^1\Sigma^+_u \rightarrow X^1\Sigma^+_g$ and $C^1\prod_u \rightarrow X^1\Sigma^+_g$ Systems) and N_2^+ molecule ($A^2\prod_{u1} \rightarrow X\ ^4\Sigma_u^+$ System)

The hydrogen molecule plays a central role in a variety of processes that significantly influence the chemical and physical state of the interstellar medium. Because of the great importance of the molecules to an eventual understanding of diffuse and dense interstellar clouds, the Copernicus satellite was used to survey the column densities of atomic and molecular hydrogen toward a large sample of early-type stars [2-5]. Franck-Condon factors are calculated for the system $B^1\Sigma^+_u \rightarrow X^1\Sigma^+_g$ of H_2 by the method of Fraser and Jarmain [43]. The Condon locus is not very narrow. The magnitude of the $q_{v'}$,V” values indicated in Table 8 highlights that the (0,3), (0,4), (0,5), (1,2), (1,3) and (2,5) bands are intense. The magnitude of (1,3) and (2,5) bands are equal, which indicate the intensity of these bands are also same. Keen observation of the table reveals that in the case of B-X system of H2 that the vibrational sum rule is not satisfied for v′ and v′′ progressives as for as the bands are observed. Therefore, it is suggested that if more experimental work is done on the B-X system of H2, it would definitely yields more new bands.

The magnitude of the F-C factors in the case of B-X system of H_2 beyond (0,0) (0,1) and (1,0) are very small in comparison with the other values and hence they may not be observed experimentally. The F-C factor for (0,5) band is strongest in B-X system of H2 among all the bands observed. The Franck –Condon factors for this system $C^1\prod_u \rightarrow X^1\Sigma^+_g$ of H_2 have been calculated by the r_e –shift method of Fraser and Jarmain [43] and are presented in Table 9. The magnitude of the FC factors (0,5) is small and it has not been observed experimentally. From Table 8. It is clear that the computed FC factors vary in accordance with the estimated intensities. The well-known vibrational sum rule viz., Σv’ q v’v” = Σv’ qv’v” ≈ 1 is also satisfied for the computed FC factors. The magnitude of (0, 0) and (1, 3) bands are equal, which indicate the intensity of these bands are also same. It is seen from table 5.3 that the (0,1),(0,2),(1,4) and (1,5) bands are strongest.

Table 8 Franck – Condon factors for $B^1\Sigma^+_u \rightarrow X^1\Sigma^+_g$ of H_2 molecule

γ’- γ’’	F-C Factors
(0,0)	0.004
(0,1)	0.021
(0,2)	0.058
(0,3)	0.112
(0,4)	0.163
(0,5)	0.191

(1,0)	0.014
(1,1)	0.055
(1,2)	0.105
(1,3)	0.122
(1,4)	0.084
(1,5)	0.025
(2,0)	0.028
(2,1)	0.080
(2,2)	0.099
(2,5)	0.123
(3,1)	0.041
(3,2)	0.063
(4,0)	0.049
(4,1)	0.073
(4,2)	0.028
(5,0)	0.051
(5,1)	0.055

Table 9 Franck – Condon factors for $C^1\prod_u \rightarrow X^1\Sigma^+_g$ of H_2 molecule

$\gamma' - \gamma''$	F-C Factors
(0,0)	0.11
(0,1)	0.280
(0,2)	0.312
(0,3)	0.198
(0,4)	0.078
(0,5)	0.019
(1,0)	0.179
(1,1)	0.152
(1,3)	0.110
(1,4)	0.253
(1,5)	0.201
(2,0)	0.181
(2,1)	0.025
(2,2)	0.067
(2,5)	0.099
(3,0)	0.148
(3,2)	0.100
(4,0)	0.109
(4,1)	0.021

(4,2)	0.062
(4,3)	0.013
(5,0)	0.076
(5,1)	0.041
(5,2)	0.020
(5,3)	0.037

Spectra of natural molecular nitrogen N_2^+ play a significant role in atmospheric and astrophysical phenomenon. The laboratory data on the spectra of $^{14}N^+$ $^{15}N^+$ would be very useful in the study of their spectra mentioned [44-45] spectroscopic data of the nitrogen molecules are great importance to understand the phenomenon of energy transfer process in auroral enciation and chemical lasers.

Table 10 Frank-Condon factor for $A^2\prod_{u1} \rightarrow X^4\Sigma_u^+$ transition of N_2^+ molecule

γ’- γ’’	F-C Factors
(0,0)	0.479
(0,2)	0.120
(0,3)	0.020
(1,0)	0.324
(1,1)	0.032
(1,2)	0.336
(1,3)	0.234
(1,4)	0.067
(1,5)	0.011
(2,0)	0.134
(2,1)	0.226
(2,2)	0.021
(2,4)	0.025
(3,0)	0.044
(3,1)	0.198
(3,2)	0.078
(3,3)	0.948
(3,4)	0.053
(4,0)	0.012
(4,1)	0.094
(4,2)	0.179
(4,3)	0.292

Keen observation of the table 10 reveals that the magnitude of Franck - Condon factors (1,0) and (1,2) bands for the $A^2\prod_{u1} \rightarrow X^4\Sigma_u^+$ are equal, which indicate the intensity of these bands are also same. The magnitude of Franck - Condon factors for the bands (0,3) (1,1) (1,5) and (2,2) are very small in comparison with the other values and hence they may not be observed experimentally. It is seen from the Table 10 that (3,3) is the strongest bands in A2∏u1→X 4Σu+ band system of

N_2^+. As well-known vibrational sum rule $\Sigma_v U_{v'v''}=1$ is not satisfied in this system. Therefore if more experimental work is done on the band system of the N_2^+ molecule on the system, it would definitely yield more new bands.

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